Advanced Materials for Radiation Dosimetry

by

Christin Gädtke

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Abstract

The motivation for this work was to find materials that have the following characteristics: good optical transparency, rapid read-out, automation of read-out, good fading characteristic, promise high sensitivity to ionising radiation, and tissue equivalence for use in medical applications. For example, there are medical applications in brachytherapy and high-energy photon therapy for the treatment of cancer. These applications benefit small dosimeters for monitoring radiation during radiotherapy or for dose verification and validation.

This thesis studies fluoroperovskite materials that were manufactured as bulk materials or nanoparticles. The techniques of photoluminescence (PL), radioluminescence (RL), thermoluminescence (TL) and optically stimulated luminescence (OSL) were employed in order to get a deeper understanding of the defect distribution in these materials. A detailed model of the trap distribution was developed from the results of these measurements. It was observed that compared to the bulk materials, the nanoparticles show a lower PL lifetime and less dependence on the dose of the RL intensity, which is due to the different defect distribution. The nanoparticles also demonstrate more low temperature peaks in the TL glow curves. PL and RL measurements of Eu^{3+} doped samples show that the crystal environment of the Eu^{3+} in the bulk material is more distorted than for the nanoparticles. For the bulk materials, the thermal coefficient of the RL is $<0.4\text{ \%}/\text{K}$, which is a desirable property of real-time dosimeters. The thermal coefficient of the RL in the nanoparticles has a high uncertainty ($\sim 7\text{ \%}/\text{K}$) compared to the bulk materials ($\sim 0.4\text{ \%}/\text{K}$). For the fluoride nanoparticles, it was observed that the PL lifetimes for the LaF_3 decreases with increasing rare earth concentrations. This can be attributed to energy transfer from luminescence ions in the core to luminescence ions near the surface followed by non-radiative decay. In comparison, the decrease of the PL lifetimes of RbMgF_3 and NaMgF_3 is predominantly due to non-radiative recombination centres inside the crystal.

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1 Introduction

Fluoroperovskite-based compounds have recently attracted interest because of the range of potential applications including optical amplifiers [21, 22] and radiation detectors [23, 24]. Bulk materials and nanoparticles have the potential to be used in small sized and remote dosimeters that can be employed in a number of applications i.e. determining the real-time radiation dose and dose rate in radiation protection, non-destructive testing, and in medical radiotherapy for monitoring the prescribed radiation for dose verification and validation. Transparent nanopartilces/ polymer composites are particularly useful for this application, because they can be used to construct long fibre optic dosimeters that take advantage of the reduced light scattering. Real-time read-out can be performed with radioluminescence (RL). This is a phenomenon that occurs from the prompt radiative recombination of charged particles after irradiation. There is a need for new RL materials that have good transparency, high sensitivity and with a response to radiation that is equivalent to that of tissue. Dose verification and validation can also be done with thermoluminescence (TL) materials, which is a phenomenon where irradiation induces carriers that become trapped. These carriers are released by heating the sample resulting in recombination and light emission. New TL materials with tissue equivalent characteristics will find applications in the area of personal dosimetry.

This work presents an investigation into the use of bulk materials and nanoparticles for real-time dosimetry and the determination of the total dose after irradiation. In chapter 2, basic theory on the quantities to describe the interaction of radiation with matter and the energy dependence is presented. Chapter 3 explains the theoretical background of

the techniques, which are employed and the luminescence characteristics of the rare earth ions. Experimental techniques and a description of sample preparations are outlined in chapter 4. In chapters 5 - 8, potential materials for tissue equivalent applications in radiation dosimetry are explored. New measurements were performed to investigate the RL and temperature dependent RL behaviour of bulk materials. The photoluminescence (PL) after heavy irradiation was also investigated. For the fluoroperovskite nanoparticles temperature dependent PL and PL lifetime measurements were performed. Their RL, TL and temperature dependent RL was determined. New defects were observed in both the bulk materials and nanoparticles and a detailed model for the trap distribution was developed. Chapter 9 presents the final results chapter and an overview of other fluoride nanoparticles and their respective RL characteristics. Chapter 10 provides a brief summary and an outlook from this thesis.

2 Basic quantities and units in radiation dosimetry

The motivation of today's research is to find new transparent dosimeters for different energy regions and applications. A good transparency is important for the samples, because during the stimulation of the sample the emitted light will not be scattered in the material. To better understand the quantities utilised in radiation dosimetry and the different energy regions for their applications, a short overview is outlined in this chapter.

To measure the radiation, which is incident on a material or person, is of great interest. For devices that are to be used in space will degrade with the amount of radiation they receive, or in the human context radiation damages the DNA in biological cells. In radiotherapy, it is desirable for thermoluminescence dosimeters (TLD) and optically stimulated luminescence (OSLD) materials to have an effective atomic number (Z_{eff}) near that of human tissue ($Z_{eff} = 7.6$). This means the response to radiation is equivalent to tissue. In personal dosimetry, the doses range from 1 μ Sv to 1 Sv and the uncertainty of the detector material should be less than 4 % for radiotherapy, otherwise the damage of healthy tissue would be too high [6]. Therefore, there is a need for dosimeters to measure the radiation to know if the dose delivered to the devices/ humans is harmful [14]. In the past, there have been many different types of dosimeters developed, for example:

Geiger Müller survey meter: secondary ionisation is caused by ionized radiation which enters the gas filled chamber, or an electron is produced during the interaction of

X-/ γ - ray with the wall material [25]

Ionisation chamber: voltage is set up that incident radiation creates only one electron-hole-pair which creates a pulse, no further generation of electron-hole-pairs

Silicon photo-diode dosimeters: where holes and electrons are produced by irradiation of the material which leads to a current pulse [26]

MOSFET dosimeters: the irradiation creates electrons and holes which are trapped in the SiO₂ which leads to a negative shift in the threshold voltage [26]

Scintillation detectors: scintillation material (crystal, liquid and polymer materials) stops incident radiation and the energy of the particle (e.g. X-ray or γ -ray (photon), α -particle, electron) will be transformed into visible light which will be detected with a photomultiplier tube (PMT) [26]

Thermoluminescence (TL) dosimeters: irradiation induces carriers which are trapped until heating the sample (read-out), this leads to recombination of the trapped charges and the emission of light, with the generation of a 'glow curve'

Optically stimulated Luminescence dosimeters (OSLD): same as TLD, the only difference is that trapped carriers are released via stimulation of the sample with light [26, 27]

Diamond detectors: a narrow strip of diamond is doped, which makes the whole diamond stack act as a diode., a charged particle, which passes through these strips, causes ionisation currents, which are detected and measured

It is also important to look at the typical dose ranges, which are applied in radiation dosimetry (see Tab. 2.1). Tab. 2.2 summarise the impact and symptoms of various doses of radiation on the human body.

Table 2.1: Typical radiation doses applied in dosimetry;

Gy is the unit Gray with $1 \text{ Gy} = 1 \text{ J/kg}$ [14].

Dose	Typical exposure	Typical effect observed
1 - 5 mGy	One year natural background	Minor risk on biological cells
4 Gy		Single exposure is a lethal dose (leading to death after one month in 50% of the cases)
10 - 20 Gy	Dose delivered to a tumour during radiotherapy	Destroys tumour, possibility of destroying healthy tissue
10 - 100 Gy	Annual dose received by a satellite	Damage of electronics
1 MGy	Dose expected in some detectors at CERN	Mechanical properties of materials alter

Table 2.2: Summary of radiation sickness after various doses of radiation (Sievert=Sv=J/kg) [15].

Dose	Effect	Symptoms
1-5 mSv per year		Average exposure of a citizen during one year (e.g. as a result of travel by plane, taking X-rays at the hospital and background radiation)
up to 0.2 Sv		Long-term consequences (cancer or modification of heritable information) could occur if the exposure happens over a long period; the only symptoms are the reduction of the red blood cells

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Table 2.2 – *Continued from previous page*

Dose	Effect	Symptoms
0.5-1 Sv		Radiation sickness with headaches, exhaustion with a high risk of infection
1-2 Sv	Light radiation sickness	10% deaths after 30 days; symptoms during 3-6 hours after irradiation: sickness with vomiting; symptoms are getting less after a short recovery but will come back after 10-14 days: absence of appetite, tiredness, loss of white blood cells and higher risk of infection
2-3 Sv	Median radiation sickness	35% deaths after 30 days: after 1-6 hours after irradiation: first symptoms like sickness with vomiting, short recovery after two days which will last until one or two weeks, after recovery again symptoms like illness tiredness, loss of hair on the whole body, recovery lasts several months; strong loss of white blood cells and very high risk of infection
3-4 Sv	Serious radiation sickness	50% deaths after 30 days: after 1-6 hours after the incident: first symptoms like sickness with vomiting, short recovery after two days but symptoms come back and additionally diarrhoea, bleeding in the mouth, under the skin and in the kidneys; strong loss of white blood cells and very high risk of infection

Continued on next page

Table 2.2 – *Continued from previous page*

Dose	Effect	Symptoms
4-6 Sv	Acute radiation sickness	90% deaths after 30 days: symptoms are in the beginning the same as after the recovery when receiving a dose of 3-4 Sv, only stronger, death usually appears because of bleeding and infection after 2-12 days
6-10 Sv	Acute radiation sickness	100% deaths after 14 days: symptoms occur after 15-30 minutes after the radiation and last usually 2 days, a short recovery of 5-10 days (walking-ghost-phase), after that death due to circulation collapse
20-80 Sv	Acute radiation sickness	100% deaths: symptoms same as 6-10 Sv, rapid death

In the above Tab. 2.2 the unit Sievert is employed, which is also defined as $1 \text{ Sv} = 1 \text{ J/kg}$ same as the unit Gray ($1 \text{ Gy} = 1 \text{ J/kg}$). The difference between these two units is that Gray is utilised to describe a physical quantity. This means it measures amount of energy per mass which is absorbed by an irradiated sample without taking the different types of radiation into account. Different types of radiation have a different effect on the cells even if they transmit the same amount of energy. Therefore, Sievert describes the damage to the cell caused by the different types of radiation. The different factors for the types of radiation are 1 for β -, γ - ray and 5-20 for neutrons, heavy particles and α - ray [28].

The purpose of measuring radiation varies and hence, some of the above named dosimeters are not practical to be employed in certain areas. For example ionisation chambers are the gold standard for medical physicists, but they are affected by climatic conditions (ambient pressure and humidity), or they have a dead time after each event during which the system is not able to record another event [25].

Scintillation detectors have the problem of quenching (optically or chemically quenching). Quenching is an effect where the light output is reduced by re-absorption of the scintillation light by a scintillation ion or by light scattering. These detectors are also affected by Cherenkov radiation, which means when electromagnetic radiation is emitted after a charged particle is passing through a dielectric medium with a speed greater than the phase velocity of light in that material. The charged particles polarise the molecules of the detector material due to rapid return to their ground state and radiation is emitted in the process [25, 26].

Diodes have the disadvantage that the material is not tissue equivalent, and the ambient temperature is important during measurement. The diodes only detect the radiation of the field, which will be used for linear accelerators or imaging plates in the hospital and not the dose.

In TLD and OSLD, the radiation induces carriers, which are trapped until a read out. During this read-out, the carriers are excited out of their traps and emit photons (luminescence) [29]. The emitted light is detected with a photomultiplier tube (PMT) and is a value for the absorbed radiation dose of the crystal [27]. So far, there is only one company which produces a commercial $\text{Al}_2\text{O}_3\text{:C}$ OSL dosimeter (OSLD). This company is Landauer® with their Luxel®+ Dosimeter. The Luxel®+ detects X-, β -, γ - and neutron radiation [30]. Commercial OSL dosimeters are capable of measurements as low as 50 μGy . McKeever also reported they can measure as low as 10 μGy . Both techniques of TL and OSL have advantages and disadvantages - optically stimulated luminescence dosimeters have the biggest advantage of a nearly real time read-out. OSL has been employed for personal dosimetry as well as the determination of environmental radiation doses absorbed by geological materials in order to date them. The OSL technique in personal dosimeters promises high sensitivity, rapid read-out, automation of read-out, good fading characteristics, and the material should have an effective atomic number like that of tissue (that means the material response to radiation is like that of tissue) [31, 32]. A tissue equivalent response to radiation is important, especially if the radiation energy of the X- or γ - rays is

between 20 keV and ~ 100 keV. In this region the photoelectric interaction is predominant (as shown in Fig. 2.1), which is a function of the third power of the atomic number and the linear attenuation coefficient for this region is given by,

$$\mu_p = \rho_e C_P \frac{Z^m}{E^n} \quad (2.1)$$

where components have been determined experimental, $m = 3.8$, $n = 3.2$ [33], ρ is the density of the electrons, C_p is an empirical constant and is 9.8×10^{-24} [34], Z is the atomic number of the detector material and E the energy of the electrons. For detector materials with a higher atomic number than tissue there will be an overresponse in the mass energy absorption coefficient for energies up to 100 keV and the measurements will be dependent of the incident energy of the photon. For materials with a similar atomic number to tissue, the measurements will become independent of the incident energy of the photon (explained in a later chapter). There is still a limitation of employing materials with an overresponse below 100 keV. Even if the average photon energy is above 100 keV secondary electrons with an energy below 100 keV will be produced. In a bremsstrahlung photon beam with a peak energy above 100 keV there are still some photons with a lower energy than 100 keV and this causes an overresponse because the measurements below 100 keV are not independent of the photon energy [35].

Figure 2.1: Graph of the Rayleigh, photoelectric, Compton, pair production, and total mass attenuation coefficient for soft tissue ($Z=7$) as a function of energy [1].

OSL dosimeters constructed of fluoroperovskite compounds as will be explained in this thesis, have the advantage of multiple read-out or the same event [31] as well as the detection of the absorbed dose and the dose rate of an event. In general, the detectors can be produced in a smaller size compared to the ion chambers, which are mainly utilised at the hospital these days. With these materials, it is possible to shift the emission to high wavelengths and therefore Cherenkov radiation is not an issue anymore. Furthermore, large area detectors can be produced to "image" the radiation field [27]. OSL dosimeters can also be combined with radioluminescence dosimeters (RLD) [23, 24, 36]. The bulk materials which are observed in this thesis show OSL [3] and RL [10, 11, 12]. RLD have the advantage for real-time read-out, which means the absorbed dose in the material can be measured as a function of the intensity of the emitted light. This application is important for dosimeters employed for patients in a hospital, i.e.. The medical physicist is able to immediately stop a treatment if there is an over or under dose.

2.1 Radiometric quantities

To describe a radiation field, which includes all types of radiations, one can utilise the particle fluence, Φ , which is the quotient of the number of the particles δN incident on cross-sectional area δa ,

$$\Phi = \frac{\delta N}{\delta a} \quad (\text{unit m}^{-2}) \quad (2.2)$$

With the corresponding fluence rate of particles, ϕ ,

$$\phi = \frac{\delta^2 N}{\delta a \delta t} \quad (\text{unit m}^{-2}\text{s}^{-1}) \quad (2.3)$$

The same applies for the energy fluence, Ψ , and energy fluence rate, ψ ,

$$\Psi = \frac{\delta R}{\delta a} \quad (\text{unit Jm}^{-2}) \quad (2.4)$$

With δR being the radiant energy emitted, transferred or received on a cross-sectional area δa [3, 37].

$$\psi = \frac{\delta^2 R}{\delta a \delta t} \quad (\text{unit Wm}^{-2}) \quad (2.5)$$

2.2 Interaction of radiation with matter and their energy dependence

2.2.1 Interaction of radiation with matter

The interaction of charged and uncharged particles are determined by measuring the cross section σ , which is usually characterised in the unit barn ($1 \text{ b} = 10^{-24} \text{ cm}^2 = 10^{-28} \text{ m}^2$). The sum of all the cross sections σ_J of each particle J multiplied with the quotient of the Avogadro constant N_A and the molecular mass M of the target material is equal to the quotient between the linear attenuation coefficient μ and the density of the absorbing material ρ [38].

$$\frac{dN}{dl} = N\mu \quad (2.6)$$

$$\frac{\mu}{\rho} = \frac{1}{\rho dl} \frac{dN}{N} = \frac{N_A}{M} \sum_J \sigma_J \quad (\text{unit m}^2\text{kg}^{-1}) \quad (2.7)$$

dN/N is the number of particles, which interact with other particles during their transit with a distance dl . In the following equation 2.9, the mass energy transfer coefficient is shown. $\delta R_{tr}/R$ is the amount of incident energy that is transferred as kinetic energy by the charged particles during interaction in the distance dl . The kinetic energy is converted from the radiation energy of these particles. μ_{tr}/ρ includes the energy loss caused by radiative processes.

$$\frac{dR_{tr}}{dl} = \mu_{tr} R_{tr} \quad (2.8)$$

$$\frac{\mu_{tr}}{\rho} = \frac{1}{\rho \delta l} \frac{\delta R_{tr}}{R} \quad (\text{unit m}^2\text{kg}^{-1}) \quad (2.9)$$

The mass energy absorption coefficient is more a quantity for dosimetric calculations. The linear attenuation coefficient μ/ρ describes the total energy, which is absorbed by the material. The mass energy transfer coefficient μ_{tr}/ρ presents a value of the radiation caused from secondary electrons, and describes the biological damage caused in the material.

$$\frac{\mu_{en}}{\rho} = \frac{\mu_{tr}}{\rho} (1 - g) \quad (\text{unit m}^2\text{kg}^{-1}) \quad (2.10)$$

In this equation 2.10, g represents the energy loss during the radiative process. Equation 2.10 changes for compounds as a fact of the independence of the components.

$$\left(\frac{\mu_{en}}{\rho}\right)_{\text{compound}} = \sum_i w_i \left(\frac{\mu_{en}}{\rho}\right)_i \quad (2.11)$$

The corresponding mass energy absorption cross section σ_{en} is,

$$(\sigma_{en})_{\text{compound}} = \frac{(\mu_{en}/\rho)_{\text{compound}}}{N_A \sum_i w_i/A_i} \quad (2.12)$$

with,

$$w_i = \frac{A_i}{\sum_j A_j} \quad (2.13)$$

as the fraction of the abundance by weight and A_i the atomic weight of the i^{th} component (equation 2.12). For charged particles, the *mass stopping power* is expressed by following equation 2.14,

$$\frac{S}{\rho} = \frac{1}{\rho} \frac{\delta E}{\delta l} \quad (\text{unit Jm}^2\text{kg}^{-1} \text{ or eVm}^2\text{kg}^{-1}) \quad (2.14)$$

which describes the energy loss δE of a charged particle during a distance δl [3].

The restricted linear collision stopping power defines the energy loss (dE_Δ) of a charged particle during soft and hard collision along a distance dl minus the total kinetic energy of charged particles that are released with an excess kinetic energy of the value Δ .

$$L_\Delta = \frac{dE_\Delta}{dl} \quad (\text{unit } \text{Jm}^{-1} = \text{eVm}^{-1}) \quad (2.15)$$

By dividing L_Δ by the density of the material, the restricted mass collision stopping power is defined. The sum of the collision mass stopping power and the radiative mass stopping power is the total mass stopping power. In Fig. 2.2, the total unrestricted and restricted electron mass stopping power of carbon is shown [2].

Figure 2.2: Unrestricted S/ρ and restricted $((L/\rho)_\Delta$ with $\Delta = 10$ and 100 keV) total mass stopping powers for carbon ($\rho = 1.70 \text{ g/cm}^3$). Vertical lines indicate the points at which restricted and unrestricted mass stopping powers begin to diverge as the kinetic energy increases [2].

2.2.2 Energy dependence of a radiative process

For personal dosimetry or radiotherapy, it is essential that the materials show tissue equivalence. Therefore, the main focus in today's research is to find materials, which have the

same absorption cross-section as human tissue has. This chapter will focus on the considerations, which have to be taken into account for the design of a detector or a dosimeter with these properties. In Fig. 2.3, the mass energy absorption coefficient for tissue and common detector materials are illustrated.

Figure 2.3: Mass energy absorption coefficients for detector materials.

The photons usually have energies in the range between several hundred eV (soft X-rays) to several MeV (hard X-rays) and can be up to 20 MeV for photon radiotherapy. Radiation defects are usually calculated by the mass-energy-absorption, which was expressed in equation 2.10. In tissue, the photoelectric contribution is large at lower energies and at these energies the photon energy becomes dependent on $\sim Z^4/E^3$. This effect is dependent on the atomic number of the material and therefore, the cross over energy from the photoelectric to the Compton contribution increases with increasing Z . The probability for the Compton effect is independent of the atomic number of the material; it is only an interaction with the electrons of the absorber. The energy of the emitted photon is dependent on the angle of the emission and on the incident photon energy. The energy dependence ED for a dosimeter material to the photon energy E is shown in the following equation 2.16 in the large detector limit, which means equation 2.16 is not valid for finite

sized detectors, which is explained in the Burlin cavity theory (as explained later in this chapter) [1, 2, 39].

$$ED = \frac{(\mu_{en}(E)/\rho)_{detector}}{(\mu_{en}(E)/\rho)_{reference}} / \frac{(\mu_{en}(E_0)/\rho)_{detector}}{(\mu_{en}(E_0)/\rho)_{reference}} \quad (2.16)$$

Furthermore, it is assumed that the energies are low enough so that thermal neutron production can be ignored (below ~ 10 MeV). The mass energy absorption coefficient of the detector and the reference material are given by $(\mu_{en}/\rho)_{detector}$ and $(\mu_{en}/\rho)_{reference}$, respectively, and E_0 is the photon energy of a reference radiation. ED values are shown in Fig. 2.4 for some detector materials.

Figure 2.4: Energy response of detector materials compared to tissue.

With s_d and s_m expressing the mass collision stopping powers of the detector and the medium, respectively. The quotient of the absorbed dose in the detector and the surrounding medium is [40],

$$\frac{D_d}{D_m} = f = d \frac{\bar{s}_d}{s_m} + (1 - d) \frac{(\mu_{en}/\rho)_d}{(\mu_{en}/\rho)_m} \quad (2.17)$$

d is expressed in the following equation 2.18. d is also related to the size of the cavity and it becomes zero for large cavities and approaches unity for small ones. As a result of this, equation 2.17 must be considered for energies above ~ 1 MeV as the cavity behaves as an

intermediate cavity, and the Burlin cavity theory needs to be applied and small cavity size is only obtained for energies above 20 MeV (see also Fig. 2.5) [1],

$$d = \frac{1 - e^{-\beta g}}{\beta g} \quad (2.18)$$

with β the effective mass attenuation coefficient for electrons and g the average path length. For a small sized cavity, as explained in the Bragg-Gray cavity theory, the quotient of the average absorbed dose in the cavity and the absorbed dose in the medium around the scintillator (without the scintillator) is equal to the quotient of the average mass collision stopping powers of the cavity and the medium. For large cavities, the quotient of the doses is equal to the quotient of the average mass-energy-absorption coefficients of the cavity and the medium. In the latter case, it is assumed that charged particles are completely generated by photon interactions in the cavity and the energy of the particles is absorbed in the cavity. Burlin explains the gap between these two other theories [1].

Figure 2.5: Burlin cavity theory parameter d as a function of photon energy for two cylindrical plastic scintillator sizes. This parameter represents the fraction of the dose deposited in the cavity due to electrons generated outside the cavity [1].

The energy response is then expressed by equation 2.19.

$$ED = \frac{D_d(E)}{D_m(E)} / \frac{D_d(E_0)}{D_m(E_0)} \quad (2.19)$$

Important for this work is the energy dependence of the fluoroperovskites, especially RbMgF_3 and NaMgF_3 , which will be mainly investigated [3].

2.2.3 Effective atomic number

The mass energy absorption cross section defines the interactions caused by the radiation. For photon energies below 1 MeV, the photoelectric effect is dependent on the effective atomic number of the material. The effective atomic number calculates the average atomic number of a compound. Hence, the effective atomic number is equivalent to the atomic number Z of an element, which has the same cross section as the compound. In cases for photon energies below 1 MeV, the energy response of a compound with one number is employed to describe the cross section rather than using the whole ED curve. Therefore, a low energy approximation to the photoelectric cross section for the effective atomic number is presented by the following equation [41],:

$$Z_{effEMP} = \sqrt[3]{\frac{\sum n_i Z_i^4}{\sum n_i Z_i}} \quad (2.20)$$

with n_i as the molar fraction and Z_i the atomic number of the i^{th} component. If the material has a high atomic number the value will be overestimated. Tissue has a value of 7.62 calculated with the equation described above [3]. A material is considered to be useful for medical applications with a $Z_{eff} < 14$. The effective atomic numbers of some of our materials are given below:

$$Z_{eff} = 10.8 \text{ for } \text{NaMgF}_3:\text{Mn}^{2+}$$

$$Z_{eff} = 13.6 \text{ for } \text{NaMgF}_3:\text{Eu}^{2+}$$

$$Z_{eff} = 31.3 \text{ for } \text{RbMgF}_3:\text{Mn}^{2+}$$

$$Z_{eff} = 31.7 \text{ for } \text{RbMgF}_3:\text{Eu}^{2+}$$

2.2.4 Radiation protection dosimetry

To determine the effect of absorbed radiation on a biological cell, the quality factor Q has been introduced. The quantity factor considers the different types of radiation. The product of the quality factor Q and the absorbed dose D is the dose equivalent H [37, 42].

$$H = QD \quad (\text{unit Jkg}^{-1}) \quad (2.21)$$

The dependence of the quality factor Q on the linear energy transfer L in water has been specified by the ICRP.

$$Q(L) = \begin{cases} 1 & \text{for } L \leq 10, \\ 0.32L - 2.2 & \text{for } 10 < L < 100, \\ 300/\sqrt{L} & \text{for } L \geq 100. \end{cases} \quad (2.22)$$

L has the unit keV/ μm [37, 42].

2.3 Dosimetric quantities

Kerma means kinetic energy relaxed per unit mass and describes the sum of the kinetic energy (dE_{tr}) of charged particles, which is transferred to uncharged particles in a mass dm [3, 37, 43].

$$K = \frac{dE_{tr}}{dm} = \int \Phi_E E \frac{\mu_{tr}}{\rho} dE \quad (\text{unit Gy}=\text{Jkg}^{-1}) \quad (2.23)$$

Where $\Phi_E = d\Phi/dE$ is a given particle fluence energy distribution and Gy is the unit Gray with,

$$1 \text{ Gy} = 1 \frac{\text{J}}{\text{kg}} = 100 \text{ rad}. \quad (2.24)$$

The corresponding kerma rate is,

$$\dot{K} = \frac{dK}{dt} \quad (\text{unit Gys}^{-1}=\text{Wkg}^{-1}) \quad (2.25)$$

The absorbed dose D is the quotient of the mean energy imparted $d\bar{\epsilon}$ to a mass dm .

$$D = \frac{\bar{\epsilon}}{dm} \quad (\text{unit Gy}=\text{Jkg}^{-1}) \quad (2.26)$$

With the corresponding dose rate,

$$\dot{D} = \frac{dD}{dt} \quad (\text{unit Gys}^{-1}=\text{Wkg}^{-1}) \quad (2.27)$$

Kerma and the absorbed dose have the same units but kerma is a microscopic quantity, which describes the radiation field, and the absorbed dose is a macroscopic quantity [3, 37, 43].

2.4 Fields of dosimetry

2.4.1 Personal dosimetry

The aim of implementing personal dosimeters is to monitor the radiation for employees exposed to radiation, i.e. in radiology, at nuclear power plants, radiation therapy or teaching facilities like universities. As mentioned in the introduction section, it is important that the dosimeter has a nearly tissue equivalent energy dependence. Therefore, the TL dosimeters (TLD) are to be employed in this field, but also film badge, scintillators, OSLD, or diodes for real-time measurements [6].

To monitor the penetration of radiation of an area, the ambient dose equivalent $H^*(d)$, with $d = 10$ mm, is utilised. In this case, $H^*(d)$ is also written as $H^*(10)$ and the value should be independent of the directional distribution of the dosimeter [44, 45]. For monitoring a low-penetration of radiation, the directional dose equivalent $H'(d, \Omega)$, with $d = 0.07$ mm or $d = 3$ mm, is utilised. The directional dose equivalent is the dose which is to be measured in an actual radiation field with Ω as the specific direction of the field at a depth d . $H'(3, \Omega)$ is to be chosen when monitoring the radiation to the eye lens, but in almost all cases $H'(0.07, \Omega)$ is employed for monitoring low- penetration of radiation [44, 45].

$H_p(d)$ is the personal dose equivalent, which considers the dose equivalent in tissue at a depth d in a human body where the actual personal dosimeter should be worn. In this case, $H_p(0.07)$ and $H_p(10)$ are defined as the skin dose at a depth of $d = 0.07$ mm and the effective dose at $d = 10$ mm in the body, respectively. However, they are to be measured by the dosimeter wearing on the body. $H_p(3)$ is employed in rare cases as the dose to the lens of an eye at a depth of $d = 3$ mm. These values are defined for all types of radiation, and also include the backscattering of the body [44, 45].

2.4.2 Medical dosimetry

Radiation is utilised in two main areas in medicine: One is radiation imaging (i.e. computed tomography (CT), projection radiography, mammography) and the other is radiotherapy (i.e. external beam radiotherapy, brachytherapy and systemic radioisotope therapy). For over 120 years, radiation imaging has been employed to examine the whole body or parts of it for clinical diagnostics. These imaging processes have since been improved and the doses have been optimised to reduce the harm of radiation to biological cells. In radiation therapy, the property of ionising radiation to damage human tissue cells is utilised to treat cancer. Compared to medical imaging a higher dose is exposed to the body during radiation therapy. This implies different requirements for dosimeters between these regimes.

Medical imaging

There are several methods for medical imaging including X-ray examinations, fluoroscopy, CT and mammography. The dose exposed to the body is measured in mSv and various doses are employed within the different methods [46, 47, 48].

X-ray examination or projection radiography is a technique where X-rays are transmitted through the body and then are captured in a plate of sensors to produce an image. On the other hand, fluoroscopy is a method to produce real-time images during a procedure.

Therefore, it needs a constant input of X-rays and works with contrast media to visualise the organs as they work [15, 16, 17].

CT or X-ray computed tomography is employed to create a 3D image of the body. 3D data of the patient anatomy is produced via reconstruction of many beamlets or rays (2D slides) [15, 16, 17].

Mammography is usually utilised for breast screening to detect breast cancer. The mechanism is similar to X-ray examination but it uses lower doses than CT [15, 16, 17].

In Tab. 2.3, the different methods of radiation imaging with their various scan doses are listed.

Table 2.3: Typically effective doses applied during medical examination [15, 16, 17].

Type of examination	Typically effective dose (mSv)
Intraoral X-ray (dental)	0.005
Chest X-ray	0.1
Mammography	0.4
Head CT	1.5
Chest CT (low dose)	1.5
Screening mammography	3
Abdomen CT	5.3
Chest CT	7
Chest, abdomen and pelvis CT	9.9
CT-abdomen and pelvis	15
Coronary CT angiography (CTA-heart)	16
Fluoroscopy	0.9

The natural background radiation to a person is around 1-5 mSv per year.

To measure the dose received to the patient, measurements are usually performed free-in-air, on phantoms or directly on the patients with TL dosimeters. To protect the patient from the harm from the radiation during this diagnostic process, there is a demand for tissue equivalent dosimeters, which measure the absorbed dose to the patient in real time [3].

Radiation therapy

Radiation therapy is a very complex area and medical physicists in the hospital need special education and extensive experience before becoming a certified medical physicist. In general, there are three different methods of radiation therapy, which will be briefly explained in the following section.

External beam radiotherapy employs a linear accelerator to produce 2D cross section beams. By control of couch, collimator, and gantry angles, the patient can be irradiated from any given angle. Dosimeters are needed for dose verification and validation to check in vivo dose to the patient or the treatment plan prior to radiation. Currently, diodes and TL, OSL dosimeters are utilised in this area.

Another way to treat the cancer is to place radiation source(s) proximal to the tumour, which is applied in brachytherapy. For this, the source(s) may be applied as a permanent implant, or delivered from an afterloader for a temporary exposure. This means, there can be a higher radiation dose applied to the cancer cells while healthy tissue remains minimally affected [15, 16, 17].

For some techniques, the cancer is targeted via a radioactive isotope that is ingested or infused to the bloodstream [15, 16, 17]. The dose applied to cancer during radiation therapy also depends on the type and stage of the cancer. Tab. 2.4 shows some typical doses applied in photon radiation therapy [15, 16, 17].

Table 2.4: Types of cancer treatment with typically applied doses (in Gy) [15, 16, 17].

Type of treatment	Applied dose (Gy)
Curative	60-80
Lymphomas (curative)	20-40
Preventive (adjuvant)	45-60

The dose to treat the cancer is fractionated. This means, the total dose is not applied all at once. Healthy tissue exhibits better repair mechanisms, so fractionation allows the healthy cells time to recover while the more radiosensitive tumour cells does not. The dose applied to the cancer also depends on the specific radiosensitivity of the cancer. For example, leukaemia, most lymphomas or germ cell tumours are highly radiosensitive when a lower dose is applied. Most of the epithelial cancers are more radiosensitive, and usually a dose up to 60-70 Gy is applied. Radiosensitive are renal cells cancer and melanoma [15, 16, 17].

Currently, the absorbed dose is calculated before the treatment and any required measurements are carried out on a phantom. For complex techniques, medical physicists are interested in measuring the dose received by the patient in real time as well as new methods for dose verification and validation. Time-resolved measurements can better indicate where delivery issues exist. Measurement methods, which have been employed so far involve are semiconductor dosimeters, TLD and OSL dosimeters [49, 50, 51]. Most of the detectors do not demonstrate tissue equivalence nor provide ideal spatial resolution (e.g. ionisation chambers) for the new treatment regimes. TLD does not provide real time dose information but as they are non-invasive, they are widely used. Therefore, there is a need for small, tissue-equivalent detectors to measure the actual absorbed dose on the patient in real time. Currently, plastic scintillators are the only commercial provided OSL dosimeter is used to measure the actual dose received by the patient [3, 52].

2.4.3 Environmental dosimetry

Environmental radiation means, the radiation a person is receiving through cosmic radiation, terrestrial radiation (natural radionuclide in the earth crust) and radiation from man-made radiation (medical treatments, radiation sources being moved, nuclear power plants, coal-fired power plants and nuclear weapons testing i.e.). Therefore, environmental dosimetry measures the exposure of radiation by nuclear and radiological facilities to the environment. A high sensitivity for dosimeters is required (monthly radiation levels around 40-80 μGy), as well as robustness and insensitivity to extreme environmental conditions (humidity, temperature, mechanical stress). TL dosimeters are mostly to be employed in this area of application [53, 54, 55].

2.4.4 Retrospective dosimetry

Retrospective dosimetry monitors radiation caused by human factors e.g. by nuclear power plant accidents. A sample of an inorganic material is collected and measured with TL, OSL dosimeters or ESR (electron spin resonance) [56]. The same techniques are utilised for geological or archaeologically dating. Requirements for the detector should be an equal effective atomic number as the investigated material. As mentioned in the previous section, the measured doses are quite low and therefore a high sensitivity is needed [56].

3 Theoretical Background

This chapter outlines a theoretical overview of the materials to be investigated, explains the principles of the techniques and equipment employed to measure the properties of the samples.

3.1 Fluoroperovskite

Fluoroperovskites are part of the group of the perovskites. A perovskite structure is any material with the same type of crystal structure as calcium titanium oxide (CaTiO_3). The fluoroperovskites have the structure ABF_3 , where A is a cation, B a metal (in this case Mg) and F is the chemical symbol of fluorine. These structures have been recently of great interest for their range of electronic, magnetic and optical properties. The crystal structure of the fluoroperovskites would be ideally cubic. However, due to the small size of the cation the structure changes and produces a lower symmetry. The undistorted structure of the perovskite is cubic ($=1$). The degree of distortion of the cubic structure can be estimated from the tolerance factor t by Goldschmidt [57],

$$t = \frac{r_A + r_F}{\sqrt{2}(r_B + r_F)} \quad (3.1)$$

where r_A is the radius of the cation, r_F the radius of fluorine and r_B the radius of the metal. From $0.76 \leq t \leq 0.88$ the structure of the crystal will be orthorhombic, like GdFeO_3 , and $0.89 \leq t \leq 1.02$ cubic structures are expected, like BaTiO_3 , and >1 hexagonal structures

are expected, like BaNiO_3 [57]. NaMgF_3 has a Goldschmidt factor of 0.83 and the structure is orthorhombic with the space group of P_{bnm} . In this case, Eu substitutes for Na^+ and Mn^{2+} for Mg^{2+} . For RbMgF_3 the Goldschmidt factor is 1.02 and the structure is therefore hexagonal with a space group of $P_{63/mmc}$. Eu substitutes for Rb^+ and Mn^{2+} for Mg^{2+} , see Fig. 3.1.

Figure 3.1: (a) Orthorhombic structure of NaMgF_3 and
(b) Hexagonal structure of RbMgF_3 [3].

3.2 Photoluminescence

The excitation of an electron to a higher energy state due to the absorption of a photon of a certain energy and the decay to a lower energy state while emitting a photon is called photoluminescence (PL). The wavelength of the emitted photon and the wavelength of the photon to excite the material are collected and from this information the structure of the material will be obtained.

In this thesis, spectra of rare earth (RE) ions within the host crystal will be observed. No PL was detected from undoped samples. RE show the presence of deep 4f shell, which is not completely filled and electrons in this shell are shielded by electrons in an outer shell.

Hence, their emission will result in a sharp line spectra. There is a difference between the emission of a free RE and RE in solids, because the transition takes place within the 4f shell in the crystal. Therefore, the absorption and emission takes place between different levels, and this results in a shift in the spectral position compared to the free RE ions. This shift is called "Stokes Shift", which is illustrated in Fig. 3.2 in a configuration coordinate diagram. In Fig. 3.2, E is the energy of the levels and Q is the configuration coordinate.

In the process of PL, an absorption of a photon takes place and an electron gets excited from a ground state to a higher excited state. This excitation is too fast and hence the lattice does not have time to relax. Therefore, multi phonon emissions take place and the electron moves into a lower excited state while losing energy to the lattice. The electron emits a photon while going back to the ground and this photon has less energy as the absorbed photon ("Stokes Shift") [18].

Figure 3.2: Photoluminescence process.

Electric dipole transitions within a 4f shell are forbidden in a free ion because the parity does not change within the shell, but they are allowed for magnetic dipole transitions. Therefore, it is expected that only magnetic dipole transitions will occur. However, for an ion in a crystal there can be a mixture of the $4f^n$ states with opposite parity states of

the $4f^n-5d$ configuration due to an odd-parity crystal field. The magnetic dipole process is five orders of magnitude smaller than the electric dipole one for a free ion. This means, in a crystal even a small amount of this crystal field mixing can result in the majority of the intensity arising from this "forced" or "induced" electric dipole transition. Transitions within the $4f$ shell can also become allowed through mechanism such as the coupling of $4f$ electrons with transient dipoles, which are induced in the ligands by the radiation field, leading to an increase in intensity of even parity transitions. These transitions are called "hypersensitive" transitions because they show large variations in oscillator strengths depending on the surrounding environment. These transition are discussed in more detail by Grller-Walrand and Binnemans, but are also known as "pseudo-quadrupole" transitions because the relevant selection rules follow those of true quadrupole transitions [58]. Selection rules for all these processes are listed in Tab. 3.1 and are assumptions for the Judd-Ofelt theory summarised by Walsh e.g. [18, 19, 20].

Table 3.1: Selection rules for the forced electric dipole process, magnetic dipole process and pseudo electric quadrupole transition [18, 19, 20].

Process	S	L	J (No $0 \leftrightarrow 0$)	Parity
Forced electric dipole	$\Delta S = 0$	$\Delta L \leq 6$	$\Delta J \leq 6$, if $\Delta J=2,4,6$ (J or $J' = 0$)	opposite
Magnetic dipole	$\Delta S = 0$	$\Delta L = 0$	$\Delta J = 0, \pm 1$ ($0-0$ forbidden)	same
Pseudo electric quadrupole	$\Delta S = 0$	$\Delta L = 0, \pm 1, \pm 2$	$\Delta J = \pm 1, \pm 2$	opposite

3.2.1 Photoluminescence of Eu^{2+} in fluoroperovskites

Europium has an atomic number of 63 and its electron configuration is $6s^2 4f^7$, which means the f shell is only half filled and the electrons in the ground state have all the same

spin. The optical absorption of Europium depends on the host in the crystal. The ground state of Europium²⁺ with the electron configuration $[Xe] 4f^7$ is $^8S_{7/2}$ and this state is lifted into two excited states $4f^6 5d (T_{2g})$ and $4f^6 5d (E_g)$ due to the crystal field. The $4f^6 5d (T_{2g})$ level is significantly lower than the $4f^7 ({}^6P_{7/2})$, which leads to a broad d-f electron absorption and emission (several 1000 cm⁻¹), which was reported for Eu²⁺ in KMgF₃ and RbMgF₃ by J. Garcia et al. [59].

The detection of only one broad band leads to the suggestion that the splitting of the crystal field, 10 Dq, of the compound is small. But since the splitting still exists, the $4f^6 5d (E_g)$ level is above the $4f^7 ({}^6P_{7/2})$. This is proved by a sharp line emission from the 4f-4f transition. The 4f-4f transition is spin and parity forbidden in the electric dipole approximation. They can occur via state mixing, magnetic dipole, electric quadrupole, etc.. They take place at a lower rate and therefore these transitions have a longer lifetime than the 5d-4f transition, which are allowed transitions. The 5d-4f transition is allowed, and hence has a shorter lifetime. The coordination number of the Eu²⁺ ion in the compounds KMgF₃ and RbMgF₃, for example, is 12 as it is found on the Rb⁺ and K⁺ site because it is too large for the Mg²⁺ - ion [59]. Fig. 3.3 shows the configuration coordinate diagram for RbMgF₃:Eu²⁺ and the splitting of the different levels by the crystal field.

Figure 3.3: Configuration coordinate diagram of Eu^{2+} in RbMgF_3 [4].

3.2.2 Photoluminescence of Mn^{2+} in fluoroperovskites

Manganese is on the 25th place in the periodic table of elements and has an electronic configuration of $4s^2 3d^5$, which means the d shell is only half filled and the electrons in the ground state form the spin sextet 6S . The excited d states have lower spin multiplicity, which means the corresponding transitions are spin and parity forbidden in the electric dipole approximation, but maybe partly allowed due to mixing of electron states and phonon modes with opposite symmetries as explained in the previous section.

A calculation of the energy levels for this electron configuration has been made by Tanabe and Sugano for the Mn^{2+} in octahedral coordination (O_h symmetry). This means in an octahedral complex 6 ligands surround a metal centre with a single pair on each axis. In this calculation, it has also been considered that the d electron states (quartet states: 4F , 4D , 4P , 4G) are split by the crystal field when excited. This means, several optical

transitions can be seen. These four quartet states can be seen on the left hand side of the Tanabe-Sugano diagrams. On the right hand side in the diagram, the different levels can be seen for a crystal field $10Dq \neq 0$ (10 Dq is the splitting energy of the crystal field and is positive for octahedral coordination and negative for tetrahedral and cubic coordination) and the ground state as the x -axis. The right axis in the Tanabe-Sugano diagram shows the symmetry properties, and the letters in the brackets lead to the energy level outside the crystal field. The superscripts are calculated by $2S+1$ where S is the total spin number of the crystal and the capital letters in the states (6S , 4F , 4D , 4P , 4G) are the total orbital angular momentum L . The levels have a degeneracy of $2L+1$, which can be lifted by the crystal field. In Fig. 3.4 the Tanabe-Sugano diagram of Mn^{2+} is shown [3, 57].

Figure 3.4: Energy levels of Mn^{2+} in a crystal field 10 Dq [3].

3.2.3 Judd-Ofelt theory

The Judd-Ofelt theory presents information on the local environment characteristics around a trivalent rare-earth ion and describes the transition intensities of these in a solid [20, 60]. The absorption spectra of the rare earth ions will be normally employed for calculation of the Judd-Ofelt parameters, but for Eu^{3+} , which mainly will be investigated in this thesis, the corrected PL emission spectra can be employed. The reason for this is the nature of the Eu^{3+} transitions. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is a magnetic dipole transition where the oscillator strength is not influenced by the crystalline environment. This means, this transition can be utilised to compare the different spectra and calculate the Judd-Ofelt parameters from it [22]. This transition rate can be calculated with [61, 62, 63],

$$A_{0-1} = \frac{64\pi^2\nu^3}{3h(2J+1)}n^3S_{md} = 0.31 \times 10^{-11}n^3\nu_{0-1}^3 \quad (3.2)$$

with h as the Planck's constant, ν_{0-1} as the transition energy in cm^{-1} , n the effective refractive index with $n = 1.364$ for NaMgF_3 and $n = 1.419$ for RbMgF_3 and S_{md} the magnetic line strength which is independent of the host. The other transitions are electric dipoles where the oscillator strength depends on the crystal field. These transition rates can be estimated from [63, 64],

$$A_{0-J} = A_{0-1} \frac{I_{0-J}\nu_{0-1}}{I_{0-1}\nu_{0-J}} \quad (3.3)$$

with ν_{0-J} as the relative transition energies in cm^{-1} and I_{0-J} the integrated emission intensities of the corrected PL spectra. Therefore, for Eu^{3+} the Judd-Ofelt parameters Ω_2 and Ω_4 can be calculated from the 0-J transition rates [10, 22, 65, 66],

$$A_{0-J} = \frac{100 \times 64\pi^4\nu^3e^2}{3h \times 4\pi\epsilon_0} \frac{1}{2J+1} \chi \Omega_J \langle {}^5D_0 || U^{(J)} || {}^7F_J \rangle^2 \quad (3.4)$$

where ν is the transition energy in cm^{-1} , ϵ_0 the permittivity of free space, h the Planck's constant, e the electron charge and χ can be calculated by,

$$\chi = n((n^2 + 2)/3)^2. \quad (3.5)$$

The reduced squared matrix elements are given by $\langle {}^5D_0 || U^{(J)} || {}^7F_J \rangle^2$, which were calculated for LaF₃ but they can be employed for different systems because they are nearly independent of the crystalline environment [10, 20, 22, 66].

$$\langle {}^5D_0 || U^{(2)} || {}^7F_2 \rangle^2 = 0.0032$$

$$\langle {}^5D_0 || U^{(4)} || {}^7F_4 \rangle^2 = 0.0023.$$

Ω_2 and Ω_4 are connected with short and long range effects, respectively. Ω_2 should increase with a decreasing site symmetry, an increasing coordination number and a decreasing bond length [22].

3.2.4 Photoluminescence lifetime measurements

The average PL lifetime can be calculated from the PL decay curve, which can be fitted with multiple exponential components. The reason for fitting the PL with multi exponential fits is that the lifetime consists of a distribution of lifetimes and they can be averaged to one lifetime. The ideal case would be a single exponential fit, which shows that there exist only one lifetime of the ions. The average lifetime was then calculated using [67],

$$\tau_{ave} = \left[\int t I(t) dt / \int I(t) dt \right]. \quad (3.6)$$

where the time t is multiplied with the individual t-dependent term, $I(t)$, divided by the total t-dependence term. The radiative lifetime can be calculated as [68],

$$\tau_{rad} = \frac{1}{\sum_J A_{0-J}} \quad (3.7)$$

where A_{0-J} are the 0-J transitions rates calculated with the Judd-Ofelt theory in the previous section.

The quantum efficiency is defined as the probability of a photon being emitted to the probability of a photon being absorbed. This can be calculated from the ratio of the

measured average lifetime divided by the radiative lifetime. Hence, the quantum efficiency for the Eu^{3+} ion can be written as [69],

$$\eta = \frac{\tau_{ave}}{\tau_{rad}}. \quad (3.8)$$

3.3 Thermoluminescence

As already mentioned in the introduction of this thesis, thermoluminescence (TL) is a phenomena where irradiation induces carriers which will be trapped until heating the sample (read-out). This leads to recombination of the trapped charges and consequent emission of light, with the generation of a "glow curve". TL provides additional information of the trapping centres via the fitting of the glow curve and calculating the activation energy of the traps by first order kinetics deconvolution, as performed in this thesis.

The material is in equilibrium before applying ionised radiation. In the crystal, there exist trapping states for the electrons with concentration N and holes with concentration M . Incoming X-rays create mobile holes in the valence band with a concentration of $m_v(\text{cm}^{-3})$ and electrons in the conduction band with a concentration of $n_c(\text{cm}^{-3})$. Electrons get trapped with the probability coefficient A_n . After a thermal stimulation of these trapped electrons, some electrons might fall directly back to the trapping states and some electrons will recombine with the trapped holes with the recombination probability A_m . To get the information about the total absorbed dose by the material, thermally stimulation will be applied. By measuring the intensity of the emitted light, the received dose can be estimated. The release of energy can be via an electron-hole recombination which is illustrated in Fig. 3.5.

Figure 3.5: One-trap/ one- centre model for the TL process [5].

Furthermore, the probability of releasing a trapped charge and overcome the barrier E is presented by the Arrhenius equation:

$$p(T) = s(T)e^{-\frac{E}{kT}} \quad (3.9)$$

with k the Boltzmann's constant and $s(T)$ a frequency factor which is related to the local lattice vibrational frequency and the entropy change cause by charge release. With increasing temperature, the particle can overcome the barrier E and the particle can move into n_c . If this recombination is radiative, it is called thermoluminescence [5]. p varies over time when increasing the temperature during a TL read-out with a constant heating rate $\beta = dT/dt$. The detected TL is the so-called glow curve, which is a plot of the luminescence intensity over the temperature. A one trap model with finite re-trapping probability and one recombination centre can be modelled by the following rate equations,

$$\frac{dm}{dt} = -A_m m n_c \quad (3.10)$$

$$\frac{dn}{dt} = -n s e^{-\frac{E}{kT}} + A_n (N - n) n_c \quad (3.11)$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt} \quad (3.12)$$

with the assumption $\frac{dn_c}{dt} \ll \frac{dm}{dt}, \frac{dn}{dt}$ and,:

$$I_{TL} = -\frac{dm}{dt} \quad (3.13)$$

dn/dt can be written as,

$$\frac{dn}{dt} = -nse^{-\frac{E}{kT}} + A_n(N-n)n_c = -A_mmn_c \quad (3.14)$$

$$n_c(A_m m + A_n(N-n)) = nse^{-\frac{E}{kT}} \quad (3.15)$$

$$n_c = \frac{nse^{-\frac{E}{kT}}}{A_m m + A_n(N-n)} \quad (3.16)$$

Eliminating n_c leads to,

$$\frac{dn}{dt} = -nse^{-\frac{E}{kT}} \left(1 - \frac{A_n(N-n)}{A_m m + A_n(N-n)} \right) \quad (3.17)$$

In this thesis, the activation energies and TL peaks were calculated via first order kinetics deconvolution which is described by the Randall and Wilkins expression, and assumes that re-trapping is negligible, $mA_m \gg (N-n)A_n$ then equation 3.17 becomes,

$$\frac{dn}{dt} = -nse^{-\frac{E}{kT}} \quad (3.18)$$

and using $T(t)=T_0+\beta t$, dn/dt can be integrated to,

$$I_{TL} = n_o s \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{s}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right] \quad (3.19)$$

where n_o is the concentration at T_o , β is the heating rate and T' is a variable representing the temperature [5]. The first term in equation 3.19 represents what is happening during the stimulation and the second term describes the energy loss.

3.4 Radioluminescence

Radioluminescence (RL) has recently attracted considerable interest, because it can be employed to determine the real-time radiation dose rate for radiation protection, non-destructive testing, and in medicine for monitoring radiation dose during radiotherapy or for dose verification and validation [10, 11, 12, 70, 71]. Fig. 3.6 shows a symbolic RL

recombination process and the process involves an electron - hole generation and recombination at a luminescent ion. During this process, the X-rays get absorbed and this causes the creation of electrons and holes in the conduction and valence band. These electrons and holes are mobile and can recombine (on a luminescent ion (A^*)). The light emitted by radioluminescence after absorption of radiation is usually detected with photomultiplier tubes (PMT) or charge-couple device (CCD) detectors. Radioluminescent materials are of interest, which emit light in the region from 200 nm till 700 nm (visible light), because the PMT detects from ~ 350 nm - 700 nm and the CCD from ~ 400 nm - 800 nm [72].

Figure 3.6: Model of the one trap, one recombination centre for RL.

In Fig. 3.6, N is the total concentration of traps and M is the total concentration of hole traps. m_v and n_c are the concentration of holes and electrons in the valence and conduction band, respectively. A_{e-h} is the ionisation probability and Φ the radiation flux. A_n is the probability coefficient where electrons get trapped and A_m the recombination probability where some electrons will recombine with the trapped holes. Therefore, the following rate equations were estimated [73],

$$\frac{dn}{dt} = A_n(N - n)n_c \quad (3.20)$$

$$\frac{dn_c}{dt} = A_{e-h}\Phi - A_{mn}mn_c - \frac{dn}{dt} \quad (3.21)$$

$$\frac{dm}{dt} = -A_{mn}mn_c + A_m(M - m)m_v \quad (3.22)$$

$$\frac{dn_v}{dt} = A_{e-h}\Phi - A_m(M - n)m_v \quad (3.23)$$

$$I_{RL} \sim \frac{dm}{dt} \quad (3.24)$$

3.5 Optically Stimulated Luminescence

The process of stimulated luminescence in general means that through radiation the sample absorbs energy, which causes ionisation of valence electrons, the freed electrons and holes drift through the crystal and get trapped in defects. Energy will be absorbed via the stimulation of the sample with i.e. UV, visible or IR light, which causes recombination of trapped carriers. During a radiative recombination luminescence can be measured [6].

The material before the radiation is in equilibrium and becomes metastable during the radiation until the stimulation. After the stimulation the state of the system is in equilibrium again [6]. In OSL the intensity of the emitted luminescence is correlated to the rate of the electrons and holes which recombine. This rate is a function of the concentration of the charged particles. Usually a luminescence versus time curve is plotted and the integral of this graph is connected to the trapped particles, which is proportional to the dose of absorbed radiation [6]. For a fixed energy with a continuous illumination the probability to stimulate the trapped carriers is dependent on the energy and the illumination intensity Φ , and is not time-independent. This type of OSL is called continuous wave OSL, CW-OSL, and the shape of the OSL intensity versus time graph is a decay curve. One way to simplify the OSL process is to assume that the system has one type of electron trap and one type of hole trap (see Fig. 3.7), which is also called the one-trap/ one-centre model and equation 3.25 shows the charge neutrality for this system [74, 75].

$$n_c + n = m_v + m \quad (3.25)$$

In the above equation 3.25, n_c is the concentration of the electrons in the conduction band, n the concentrations of the electrons in the traps, m_v the concentration of the holes in the valence band and m the concentration of the recombination centres.

Figure 3.7: One-trap/ one-centre OSL model [6].

The material is in equilibrium before applying ionised radiation. N is the total concentration of electron traps and M the total concentration of hole traps. Incoming X-rays create mobile holes in the valence band with a concentration of $m_v(\text{cm}^{-3})$ and electrons in the conduction band with a concentration of $n_c(\text{cm}^{-3})$. Electrons get trapped with the probability coefficient A_n . After an optical stimulation of these trapped electrons, some electrons might fall directly back to the trapping states and A_m is the recombination probability where some electrons will recombine with the trapped holes. The derivative of equation with respect to the time t and for a one trap model with finite re-trapping probability and one recombination centre,

$$\frac{dm}{dt} = -A_m m n_c \quad (3.26)$$

$$\frac{dn}{dt} = -n p_{OSL} \quad (3.27)$$

$$\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt} \quad (3.28)$$

with the assumption of slow re-trapping $\frac{dn_c}{dt} \ll \frac{dm}{dt}, \frac{dn}{dt}$ and,

$$I_{OSL} = -\frac{dm}{dt} \quad (3.29)$$

dn/dt can be written as,

$$\frac{dn}{dt} = -n p_{OSL} + A_n (N - n) n_c = -A_m m n_c \quad (3.30)$$

$$n_c(A_m m + A_n(N - n)) = np_{OSL} \quad (3.31)$$

$$n_c = \frac{np_{OSL}}{A_m m + A_n(N - n)} \quad (3.32)$$

Eliminating n_c leads to,

$$\frac{dn}{dt} = -\frac{np_{OSL}A_m m}{A_m m + A_n(N - n)} \quad (3.33)$$

The one-trap/ one-centre model is a good way to also describe non-exponential OSL curves [6, 31, 74, 75]. Examples of traps include:

- An F-centre is a vacancy with a trapped electron and in the case of Al_2O_3 the F^+ -centres are recombination centres.
- V_k -centre or a X_2^- -centre means a hole trapped between two halide ions [3].

4 Experimental techniques

4.1 Sample preparation

In this thesis different types of samples are produced, which are described in the following paragraphs. The samples are utilised for 1D dosimeters and the starting compounds are usually polycrystalline bulk materials or nanoparticles, which are further fabricated as thin films or pressed as pellets, respectively. All samples are prepared in glove boxes under an inert atmosphere to protect the materials and ensure that the operating person does not inhale hazardous powder.

4.1.1 Polycrystalline samples

The polycrystalline bulk samples were prepared at Victoria University of Wellington. The compounds are produced by mixing the starting materials (e.g. RbF, NaF, MgF_2 , and either MnF_2 or EuF_2) in the stoichiometric ratio in a glassy carbon crucible and are sealed with a glassy carbon lid. The mixing is performed in a sealed glove box under nitrogen ("dry" or "oxygen free") atmosphere. After that, the crucible with the powder was transported to the furnace, which is connected to another glove box. The samples are then heated with a furnace consisting of a quartz tube where a central zone was heated by a radio frequency heating utilising a graphite susceptor. The samples were heated slightly above the melting temperature, and then slowly cooled down below the melting point.

With a computer program, a defined heating pattern was written for the furnace. During this heating a constant argon flow was applied. The different sample concentrations that were studied and reported in this thesis were chosen because these concentrations were used in the fibre optic dosimeter in the Wellington Hospital.

4.1.2 Nanoparticles

The motivation of preparing nanoparticles is to get transparent plates of an arbitrary size and shape for different types and application of dosimeters. The fluoroperovskite RbMgF_3 and NaMgF_3 nanoparticles doped with 1%, 2% or 5% Mn or Eu were produced using a reverse micro-emulsion method [76]. The precursors were high purity $\text{RbNO}_3 \cdot 6\text{H}_2\text{O}$, $\text{NaNO}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$, Cetyl trimethylammonium bromide (CTAB) ($(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3\text{Br}$) and NH_4F . 10g of CTAB and 50 ml of 2-octanol were placed in a flask and stirred for about 1 hour. The nanoparticles were produced by first dissolving (370.4mg, 10 mmol) NH_4F into 4.6 ml of milliQ water. This was then added to the solution containing 10 g of CTAB and 50 ml of 2-octanol and stirred for 30 minutes (flask A). 3 mmol of RbNO_3 or NaNO_3 , 2.5 mmol of MgNO_3 and x mmol of $\text{Mn}(\text{NO}_3)_3$ or $\text{Eu}(\text{NO}_3)_3$, were dissolved in 4.6 ml of milliQ water. This was then added to a solution containing 10 g of CTAB and 50 ml of 2-octanol and also stirred for 30 minutes (flask B). The contents of flask B were slowly added to flask A while stirring for about 10 minutes after which the nanoparticles precipitated. The solution was diluted with ethanol and centrifuged at 4000 rpm for 3 to 5 minutes to isolate and purify the nanoparticles. This process was repeated 5 times. Fluoride nanoparticles were manufactured with a different method which will be explained in the particular chapter.

4.2 X-ray diffraction

After the preparation of the samples (polycrystalline bulk materials, nanoparticles or the thin sheets, e.g.). The samples were characterised with X-ray diffraction (XRD) to ensure the purity and to examine if any process affects the purity of the compound. In most of the XRD measurements, the samples were ground until they form a fine powder and the diffraction pattern was recorded for the powder. The powder is placed either on aluminium powder sample holders (at Callaghan Innovation), or on silicon powder sample holders (at VUW). The X-ray diffraction patterns of the samples were performed with an X-ray generator (Model PW 1729, Philips, Holland) with crystal monochromatic Co K_α ($\lambda = 1.79 \text{ \AA}$) radiation. At Victoria University, the XRD patterns were collected with Cu K_α X-rays ($1.54 \text{ \AA}$) radiation. The patterns were then compared with reference patterns from the International Centre for Diffraction Data database. Fig. 4.1 shows the XRD patterns of RbMgF₃(a) bulks, NaMgF₃(b) bulks, RbMgF₃(c) nanoparticles and NaMgF₃(d) nanoparticles. XRD pattern for the LaF₃ and BaMgF₄ are already published elsewhere [19, 22, 77]. The JCPDS reference pattern is 01-070-8139 for NaMgF₃ and 01-076-0179 for RbMgF₃ with an orthorhombic (P_{bnm}) and hexagonal (P_{63nm}) phase for the bulk materials, respectively. For the nanoparticles, the JCPDS reference pattern is 04-012-1614 for NaMgF₃ and 04-008-2832 for RbMgF₃ with an orthorhombic (P_{bnm}) and hexagonal (P_{63nm}) phase, respectively.

Figure 4.1: XRD diffractogram of RbMgF₃(a) and NaMgF₃(b) bulks and the reference pattern for RbMgF₃ (blue lines in (a)) and NaMgF₃ (red lines in (b)).

XRD diffractogram of RbMgF₃(c) and NaMgF₃(d) nanoparticles and the reference pattern for RbMgF₃ (blue lines in (c)) and NaMgF₃ (red lines in (d)).

The crystal size l (grain size) of the nanoparticles was estimated with the Scherrer formula [78],

$$l = \frac{K\lambda}{\beta \cos(\theta)}, \quad (4.1)$$

with $\beta = \frac{1}{2}(2\theta_2 - 2\theta_1)$

where K is a constant which is close to unity (0.9) and related to the crystalline shape,

which is assumed to be spherical, λ is the X-ray wavelength and θ is the Bragg angle [78].

4.3 Thermoluminescence measurements

TL measurements were performed with a custom-built TL spectrometer. The schemata of the TL measurements are illustrated in Fig. 4.2. The samples were powdered, immersed in isopropanol and dispersed on two rectangular PT 100 resistor (sample holder) for controlled heating up to 350 °C. The sample holder was 2 mm x 3 mm big and usually a 1 mm thick layer of the powder isopropanol mixture was placed on it. The sample holder was heated up to 350 °C outside of the light-tight cylinder to evaporate all of the isopropanol. For better heat transport in the sample, the powder is usual immersed with silicon oil, but this oil shows a signal in the TL, which overlaps with the signal of the samples. Therefore, isopropanol was utilised instead. This sample holder was placed in a light-tight cylinder, which has a connection to a fibre cable on the top and to the X-ray generator on the front. All measurements were performed in a lead box, which surrounds the X-rays generator. The emission was detected with an optical fibre that was connected to a photomultiplier with a photon-counting unit or a CCD (charged-couple device). The CCD was used for a high intensity TL signal, for example with the bulk materials. It was possible to observe which transition is having an impact on the TL signal with the CCD. The nanoparticles did not have an intense TL signal and therefore the PMT (photomultiplier tubes) was utilised to detect the TL glow curve. It was not possible to get any information about the origin of the TL signal because the PMT only detects the overall signal of the TL glow curve and does not detect an extra TL intensity versus wavelength spectra for each temperature step compared to the measurements with the CCD. After each TL measurement, a black body measurement was performed to subtract the background from the actual TL signal. The X-ray irradiations were carried out with a Philips X-ray generator operating at 40 kV and 40 mA, using a W-tube. The glow curves were measured with different heating rate 1K/s and at different doses.

Figure 4.2: Schematic of the thermoluminescence measurements.

4.4 Radioluminescence measurements

The ^{241}Am RL measurements were performed with a custom-built system that was designed especially for these measurements. A schematic of this holder is illustrated in Fig. 4.3. It consists of two parts: the lower part holds the PMT and filters can be adjusted and an upper part, which holds the sample and the source. Between the upper and lower part a foil is attached, which keeps the sample in position. Right above the sample, the holder for the ^{241}Am source starts. The source can be adjusted to a different height depending on purpose of the measurements, which needs to be performed. The two parts of the holder are screwed to each other, and they are constructed of lead to protect the person who is measuring being exposed to harmful radiation. Additionally on the top of the upper holder, there is a lead screw to protect the operator from radiation, to easily remove or bring the source into the sample holder and to protect the PMT from being exposed to light from the environment during the measurement. This setup captures the whole emitted light of the sample during the exposure by the radiation source with the PMT.

Figure 4.3: Schematic of the radioluminescence measurements with the ^{241}Am -source.

Higher dose measurements were performed using a custom-built system attached to an X-ray set using X-rays generated by a cobalt X-ray tube (40 kV and 40 mA) with an Aluminium filter. The sample was located ~ 3 cm from the exit port (similar to the TL measurements, explained in the previous section). The only difference is that the sample was placed on a holder with an 45° angle. This system was also utilised to collect the RL spectra where an optical fibre was connected to an Ocean Optics USB 2000 or 4000 spectrometer that had a CCD detector array.

4.5 Radiation facilities

^{241}Am radio nuclide

The ^{241}Am source emits up to 0.4 mGy/s (at a distance of 0.1 cm) of monochromatic γ -rays with an energy of about 60 keV with an activity of 3 500 MBq. Most of the measurements or irradiations of the sample to measure RL, OSL or conversion efficiency OSL are performed by placing the source directly on the sample. For some RL measurements, the distance between the sample and the source is varied with the sample holder described

in the preceding paragraph. The dose rates on the sample vary with the distance from the source, which has to be taken into account when comparing the measurements done with a different setup.

Philips PW 1720 X-ray tube with W-anode

The X-ray beam was employed with a tube voltage of 40 kV and a current of 40 mA. The distance in this tube can be varied. It can be utilised either without a filter, with an Al filter or a quartz window.

4.6 Photoluminescence, PL lifetime and temperature dependent PL measurements

Cary Eclipse fluorescence spectrometer

Photoluminescence measurements performed at the Callaghan Innovation were carried out with the Varian Cary50 Eclipse. It operates with a pulsed Xe-lamp with a pulse of 2-3 μs and a repetition rate up to 80 Hz. The schematic configuration of the Cary Eclipse is illustrated in Fig. 4.5 [7]. The wavelength range of the pulsed Xenon lamp is from 190 nm to 1100 nm. The device offers a different range of slit widths both for the emission and excitation beam, for example 1.5, 2.5, 5, 10, 20 nm and a round slit of 10 nm. For the excitation and emission detection, there are also built-in filters as well as a possibility to insert an external filter in the device. Spectra can be detected with the fluorescence or phosphorescence mode. The total decay time, gate time and delay between the pulse and start of the measurement can be selected with the phosphorescence mode. For fluorescence measurements, the signal is measured during the excitation pulse. Lifetime measurements can be performed with a time resolution down to 1 μs [7].

Figure 4.4: Schematic configuration of the Varian Cary Eclipse fluorescence spectrometer[7].

Jobin-Yvon FluoroLog[®]

At Victoria University of Wellington, photoluminescence (PL), PL lifetime, temperature dependent PL and OSL measurements were performed using the Jobin-Yvon FluoroLog[®] spectrometer which operates over a wide wavelength range, from 250 nm until 1550 nm, by employing a Xe short-arc lamp. This spectrometer was also utilised to perform lifetime measurements from a few μs or even longer. The setup was slightly modified and three different LEDs were utilised as an excitation source (370nm, 465 nm, 498 nm). This method is called multichannel scaling single-photon-counting spectroscopy (MCS). Low temperature PL and lifetime measurements were performed for temperatures down to 10 K with an RMC-22 closed cycle refrigerator [8].

Figure 4.5: Schematic configuration of the Jobin-Yvon FluoroLog[®] spectrometer [8].

5 Bulk polycrystalline NaMgF₃

In this chapter, the optical, radioluminescent and thermoluminescent properties of Eu and Mn doped NaMgF₃ will be discussed. The samples were prepared as described in the experimental description given in section 4.1.1. 10 g of each sample was produced using high purity Sodium fluoride (NaF), Magnesium fluoride (MgF₂), Europium(II) fluoride (EuF₂) or Manganese(II) fluoride (MnF₂). NaMgF₃ is also called neighborite, and the crystal structure is orthorhombic with the space group P_{bnm} and a melting point at ~ 1030 °C. The bandgap is about 6.05 eV [79] and the $4f^65d(E_g)$ levels are above the 6P_J levels with an energy difference of $\Delta E = 1.2$ eV which is around 9700 cm^{-1} [3, 9, 79, 80, 81]. The significance of the energy difference is the bigger the gap the lower the probability of $5d4f$ transition. The samples which will be discussed were doped with either 0.2 % Eu, 0.5 % Mn and 1 % Mn. The appearance of the Eu doped sample was slightly milky and transparent. The Mn doped samples were slightly greenish and transparent, but the 1 % doped sample was a bit darker than the 0.5 % doped sample. The influence the concentration of the Mn dopant has on the PL spectra, PL lifetime, TL and RL measurements will be demonstrated.

5.1 Photoluminescence and PL lifetime measurements

5.1.1 Eu doped polycrystalline NaMgF₃

PL measurements were performed with the Jobin-Yvon FluoroLog[®]. The PL spectrum of NaMgF₃: 0.2 % Eu is shown in Fig. 5.1, which consists of transitions from the Eu²⁺ ion. The sharp peak in the PL emission is due to the transition from the ⁶P_{7/2} and ⁶P_{5/2} excited states to the ⁸S_{7/2} ground state with an emission at 360 nm, and the broad peak is from the band emission from the 4f⁶5d(E_g) excited states to the 4f⁷ ground state. In Fig. 5.1(b), it is shown that the E_g emission is at lower energies (red arrow) than the ⁶P emission (blue arrow). The excited 4f⁶5d levels are split by the crystal field into two energy levels: the lower energy level E_g and a higher T_{2g}, which was also reported for RbMgF₃ by Alcala et al. [82]. The 4f⁷ excited state consists of two ⁶P_J multiplets as illustrated in Fig. 5.1(b). These multiplets are shielded by the 5s and 5p electrons and hence their interactions with the lattice are very weak. The ⁶P_J transitions to the ground state, ⁸S_{7/2}, are spin and parity forbidden in the electric dipole approximation. Therefore, this transition has a narrow PL line emission (Fig. 5.1(a)). Dotzler et al. reported that the line emission in the PL emission spectra is a zero phonon line which is due to the transition from the excited ⁶P_J level to the ⁸S_{7/2} ground state. The smaller side peaks are Stokes and anti-Stokes vibronics which arise from higher ⁶P_J level [4].

Figure 5.1: (a) PL excitation (dashed curve, $\lambda_{em} = 360$ (blue) nm and 420 nm (black)) and emission (solid curve, $\lambda_{ex} = 256$ nm) spectra for NaMgF₃ 0.2 % Eu. (b) Configuration coordinate diagram of Eu²⁺ in NaMgF₃ [3, 9].

After measuring the PL emission and excitation spectra of NaMgF₃:Eu with the Jobin-Yvon FluoroLog[®], the sample was heavily irradiated. Thus, the sample was mounted on a transportable holder for the PL measurements and the whole holder was placed in a light-tight box for transportation to the X-ray generator. The PL holder was placed in the X-ray generator, which is operating at 40 mA and 40 kV, and the sample was irradiated up to an initial dose of 19 kGy. After radiation, the holder with sample was transported back in the light-tight box to the spectrometer and the PL measurement was repeated with the sample in the same position. Fig. 5.2(a) shows the absolute PL intensity of the emission spectra for Eu²⁺ before (solid curve) and after (dashed curve) irradiation. The PL intensity of the Eu²⁺ decreases after receiving a dose of ~ 19 kGy and the emission wavelengths of the Eu²⁺ transition remain unchanged. Although a shift in the wavelengths was expected but this could not be detected with the spectrometer. The ratio of the E_g level to the 6P_J excited states changes from 1.4:1 before irradiation to 2:1 after heavy irradiation. This is illustrated in the normalised PL plot in the inset of Fig. 5.2(a). The change of the ratio

might be due to the creation of defects nearby the Eu²⁺ site. The 5d emission seems to increase on top of the decreasing Eu²⁺ signal after heavy irradiation (Fig. 5.2(a)). Fig. 5.2(b) shows the PL excitation and emission spectra of Eu³⁺ where the transitions from Eu³⁺ are indicated.

Figure 5.2: (a) Absolute PL intensity of the emission spectra, $\lambda_{ex} = 256$ nm, for NaMgF₃ 0.2 % Eu before (solid curve) and after irradiation with a dose of ~ 19 kGy (dashed curve). Inset: Normalised PL of the emission spectra, $\lambda_{ex} = 256$ nm, for NaMgF₃ 0.2 % Eu before (solid curve) and after irradiation with a dose of ~ 19 kGy (dashed curve). (b) PL excitation at $\lambda_{em} = 610$ nm (blue: solid curve - before irradiation, dashed curve - after irradiation with a dose of ~ 19 kGy) and emission at $\lambda_{ex} = 396$ nm (red: solid curve - before irradiation, dashed curve - after irradiation (with ~ 19 kGy)) spectra for the Eu³⁺ ion.

The normalised excitation spectrum measured at 610 nm before (solid curve) and after (dashed curve) irradiation are plotted in Fig. 5.3(a). The excitation spectrum before irradiation consist of the transition from the ⁷F₁ level of Eu³⁺ and one peak centred at 340 nm. After heavy irradiation, the intensity of the broad peak centred around 340 nm increases and a second peak centred at 470 nm appears (dashed curve in Fig. 5.3(a)). The

transitions from the 7F_1 level were not detected after irradiation because the intensity of the unknown defect centred at 470 nm overlaps the 7F_1 transitions.

The Eu^{3+} emission spectra excited at $\lambda_{ex} = 396$ nm shows transitions from 5D_0 and 5D_1 levels (Fig. 5.2(b)) and an additional large peak around 450 nm (see Fig. 5.3(b)). This new band at 450 nm can be assigned to some defects. The precise origin of these defects is unknown, but can probably be ascribed to the same defect observed in the nanoparticles and will be discussed further in the next chapter. However this defect with a peak at 450 nm could be from oxygen. After heavy irradiation, the intensity of the broad peak around 450 nm increases on top of an increase of the ${}^5D_0 \rightarrow {}^7F_1$, 7F_2 transitions (Fig 5.3(c+d)). The ratio of ${}^7F_2: {}^7F_1$ changes from 2:1 before irradiation to 1:1 after heavy irradiation (Fig. 5.3(c)). The ${}^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition and therefore almost independent of the crystalline structure as discussed by Görller-Walrand and Binnemans [58]. Whereas the ${}^5D_0 \rightarrow {}^7F_2$ transition is a hypersensitive transition and so very dependent on the crystalline environment. This means before irradiation the environment was highly distorted because the ratio of ${}^7F_2: {}^7F_1$ was 2:1. The reason for this could be that the charge balance requires the existence of V_k or Na vacancies (V_A centres), which can be close to the Eu^{3+} ions. The average Eu^{3+} ions of the newly created Eu^{3+} ions are less distorted than the already existing ones, which is shown in the decreases of the ${}^7F_2: {}^7F_1$ ratio. Hence, there are two Eu^{3+} in the crystal after irradiation of ~ 19 kGy: one distorted site and one less distorted site.

After the irradiation, the average crystal environment of Eu^{3+} was less distorted because the ratio of ${}^7F_2: {}^7F_1$ changes from 2:1 to 1:1. The reason for this might be the additional generation of H- or F- centres by the X-rays, which do not have to be near the Eu^{3+} sites (Fig. 5.3(c)). To measure the change of ratio of these transitions, the unknown defect was subtracted from the PL data by creating a baseline with the OriginLab program. Fig. 5.3(d) shows the PL excitation spectra measured at 450 nm before (solid curve) and after (dashed curve) irradiation. The new band at 450 nm cannot be attributed to the ${}^8S_{7/2} \rightarrow E_g$ transition because the emission from the E_g level has a peak from 250 nm until 400

nm as shown in Fig. 5.1. The peak intensity of the defect centred at 340 nm increases after heavy irradiation.

Figure 5.3: (a) Absolute PL intensity of the excitation spectra, $\lambda_{em} = 610$ nm, before (solid curve) and after irradiation with a dose of ~ 19 kGy (dashed curve). (b) Absolute PL intensity of the emission spectra, $\lambda_{ex} = 396$ nm, before (solid curve) and after irradiation with a dose of ~ 19 kGy (dashed curve). (c) PL emission spectra of Eu³⁺ corrected for the broad unknown peak before (solid curve) and after heavy irradiation with a dose of ~ 19 kGy (dashed curve). (d) Absolute PL excitation spectra at $\lambda_{em} = 450$ nm before (solid curve) and after heavy irradiation with a dose of ~ 19 kGy (dashed curve).

Radiation damage might lead to defects near the Eu²⁺ ions. This could change the crystal field and lead to a shift in the 5d4f level so that the energy difference between the 5d4f and excited 4f levels is smaller (Fig. 5.4(a)). Fig. 5.4(b) illustrates the increase of the Eu³⁺ signal. Due to the damage induced by radiation, more defects are generated near to the Eu²⁺ ions. An electron which is stimulated from the Eu²⁺ site recombines in a very deep non-optical or non-thermal stimulated trap. Hence, more Eu³⁺ will be detected.

Figure 5.4: (a) Change of the crystal field leading to a shift in the 5d4f level in Eu²⁺.

(b) Electron from Eu²⁺ recombines in a deep non-optical or non-thermal trap.

Fig. 5.5 shows the PL lifetime decay curve (solid curve) with the exponential fit (dashed curve) for the 0.2 % Eu doped NaMgF₃ same at $\lambda_{em} = 360$ nm (a) and (b) $\lambda_{em} = 390$ nm, when excited at $\lambda_{ex} = 256$ nm.

Figure 5.5: (a) PL lifetime decay of 0.2 % Eu doped NaMgF₃ at $\lambda_{em}= 360$ nm (solid curve) and (b) $\lambda_{em}= 390$ nm emission (solid curve). The dashed curve is the exponential fit. Both lifetimes were measured at $\lambda_{ex}= 256$ nm.

The average PL lifetimes for the 0.2% Eu²⁺ ions were measured with the Cary 50. The PL lifetime for the Eu³⁺ and the unknown defect were measured with the Jobin-Yvon FluoroLog[®] spectrometer. The PL lifetime remains unchanged after heavy irradiation. The PL decay could be fitted two-exponential which can be described by two exponential components,

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) + I_0 \quad (5.1)$$

For an emission wavelength of 360 nm the calculated average lifetime was 0.63 ± 0.06 ms, while for a wavelength of 390 nm a lifetime of 0.42 ± 0.04 ms was obtained ($\lambda_{ex}= 256$ nm). The reason for the different lifetimes is already discussed in section [?]. The average lifetime was estimated from [67],

$$\tau_{ave} = \left[\int t I(t) dt / \int I(t) dt \right]. \quad (5.2)$$

For an emission wavelength of 592 nm the calculated average lifetime was 11.1 ± 1.1 ms ($\lambda_{ex}= 375$ nm) and it was measured with the Jobin-Yvon FluoroLog[®]. The unknown defect centred at ~ 460 nm had an average PL lifetime of 67 ± 7 ms ($\lambda_{ex}= 375$ nm). The PL lifetime of the unknown defect could only be fitted with a three exponential decay as

summarised in Tab. 5.2. The lifetime of the unknown defect is large compared to the measured PL lifetimes of the Eu ions. This new band at 450 nm can be assigned to some defects. The precise origin of these defects is unknown and it cannot arise from the Eu²⁺ or Eu³⁺ transitions. Maybe the unknown defect is from oxygen as discussed by Williams et al. [10]. The different compounds of the average PL lifetimes are listed in Tab. 5.1. The average lifetime measured for an emission wavelength of 360 nm showed two separate sites with different lifetimes of 0.28 ± 0.03 ms and 0.85 ± 0.09 ms. For an emission wavelength of 390 nm the lifetime decay shows distributions of two sites with calculated lifetimes of 0.22 ± 0.02 ms and 0.69 ± 0.07 ms. The lifetime measured at 592 nm shows a big distribution of lifetimes where one site has a lifetime of 2.0 ± 0.2 ms and the other one shows a lifetime of 16.7 ± 1.7 ms. There are three sites calculated of the PL lifetime in the unknown defect with lifetimes of 5.2 ± 0.5 ms, 33.2 ± 3.3 ms and 107 ± 11 ms.

Table 5.1: Different compounds with the pre factors of the PL lifetimes of 0.2 % Eu doped NaMgF₃.

λ_{em} (nm)	factor A ₁	τ_1 (ms)	factor A ₂	τ_2 (ms)	factor A ₃	τ_3 (ms)
360	42	0.28 ± 0.03	26	0.85 ± 0.09		
390	233	0.22 ± 0.02	54	0.69 ± 0.07		
500	46	5.2 ± 0.5	6	33.2 ± 3.3	5	107 ± 11
592	236	2.0 ± 0.2	47	16.7 ± 1.0		

Table 5.2: Average PL lifetimes of 0.2 % Eu doped NaMgF₃.

λ_{em} (nm)	τ_{ave} (ms)
360	0.63 ± 0.06
390	0.42 ± 0.04
500	11.1 ± 1.1
592	67 ± 7

5.1.2 Mn doped polycrystalline NaMgF₃

PL emission and excitation spectra for NaMgF₃ samples doped with 1 % Mn are shown in Fig. 5.6. The PL emission spectrum was excited at 396 nm (see Fig. 5.6(b)). The spectrum consists of two peaks: one at 500 nm and the other one at 600 nm (solid curve). Fig. 5.6(b) shows the PL emission spectrum of the 0.5 % Mn doped NaMgF₃ sample (dashed curve). The intensity of the peak centred at 500 nm has nearly the same intensity as the peak of the regular Mn²⁺ site centred at 600 nm. This is different for the 1 % Mn doped sample where the ratio of the intensity of the distorted peak is smaller compared to the intensity of the regular peak (Fig. 5.6(b)). The change in ratio of the regular site compared to the distorted site is 1:1 for the 0.5 % Mn doped sample and 3:1 for the 1 % doped Mn sample. The reason for the change could be the existence of fewer distorted defects in the sample with the higher concentration. The PL excitation spectrum for the 600 nm emission (solid curve in Fig. 5.6(a)) can be attributed to transitions to the ⁶A_{1g} ground state and the excited state levels are indicated in Fig. 5.6(a). The two Mn²⁺ sites plotted in Fig. 5.6(b) are unexpected because the space group of NaMgF₃ is *P_{bnn}* and Mn²⁺ is believed to substitute for the Mg site. Thus, PL emission from only one Mn²⁺ site is expected.

Figure 5.6: (a) PL excitation spectrum at $\lambda_{em}=500$ nm (dashed curve) and $\lambda_{em}=600$ nm emission (solid curve) for the 1 % Mn doped NaMgF₃ sample.
 (b) PL emission spectrum for NaMgF₃ doped with 0.5 % Mn (dashed curve) and 1 % Mn (solid curve) excited at 396 nm.
 (c) Broadening of the peaks in the PL excitation spectra for the distorted Mn^{2+} site.
 (d) Splitting of the energy levels of Mn^{2+} in an octahedral crystal field.

The PL excitation spectrum from the 500 nm emission was also measured and it is plotted

in Fig. 5.6(a) (dashed curve). The peak centred at ~ 396 nm can be attributed to the Mn^{2+} ${}^6\text{A}_{1g}$ and ${}^4\text{E}_g$ levels. All of the distorted Mn^{2+} transitions are significantly broader. The broadening of the excitation spectra for the 500 nm emission can be explained with a model illustrated in Fig. 5.6(c). The regular Mn^{2+} site shows distinct peaks in the excitation spectra, which can be distinguished in the PL. The distorted site shows traps that are close to each other resulting in transitions that cannot be distinguished in the PL excitation spectrum. Therefore, the peaks are broader in the PL excitation spectrum for the second Mn^{2+} site centred at 500 nm. Due to the crystal field, the ${}^4\text{E}_{2g}$, ${}^4\text{T}_{2g}$ and ${}^4\text{T}_{1g}$ levels shift with the crystal field parameter and the ${}^4\text{A}_{1g}$ and E_g levels are not affected by the crystal field (Fig. 5.6(d)). Therefore, the ${}^4\text{A}_{1g}$ and E_g levels still show a distinct peak and the other levels are broader. Therefore, it is likely that the 500 nm PL emission comes from a distorted Mn^{2+} site. There were no additional peaks before and after heavy irradiation with ~ 12 kGy observed and these measurements were explicit discussed in the Ph.D. thesis of Christian Dotzler [3].

Figure 5.7: (a) PL lifetime decay of 1 % Mn doped NaMgF₃ at $\lambda_{em}=500$ nm (solid curve) and (b) $\lambda_{em}=600$ nm emission (solid curve). The dashed curve is the exponential fit. Both lifetimes were measured at $\lambda_{ex}=465$ nm.

Fig. 5.4 shows the PL lifetime decay curve (solid curve) with the exponential fit (dashed

curve) for the 1 %Mn doped NaMgF₃ measured at $\lambda_{em} = 500$ nm (a) and (b) $\lambda_{em} = 600$ nm ($\lambda_{ex} = 465$ nm). The lifetimes of the Mn doped samples were measured with the Jobin-Yvon FluoroLog[®]. They could be fitted in a two exponential decay and the distribution of the lifetimes are listed in Tab. 5.3. Both Mn²⁺ sites have two compounds of the PL lifetime: a shorter lifetime which is from a more distorted site and a longer lifetime from a less distorted site.

Table 5.3: Different compounds with the pre factors of the PL lifetimes of Mn doped NaMgF₃.

λ_{em} (nm)	factor A ₁	τ_1 (ms)	factor A ₂	τ_2 (ms)
0.5 % 500	8342	12.2±1.2	226	30.9±3.1
0.5 % 600	2179	52.8±5.3	7776	104±10
1 % 500	505	5.9±0.6	880	14.4±1.4
1 % 600	11105	53.9±5.4	24219	101±10

For the regular site of Mn in the NaMgF₃ an average lifetime of 98±10 ms and 91.4±9.1 ms for the 0.5 % and the 1 % doped sample was calculated ($\lambda_{em} = 600$ nm), respectively. An average PL lifetime of 13.5±1.4 ms and 12.8±1.3 ms was measured for the distorted Mn²⁺ site for the 0.5 % and 1 % doped sample ($\lambda_{em} = 500$ nm), respectively. The transitions of the regular Mn²⁺ site are spin and parity forbidden. F-centres next to the regular Mn²⁺ site make this transition only parity forbidden resulting in a high average PL lifetime. The distorted Mn²⁺ site is only parity forbidden and it shows a distribution of the crystal fields. This results in a mixing of crystal field symmetry and therefore, more defects near this site. Thus, the distorted site of Mn²⁺ shows a shorter measured PL lifetime due to the shift in the levels, which is illustrated in Fig. 5.6(d). The PL lifetime of the regular site decreases by 10% with the increasing Mn concentration. This can be a result of the energy transfer between the Mn²⁺ site and the recombination at a non-radiative recombination centre. The probability of this energy transfer is proportional to the distance of the atoms which

is depending on the Mn concentration, $\frac{1}{\tau^6} \sim \frac{1}{conc^2}$. This model was used to explain the decrease of the average PL lifetimes in Eu³⁺ doped samples [11, 12, 22, 64, 83, 84, 85, 86].

Table 5.4: Average PL lifetimes of distorted and regular Mn²⁺ sites in NaMgF₃.

Mn concentration (%)	τ_{500nm} (ms)	τ_{600nm} (ms)
0.5	13.5±1.4	98±10
1	12.8±1.3	91.4±9.1

5.2 Thermoluminescence measurements

The TL measurements were performed with a custom-built TL spectrometer in the manner explained in section 4.3.

5.2.1 Eu doped polycrystalline NaMgF₃

The NaMgF₃ sample doped with 0.2 % Eu was irradiated for with a Philips X-ray generator operating at 40 kV and 40 mA, using a W-tube with an Aluminium filter. The glow curves were obtained using a heating rate of 1K/s and an irradiation time of 1 minute was used when the data was collected using a PMT and 5 min for the CCD. The advantage of collecting the data with a CCD detector is that it is possible to distinguish the wavelengths of the TL transitions. The TL spectrum is plotted in Fig. 5.8(a+b) and the activation energies of the peaks of the glow curves are summarised in Tab. 5.5. They were obtained using first order kinetics glow curve deconvolution software and by minimizing the number of peaks during fitting of the glow curve (see also Fig. 5.8(a) - dashed curves). Fig. 5.8(b) shows the TL intensity plotted against the wavelength for different temperatures. The units for the TL intensity in Fig. 5.8(a+b) are different because for the deconvolution the whole peak from 360 nm to 420 nm was integrated and hence the y-axis in Fig. 5.8(a) shows a higher TL intensity than the peak maximum at 360 nm in Fig. 5.8(b). Potential

additional peaks above 620 K could not be detected due to the temperature limitation of the equipment used.

Figure 5.8: (a) TL for the NaMgF₃ sample doped with 0.2 % Eu (solid curve). The TL data was detected with the CCD after 5 min X-ray irradiation (40 kV, 40 mA) at a heating rate of 1 K/s. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves).
 (b) TL spectra vs. wavelength for the different temperatures.
 (c) Model for the probability of the emission from the 4f and 5d levels to the ground states for higher temperatures.

Table 5.5: The activation energies of the individual glow curve peaks for the NaMgF₃:0.2 % Eu sample obtained by first order kinetics glow curve deconvolution. The top line is the peak temperature for the glow curve.

	363 K	386 K	459 K
0.2 % Eu	0.76±0.07 eV	0.61±0.06 eV	0.50±0.05 eV
peak height	164000	54000	76000

The TL signal arises mainly from the Eu²⁺ transition (see Fig. 5.8(b)). The 5d emission seems to increase with increasing temperature as shown in Fig. 5.8(a). The probability for the transition between the 4f and 5d level, $\tau_{f \rightarrow d}$, is dependent on the energy difference between the d $\rightarrow$ f level, Δ , and the temperature, T. This can be estimated from the following equation,

$$\tau_{f \rightarrow d} = \tau_o e^{-\frac{\Delta}{kT}} \quad (5.3)$$

where k is the Boltzmann's constant. This means that with increasing temperature the energy difference between the 4f and 5d level is decreasing and this will result in a higher probability for the transition from the 4f to the 5d levels. Therefore, at higher temperatures more of the 4f levels emission will be quenched by the 5d level resulting in an increase of the emission from the 5d level. Therefore, there is hardly any line emission detected in the TL spectra (Fig. 5.8(c)). The energy difference, Δ , between the d $\rightarrow$ f level is around 9700 cm⁻¹ (1.2 eV). The value Δ/k can be estimated from,

$$\frac{\Delta}{k} = 1.39 \times 10^4 \text{K} \quad (5.4)$$

Another possibility of a decrease in the line emission with increasing temperature is the probability of exciting into the 5d level becomes more likely with increasing temperature. The glow curve consists out of two main peaks located at 363 K and 459 K. There is also a weaker peak detected at 385 K. The activation energies of the peaks centred at 363 K, 386 K and 459 K are 0.76 eV, 0.61 eV and 0.5 eV, respectively.

5.2.2 Mn doped polycrystalline NaMgF₃

For the NaMgF₃ doped with Mn²⁺ the TL spectrum was measured for the 0.5 % and 1 % sample (Fig 5.9 - 5.11). The TL spectrum for the 0.5 % sample was measured using a heating rate of 1K/s when irradiating for 1 min with the X-ray generator (40 kV, 40 mA), as plotted in Fig. 5.9 (solid curve) and the first order kinetics glow curve deconvolution (dashed curve). The glow curve peaks were summarised in Tab. 5.6. The TL emission arises from the ⁶A_{1g} emission at 600 nm, plotted in Fig. 5.9(b) and Fig. 5.10(e). No TL emission arises from the distorted Mn²⁺ site which was detected at 500 nm in the PL emission spectrum. A reason could be that a F-centres might be closer to the regular Mn²⁺ site and more likely to recombine with this site. The electron from the F-centre is stimulated into the conduction band and gets trapped in the excited Mn^{2+*}, as shown in Fig 5.9(d). The detrapping out of this Mn^{2+*} site leads to a higher TL signal of the regular site. Another reason could be that the distorted site might show a non-radiative recombination. Fig. 5.9(c) shows the normalised TL emission curve at 443 K (blue curve) and 622 K (black curve). It was observed that the maximum of the TL emission shifts towards higher energies with increasing temperature and the peak broadens with increasing temperature. The shift is from 595 nm → 588 nm for the 0.5 % Mn doped sample. This phenomenon is similar to the process of the temperature dependence of the bandgap of semiconductors [87, 88, 89, 90].

Figure 5.9: (a) TL for the NaMgF₃ sample doped with 0.5 % Mn (solid curve). The TL data was detected with the PMT after 1 min X-ray irradiation (40 kV, 40 mA) at a heating rate of 1 K/s. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves).
 (b) TL spectra vs. wavelength for the different temperatures detected after 5 min of X-ray irradiation (40 kV, 40 mA) detected with the CCD.
 (c) Normalized TL intensity of the TL curves at 443 K (blue curve) and 622 K (black curve).
 (d) Model for F-centre recombination close to the regular Mn²⁺ site.

Figure 5.10: TL for the NaMgF₃ sample doped with 1 % Mn (solid curve). The TL data was detected with the PMT after 1 min (a), repeated after another 5 min (b) and repeated again after 1 min (c) of X-ray irradiation (40 kV, 40 mA) at a heating rate of 1 K/s. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves). (d) TL spectra vs. wavelength for the different temperatures detected after 5 min of X-ray irradiation (40 kV, 40 mA) detected with the CCD.

An irradiation time of 1 minute, 5 minutes and again 1 minute was used for TL measurements of the 1% Mn doped sample and using a heating rate of 1K/s when the data was collected using a PMT (Fig. 5.10)(a-d). This was performed to observe the dependence

of the TL signal on an initial dose. The TL after 5 min irradiation was collected using a PMT as well as a CCD (Fig. 5.10(b+d)). The TL emission mainly arises from the Mn²⁺ emission at 600 nm (Fig. 5.10(d)). There is no TL emission detected from the 500 nm emission. The peaks of the glow curves were all fitted with first order kinetics glow curve deconvolution for the different samples and doses but this will only be shown for the TL after 5 min of irradiation (see Fig.5.10(b)).

Fig. 5.11(a) shows that the TL intensity is dependent on dose and the history of the initial dose. The sample was irradiated with a dose of 96 Gy and TL was measured. After this, the sample was irradiated again with a dose of 228 Gy and TL was measured again. Then, the sample was irradiated again with a dose of 96 Gy, which leads to a total dose of 420 Gy. TL measurements were performed again. The TL glow curve shows a different shape after receiving a dose of 96 Gy compared to receiving a total dose of 420 Gy. This might be due to the probability of filling traps at a higher temperature is more likely after receiving a higher dose. The shape of the curve above 550 K seems broader, and if fitting the TL glow curve with a minimum number of peaks with the first order kinetics glow curve deconvolution, the peak above 600 K shifts towards higher temperatures. But this might just be due to the fact that this peak could also be fitted with two peaks: one at 608 K and one at higher temperature, which result in the filling of additional traps after receiving a higher dose.

Fig. 5.11(b) shows the shift of the maximum of the TL emission with increasing temperature of the 1 % Mn doped sample. The shift is from 593 nm to 586 nm for the 1 % sample. The glow curve is also broader for higher temperatures. The effect is similar to the temperature dependence of the band gap in semiconductors where the amplitude of atomic vibrations increases leading to larger spacing between atoms with increasing temperature [87, 88, 89, 90].

Figure 5.11: (a) TL for the NaMgF₃ sample doped with 1 % Mn (solid curve). The TL data was detected with the PMT after 1 min, 5 min and again 1 min X-ray irradiation.
 (b) Normalized TL intensity of the TL curves at 427 K (blue curve) and 622 K (black curve).

All of the glow curves have a low temperature peak at 412 K and an activation energy of 0.5 eV was calculated. An activation energy of 0.5 eV was calculated for the second peak at 473 K for the 1 % doped samples and at 464 K for the 0.5 % doped sample. This peak shifts to lower temperatures for the 0.5 % Mn doped sample. The temperature for the 3rd peak was measured at ~525 K for the 0.5 % Mn and at ~557 K for the 1 % Mn doped sample with an activation energy of 0.51 eV. The 4th peak shifts from 608 K for the 1 % doped sample without any initial dose to 618 K for the highest initial dose and shows an activation energy of 1.42 eV. This peak shift might be a result of radiation damages in the material which induces deeper defects. The higher the initial dose, the higher the temperature for the 4th peak of the glow curve becomes. For the 0.5 % doped sample, the temperature of the 4th peak was around 619 K.

Table 5.6: The activation energies of the individual glow curve peaks for NaMgF₃ doped with different concentrations of Mn obtained by first order kinetics glow curve deconvolution. The top line is the activation energy for the different peaks for the glow curves.

	0.50±0.05 eV	0.50±0.05 eV	0.51±0.05 eV	1.42±0.14 eV
0.5 % (1 min)	411 K	464 K	580 K	619 K
peak height	500	2300	15000	3700
1 % (1 min)	412 K	473 K	557 K	608 K
peak height	120	1500	6400	700
1 % (repeat 5 min)	412 K	4730 K	557 K	616 K
peak height	900	5500	25000	24000
1 % (repeat 1 min)	412 K	473 K	557 K	619 K
peak height	400	700	4500	9700

These values compare well with the values obtained for the NaMgF₃ samples doped with Eu. It can be assumed that this peak is from the same defect since the activation energy and peak temperatures are similar [87, 88, 89, 90].

Dotzler reported in his thesis that the TL only arises from the 600 nm emission, and additional peaks at low temperature (473 K) were observed. The main peak is around 573 K in these measurements. It is not clear where this low temperature peak is coming from, and it seems to disappear with increasing Mn concentration (> 0.2 %). The samples that were used in this thesis had Mn concentrations higher than 0.2 %, and this could be the reason for the absence of the low temperature peak around 474 K. Dotzler also reported the existence of PTTL (phototransferred thermoluminescence), which he has observed with the 0.02 % Mn doped sample [3]. These measurements were also performed: the 1 % doped sample which was irradiated for 1 min and bleached for 2 s with a 405 nm laser, using a

0.3 % neutral density filter (Fig. 5.12). There was no PTTL observed and the increase above 500 K comes from the black body radiation. Dotzler used also a different laser with less power, and it might be that the power of the laser used in this thesis is too high for the proof of PTTL [3].

Figure 5.12: TL for NaMgF_3 : 1 % Mn after 1 min irradiation and 2 s of bleaching with a 405 nm laser using a 0.3 % neutral density filter detected with the PMT.

5.3 Radioluminescence and temperature dependent RL measurements

Long-term radioluminescence measurements and temperature dependent RL measurements were performed with the X-ray generator (40 kV, 40 mA) using an Aluminium filter. For the temperature dependent RL measurements, the samples were powdered, immersed in isopropanol and dispersed on a resistor to control heating for different temperatures up to 100 °C. At a certain temperatures, the samples were also thermally bleached.

5.3.1 Radioluminescence measurements

5.3.1.1 Eu doped polycrystalline NaMgF₃

Fig. 5.13 shows the results for the RL measurements on 0.2 % Eu doped NaMgF₃. The peaks in the RL spectrum for the Eu sample can be attributed to the Eu²⁺ and Eu³⁺ transitions. The emission from 360 nm to 420 nm arises from Eu²⁺ ion and from 590 nm to 715 nm from the Eu³⁺ ion. From ~400 nm to 580 nm, a broad peak is detected at low doses and disappears for high doses (Fig. 5.13(a)). The emission wavelengths in the RL spectrum of Eu²⁺ and Eu³⁺ did not change after irradiation.

The RL spectrum as a function of dose in Fig. 5.13(b) shows that the integrated intensity (I_{RL}) of the Eu²⁺ ion increases by 50.5 % and reaches a maximum after a dose of 850 Gy. After this initial increase the I_{RL} intensity starts to decrease. After a dose of 13 kGy it has been decreased by 48.5 % which is 22.5 % smaller than the starting value. The low RL signal until 850 Gy is caused by the existence of additional electron-hole-traps next to the Eu²⁺, see Fig. 5.13(c). Electron and holes, which are mobile after irradiation, will more likely recombine on the electron and hole traps and therefore, less electrons get trapped in the Eu²⁺. This results in a low RL signal of Eu²⁺ until 850 Gy. The electron and hole traps saturate after higher irradiation and hence, the RL signal of the Eu²⁺ increases after receiving a dose of 850 Gy. Above ~1 kGy, the RL signal of the Eu²⁺ decreases (Fig. 5.13(b)), which can be due to the creation of non-radiative defects and/or the conversion of Eu²⁺ → Eu³⁺. Fig. 5.13(d) shows that radiation generates a non-radiative recombination centre next to Eu. This non-radiative centre competes with Eu and the probability for mobile carriers to recombine in this centre is higher compared to Eu. Therefore, the RL signal for Eu decreases for doses above ~1 kGy.

Figure 5.13: (a) Radioluminescence spectra for NaMgF₃: 0.2% Eu for different doses and (b) the integrated RL spectrum as a function of dose during continuous X-ray irradiation (Eu²⁺ filled squares and Eu³⁺ open squares). (c) Existence of electron and hole traps next to the Eu. (d) Dose dependence of the RL signal as a result of the generation of non-radiative recombination centres.

I_{RL} for the Eu³⁺ signal is nearly independent of dose as shown in Fig. 5.13(b). This is a desirable property for a real-time dosimeter that can detect low doses as well as high doses without being damaged. The ratio of ⁷F₂:⁷F₁ changes from 2:1 before irradiation to 1:1 after heavy irradiation in the PL spectra, and in the RL spectrum a change from 1.8:1 at 1.8 Gy and 1.4:1 at 12 kGy was observed. This means that the average crystal environment

of the Eu³⁺ ion seems less distorted after heavy irradiation with a dose of 12 kGy. The PL measurements were performed for a higher dose (19 kGy) and therefore, the change of the ratio ⁷F₂:⁷F₁ is bigger. The RL signal of the Eu²⁺ emission changes with dose, which was also observed in the PL spectra measured before and after heavy irradiation (Fig. 5.3(a)). The ratio of integrated intensity of the E_g transition to the ⁶P_J emission increases from 1.3:1 at 850 Gy to 1.7:1 at ~12.7 kGy. This is consistent with the PL emission spectra where the ratio changes from 1.4:1 before irradiation to 2:1 after irradiation with a dose of 19 kGy. That means for further irradiation up to 19 kGy the intensity of the emission of the unknown defect centred at 380 nm increases due to the creation of defects next to the Eu²⁺ ion, which results in a decrease of the energy level between the 5d and 4f level and increases the transition from the 5d level on top of the overall decrease of the Eu²⁺ emission.

The RL intensity is initially low because some of the X-ray generated electrons and holes become trapped and hence electrons and holes available for RL are low. For a high enough dose, all of the traps are filled and hence all of the X-ray generated electrons and holes are available for RL. Thus, the RL will increase with dose until all of the electron and hole traps are filled. This explains the initial increase in the RL (Fig. 5.13(c)). The RL starts to decrease at high doses due to X-ray induced radiation damage that results in non-radiative recombination sites. Thus, as shown in Fig. 5.13(d), some of the X-ray generated electrons and holes are not available for RL due to non-radiative recombination, which leads to a reduction in the RL for high doses.

The RL emission wavelength of the broad unknown defect detected from 450 nm until 580 nm is the same as observed for the PL emission spectrum (Fig. 5.13(a)). The integrated RL intensity of the unknown defect decreases with increasing dose. This might be due to the fact that the probability for the mobile charges to recombine in a non-radiative recombination site is very high and therefore, there is no RL detected of the unknown defect (Fig. 5.13(d)).

5.3.1.2 Mn doped polycrystalline NaMgF₃

The RL spectrum for both Mn concentrations can be completely attributed to the regular and highly distorted Mn²⁺ site. The peak at 500 nm arises from the highly distorted site and at 600 nm from the regular site. There is no shift in the RL emission wavelengths after heavy irradiation (Fig. 5.14(a-d)). The RL spectrum and the integrated intensity for 0.5 % Mn doped NaMgF₃ are plotted in Fig. 5.14(a+b). Fig. 5.14(b) shows I_{RL} versus the dose for the 0.5 % sample and the RL signal for the regular Mn²⁺ increases by 259.7 % and reaches a maximum after a dose of 8.5 kGy. After this initial increase the RL intensity starts to decrease. After a dose of 11.6 kGy I_{RL} has been decreased by 2.2 %, which is 251.6 % higher than the starting dose. For the distorted site, I_{RL} increases by 40 % and reaches a maximum after a dose of 5.3 kGy. After this initial increase the RL intensity starts to decrease. After a dose of 12.7 kGy I_{RL} has been decreased by 42.9 %, which is 20 % less than the value at ~1.8 Gy. The ratio of the peaks of regular to the highly distorted Mn²⁺ site changes from 18:1 at 1.8 Gy to 70:1 at 8.5 kGy.

I_{RL} for the regular Mn site for the 1 % doped sample increases by 403 % and reaches a maximum after a dose of 8.5 kGy. After this initial increase the RL intensity starts to decrease. After a dose of 12 kGy it has been decreased by 0.36 %. The RL of the highly distorted site increases by 140 % until 5.3 kGy. After this increase I_{RL} decreases by 9.4 % until 12 kGy, which is 118.2 % of the starting value. The ratio of the peaks of regular to the highly distorted Mn²⁺ change from 18:1 at 1.8 Gy to 70:1 at 8.5 kGy. For the 0.5 % Mn doped sample the ratio of the regular Mn²⁺ to the distorted Mn²⁺ site was nearly 1:1 in the PL and therefore, a higher ratio of the regular site to the distorted site was expected to be observed in the RL spectra.

Figure 5.14: (a) Radioluminescence spectra for NaMgF_3 : 0.5 % Mn for different doses and (b) the integrated RL spectra as a function of dose during continuous X-ray irradiation (regular Mn^{2+} site filled squares and highly distorted Mn^{2+} site open squares). (c) Radioluminescence spectra for NaMgF_3 :1 % Mn for different doses and (d) the integrated RL spectra as a function of dose during continuous X-ray irradiation (regular Mn^{2+} site filled squares and highly distorted Mn^{2+} site open squares).

Figure 5.15: Normalised RL spectra for low doses (blue curve) and after 12 kGy irradiation (black curve) for 0.5 % (a) and 1 % Mn (b) doped sample.

Ratio of the RL intensity of the distorted peak divided by the RL intensity of the regular peak as a function of dose for 0.5 % Mn (c) and 1 % Mn (d) doped NaMgF₃.

The normalised RL curve for low radiation and after heavy irradiation shows that the intensity of the distorted site decreases with increasing dose for both concentrations of the Mn doped samples (Fig. 5.15(a+b)). This is due to the probability for filling the distorted traps being lower than filling the traps from the regular Mn²⁺ site. In Fig. 5.15(c+d) the ratio of the RL intensity of the distorted peak to the regular peak is plotted against the

dose. This ratio is constant up to 100 Gy. After that it decreases for doses until 12.7 kGy. The decrease might be due to the generation of non - radiative defects near the distorted site.

5.3.2 Temperature dependent RL measurements

The temperature dependent measurements were performed by putting the powdered samples immersed with isopropanol on a ceramic holder and heating the holder up until a certain temperature. After the temperature had stabilized RL measurements up to a dose of 15 Gy were performed. Then the sample was thermally bleached by heating up it until 350 °C. This process was repeated for 13 different temperature settings. The total dose the sample has received at the end was ~ 200 Gy.

5.3.2.1 Eu doped polycrystalline NaMgF₃

The temperature dependent RL signal increases by 6.2 % compared to room temperature when the temperature is increased to 100 °C for the NaMgF₃: 0.2 % Eu doped sample and the RL intensity increases by 5.2 % compared to 100 °C when the temperature is decreased to 40 °C (Fig. 5.16). The RL signal for different temperature steps shows a non-linear behaviour. This might be due to the noise from the system. At low temperature, the RL signal is lower due to electron-hole-trapping overlapping the RL signal. This was already explained for the shape of the RL signal at low doses (Fig. 5.13(c)). The RL is low at room temperature due to some of the mobile carriers being trapped. The probability of thermal detrapping increases with increasing temperature. This means that a smaller fraction of the mobile electrons and holes become trapped as the temperature increases. This results in an increase in the RL with increasing temperature (Fig. 5.16(c)). For small doses and hence a negligible trapped carrier concentration, the RL should then decrease with decreasing temperature. This is not observed. It is likely that the dose at each temperature results in significant carrier trapping. Thus, as the temperature is reduced there will be a

competition between reducing the RL through reducing the thermal detrapping probability and increasing the RL due to significant trap filling at each temperature. It is apparent in Fig. 5.16(a) that the second process dominates. The thermal coefficient was estimated using the average of the temperature dependent RL curve and was around 0.11 ± 0.08 %/K.

The shape of the Eu²⁺ RL emission also changes with increasing temperature. The intensity of the sharp peak centred at 360 nm decreases compared to room temperature when the temperature is increased to 100 °C, which leads to a higher emission from the 5d level. An emission from the 4f and the 5d level is expected. With increasing temperature, the crystal field of the material changes, the energy difference between the 4f and 5d level, Δ , decreases with increasing temperature, making a transition from the 4f to the 5d level more likely. Prompt transition from the 5d to the ground state occurs, increasing the RL signal of the broad peak around 380 nm. At low temperatures, traps are only filled through process of radioluminescence. Above a certain temperature, additional deep traps will be emptied. The probability of detrapping these deep traps increases until it becomes the main process. This can be estimated from the following equation,

$$\tau_{dt} = \tau_o e^{-\frac{\Delta_1}{kT}} \quad (5.5)$$

where Δ_1 is the energy of the trap, k the Boltzmann's constant and T the temperature. Therefore, the RL signal increases with increasing temperature, which is schematically shown in Fig. 5.16(c).

Figure 5.16: (a) Temperature dependent RL for NaMgF₃: 0.2 % Eu for different temperature up to 100 °C. Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature.
 (b) RL spectra measured for different temperatures.
 (c) Model of the RL and TL trapping and detrapping in NaMgF₃ doped with Eu.

5.3.2.2 Mn doped polycrystalline NaMgF₃

For the NaMgF₃ doped with different concentration of Mn²⁺, the temperature dependent RL intensity was observed (Fig. 5.17). The blue arrows represent the regular Mn²⁺ site and the red ones represent the distorted Mn²⁺ in Fig. 5.17(a+b). In Fig. 5.17(a) the

temperature dependence of the RL intensity of the 0.5 % sample is shown. It was observed that the RL signal shows negligible hysteresis within the noise. For the highly distorted site, it was observed that the RL is not changing with increasing or decreasing temperature. For the regular site, the RL signal is dependent on the temperature. The observation of the regular Mn site is similar to the Eu doped samples (Fig. 5.16(c)).

The 1 % doped sample shows a temperature dependent RL signal. This might be due to the creation of non-radiative recombination centres next to the distorted Mn²⁺ as already explained for the RL signal. The probability of filling these traps increases with increasing temperature and therefore, the overall RL signal of the highly distorted Mn²⁺ site decreases. Since the probability of filling these traps is temperature dependent, the rate of filling these traps is decreasing with decreasing temperature from 100 °C to 40 °C. For the regular site, the RL intensity increases by 3.1 % compared to room temperature when the temperature is increased to 100 °C and decreases by 1.7 % compared to 100 °C when the temperature is decreased to 40 °C. The increase of the RL signal for higher temperatures can be explained with the same model that was used for the 0.5 % sample above. It was mentioned previously that for low temperatures, additional electron-hole-trapping overlaps the RL trapping and therefore the RL signal is lower for low temperatures. With increasing temperature the thermal excitation is increasing and additional trapping and detrapping occurs which increases the RL signal. The probability of detrapping deep traps also increases with increasing temperature (Fig. 5.16(c)).

Figure 5.17: (a) Temperature dependent RL for 0.5 % Mn and (b) for 1 % Mn doped NaMgF₃ for different temperature up to 100 °C. Blue indicates the regular Mn²⁺ site and red the highly distorted site. (c) Total RL signal of the distorted and the regular site versus the temperature for the 1 % doped sample (top graph) and the 0.5 % sample (bottom graph). (d) RL spectra measured for different temperatures for 1 % Mn doped NaMgF₃.

Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature. Black curves show the trend of the temperature dependent RL.

Fig. 5.17(d) shows the RL intensity plotted against the wavelength for different temperatures up to 100 °C. For higher temperatures, the distance between atoms increases which should lead to a change in the emission spectrum. This could result in a shift of the peak towards higher energies or a broadening of the peaks [87, 88, 89, 90]. There was no observable shift in the emission wavelength towards lower wavelengths, in the ratio of the peaks nor in the width of the peaks, which would have been expected because with increasing temperature, the spacing between atoms gets larger with a temperature change from 40 °C to 100 °C. The total temperature dependent signal of both concentrations is plotted in Fig. 5.17(c). The 0.5 % Mn sample shows a nearly temperature independent RL. The variation of the RL signal with increasing or decreasing temperature is more dependent on the RL signal of the regular Mn²⁺ site because this signal has a higher intensity than the distorted site. Tab. 5.7 summarises the temperature changes for different Mn doped samples. The thermal coefficients of the RL were calculated using the average RL signal for each temperature. The 1 % doped sample shows the biggest dependence of the RL signal on increasing temperature. Whereas the distorted site of the 0.5 % sample shows a nearly independent RL signal with increasing temperature, only the regular site shows an increase of the RL intensity with increasing temperature. All of the thermal coefficients of the RL are smaller than 0.1 %/K, which is a desirable property of a real-time dosimeter.

Table 5.7: Summary of temperature changes of the RL signal for different doped samples and different Mn²⁺ sites.

Concentration (%)	distorted (%/K)	regular (%/K)	total (%/K)
0.5	0±0.02	0.02±0.1	0.01± 0.1
1	0.03±0.02	0.03±0.07	0.03±0.07

5.4 Optically stimulated luminescence measurements

Optically stimulated luminescence (OSL) measurements were only performed for the Eu²⁺ ions in the NaMgF₃ sample. The sample was transported in a light-tight box between all the measurements. The OSL measurements were performed for different doses as shown in Fig. 5.18(a). After each irradiation, the sample was taken out of the X-ray generator and OSL was measured with an emission wavelength of 360 nm and detected at 410 nm. The irradiation was performed with an X-ray generator operator operating at 40 mA and 40 kV.

The total intensity of the OSL signal was calculated and plotted against the dose in Fig. 5.18(b). The OSL signal rapidly increases until a dose of ~ 1 kGy, and then it increases at a slower rate. The signal will probably saturate at higher doses. This is consistent with the dose dependence of the RL intensity. It was shown that the I_{RL} is increasing for doses up to ~ 850 Gy, and then is decreasing up to 12.7 kGy (Fig. 5.13(b)). The decrease of the RL signal for doses above 1 kGy results in a slower increase of the OSL signal for doses up to 19 kGy. This result leads to the assumption that the carriers are recombining at the same traps. Fig. 5.18(c) shows the change of the OSL signal (ΔOSL) divided by the change of dose versus the total dose. The signal of $\Delta\text{OSL}/\Delta\text{dose}$ is nearly constant until ~ 1 kGy and decreases until 19 kGy. This suggests that a degradation effect is occurring at higher doses, leading to a decrease of the ΔOSL signal. The OSL intensity at around 200 Gy was significantly lower than expected. This might be a result of the method of transportation the sample. During the process of irradiation and measuring the OSL, the sample could have flipped over or could have been accidentally illuminate. Therefore, there was a smaller intensity of the OSL measured. To investigate this hypothesis, measurements were repeated for 211 Gy, 4 kGy and again 211 Gy (Fig. 5.18(d)). The sample was mounted on a transportable holder for photoluminescence measurements and the whole holder was placed in the X-ray generator. After radiation the holder with sample was transported back in the light-tight box to the spectrometer and the OSL measurement was repeated with the sample in the same position. It can be seen that the OSL signal decreases after

receiving a heavy dose of 4 kGy (and a total dose of 4.2 kGy). The second measurement after receiving an additional dose of 211 Gy (total dose of 4.4 kGy) also shows a decrease in the OSL signal compared to the first measurement after a dose of 211 Gy.

Figure 5.18: (a) Absolute OSL signal versus time for the different doses.
 (b) The total OSL signal plotted versus the total dose.
 (c) The change of the OSL signal (ΔOSL) divided by the change of dose versus the total dose.
 (d) $\Delta\text{OSL}/\Delta\text{dose}$ versus the change of the dose (Δdose).

5.5 Conclusion

PL, TL, RL and OSL were observed for polycrystalline NaMgF₃ doped with Eu. Photoluminescence measurements show the presence of Eu²⁺ and Eu³⁺ ions in the Eu doped sample as well as an unknown defect centred around 470 nm. PL measurements of the Eu doped samples before and after irradiation show that the total PL emission signal of the Eu²⁺ site decreases after heavy irradiation. The Eu³⁺ signal could not be detected due to the increased broad defect centred at 470 nm for the excitation spectra after irradiation. The Eu³⁺ transitions, when excited at 396 nm, increase after irradiation with an initial dose of 19 kGy. This could be observed after subtracting the unknown defect centred at 470 nm in the PL spectra. The newly created Eu³⁺ ions are less distorted since the ratio of ⁷F₂:⁷F₁ decreases from 2:1 before to 1:1 after irradiation. TL measurements for NaMgF₃ doped with Eu show three peaks with a main peak at low temperatures (~ 363 K). Eu²⁺ and Eu³⁺ were also observed in the RL spectra and their emission wavelengths are the same wavelengths as observed in the PL spectra. The integrated RL intensity for the Eu²⁺ ion increases until it reaches a maximum above 850 Gy. After this increase it decreases again until 13 kGy. The ratio of the broad peak centred at 400 nm to the sharp peak centred at 360 nm increases with a higher dose. This was also observed for the PL emission spectra and can be explained with the creation of defects near the Eu²⁺ site. These defects shift the 5d and 4f level which increases the transition of the 5d level on top of the decrease of the Eu²⁺ signal. The RL signal of the Eu³⁺ is nearly independent of dose, which is a desirable property for a real-time dosimeter. For the unknown defect, a decrease of RL intensity versus dose was observed, which is due to the higher probability of filling traps with non-radiative recombination centres next to the unknown defect. The temperature dependent RL measurements for the Eu²⁺ ion are mainly dominated by detrapping deep traps. Hence, only corrections for this effect need to be taken into account when using these materials as dosimeters. The value of the temperature dependence of the RL intensity is 0.11 ± 0.08 %/K and the value is within the range as expected for dosimeters (< 0.4 %/K). The shape of the Eu²⁺ RL emission curve also changes with increasing temperature. The

intensity of the sharp peak centred at 360 nm decreases with increasing temperature from room temperature up to 100 °C leading to a higher emission from the 5d level. Due to an increase in temperature, the energy difference between the 4f to the 5d level, Δ , decreases and the probability of exciting into the 5d level increases with higher temperature, making TL transition from the 4f to the 5d level more likely. There was no shift in RL emission wavelengths with increasing temperatures for the NaMgF₃ samples doped with Eu observed. The thermal coefficient was estimated using the average of the temperature dependent RL curve and was around 0.11 ± 0.08 %/K. The total OSL signal rapidly increases until 1 kGy and decreases above 19 kGy. The change of the OSL signal divided by the change of the dose versus the total dose shows the same behaviour as the integrated RL signal versus the dose. This leads to the suggestion that this effect is due to the generation of the same traps.

For the 0.5 % and 1 %Mn doped samples, an additional high distorted peak of a Mn²⁺ site was observed in the PL spectrum. The PL lifetime of the highly distorted Mn²⁺ peak centred at 500 nm was lower than the lifetime of the regular Mn site centred at 600 nm. The transition of the distorted site more likely because it is only parity forbidden and therefore shows a lower lifetime. The TL glow curve for the Mn doped samples could be fitted with a deconvolution and consist of four peaks, both of the concentrations had two main peaks with similar peak temperatures and an activation energies of 0.5 eV. The high temperature peak above 608 K shifts towards higher temperatures for higher concentrations of Mn and with a higher initial dose. There was no PTTL observed. The RL spectra show that the ratio of the two Mn²⁺ sites decreases with increasing concentration. The decrease of the ratio of the distorted site to the regular site with increasing Mn concentration means there are less distorted defects in the sample with increasing Mn concentration. For the regular Mn site and both Mn concentrations, The integrated RL intensity increases until it reaches a maximum above a dose of ~ 8.5 kGy. After this initial increase the RL signal decreases up to a dose of 13 kGy. For both Mn concentrations, the distorted site shows an increase of I_{RL} until it reaches a maximum above a dose of ~ 5.3 kGy. After this dose the

RL intensity decreases until a dose of ~ 13 kGy. The temperature dependent RL intensity for the Mn doped samples depends more on the regular site because it has a higher RL signal as the distorted site. The RL intensity is temperature independent for the distorted site in the 0.5 % sample. The 1 % doped sample shows an increase of the RL signal for the regular site because of the increase of the probability of detrapping deep traps with increasing temperature. The thermal coefficient of the RL for the regular site is around 0.01 ± 0.1 %/K for the 0.5 % Mn doped sample and 0.03 ± 0.07 %/K for the 1 % sample. This is a good value for application as a real-time dosimeter.

6 NaMgF₃ nanoparticles

The nanoparticles were either doped with 0.1 %, 0.5 %, 1 %, 2 % and 5 % Eu or 1 %, 2 % and 5 % Mn. Their optical, radioluminescent and thermoluminescent properties will be discussed in this chapter. The samples were prepared with the method described in chapter 4.1.2 [76]. The crystal structure is orthorhombic with the space group P_{bnm} and from XRD measurements, the crystal size was calculated with the Scherrer formula from the XRD spectra shown in Fig. 4.1, which was ~ 25 nm. These nanoparticles had a smaller crystal size than the ones observed by Williams et al., which had an average size of 53 nm for the Mn samples, and 57 nm for the 1 % Eu and 77 nm for the 5 % Eu doped samples [10]. It is not clear why the size of the nanoparticles is smaller. This might be caused by the production process. To perform PL, PL lifetime and RL measurements, the nanoparticles were pressed into pellets with a diameter of ~ 6 mm and a thickness between 0.5 mm and 1.5 mm. The appearance of the pressed pellets was whitish. The influence of the concentration of the dopant on the PL spectra, PL lifetime, TL and RL measurements will be examined. There was no OSL observed for any of the nanoparticles.

6.1 Photoluminescence and PL lifetime measurements

PL measurements were performed with the Jobin-Yvon FluoroLog[®].

6.1.1 Eu doped NaMgF₃ nanoparticles

The PL spectrum of NaMgF₃: 5 % Eu is plotted in Fig. 6.1(a+b). The PL excitation spectra detected at 590 nm arises mainly from the 7F_1 transition of Eu³⁺ (solid curve in Fig. 6.1(a)). Eu²⁺ was detected for an emission at 360 nm (dashed curve in Fig. 6.1(a)). When exciting the sample at 396 nm Eu³⁺ emission was observed (Fig. 6.1(b)) and when exciting at 256 nm Eu²⁺ emission was detected (see inset in Fig. 6.1(b)). The sharp peak centred at 360 nm in the PL emission spectrum is due to the transition of $^6P_{7/2}$ and $^6P_{5/2}$ excited states to the $^8S_{7/2}$ ground state and the broad peak centred at 380 nm is from the band emission from the $4f^65d(E_g)$ excited states to the $4f^7$ ground state from the Eu²⁺ ion. When exciting at 396 nm the PL emission mainly arises from the 5D_1 and 5D_0 level. The solid curve in the PL emission is from the 5 % Eu doped sample and the dashed curve from the 1 % doped sample (Fig. 6.1(b)). The ratio of Eu²⁺/Eu³⁺ is 1.8:1 for the 5 % doped sample. The transitions of the excited states to the ground state are indicated in Fig. 6.1(a+b) for the Eu²⁺ and Eu³⁺ emission.

Figure 6.1: (a) PL excitation for the Eu²⁺ (λ_{em} = 360 nm - dashed curve) and Eu³⁺ (λ_{em} = 592 nm - solid curve) and (b) emission (λ_{ex} = 396 nm; inset λ_{ex} = 256 nm) spectra for NaMgF₃ doped with 1 % Eu (dashed curve) and 5 % Eu (solid curve).

The PL spectra for low temperatures are plotted in Fig. 6.2. An additional broad peak between the Eu²⁺ and Eu³⁺ emission appears. This unknown defect has a maximum at ~ 470 nm and the emission of this defect is weaker at room temperature. The excitation spectrum of the defect at ~ 470 nm is shown in the inset and it consists of one peak at 360 nm for the measurements at 300 K. At 10 K the excitation spectrum consists out of two peaks, one centred at 300 nm and one at 360 nm. This new band at 470 nm can be assigned to some defects. The precise origin of these defects is unknown, but can probably be ascribed to the same defect previously observed in NaMgF₃:Eu bulk material (see Fig. 5.3(b)). The emission of the Eu³⁺ are also weaker at room temperature. This leads to the assumption that non-radiative recombinations increase with increasing temperature. The ratio of I_{7F_2}/I_{7F_1} is 1:1.6 for the 0.1 % sample, 1:1 for the 0.5 % sample, 1:1.3 for the 1 % one and further decreasing to 1:1.2 for the 5 % sample. The average crystal environment of Eu³⁺ seems to get more distorted with increasing Eu³⁺ concentration. This was also later observed in this chapter when calculating the average PL lifetime and it will be shown that with increasing Eu³⁺ concentration, the energy transfer from Eu³⁺ away from the surface to Eu³⁺ sites near the surface increases [10, 11, 12, 22, 83].

Figure 6.2: (a) PL emission spectra for 0.1 %, (b) 0.5 %. (c) 1 % and (d) 5 % Eu doped NaMgF₃ at $\lambda_{ex} = 396$ nm at 10 K (solid curve) and at room temperature (dashed curve). Inset: PL excitation spectra detected at $\lambda_{em} = 450$ nm for the different Eu concentrations of NaMgF₃.

Temperature dependent PL lifetime measurements from the Eu³⁺ ion were performed for the 1 % Eu (Fig. 6.3) and 5 % Eu (Fig. 6.4) doped sample. The measurements were performed while cooling the samples down until 10 K with a cryostat and then increasing the temperature in 30 K steps. The PL decay can be fitted with multiple exponential components and the average lifetime was estimated as mentioned in section 3.2.4.

The radiative lifetime from Eu³⁺ can be estimated from the ⁵D₀ → ⁷F_J emission as mentioned in section 3.2.4. τ_{rad} was calculated employing the corrected PL emission spectra of the Eu³⁺ transition and subtracting the signal from the broad unknown defect centred at ~470 nm. These average lifetimes are listed in Tab. 6.1. τ_1 and τ_2 seemed to be less temperature dependent than τ_3 (Fig. 6.3(a)). The values of τ_3 are always bigger than the radiative lifetime of 9.9 ± 1.0 ms (values up to 33.5 ± 3.4 ms for 10 K) and strongly temperature dependent. For low temperatures down to 10 K, the average lifetime was as high as 13.8 ± 1.4 ms when taking all three components into account. This is much higher than the measured radiative lifetime of around 9.9 ± 1.0 ms. Therefore, it is likely that τ_3 is from the defect which causes the broad emission peak centred at 470 nm. Hence, these values were not added in the summation of the Eu³⁺ lifetime (Fig. 6.3(b)). This gives an average PL lifetime of around 7.85 ± 0.79 ms at room temperature. This effect was already reported for NaMgF₃ nanoparticles [10, 11, 12, 22, 83]. Williams et al. reported that the temperature dependence of τ_3 might occur because thermal quenching resulting in two decays: One radiative and one thermally active non-radiative. They suggested that τ_3 can be estimated from the following equation,

$$\frac{1}{\tau_3} = \frac{1}{\tau_{3,0}} + f \times e^{-\frac{E_A}{k_B T}} \quad (6.1)$$

with $\tau_{3,0}$ as the intrinsic effective decay time at 0 K, E_A the activation energy, k_B the Boltzmann's constant and f the attempt frequency [10]. At 592 nm $\tau_{3,0}$ is 32.5 ± 3.3 ms and E_A is 104 ± 36 meV.

Figure 6.3: (a) Temperature dependent average PL lifetime of 1 % Eu doped NaMgF₃ ($\lambda_{em} = 592$ nm; $\lambda_{ex} = 375$ nm) from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles), τ_3 (filled triangles) and the average lifetime, $\tau_{123,ave}$ (open squares). τ_3 was fitted using equation 6.1. (b) Temperature dependent average PL lifetime of 1 % Eu doped NaMgF₃ from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles) and the average lifetime, $\tau_{12,ave}$ (open squares) when only using the first and the second component.

Fig. 6.4(a) shows the average PL lifetime of the three components when fitting the decay curve multi - exponential and Fig. 6.4(b) shows the fit with only two of the components for the 5 % Eu doped sample. When adding all three components to the lifetime, $\tau_{123,ave}$, gets as high as 13.9 ± 1.4 ms at 10 K with a τ_3 component of 31.3 ± 3.1 ms. Therefore, the τ_3 component was excluded from τ_{ave} . Fig. 6.4(b) shows that $\tau_{12,ave}$ gets as low as 7.4 ± 0.7 ms at room temperature. τ_3 was also fitted with equation 8.1 and at 592 nm $\tau_{3,0}$ is 17.9 ± 1.8 ms with a calculated E_A of 95 ± 40 meV (Fig. 6.4(a)). This value of E_A is the same as within the experimental uncertainty for the 1 % doped sample where an E_A of 104 ± 36 meV was calculated. Williams et al. reported an E_A of 169 ± 39 meV for the 1 % Eu doped NaMgF₃ sample and an E_A of 206 ± 49 meV for the 5 % sample measured at 592

nm. For the measurement at 500 nm Williams et al. reported an value of 139 ± 20 meV for E_A . This E_A is closer to the values calculated for the nanoparticles in this thesis which have a smaller crystal size [10].

Figure 6.4: (a) Temperature dependent average PL lifetime of 5 % Eu doped NaMgF₃ ($\lambda_{em} = 592$ nm; $\lambda_{ex} = 375$ nm) from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles), τ_3 (filled triangles) and the average lifetime, $\tau_{123,ave}$ (open squares). τ_3 was fitted using equation 6.1. (b) Temperature dependent average PL lifetime of 5 % Eu doped NaMgF₃ from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles) and the average lifetime, $\tau_{12,ave}$ (open squares) when only using the first and the second component.

Table 6.1: Summary of the different measured PL lifetimes, $\tau_{12,ave}$, the radiative lifetime, τ_{rad} , and the quantum efficiency, η , for NaMgF₃ doped with different concentrations of Eu.

Concentration (%)	$\tau_{12,ave}$ (ms)	τ_{rad} (ms)	η (%)
0.1	0.64 ± 0.06 (em @ 360 nm)		
	0.51 ± 0.05 (em @ 380 nm)		

Continued on next page

Table 6.1 – *Continued from previous page*

Concentration (%)	$\tau_{12,ave}$ (ms)	τ_{rad} (ms)	η (%)
	49.4±4.9 (em @ 500 nm) 9.5±1.0 (em @ 592 nm)	11.0	86.4
0.5	0.60±0.06 (em @ 360 nm) 0.46±0.05 (em @ 380 nm) 44.5±4.5 (em @ 500 nm) 9.1±0.9 (em @ 592 nm)	9.1	99.7
1	0.62±0.06 (em @ 360 nm) 0.50±0.05 (em @ 380 nm) 41.7±4.2 (em @ 500 nm) 7.9±0.8 (em @ 592 nm)	9.9	79.5
2	0.67±0.07 (em @ 360 nm) 0.52±0.05 (em @ 380 nm) 39.2±3.9 (em @ 500 nm) 7.36±0.74 (em @ 592 nm)	10.4	71.0
5	0.65±0.06 (em @ 360 nm) 0.50±0.05 (em @ 380 nm) 35.5±3.6 (em @ 500 nm) 7.34±0.73 (em @ 592 nm)	9.2	79.4

PL lifetime measurements for the Eu³⁺ were performed with the Jobin-Yvon FluoroLog[®] and for the Eu²⁺ with the Cary50. A summary of the different lifetimes for the different Eu-ions in NaMgF₃ is listed in Tab. 6.1 and Fig. 6.5 shows the lifetimes for an emission at 592 (a) and 500 nm (b). The measurements for the Eu²⁺ were performed for an emission at 360 nm and 380 nm (λ_{ex} = 256 nm). For an emission wavelength of 592 nm the lifetime for Eu³⁺ ion were measured (λ_{ex} = 375 nm). The average lifetimes for the unknown defect centred at 500 nm were measured at an excitation wavelength of 375 nm.

Figure 6.5: (a) Average PL lifetime for Eu³⁺ ($\lambda_{em} = 592$ nm, $\lambda_{ex} = 375$ nm) doped NaMgF₃ nanoparticles against the rare earth concentration.

(b) The PL lifetime for the unknown broad peak was measured at $\lambda_{em} = 500$ nm and $\lambda_{ex} = 375$ nm.

All measurements were done at room temperature.

A radiative lifetime for the Eu³⁺ ion of up to 11.2 ± 1.1 ms was calculated for the 0.1 % Eu doped sample and the lifetime was as low as 9.1 ± 0.9 ms for the 0.5 % doped sample (see Tab. 6.1). Fig. 6.6(a) shows a PL lifetime decay curve for the 5 % Eu doped NaMgF₃ sample for an emission wavelength of 590 nm (solid curve) and the dashed curve represents the exponential fit ($\lambda_{ex} = 375$ nm). A decrease of the decay curves for the different Eu³⁺ concentrations is illustrated in Fig. 6.6(b).

Figure 6.6: (a) PL lifetime decay of 5 % Eu doped NaMgF₃ at $\lambda_{em} = 590$ nm (solid curve). The dashed curve is the exponential fit. The lifetime was measured at $\lambda_{ex} = 375$ nm. (b) The lifetime decay curves at $\lambda_{em} = 590$ nm emission for the different Eu concentrations in NaMgF₃.

τ_{ave} does not change significantly with the Eu concentration for Eu²⁺ ions but it decreases with increasing Eu³⁺ concentration. The resultant quantum efficiencies, η , are as high as 99.7 %. A systematic decrease in the Eu PL lifetimes, $\tau_{12,ave}$, can be attributed to energy transfer between Eu³⁺ sites and a high concentration of surface non-radiative recombination sites that results in a lower PL lifetime for Eu³⁺ at the surface. The decrease in τ_{500} for high Eu concentrations observed in this study suggests that there is also energy transfer between the unknown defects to sites with higher non-radiative decay rates. The average PL lifetime of the unknown defect in the polycrystalline bulk materials was around 67 ms for an emission wavelength of 460 nm. This lifetime is larger than the calculated lifetimes of Eu²⁺ and Eu³⁺. These non-radiative decay surface sites were previously observed in other nanoparticles and it was shown that only luminescent ions near the surface will experience non-radiative decay [85, 86]. This reduction in the PL lifetime was observed for LaF₃ nanoparticles and also reported for NaMgF₃ ones [10, 11, 12, 22, 83]. The energy transfer

occurs in terms of a transfer from Eu³⁺ in Eu sites near the surface or Eu³⁺ ion sites away from the surface. This energy transfer between Eu³⁺ ions could occur by a dipole-dipole or dipole-quadrupole mechanism which have a r^{-6} or r^{-8} dependency, respectively [91]. This means for the dipole-dipole mechanism as the average distance between nuclei decreases cubically with the Eu³⁺ concentration the energy transfer increases quadratically with Eu³⁺ concentration. It seems for $\tau_{12,ave}$ that from a certain concentration the amount of extra Eu does not matter anymore because the energy transfer is already very efficient and hence does not cause an extra decrease in lifetime, see Fig. 6.5(a). For the polycrystalline NaMgF₃:Eu bulk materials, an average PL lifetime of 0.63 ± 0.06 ms for an emission wavelength of 360 nm, 0.42 ± 0.04 ms for an emission wavelength of 380 nm and 11.1 ± 0.1 ms for an emission wavelength of 592 nm was calculated. The PL lifetimes for the Eu²⁺ emission are similar in the nanoparticles. The lifetime of the Eu³⁺ lifetime is slightly higher in the bulk materials.

The Judd-Ofelt parameters, Ω_2 and Ω_4 , for the Eu³⁺ ions were also calculated [65, 66, 92]. The parameters were estimated from equation 3.4, where I_{0-J} are the intensity values from the PL spectra in Fig. 6.2 at room temperature after subtracting the unknown broad defect centred at 470 nm. The resulting Ω_2 and Ω_4 values are listed in Tab. 6.2. Ω_2 and Ω_4 are 6.87×10^{-20} cm² and 25.0×10^{-20} cm² for the 1 % doped Eu sample and 7.52×10^{-20} cm² and 27.9×10^{-20} cm² for 5 % Eu. Williams et al. calculated the values of Ω_2 and Ω_4 as 6.95×10^{-20} cm² and 15.7×10^{-20} cm² for 1 % Eu and 11.3×10^{-20} cm² and 22.8×10^{-20} cm² for 5 % Eu doped NaMgF₃ [10]. These values are also summarised in Tab. 6.2. It was observed that for smaller nanoparticles the resultant Ω_2 is also smaller. This indicates that, on average, the Eu³⁺ is in less distorted sites [10]. It was not possible to see any dependence of Ω_2 of the Eu concentration for the different nanoparticles. It was reported that Ω_2 is to be found in ranges of $\sim 1 \times 10^{-20}$ cm² to 33×10^{-20} cm² in other nanoparticle compounds [22, 93, 94, 95]. Brito et al. reported that Ω_2 is connected to short range effects and if the symmetry of the Eu³⁺ site is reduced Ω_2 will increase [93]. Therefore, the higher Ω_2 is, the more Eu³⁺ is in a distorted site. Eu³⁺ is more distorted near the surface which

was already observed for other nanoparticle compounds [10, 11, 12, 22]. Ω_4 is connected with long range effects [93], and it is found in ranges from (0.2 to 13) $\times 10^{-20}$ cm². It is not clear why Ω_4 is higher than ranges found in other compounds.

Table 6.2: The Judd-Ofelt parameters Ω_2 and Ω_4 for $^5D_0 \rightarrow ^7F_2$ transitions for different concentrations of Eu doped NaMgF₃ nanoparticles measured using the PL emission.

Concentration (%)	Ω_2 (10^{-20} cm ²)	Ω_4 (10^{-20} cm ²)	Ω_2 (10^{-20} cm ²)[10]
0.1	5.3 $\pm$ 0.5	22.2 $\pm$ 2.2	
0.5	8.3 $\pm$ 0.8	26.7 $\pm$ 2.7	
1	6.9 $\pm$ 0.7	25.0 $\pm$ 2.5	6.95
2	5.9 $\pm$ 0.6	24.9 $\pm$ 2.5	
5	7.5 $\pm$ 0.8	27.9 $\pm$ 2.8	11.3

6.1.2 Mn doped NaMgF₃ nanoparticles

The PL emission spectrum for NaMgF₃ doped with 5 % Mn is plotted in Fig. 6.7(a) and the excitation spectrum for different concentrations of Mn is shown in Fig. 6.7(b). NaMgF₃ nanoparticles show a distorted peak centred at 500 nm in the PL spectrum. This was also observed for the NaMgF₃ bulk materials. For the excitation spectrum was detected for an emission wavelength of 500 nm for the distorted site and 600 nm for the regular site (Fig. 6.7(a)). The emission spectra was excited at 396 nm (Fig. 6.7(b)). For the NaMgF₃:Mn bulk materials, the PL spectra was measured for the different Mn concentrations and it was observed that the distorted site centred at 500 nm increases for smaller concentrations of the dopant in the material (see Fig. 5.6(b)). For the nanoparticles, it was observed that the PL intensity of the Mn site centred at 500 nm increases for Mn concentrations and reaches a maximum after a concentration of 2 % Mn. After this initial increase the PL intensity starts to decrease until a concentration of 5 % Mn.

Figure 6.7: (a) PL excitation spectra for 5 % Mn doped NaMgF₃ at $\lambda_{em}=500$ nm (dashed curve) and $\lambda_{em}=600$ nm (solid curve) for the distorted Mn²⁺ site.
 (b) PL emission spectrum for NaMgF₃ doped with 1 % Mn (red), 2 % (blue) and 5 % Mn (black) excited at 396 nm.

Average PL lifetime was measured when exciting the sample at 465 nm for the regular Mn²⁺ site ($\lambda_{em}=600$ nm) and the distorted Mn²⁺ site ($\lambda_{em}=500$ nm). These measurements were carried out with the Jobin-Yvon FluoroLog[®]. The average PL lifetime, τ_{ave} , could be fitted in a two - exponential decay (the same as the bulk materials). PL lifetime measurements showed a dependence of τ_{ave} on the Mn concentrations (Fig. 6.9 and Tab. 6.3). The highest lifetime was measured for the 2 % doped sample and τ_{ave} was the lowest for the 1 % doped sample (Fig. 6.8(a+b)). The average PL lifetime for the distorted Mn²⁺ site ranged from 11.1 ± 1.1 ms until 11.6 ± 1.2 ms. It was lower than the calculated lifetime of the regular site which ranges from 62 ± 6 ms until 80.1 ± 8.0 ms (Tab. 6.3). The lower τ_{ave} for the distorted site may suggest that these sites are near a non-radiative recombination site, which makes the transition more allowed.

Figure 6.8: (a) PL lifetime decay of 1 % Mn doped NaMgF₃ at $\lambda_{em}=500$ nm (solid curve) and (b) $\lambda_{em}=600$ nm (solid curve). The dashed curve is the exponential fit. The lifetime was measured at $\lambda_{ex}=465$ nm.

The average lifetime of the distorted site for the NaMgF₃ bulk materials was 13 ± 1.3 ms for both concentrations. This is similar to the lifetimes calculated for the distorted site in the nanoparticles. The regular site shows a lifetime as high as 98 ± 10 ms for the 0.5 % doped sample for the bulk materials, which is higher than calculated for the nanoparticles. The lower lifetime of the regular site in the nanoparticles means that this site is more distorted and transitions are more allowed.

Figure 6.9: Average PL lifetime for the distorted Mn²⁺ site (λ_{em} = 500 nm red squares) and the regular Mn²⁺ site (λ_{em} = 600 nm blue squares) doped NaMgF₃ nanoparticles versus the rare earth concentration.

Table 6.3: Summary of different measured PL lifetimes, τ_{ave} , for NaMgF₃ doped with different concentrations of Mn.

Concentration (%)	τ_{ave} (ms)
1	11.1±1.1 (em @ 500 nm)
	62.0±6.2 (em @ 600 nm)
2	11.6±1.2 (em @ 500 nm)
	80±8 (em @ 600 nm)
5	11.4±1.1 (em @ 500 nm)
	74±7 (em @ 600 nm)

6.2 Thermoluminescence measurements

6.2.1 Eu doped NaMgF₃ nanoparticles

The Eu doped NaMgF₃ nanoparticles hardly show any TL. Therefore, the TL of the 0.5 % and the 5 % doped samples were only plotted in Fig. 6.10(a+b). The samples were irradiated for 20 min with an X-ray generator operating at 40 kV and 40 mA using an Aluminium filter. Afterwards, the samples were heated up to 350 °C with a heating rate of 1 K/s and glow curve data was collected using a PMT. The PMT could not detect the origin of the TL transition. Glow curve peaks were fitted using first order kinetics glow curve deconvolution. The glow curve peaks are listed in Tab. 6.4.

Figure 6.10: TL glow curves for NaMgF₃ doped with 0.5 % (a) and 5 % (b) Eu after 20 min irradiation with the X-ray generator operating at 40 kV and 40 mA (solid curves). The TL was detected with the PMT. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves).

The values for the 5 % Eu doped sample compare to the values obtained for the bulk materials (see Tab. 5.5). There is only an additional high temperature peak at ~551 K which was not observed for the bulk materials. The first peak centred at 363 K has the

highest TL intensity in the bulk samples but it shows a low intensity for the nanoparticles. The peak intensity for the peak at 386 K for the 5 % Eu doped nanoparticle also has a lower intensity (Fig. 6.4(b)) compared to the bulk samples (see Fig. 5.8). The peak intensities of the TL glow curve peaks centred at 459 K and 551 K are similar for both concentrations of Eu in the nanoparticles. The glow curve peak at 363 K has the lowest TL intensity for both Eu doped samples. The 2nd glow curve peak shifts towards lower temperatures for the 5 % Eu doped sample, the peak intensity also increases compared to the 0.5 % sample. Although the TL measurements were detected with the PMT and it could not be distinguished if the TL signal arises from the Eu²⁺ ions or the Eu³⁺ ones. The activation energies obtained from the nanoparticles were similar to the bulk sample. Therefore, it can be assumed that the TL signal is due to same traps from the Eu²⁺ emission. Potential additional peaks above 620 K could not be detected due to the temperature limitation of the equipment used.

Table 6.4: The activation energies of the individual glow curve peaks for the NaMgF₃: 0.5 % and 5 % Eu sample obtained by first order kinetics glow curve deconvolution. The top line is the activation energy for the glow curve.

	0.76±0.08 eV	0.61±0.06 eV	0.50±0.05 eV	0.50±0.05 eV
0.5 %	363 K	411 K	459 K	551 K
peak height	10	40	30	200
5 %	363 K	386 K	459 K	551 K
peak height	10	10	40	20

6.2.2 Mn doped NaMgF₃ nanoparticles

The TL glow curves for the Mn doped samples with different concentrations are plotted in Fig. 6.11 and activation energies for the individual glow curve peaks are listed in Tab. 6.5. The TL glow curve peaks were calculated with the first order kinetics glow curve

deconvolution. The TL data was collected using a PMT after an irradiation of 20 min with a X-ray generator (40 kV, 40 mA) using an Aluminium filter at a heating rate of 1 K/s.

The nanoparticles show different activation energies and their peak maximums are found at different temperatures compared to the bulk materials. The main peaks for the bulk materials are observed for higher temperatures, where the nanoparticles have their main peaks at lower temperatures up to ~ 500 K. The high temperature glow curve peak shifts from ~ 516 K to ~ 535 K with increasing Mn concentration of the sample. The other peak maxima are constant within a range of 4 K. The low temperature peak centred at 354 K shows an activation energy of 0.76 eV. For the 1 % Mn doped nanoparticles the main three peaks are found at 381 K, 401 K and 450 K, with respectively an activation energies of 0.6 eV, 0.54 eV and 0.5 eV. For the 5 % doped sample the activation energy was 0.54 eV and 0.5 eV for peaks centred at 401 K and 464 K, respectively. For the 1 % doped sample, additional TL measurements were performed after irradiating the sample with different doses to investigate the dependence of the TL intensity on the initial dose (Fig. 6.11(d)). Therefore, the sample was irradiated with a dose of 1056 Gy and TL was measured. After this, the sample was irradiated again with a dose of 3168 Gy, which gives a total dose of 4224 Gy. TL was measured again. Then, the sample was irradiated again with a dose of 1056, which leads to a total dose of 5280 Gy. TL measurements were performed again. The TL glow curve shows a different shape after receiving a dose of 1056 Gy compared to receiving a total dose of 5280 Gy. The reason for this is that the probability of trapping changes after receiving a higher dose. For higher doses the filling of additional traps might increase resulting in a less sharp peak at 375 K when receiving a total dose of 4224 Gy. Fig. 6.11(d) shows the TL intensity decreases when receiving a total dose of 5280 Gy compared to TL measurements when receiving a dose of 1056 Gy. No significant change in activation energies or temperatures after receiving different doses was observed. Only the concentration of the dopant has an influence on the temperature shift of the glow curves peaks.

Figure 6.11: TL glow curves for NaMgF₃ doped with 1% Mn (a), 2 % Mn (b), 5 % Mn (c) after 20 min irradiation and for 1 % Mn after 10 min, 30 min and again 10 min (d) irradiation with the X-ray generator operating at 40 kV and 40 mA (solid curves). The TL was detected with the PMT. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves).

The intense glow curve peaks are found at 380 K, 403 K and 450 K. The peak at temperatures above 510 K show a lower TL glow curve height for the 1 % and 5 % doped samples. In comparison with the Mn doped bulk materials, the TL glow curve peak at a temperature of ~ 464 K with an activation energy of 0.5 eV was similar (see Tab. 5.6). These values compare well with the values obtained for the Eu doped NaMgF₃ bulk material (Tab. 5.5

and Tab. 6.4). It is likely that these defects arise from the same defects. The TL signal intensity was too low to be detected with the CCD detector but as the temperatures and the activation energies for the Mn doped nanoparticles are comparable to the Mn doped bulk materials it is more likely that the TL signal arises from the 600 nm emission. Potential additional peaks above 620K could not be detected due to the temperature limitation of the equipment used.

Table 6.5: The activation energies of the individual glow curve peaks for NaMgF₃ doped with different concentration of Mn²⁺ obtained by first order kinetics glow curve deconvolution. The top line is the activation energy for the different peaks for the glow curves.

	0.76±0.08 eV	0.60±0.06 eV	0.54±0.05 eV	0.50±0.05 eV	0.50±0.05 eV
1 % (10 min)	359 K	379 K	401 K	449 K	516 K
peak height	100	280	130	180	140
1 % (20 min)	357 K	376 K	404 K	449 K	519 K
peak height	350	550	260	170	60
1 % (30 min)	357 K	373 K	403 K	449 K	516 K
peak height	50	390	390	380	270
1 % (10 min-repeat)	357 K	373 K	403 K	449 K	516 K
peak height	60	130	130	100	80
2 % (20 min)	351 K	374 K	401 K	450 K	520 K
peak height	100	200	340	310	230
5 % (20 min)	356 K	381 K	400 K	464 K	535 K
peak height	270	600	630	470	80

6.3 Radioluminescence and temperature dependent RL measurements

Radioluminescence measurements were performed on pressed pellets. The temperature dependent RL measurements were performed on the pulverised samples, immersed with isopropanol and dispersed on a ceramic heat element to control heating.

6.3.1 Radioluminescence measurements

6.3.1.1 Eu doped NaMgF₃ nanoparticles

In Fig. 6.12 to 6.14, the RL measurements of the Eu doped NaMgF₃ nanoparticles are plotted. RL was measured using a CCD while irradiating the sample with an X-ray generator. For lower doses the sample was irradiated with an ²⁴¹Am source and the data was collected using a PMT (solid curve in Fig. 6.14(b)). The RL arises mainly from Eu²⁺ and Eu³⁺ emission and their energies are the same as those observed in the PL spectra. There is no shift of RL emission wavelengths in the spectra for transitions of the two ions after heavy irradiation. The RL intensity against the dose shows the same behaviour for all different concentrations of Eu. I_{RL} decreases at a slower rate for the Eu³⁺ ion compared to the Eu²⁺ ion. It was calculated that the integrated RL intensity of the Eu²⁺ ion decreases by 28.5 % at 1 kGy and by 77.4 % at 12.7 kGy for the 0.1 % doped sample. I_{RL} decreases by 2.6 % 1 kGy and by 8 % at 12.7 kGy for the Eu³⁺ ion (Fig. 6.12(a+b)). A change in the ratio $I_{Eu^{3+}}/I_{Eu^{2+}}$ from 1.3:1 at 35 Gy to 5.3:1 at 12.7 kGy was observed.

Figure 6.12: Radioluminescence spectra for NaMgF₃ nanoparticles doped with 0.1 % Eu (a) and 0.5 % Eu (c) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 0.1 % Eu (b) and 0.5 % Eu (d) doped samples (Eu²⁺ open squares and Eu³⁺ filled squares).

For the 0.5 % sample, the integrated intensity (I_{RL}) decreases by 12.3 % at 1 kGy and by 56.7 % at 12.7 kGy for the Eu²⁺ ion. The RL intensity decreases by 0.3 % 1 kGy and by 2.6 % at 12.7 kGy for the Eu³⁺ ion (Fig. 6.12(c+d)). A change $I_{Eu^{3+}}/I_{Eu^{2+}}$ from 5.8:1 at 35 Gy to 18:1 at 12.7 kGy was calculated.

Figure 6.13: Radioluminescence spectra for NaMgF₃ nanoparticles doped with 1 % Eu (a) and 2 % Eu (c) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 1 % Eu (b) and 2 % Eu (d) doped samples (Eu²⁺ open squares and Eu³⁺ filled squares).

I_{RL} decreases by 21.2 % at 1 kGy and by 64.8 % at 12.7 kGy for the Eu²⁺ ion. The RL intensity decreases by 3.1 % 1 kGy and by 8.6 % at 12.7 kGy for the Eu³⁺ ion for NaMgF₃: 1 % Eu (Fig. 6.13(a+b)). In this case $I_{Eu^{3+}}/I_{Eu^{2+}}$ changes from 6.3:1 at 52 Gy to 16:1 at 12.7 kGy. The 2 % doped sample shows a decrease by 28.7 % at 1 kGy and by 77.8 % at 12.7 kGy for the Eu²⁺ ion. I_{RL} decreases by 5.2 % 1 kGy and by 14.7 % at 12.7 kGy for the Eu³⁺ ion (Fig. 6.13(c+d)). A ratio of 21:1 for $I_{Eu^{3+}}/I_{Eu^{2+}}$ at 35 Gy and 75:1 at 12.7

kGy was estimated.

Figure 6.14: Radioluminescence spectra for NaMgF₃ nanoparticles doped with 5 % Eu (a) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 5 % Eu (b) doped samples (Eu²⁺ open squares and Eu³⁺ filled squares, solid line ²⁴¹Am irradiation). The γ -ray RL was scaled to match the X-ray RL.

The highest decrease of the integrated RL intensity of the Eu²⁺ was observed for the 5 % doped sample. The intensity decreases by 35.5 % at 1 kGy and by 84.4 % at 12.7 kGy for the Eu²⁺ ion. The RL intensity decreases by 5.6 % 1 kGy and by 13.6 % at 12.7 kGy for the Eu³⁺ ion (Fig. 6.14(a+b)). The $I_{Eu^{3+}}/I_{Eu^{2+}}$ ratio changes from 23:1 at 35 Gy to 125:1 at 12.7 kGy. The decrease in I_{RL} for the Eu³⁺ at high doses is likely to occur through the generation of defects that act as non-radiative decay centres. It is not clear why the RL integrated intensity increases at a faster rate for Eu²⁺ [10, 11]. For example, it decreased by 84.4 % at 12.7 kGy for the 5 % sample. It might be because radiation induced defects preferentially occur near Eu²⁺ sites leading to more quenching of the Eu²⁺ RL compared with the Eu³⁺ intensity. It is apparent in Fig. 6.14(b) that the Eu³⁺ RL is dose-independent down to at least 10 mGy for low doses for the 5 % Eu sample. This was measured with the ²⁴¹Am source, which emits γ -rays. The decrease of the integrated RL

signal might be due to the creation of additional point defects, resulting in non-radiative decay [10]. The ratio of I_{7F_2}/I_{7F_1} does not change after heavy irradiation and it is around 1:1.7 for all doses and concentrations. In the PL spectra, the ratio of I_{7F_2}/I_{7F_1} is dependent on the Eu^{3+} concentration. It was calculated as 1:1.6 for the 0.1 % sample, 1:1.3 for the 1 % sample and decreases to 1:1.2 for the 5 % sample. The average crystal environment of Eu^{3+} seem to be more distorted with increasing Eu^{3+} concentration.

The 5 % doped sample shows the biggest change in the ratio of the intensity of $\text{Eu}^{3+}/\text{Eu}^{2+}$ in the RL spectra and it changes from 23:1 to 125:1. This decrease of I_{RL} for the Eu^{2+} ion might be due to the conversion from Eu^{2+} to Eu^{3+} , which was reported for the bulk materials (see chapter 5). The ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$ is 1.8:1 in the PL spectrum for the 5 % doped sample. There is no RL transition detected from the unknown defect between 400 nm to 500 nm but this was observed in the RL spectrum for the bulk materials (see Fig. 5.13(a)).

In a recent paper, Williams et al. reported the RL behaviour of Eu^{2+} and Eu^{3+} for doses up to 30 kGy. They showed that the integrated RL intensity of Eu^{2+} and Eu^{3+} for a 1 % Eu doped sample decreases up to ~ 10 kGy and decreases at a slower rate above ~ 10 kGy, which is shown in Fig. 6.15. The size of the nanoparticles was 57 nm for the 1 % Eu doped sample, which were investigated in the paper [10]. The size of the nanoparticles researched in this thesis were 25 nm.

Figure 6.15: The integrated Eu³⁺ (filled squares, left axis) and Eu²⁺ (open squares, right axis) RL spectra as a function of radiation dose for NaMgF₃:1 % Eu nanoparticles with a crystal size of 57 nm [10].

6.3.1.2 Mn doped NaMgF₃ nanoparticles

The following Fig. 6.16 and 6.17 are showing the RL spectra against dose for NaMgF₃ doped with different concentrations of Mn.

Figure 6.16: Radioluminescence spectra for NaMgF₃ nanoparticles doped with 1 % Mn (a) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 1 % Mn (b) doped samples.

For all of the nanoparticles, the RL of the distorted site centred at 500 nm was too weak and therefore, the dose dependence could not be calculated from the RL emission spectra. The strongest decrease of the integrated RL signal with increasing dose was observed for the 1 % Mn doped sample (Fig. 6.17(b)). The RL intensity for the regular site decreases by 2.7 % at 1 kGy and decreases until 20.9 % at 12 kGy (Fig. 6.17(b)).

Figure 6.17: Radioluminescence spectra for NaMgF₃ nanoparticles doped with 2 % Mn (a) and 5 % Mn (c), for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 2 % Mn (b), and 5 % Mn (d) doped samples, solid line ²⁴¹Am irradiation. The γ -ray RL was scaled to match the X-ray RL.

A decrease by 2.9 % at 1 kGy and by 9.6 % at 12 kGy was calculated for the 2 % Mn doped nanoparticles. The lowest dose dependence of RL signal was observed at the 5 % doped sample. The signal decreases by 0.2 % at 1 kGy and by 7.52 % at 12 kGy. Fig. 6.17(d) shows RL measurements down to ~ 10 mGy for the 5 % Mn doped sample. These measurements were performed with an ^{241}Am nuclide that emits γ -rays.

Fig. 6.18 shows long-term RL measurements of NaMgF₃ doped with 1 % Mn, which were measured up to a dose of 20 kGy. These measurements were performed by Williams et al. for nanoparticles with a bigger crystal size (53 nm) [10]. The size of the nanoparticles researched in this thesis was 25 nm. Williams et al. reported, the integrated RL intensity decreases up to a dose of ~ 10 kGy and I_{RL} saturates above ~ 10 kGy. The RL signal for the Eu doped samples decreases with increasing dose (see Fig. 6.13). This indicates that the decreasing RL signal is caused by the creation of point defects with non-radiative recombination centres near the Mn^{2+} [10].

Figure 6.18: The integrated RL spectra as a function of radiation dose for NaMgF₃:1 % Mn^{2+} nanoparticles with a crystal size of 53 nm [10].

6.3.2 Temperature dependent RL measurements

6.3.2.1 Eu doped NaMgF₃ nanoparticles

Temperature dependent RL measurements were performed with a custom-built TL setup employing pulverized samples, immersed in isopropanol and dispersed on a ceramic holder. The integration time for each measurement was 5 s and 10 measurements were taken at each temperature step. The sample was heated from 40 °C to 100 °C in 10 °C steps. At a certain temperature, the samples were thermally bleached with temperatures as high as 350 °C. The sample received a total dose of 1.2 kGy at the end of these measurements.

The temperature dependent RL spectra for the 0.1 % and 5 % Eu doped samples are shown in Fig. 6.19(a-d). In Fig. 6.19(a) it was observed that the RL intensity is not decreasing until it reaches the initial measured RL intensity at 40 °C. The intensity of the last measurement at 40 °C is smaller than the intensity at the first measurement at 40 °C. For the 0.1 % RL intensity increases by 0.2 % compared to room temperature when the temperature is increased to 100 °C, and decreases by 11.8 % compared to 100 °C when decreasing the temperature to 40 °C leading to a total difference of 11.6 %. The integrated RL intensity for the Eu²⁺ ion decreases by 2.8 % compared to room temperature when the temperature is increased to 100 °C and decreases by 15.1 % compared to 100 °C when decreasing the temperature to 40 °C. The total difference of the integrated intensity was 17.5 %. The RL is low at room temperature due to some of the mobile carriers being trapped. The probability of thermal detrapping increases with increasing temperature. This means that a smaller fraction of the mobile electrons and holes become trapped as the temperatures increases. This results in an increase in the RL signal with increasing temperature (see model in Fig. 5.16(c)). The sample received a total dose of ~1.2 kGy and it is possible that some non-radiative recombination sites are generated by X-ray irradiation that leads to a reduction in the RL. As can be seen in Fig. 6.12(b), the RL systematically decreases with increasing dose for doses above ~100 Gy.

Figure 6.19: Temperature dependent RL spectra for NaMgF₃ nanoparticles doped with 0.1 % Eu (a), and 5 % Eu (c) for different temperatures up to 100 °C and the respective RL spectra versus the wavelength for different temperatures ((b) for 0.1 % Eu and (d) for 5 % Eu).

Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature. Eu²⁺ is indicated by the red colour and Eu³⁺ by the blue colour. The lines are guided to the eye.

The 5% Eu sample shows a decrease in the Eu²⁺ and Eu³⁺ RL compared to room temperature as the temperature is increased to 100 °C. Decreasing the temperature from 100 °C to 40 °C results in a further decrease in the RL where the RL at 30 °C is lower than the

initial value. The initial decrease in the RL with increasing temperature may be due to thermal activation to non-radiative recombination centres as shown in Fig. 6.20. In this model, the RL should then increase as the temperature is reduced from 100 °C to 30 °C. However, this does not occur. It is possible that some non-radiative recombination sites are generated by X-ray irradiation that leads to a reduction in the RL. This is possible because the total dose during the experiment was ~ 1.2 kGy. As can be seen in Fig. 6.14, the RL systematically decreases with increasing dose for doses above ~ 100 Gy.

Figure 6.20: Access of non-radiative traps with increasing temperature.

The thermal coefficient of the RL could not be estimated. There was no observable shift in the RL emission wavelengths of Eu²⁺ transitions with increasing temperature because the temperature change was too low.

6.3.2.2 Mn doped NaMgF₃ nanoparticles

In Fig. 6.21 and 6.22, the temperature dependent integrated RL spectra of 1 % Mn and 5 % Mn doped NaMgF₃ and their RL spectra against the wavelength for different temperatures are plotted. I_{RL} for the 1 % Mn doped sample decreases by 12.1 % compared to room temperature when increasing temperature up to 100 °C and decreases by 1.7 % compared to 100 °C when decreasing temperature at 40 °C leading to a total decrease by 13.7 %. The

decrease of the RL intensity with increasing temperature might be due to an energy transfer to a non-radiative recombination site. Therefore, the overall RL intensity decreases (Fig. 6.21(a)). The 1% Mn sample shows a decrease in the RL compared to room temperature when the temperature increases up to 100 °C. Decreasing the temperature from 100 °C to 40 °C results in a further decrease in the RL where the RL intensity when measuring it again at 40 °C is lower than the initial value. The initial decrease in the RL with increasing temperature may be due to thermal activation to non-radiative recombination centres as shown in Fig. 6.20. In this model, the RL should then increase as the temperature is reduced from 100 °C to 40 °C. However, this does not occur. The further decrease of the RL signal with decreasing temperature from 100 °C to 40 °C is due to the dose dependence of the RL signal. The sample has received a total dose of ~ 1.2 kGy, and RL measurements showed that the signal will decrease by 2.7 % at this dose (see Fig. 6.16(a)).

Figure 6.21: Temperature dependent RL spectra for NaMgF₃ nanoparticles doped with 1 % Mn (a) for different temperatures up to 100 °C and the respective RL spectra versus the wavelength for different temperatures ((b) for 1 % Mn).

Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature. The lines are guided to the eye.

A different behaviour was observed for the 5 % Mn doped sample (Fig. 6.22). At first, the

signal decreases by 3.2 % compared to room temperature as the temperature is increased to 100 °C and increases by 16.4 % compared to 100 °C when decreasing temperature at 40 °C leading to a total increase by 13.7 %. At low temperatures, the traps start to get filled. They are not filled unless there is a high enough dose. The appearance of RL does not depend on the filling of the traps. If the temperature increases, the probability of hopping increases. This means that the carriers overcome an energy barrier, Δ , and could recombine in non-radiative recombination centres (Fig. 6.22(c)). For small doses and hence a negligible trapped carrier concentration, the RL signal should decrease with decreasing temperature. This is here not observed. However, it is likely that the dose at each temperature results in a significant carrier trapping. Therefore, as the temperature decreases there may be a competition between reducing the RL via reducing the thermal detrapping probability and increasing the RL due to significant trap filling at each temperature. It is apparent that the second process dominates in Fig. 6.22(a). The same process was also shown in Fig. 5.16(a) for the NaMgF₃ polycrystalline materials. The thermal coefficient could not be calculated from the measurements since the difference in the RL intensities is too large for increasing and decreasing temperatures. The temperature was not high enough to observe a shift in the RL emission wavelengths.

Figure 6.22: Temperature dependent RL spectra for NaMgF₃ nanoparticles doped with 5 % Mn (a) for different temperatures up to 100 °C and the respective RL spectra versus the wavelength for different temperatures ((b) for 5 % Mn). Arrows facing up signal an increase of temperature, and arrows facing down signal an decreases in temperature. The lines are guided to the eye. (c) Non-radiative recombination near a Mn site.

6.4 Conclusion

Eu²⁺, Eu³⁺, and a unknown defect centred at around 470 nm were observed in the PL spectra of the nanoparticles as it previously was observed for the polycrystalline bulk ma-

terials. Temperature dependent PL measurements for the Eu doped samples show that the unknown defect centred at 470 nm increases with decreasing temperature. The peak of the unknown defect in the PL excitation spectra is broader at low temperature. The PL intensity of the unknown defect is also dependent on the concentration of the dopant, which means it increases with decreasing Eu concentration. The PL lifetimes of the Eu doped nanoparticles are similar to the bulk materials, when calculated with the 1st and 2nd component of the multi-exponential fit from the PL decay curve. $\tau_{12,ave}$ of the Eu³⁺ ion decreases with increasing Eu concentration, which can be attributed to an energy transfer from Eu³⁺ sites away from the surface to Eu³⁺ sites near the surface. The quantum efficiency was as high as 99.7 %. Temperature dependent PL lifetime measurements show that $\tau_{12,ave}$ is nearly constant for decreasing temperature. The unknown defect has a long PL lifetime of 49.4 ms for the 0.1 % sample and the lifetime decreases to 35.5 ms for the 5 % Eu doped sample. It shows thermally activated behaviour with an activation energy of 104 ± 36 meV for the 1 % doped sample and 95 ± 40 meV for the 5 % sample. The Judd-Ofelt parameters have been calculated and Ω_2 seems to be in the range of other nanoparticle compounds. Ω_4 is higher than Ω_2 and higher than observed in other compounds as LaF₃. The NaMgF₃:Eu nanoparticles showed similar activation energies of the TL glow curves peaks as it was researched for the Eu doped bulk materials. This means that the peaks might arise from the same defects. Eu²⁺ and Eu³⁺ were measured in the RL spectra. The unknown defect centred at ~ 470 nm was not observed in the RL spectra of the Eu doped samples. I_{RL} is independent of dose from 10 mGy to ~ 500 Gy. For doses higher than 500 Gy, the RL intensity decreases. The integrated RL intensity of the Eu³⁺ for the 0.5 % sample decreases by 2.6 % at 12.7 kGy. The 5 % doped nanoparticles show the highest decrease by 13.6 % at 12.7 kGy for the Eu³⁺ ion. The RL intensity of the Eu²⁺ ion decreases at a faster rate for all of the samples. In general, the RL intensity is less dependent on the dose as it was observed for the bulk samples, which means there are different defect distributions in the nanoparticles. The RL intensity shows a higher dependence on the temperature than the bulk materials and the difference in the RL signal for increasing and decreasing temperature is too large to calculate the thermal coefficient of the RL intensity.

PL measurements show the regular Mn²⁺ site centred at 600 nm and also an additional highly distorted site centred at 500 nm, which also was observed for the NaMgF₃ bulk materials. The PL decay curve of the Mn²⁺ nanoparticles could be fitted two-exponential. The regular site shows a higher lifetime than the distorted site, which might suggest that the distorted site is near a non-radiative centre. TL measurements for the Mn doped nanoparticles show more low temperature peaks and different activation energies for the peaks compared to the Mn doped bulk materials. This means that there is a different defect distribution compared to the bulk materials. Mn²⁺ was observed in the RL spectra and the integrated intensity slightly decreases above ~ 1 kGy for 5 % Mn²⁺. For the 1 % and 2 % Mn doped samples, the integrated RL intensity decreases at a faster rate. The RL of the Mn doped nanoparticles is dependent on the temperature, but the thermal coefficient of the RL could not be calculated. As previously mentioned in chapter 5 for the polycrystalline NaMgF₃ materials, optical bleaching of the nanoparticles after the temperature change should be applied.

7 Bulk polycrystalline RbMgF₃

In this chapter, the optical, radioluminescent and thermoluminescent properties of Eu and Mn doped RbMgF₃ will be discussed. The samples were prepared as described in the experimental description given in chapter 4.1.1. 10 g of each sample was produced using high purity Rubidium fluoride (RbF), Magnesium fluoride (MgF₂), Europium(II) fluoride (EuF₂) or Manganese(II) fluoride (MnF₂). RbMgF₃ has a hexagonal crystal structure with the space group $P_{63/mmc}$ and a melting point of ~ 912 °C. The bandgap is about 7.32 eV [79], and the crystal field splitting between the 4f-5d level is around 970 cm^{-1} (0.12 eV) [59]. The samples which will be discussed were doped with 0.2 % Eu or 0.2 % Mn and their appearance was transparent.

7.1 Photoluminescence and PL lifetime measurements

PL measurements were performed with the Jobin-Yvon FluoroLog[®].

7.1.1 Eu doped polycrystalline RbMgF₃

The PL spectrum of RbMgF₃: 0.2 % Eu is shown in Fig. 7.1, which arises from the Eu²⁺ transitions. The sharp peak in the PL emission is due to the transition from the ⁶P_{7/2} and ⁶P_{5/2} excited states to the ⁸S_{7/2} ground state with an emission at 360 nm, and the broad peak is from the band emission from the 4f⁶5d(E_g) excited states to the 4f⁷ ground state.

RbMgF₃ does not show a broad peak of the 5d level in the linear PL spectra as it was observed for the NaMgF₃ (Fig. 5.1). This is due to the energy difference between the 4f and 5d levels. The energy difference is $\sim 9700 \text{ cm}^{-1}$ (1.2 eV) for NaMgF₃, and $\sim 970 \text{ cm}^{-1}$ (0.12 eV) for RbMgF₃ [9, 59, 79, 80, 81]. Although the 5d transition could be observed in the PL spectra when plotting it logarithmic (Fig. 7.1(b)) [4]. The small energy difference causes the 5d to be quenched by the 4f (Fig. 7.1(a)). The sharp peak at 360 nm from the 4f level is also detected at 360 nm in the NaMgF₃ bulk materials (Fig. 5.1). The reason there is no shift is that 4f transitions are shielded by the electrons in 5d and therefore, not strongly affected by the crystal field.

Figure 7.1: (a) PL excitation (dashed curve, $\lambda_{em} = 360$ (blue) nm and 420 nm (black)) and emission (solid curve, $\lambda_{ex} = 256$ nm) spectra for RbMgF₃ 0.2 % Eu.
(b) Logarithmic plot of the PL emission spectra at $\lambda_{ex} = 256$ nm.

PL measurements were done before and after heavy irradiation. In order to perform this, the sample was placed on the holder for the PL measurements. The holder was transported in a light-tight box to the X-ray generator. The sample was irradiated up to a dose of ~ 12.7 kGy with the X-ray generator operating at 40 mA and 40 kV. After radiation, the holder with sample was transported back in the light-tight box to the spectrometer and the PL measurement was repeated with the sample in the same position.

Figure 7.2: (a) Absolute PL intensity of the emission spectra, $\lambda_{ex} = 256$ nm, for RbMgF_3 0.2 % Eu before (solid curve) and after irradiation with a dose of 12.7 kGy (dashed curve).
 (b) PL excitation at $\lambda_{em} = 590$ nm (blue: solid curve - before irradiation, dashed curve - after irradiation) and emission at $\lambda_{ex} = 396$ nm (red: solid curve - before irradiation, dashed curve - after irradiation with a dose of 12.7 kGy) spectra for the Eu^{3+} ion.
 (c) Absolute PL intensity of the excitation spectra, $\lambda_{em} = 590$ nm, before (solid curve) and after irradiation with a dose of 12.7 kGy (dashed curve).
 (d) Absolute PL intensity of the emission spectra, $\lambda_{ex} = 396$ nm, before (solid curve) and after irradiation with a dose of 12.7 kGy (dashed curve).

Fig. 7.2(a) shows the absolute PL intensity of the emission spectra for Eu^{2+} before (solid curve) and after (dashed curve) heavy irradiation. The PL intensity decreases by 24 % after receiving a dose of ~ 12.7 kGy, but the shape of the Eu^{2+} transition remains unchanged. When exciting the sample at 396 nm no Eu^{3+} emission is observed (Fig. 7.2(b)). In Fig. 7.2(c), the excitation spectra for an emission at 590 nm is plotted. The excitation spectrum before irradiation consists out of two peaks, one centred at 340 nm and one at 365 nm and these ones are indicated in Fig. 7.2(c). After heavy irradiation with a dose of ~ 12.7 kGy, the peaks at 340 nm and 365 nm increase and an additional peak at 470 nm appears. These additional peak was also observed for NaMgF_3 bulk samples (see Fig. 5.3(c)). The emission spectra, which was excited at $\lambda_{ex} = 396$ nm, peak around 505 nm before irradiation (Fig. 5.3(d)), while after irradiation this broad band increases and a new peak with a maximum at 455 nm appears. This new band at 455 nm can be assigned to some defects. The precise origin of these defects is unknown, but can probably be ascribed to the same defect previously observed in $\text{NaMgF}_3\text{:Eu}$ bulk materials (see Fig. 5.3(c+d)). For the NaMgF_3 sample doped with Eu, the unknown defects were observed at 340 nm and 470 nm in the PL excitation spectra. There was no extra peak detected at 365 nm (Fig. 5.3(c)). The peaks were detected at ~ 450 nm and ~ 520 nm for the NaMgF_3 polycrystalline samples (Fig. 5.3(d)). Therefore, it can be assumed that these unknown defects arise from the same defects.

PL lifetime measurements were performed with the Jobin-Yvon FluoroLog[®] for the Eu^{3+} and with the Cary50 for the Eu^{2+} sites. The PL lifetimes for the 0.2 % Eu^{2+} doped sample were calculated by fitting the curve with a two-exponential decay with the method explained in section 3.2.4. For an emission wavelength of 360 nm the calculated lifetime was 1.95 ± 0.20 ms, while for a wavelength of 400 nm a lifetime of 0.51 ± 0.05 ms was obtained ($\lambda_{ex} = 256$ nm), see Fig. 7.3(a+b). The lifetime of the 360 nm emission in the RbMgF_3 sample is slightly higher than the lifetime for NaMgF_3 samples which was calculated with 0.63 ± 0.06 ms, which can result from a different symmetry of the crystal field. For the unknown defect an average PL lifetime of 48.5 ± 4.9 ms (at $\lambda_{em} = 460$ nm and $\lambda_{ex} = 375$

nm) was measured. NaMgF₃: Eu had a PL lifetime of 68 ± 7 ms for the unknown peak.

Figure 7.3: (a) PL lifetime decay of 0.2 % Eu doped RbMgF₃ at $\lambda_{em} = 360$ nm (solid curve) and (b) $\lambda_{em} = 400$ nm emission (solid curve). The dashed curve is the exponential fit. Both lifetimes were measured at $\lambda_{ex} = 256$ nm.

The different compounds of the average PL lifetimes are listed in Tab. 7.1. For the Eu²⁺ emission at 360 nm, the existence of two separate sites with different lifetimes of 0.90 ± 0.09 ms and 2.22 ± 0.22 ms was observed. The Eu²⁺ emission at 400 nm also showed two sites with lifetimes of 0.09 ± 0.01 ms and 0.79 ± 0.08 ms. For the unknown peak, two different lifetimes of 8.74 ± 0.88 ms and 106 ± 11 ms were observed. The longer the lifetime, the less distorted the site is.

Table 7.1: Different compounds with the pre factors of the PL lifetimes of Eu doped RbMgF₃.

λ_{em} (nm)	factor A_1	τ_1 (ms)	factor A_2	τ_2 (ms)
360	18	0.90 ± 0.09	28	2.22 ± 0.22
400	240	0.09 ± 0.01	42	0.79 ± 0.08
500	703	8.74 ± 0.87	88	106 ± 11

7.1.2 Mn doped polycrystalline RbMgF₃

The PL emission and excitation spectra for the RbMgF₃ samples doped with 0.2 % Mn are plotted in Fig. 7.4(a+b). The PL excitation and emission peaks are consistent with Mn²⁺. Mn²⁺ substitutes for Mg, and RbMgF₃ has the P_{63/mmc} space group with two inequivalent Mg sites. Therefore, two Mn²⁺ sites were expected: one site, Mn1, has C_{3v} symmetry and the other site, Mn2, has D_{3d} symmetry [3]. The difference in the crystal field between the two sites in the compound is large enough to be detected in the PL excitation spectra resulting in a shift in the PL excitation peaks, when detecting the emission at 550 nm or 580 nm [96, 97]. The PL emission, when excited at 396 nm, exists of one peak at 580 nm. For the NaMgF₃: Mn bulk materials, the transition from the ⁶A_{1g} was found at 600 nm. There are no additional peaks observed from a highly distorted Mn site as it was detected in NaMgF₃ samples at 500 nm (Fig. 7.4(b)).

Figure 7.4: (a) PL excitation spectrum at $\lambda_{em}=550$ nm (dashed curve) and $\lambda_{em}=580$ nm emission (solid curve).

(b) PL emission spectrum for RbMgF₃ doped with 0.2 % Mn excited at 396 nm.

Figure 7.5: (a) PL lifetime decay of 0.2 % Mn doped RbMgF_3 at $\lambda_{em} = 550$ nm (solid curve) and (b) $\lambda_{em} = 580$ nm emission (solid curve). The dashed curve is the exponential fit. Both lifetimes were measured at $\lambda_{ex} = 465$ nm.

The average PL lifetime measurements were performed with the Jobin-Yvon FluoroLog[®] for the Mn^{2+} sites. For the 0.2 % Mn doped sample, an average lifetime of 87.7 ± 8.8 ms for the 550 nm emission and 62.9 ± 6.3 ms for the 580 nm emission was measured (at $\lambda_{ex} = 465$ nm), using a two-exponential fit for the PL lifetime decay as explained in section 3.2.4. The different compounds of the average PL lifetimes are listed in Tab. 7.2. For the Mn^{2+} emission at 550 nm, the existence of two separate sites with different lifetimes of 21.8 ± 2.2 ms and 96 ± 10 ms were observed. The Mn^{2+} emission centred at 580 nm also showed two sites with lifetimes of 25.0 ± 2.5 ms and 97 ± 10 ms. The different symmetry of the two sites of Mn^{2+} could cause the different lifetimes of the 550 nm and 580 nm emission. The PL lifetime for the NaMgF_3 Mn doped samples was 98 ± 10 ms for 0.5 % Mn, and 91.4 ± 9.1 ms for 1 % Mn for the regular Mn^{2+} site.

Table 7.2: Different compounds with the pre factors of the PL lifetimes of Mn doped RbMgF₃.

λ_{em} (nm)	factor A ₁	τ_1 (ms)	factor A ₂	τ_2 (ms)
550	145	21.8±2.2	267	96±10
580	1275	25.0±2.5	366	97±10

7.2 Thermoluminescence measurements

The TL measurements were performed using the same method as previously described in section 5.2 for NaMgF₃. The glow curves were obtained after irradiating the sample for 5 min and using a heating rate of 1K/s.

7.2.1 Eu doped polycrystalline RbMgF₃

The TL glow curve is plotted in Fig. 7.6(a) and activation energies of the peaks of the glow curves are summarised in Tab. 7.3. The glow curve peaks were obtained using first order kinetics glow curve deconvolution software and by minimizing the number of peaks during fitting of the glow curve (see also Fig. 7.6(a) - dashed curves). Fig. 7.6(b) shows the TL intensity plotted against the wavelength for different temperatures. There was no TL from Eu³⁺ detected but the TL spectra consists of a broad peak centred around ~560 nm as well as the peak at 360 nm (Fig. 7.6(b+c)). This band at 560 nm could not arise from Mn²⁺, because there was no evidence of Mn²⁺ in the PL spectra (Fig. 7.1(a)). The deconvolution of the glow curve was performed for the TL emission at 360 nm (Fig. 7.6(a)) and for the peak around 560 nm (Fig. 7.6(c)). The Eu²⁺ ion in the polycrystalline RbMgF₃ bulk sample has two low temperature peaks at ~373 K and ~408 K with activation energies of 0.53 eV and 1.07 eV, respectively. The main three peaks are found at 482 K, 552 K and 555 K, with respectively an activation energy of 0.92 eV, 0.5 eV and 1.7 eV. Neither

NaMgF₃ or RbMgF₃ bulk materials had similar TL glow curve peaks (Tab. 5.8). The NaMgF₃ nanoparticles showed a TL peak at ~ 551 K with an activation energy of 0.5 eV (Tab. 6.10), which was also observed in the RbMgF₃ bulk materials. The 5d emission seems to increase with increasing temperature as shown in Fig. 7.6(a) and this might be due to the same effect as for the NaMgF₃ samples where it has been explained previously. The probability for the transition between the 4f and 5d level, $\tau_{f \rightarrow d}$, is dependent on the energy difference between the 4f and 5d level, Δ , and the temperature, T. This can be estimated from the following equation,

$$\tau_{f \rightarrow d} = \tau_o e^{-\frac{\Delta}{kT}} \quad (7.1)$$

where k is the Boltzmann's constant (Fig. 5.8(c)). This means that with increasing temperature the energy difference between the 4f and 5d level is decreasing and this will result in a higher probability for the transition from the 4f to the 5d levels. Therefore at higher temperatures more of the 4f levels emission will be quenched by the 5d level resulting in an increase of the emission from the 5d level (Fig. 7.6(b)).

The TL glow curve of the unknown defect with a peak at ~ 560 nm is plotted in Fig. 7.6(c). It has a similar behaviour as the TL emission of the Eu²⁺ ion (Fig. 7.6(a)). In Tab. 7.3, the temperatures and activation energies of the TL glow curve peaks are listed and it can be observed that these are similar for the unknown defect and for the Eu²⁺ ion. The TL peak intensities of the unknown defect and Eu²⁺ are similar as well. The highest TL intensity arises from the peak with a maximum at ~ 550 K. In the PL spectra a broad peak was observed at 470 nm (Fig. 7.2(d)) and it is likely that the unknown peak in the TL spectra arises from the same defect. No TL emission from the broad peak at 560 nm was observed in the NaMgF₃ bulk materials or nanoparticles. Potential additional peaks above 620K could not be detected due to the temperature limitation of the equipment used.

Figure 7.6: (a) TL for the RbMgF_3 sample doped with 0.2 % Eu (solid curve). The TL data was detected with the PMT after 5 min X-ray irradiation (40 kV, 40 mA) at a heating rate of 1 K/s. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves).
 (b) TL spectra vs. wavelength for the different temperatures detected with the CCD after 5 min X-ray irradiation.
 (c) TL for the unknown peak between 500 nm and 650 nm (solid curve). TL was detected with the CCD after 5 min of X-ray irradiation and the peaks were fitted using first order kinetics glow curve deconvolution (dashed curves).

Table 7.3: The activation energies of the individual glow curve peaks for the RbMgF₃:0.2 % Eu sample obtained by first order kinetics glow curve deconvolution. The top line is the activation energy of the peaks for the for the glow curve.

	0.53±0.05 eV	1.07±0.11 eV	0.92±0.09 eV	0.50±0.05 eV	1.70±0.17 eV
0.2 % Eu	373 K	408K	482 K	552 K	555 K
peak height	13500	8900	54600	113100	17600
unknown peak	373 K	410 K	478 K	549 K	544 K
peak height	12600	8500	20900	64500	10100

7.2.2 Mn doped polycrystalline RbMgF₃

TL spectra from a polycrystalline RbMgF₃ sample doped with Mn²⁺ are plotted in Fig. 7.7 and the activation energies of the fitted peaks are summarised in Tab. 7.4. An irradiation time of 1 minute was used when the data was collected using a PMT (Fig. 7.7(a)) and 5 min for the CCD (Fig. 7.7(b)). The TL emission mainly arises from the Mn²⁺ ions with an emission band around 580 nm. The TL glow curves were fitted using first order kinetics glow curve deconvolution and by trying to minimise the number of peaks. The glow curve consists out of two main peaks located at 346 K and 555 K. There are also two weaker peaks detected at 375 K and 595 K. The activation energy of the ~346 K peak is 0.58 eV, while it is 0.5 eV at ~375 K. The values of RbMgF₃ compare well with the values obtained for the NaMgF₃: 0.2 % Mn and RbMgF₃: 0.2 % Eu. Potential additional peaks above 620K could not be detected due to the temperature limitation of the equipment used.

Figure 7.7: (a) TL for the RbMgF_3 sample doped with 0.2 % Mn (solid curve). The TL signal was detected with the PMT after 1 min X-ray irradiation (40 kV, 40 mA) at a heating rate of 1 K/s. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves).
 (b) TL spectra vs. wavelength for the different temperatures detected with the CCD after 5 min X-ray irradiation.
 (c) Normalised TL spectra at 341.5 K, 477 K and 622 K.

Fig. 7.7(c) shows the normalised TL emission at 341.5 K, 477 K and 622 K. For higher temperatures the peak maximum shifts towards higher energies and the peak is broader, which was also observed for the NaMgF_3 bulk materials (see Fig. 5.9(c)). This phenomenon

is similar to the temperature dependence of the band gap of semiconductors. This means that the band gap increases with increasing temperature [87, 88, 89, 90].

Table 7.4: The activation energies of individual glow curve peaks for the RbMgF₃:0.2 % Mn sample obtained by first order kinetics glow curve deconvolution. The top line is the peak temperature for the glow curve.

	346 K	375 K	555 K	595 K
0.2 %	0.58±0.06 eV	0.50±0.05 eV	0.89±0.09 eV	0.78±0.08 eV
peak height	26500	14600	608100	205500

7.3 Radioluminescence and temperature dependent RL measurements

Radioluminescence and temperature dependent RL measurements were performed with the same methods as described in section 5.3.1 for the measurements on NaMgF₃.

7.3.1 Radioluminescence measurements

7.3.1.1 Eu doped polycrystalline RbMgF₃

RL spectra of RbMgF₃ doped with Eu are shown in Fig. 7.8. The RL intensity against wavelength is plotted in Fig. 7.8(a), while the RL intensity against dose is shown in Fig. 7.8(b). The RL spectra during continual X-ray excitation can be attributed to Eu²⁺ and Eu³⁺ emission. A broad peak around 420 nm was detected and its intensity increases with increasing dose. The energy of the Eu²⁺ emission is the same as observed in the PL spectra. Additional emission bands from Eu³⁺ ions were detected and the emission wavelengths remain unchanged (Fig. 7.8(a)). No sign of Eu³⁺ ions was detected in the

PL spectra, most likely because of the intensity of the broad peak around 470 nm was too high. The integrated RL intensity is plotted for Eu^{2+} (filled squares) and Eu^{3+} (open squares) in Fig. 7.8(b). I_{RL} for Eu^{2+} increases by 48.8 % and reaches a maximum after a dose of 211Gy. After this initial increase the RL intensity starts to decrease. After a dose of 12KGy it has been decreased by 73.9 % at 12 kGy. This results in a total difference of 61.1 % between the start point and the end point. The RL intensity is initially low because some of the X-ray generated electrons and holes become trapped and hence the amount of electrons and holes available for RL is low. After a high enough dose, all the traps will be filled and hence all the X-ray generated electrons and holes are available for RL. Thus, the RL will increase with dose until all the electron and hole traps are filled. This explains the initial increase in the RL (Fig. 7.8(c)). The RL starts to decrease at high doses due to X-ray induced radiation damage that results in non-radiative recombination sites. Thus, as shown in Fig. 7.8(d), some of the X-ray generated electrons and holes are not available for RL due to non-radiative recombination, which leads to a reduction of the RL at high doses. This non-radiative centre competes with Eu as recombination centre and the probability for mobile carriers to recombine in this centre is higher compared to Eu. On the other hand an increase with 55.8 % after a dose of 211 Gy and a further increase with 87.2 % after 12 kGy was observed for the I_{RL} of the Eu^{3+} ions. The RL spectra contains a broad band between 400 nm and 500 nm. This band can probably be assigned to a defect of unknown origin. During irradiation the intensity of this band increases and the maximum shifts from 400 nm towards 420 nm. The integrated radioluminescence intensity increases by 86.5 % after a dose of 1 kGy and by 155 % after a large dose of 12.7 kGy (Fig. 7.8(b)). This behaviour is different than previously observed for NaMgF_3 . In NaMgF_3 the RL intensity of the unknown defect decreased with dose as demonstrated in section 5.3.1 and shown in Fig. 5.13(b).

Figure 7.8: (a) Radioluminescence spectra for RbMgF_3 : 0.2 % Eu versus the dose and (b) the integrated RL spectra as a function of dose during continuous X-ray irradiation (Eu^{2+} : filled squares, Eu^{3+} : open squares, unknown defect: circles). (c) Existence of electron and hole traps next to the Eu. (d) Dose dependence of the RL signal as a result of the generation of non-radiative recombination centres.

Fig. 7.9 shows the emission spectra of the unknown defect centred at 470 nm for the PL, TL and RL measurements. The PL spectrum was excited at 396 nm, the TL spectrum was measured at a temperature of 620 K and the RL was measured using an X-ray excitation and after an initial dose of 12 kGy. The emission wavelengths of the unknown defect are different for every measurement. The PL spectra consists out of two maxima. The first around 455 nm and the second at 505 nm. On the other hand the TL spectra consists out

of a broad peak around 580 nm and a shoulder at 420 nm. While the RL spectra show a broad peak centred at 420 nm, and a smaller one at around 560 nm. From the differences of these spectra it seems that the unknown defect has different defect distributions. For the RL and TL the probability of the mobile carriers to get trapped in other defects is higher Fig. 7.9(b). Thus, the unknown peak observed in the PL spectra will not necessarily be detected in the RL and TL spectra (Fig. 7.9(a+b)).

Figure 7.9: (a) PL, TL and RL emission spectra for the broad peak around 400 nm to 580 nm.

(b) Different excitation regions for PL and RL.

7.3.1.2 Mn doped polycrystalline RbMgF_3

The Mn doped polycrystalline sample of RbMgF_3 was also irradiated continuously up to a dose of 12.7 kGy. Fig. 7.10(a) shows the RL emission spectra plotted against the wavelength for different doses, while Fig. 7.10(b) shows the dose dependence of the integrated RL intensity. The luminescence in the RL spectra of this sample can be completely attributed to Mn^{2+} with an emission band at 580nm. There is no spectral change of the RL or PL emission after heavy irradiation. Fig. 7.10(b) shows the integrated RL intensity plotted against the X-ray dose and the RL increases by 125.4 % at $\sim 1 \text{ kGy}$ and afterwards

decreases by 9.4 % at 12 kGy. NaMgF_3 : Mn showed also an increase of the RL signal with a doses up to 8.5 kGy and then the signal would decrease (Fig. 5.14(b)). The behaviour of the RL signal can be explained with the same model as used previously for the Eu doped samples (see Fig. 7.8(c+d)). The RL intensity is initially low because some of the X-ray generated electrons and holes become trapped and hence electrons and holes available for RL are low. For a high enough dose, all of the traps are filled and hence all of the X-ray generated electrons and holes are available for RL. Thus, the RL will increase with dose until all of the electron and hole traps are filled. This explains the initial increase in the RL until 1 kGy Fig. 7.8(c). The decrease of the RL signal for doses above 1 kGy is due to X-ray induced radiation damage that results in non-radiative recombination sites. Thus, as shown in Fig. 7.8(d), some of the X-ray generated electrons and holes are not available for RL due to non-radiative recombination, which leads to a reduction in the RL for high doses. Additionally, there could be a conversion of $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$. No Mn^{3+} was detected in the PL spectra, but this might be due to the signal of Mn^{3+} being too low.

Figure 7.10: (a) Radioluminescence spectra for RbMgF_3 : 0.2% Mn for versus the dose and (b) the integrated RL spectra as a function of dose during continuous X-ray irradiation.

7.3.2 Temperature dependent RL measurements

Temperature dependent RL measurements were performed on powdered samples using a method similar as previously mentioned for NaMgF_3 in section 5.3.2.

7.3.2.1 Eu doped polycrystalline RbMgF_3

The temperature dependent measurements were done by powdering the samples, which were saturated with isopropanol, on a ceramic holder and heating the holder up until a certain temperature. After the temperature had stabilized RL measurements up to a dose of 15 Gy were performed. Then the sample was thermally bleached by heating it up until 350 °C. This bleaching empties shallow traps as previously observed in the NaMgF_3 samples. Hence, future measurements should have been performed with an optical bleaching step after each temperature change. This process was repeated for 13 different temperature settings. The total dose the sample received at the end was ~ 200 Gy.

The RbMgF_3 sample shows a decrease in the Eu^{2+} RL compared to room temperature when the temperature is increased to 100 °C. The initial decrease in the RL with increasing temperature may be due to thermal activation of trapped charges to non-radiative recombination centres as shown in Fig. 7.11(c). The appearance of RL does not depend on the filling of the traps. If the temperature increases, the probability of hopping increases. This means that the carriers overcome an energy barrier, Δ , and could recombine in non-radiative recombination centres (Fig. 7.11(c)). For small doses and hence a negligible trapped carrier concentration, the RL signal is expected to decrease with decreasing temperature, which is not observed. Thus, it is likely that the dose at each temperature results in a significant carrier trapping. Therefore, as the temperature decreases there may be competition between reducing the RL through reducing the thermal detrapping probability and increasing the RL due to significant trap filling at each temperature. It is apparent that the second process dominates in Fig. 7.11(a). The same process was also shown in Fig. 5.16(a) for the NaMgF_3 polycrystalline materials. The thermal coefficient of

the RL was calculated using the average for each temperature dependent RL intensity, and was around 0.13 ± 0.1 %/K. There was no observable shift in the RL emission wavelengths of Eu^{2+} transitions with increasing temperature because the temperature change was too low.

Figure 7.11: (a) Temperature dependent RL for RbMgF_3 : 0.2 % Eu for different temperature up to 100 °C. Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature.

(b) RL spectra measured at different temperatures.

(c) Hopping of the carriers to a deep non-radiative trap due to increasing temperature.

7.3.2.2 Mn doped polycrystalline RbMgF_3

Fig. 7.12 shows the temperature dependent RL intensity for the Mn doped polycrystalline RbMgF_3 sample. The RL signal shows a similar temperature dependent behaviour as previously discussed for the Eu doped samples. At low temperatures, the traps become partially filled but they will not be completely filled after a high enough dose. The shape of the temperature dependent RL intensity does not depend on the filling of the traps. With increasing temperature the probability of hopping increases. This means that the carriers overcome an energy barrier, Δ , and could recombine in non-radiative recombination centres as shown in Fig. 7.11(c). For small doses and hence a negligible trapped carrier concentration, the RL signal should decrease with decreasing temperature. The opposite was observed. It is likely that the dose at each temperature results in a significant carrier trapping. As the temperature is reduced, there will be a competition between reducing the RL through reducing the thermal detrapping probability and increasing the RL due to significant trap filling at each temperature. It is apparent that the second process dominates in Fig. 7.12(a). The same process was also shown in Fig. 5.16(a) for the NaMgF_3 polycrystalline materials. The thermal coefficient of the RL was calculated using the average for each temperature dependent RL curve, and was around 0.06 ± 0.1 %/K. For the NaMgF_3 doped with Mn the RL signal increases with increasing temperature and decreases for measurements from 100 °C to 40 °C. There was no observable shift in the RL emission wavelengths of Mn^{2+} transitions with increasing temperature because the temperature change was too low.

Figure 7.12: (a) Temperature dependent RL for RbMgF_3 : 0.2 % Mn for different temperature up to 100 °C. Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature.
 (b) RL spectra measured for different temperatures.

7.4 Conclusion

PL, TL and RL were observed for polycrystalline samples of RbMgF_3 doped with Eu or Mn. Photoluminescence measurements show the presence of Eu^{2+} ions in the Eu doped samples. PL measurements of the Eu doped samples before and after heavy irradiation show that the total intensity of the Eu^{2+} emission decreases, but the peak intensity of the unknown defect increases. The measured lifetimes for the sharp emission band of Eu^{2+} located at 360 nm is higher for the RbMgF_3 samples compared to the NaMgF_3 samples. This is because there are less non-radiative recombination sites in the RbMgF_3 crystal. Further work should be performed to find the origin of the unknown peak and if it is a F-centre or other defects. One possibility could be, to measure the sample with electron paramagnetic resonance (EPR). If the unknown peak is dominated by F-centres, it would be possible to detect this with EPR [98]. Another possibility would be, to powder the sample and heat it up. Oxygen will diffuse through most of the sample when the particles

are small comparable to the oxygen diffusion mean free path. If afterwards an increase in the PL intensity is observed, it would mean that these defects are caused by oxygen. Oxygen can also be detected by performing vacuum UV-PL on the peak. TL measurements on the Eu samples show that the defects are different compared to the NaMgF₃: Eu bulk materials TL peaks. TL was observed for the unknown defect centred at 400 nm to 560 nm for RbMgF₃ sample. The calculated activation energies for the unknown defect were similar to the Eu²⁺ ones. There was no TL observed for the unknown defect observed in the NaMgF₃ samples. The RL intensity of the unknown defect decreases with dose for the NaMgF₃ samples but it increases with dose for the RbMgF₃ samples. The thermal coefficient of RL is 0.13 ± 0.1 %/K for RbMgF₃: 0.2 %.

Photoluminescence measurements show the presence of two regular sites of Mn²⁺. There was no presence of a peak around 500 nm from a distorted Mn²⁺ site as was observed for manganese doped NaMgF₃. The two Mn²⁺ sites in RbMgF₃ show different average lifetimes, a higher lifetime for the site at 550 nm and a lower one for the Mn²⁺ site at 580 nm. This might be due to a lower concentration of non-radiative recombination sites at Mn²⁺ site at 580 nm, or due to the different symmetry caused by the different crystal field. EPR measurements should also be performed on RbMgF₃: Mn to observe the decrease of the RL above 1 kGy, and to investigate if it is caused from a conversion from Mn²⁺ → Mn³⁺ by irradiation [98]. The RL signal of the RbMgF₃: Mn has a similar behaviour to NaMgF₃: Mn bulk materials, and it can be assumed that the defects have the same origin. The thermal coefficient of RL is 0.06 ± 0.1 %/K for RbMgF₃: 0.2 % Mn. The temperature dependence of the RL mainly arises from deep traps, and thermal bleaching is not enough to empty them. Therefore, future measurements should be performed with optical bleaching after each temperature change.

8 RbMgF₃ nanoparticles

The nanoparticles were either doped with 0.1 %, 0.5 %, 1 %, 2 % and 5 % Eu or 1 %, 2 % and 5 % Mn. The sample preparation was already mentioned in chapter 4.1.2. The crystal structure is hexagonal crystal structure with the space group $P_{63/mmc}$ and from XRD measurements, the crystal size was calculated with the Scherrer formula from the XRD spectra shown in Fig. 4.1, which was ~ 25 nm. To perform PL, PL lifetime and RL measurements, the nanoparticles were also pressed into pellets with a diameter of ~ 6 mm and a thickness between 0.5 mm and 1.5 mm. The appearance of the pressed pellets was whitish. The influence of the concentration of the dopant on the PL spectra, PL lifetime, TL and RL measurements will be investigated. There was no OSL observed for the nanoparticles.

8.1 Photoluminescence and PL lifetime measurements

PL measurements were performed with the Jobin-Yvon FluoroLog[®]. The spectra were all normalised to the maximum.

8.1.1 Eu doped RbMgF₃ nanoparticles

Fig. 8.1 shows the PL excitation spectra (a) and emission spectra (b) for RbMgF₃ doped with Eu. The PL excitation spectra was measured with an emission wavelength of 360

nm for the Eu^{2+} ions (dashed curve) and with an emission wavelength of 592 nm for the transition from ${}^7\text{F}_1$ level of the Eu^{3+} ion (Fig. 8.1(a)). In Fig. 8.1(b), the PL emission spectra for the Eu^{3+} ion of the 1 % (dashed curve) and 5 % doped sample (solid curve) are plotted. The spectra of the Eu^{3+} site consists of the ${}^5\text{D}_1$ and ${}^5\text{D}_0$ transitions, which are indicated in Fig. 8.1. The ratio ${}^7\text{F}_1/{}^7\text{F}_2$ decreases from 1.4:1 for the 1 % sample to 0.8:1 for the 5 % sample. An unknown defect centred at 470 nm was detected. The PL intensity of the broad defect remains unchanged for the measurements of the 1 % sample and the 5 % Eu sample as shown in Fig. 8.1(b). The PL intensity of the unknown defect in the $\text{NaMgF}_3:\text{Eu}$ nanoparticles decreased with increasing Eu^{3+} concentration. The inset in Fig. 8.1(b) shows the PL emission while excited at 256 nm. The PL emission mainly arises from the transitions of ${}^6\text{P}_{7/2}$ and ${}^6\text{P}_{9/2}$ to the ground state, ${}^8\text{S}_{7/2}$ - sharp peak centred at $\lambda_{em}=360$ nm. The broad peak centred at 380 nm arises from transitions from the E_g level to the ${}^8\text{S}_{7/2}$ ground state.

Figure 8.1: (a) PL excitation for the Eu^{2+} ($\lambda_{em}=360$ nm - dashed curve) and Eu^{3+} ($\lambda_{em}=592$ nm - solid curve) and (b) emission ($\lambda_{ex}=396$ nm; inset $\lambda_{ex}=256$ nm) spectra for RbMgF_3 doped with 1 % Eu (dashed curve) and 5 % Eu (solid curve).

Temperature dependent PL measurements of $\text{RbMgF}_3:\text{Eu}$ doped pellets were performed

and the PL plots of the 0.1 % (a), 1 % (b) and 5 % (c) samples are shown in Fig. 8.2. The solid curves show measurement performed at 10 K and the dashed curves were measured at 300 K. The insets in Fig. 8.2 show the PL spectra detected for an emission wavelength at 450 nm at 10 K (red curve) and 300 K (black curve). The 0.1 % Eu doped RbMgF₃ sample shows a shoulder centred at 450 nm and a broad peak centred at 550 nm for the measurements at 10 K. The transitions from Eu³⁺ were quenched by the higher intensity of the broad defect centred at 550 nm (Fig. 8.2(a)). The unknown defect with a peak centred at 550 nm disappears for measurements at 300 K. Therefore, Eu³⁺ transitions can be detected as well as an unknown defect centred at 470 nm (Fig. 8.2(a)). The inset in Fig. 8.2(a) shows the PL excitation spectrum with an emission wavelength at 450 nm. In the PL spectrum consists of two peaks, one centred at 290 nm and another at 400 nm for measurements at 10 K. These peaks broaden and shift towards higher energies for measurements at 300 K.

For the 0.5 % doped sample, a shoulder centred at 450 nm, an additional unknown defect with centred at ~ 550 nm and Eu³⁺ transitions were detected (Fig. 8.2(b)). Peak intensities from the emission below 570 nm decrease with increasing temperature. In the inset of Fig. 8.2(b), the PL was measured for an emission wavelength at 450 nm and the spectrum consists of two broad peaks, one centred at ~ 290 nm and another one at ~ 400 nm for measurements at 10 K. The intensity of the first peak centred at ~ 290 nm decreases for measurements at room temperature.

The 1 % Eu doped pellets show only one broad peak with a maximum at 470 nm at 10 K. The PL intensity of this unknown defect centred at ~ 470 nm decreases for measurements at room temperature (Fig. 8.2(c)). The inset in this graph shows the PL excitation spectra, which is detected at 450 nm for both temperatures at 10 K and 300 K. The spectra consists of two broad peaks, one centred at ~ 290 nm and another one at ~ 370 nm. The intensity of the peak centred at ~ 300 nm decreases with increasing temperature. The centre of the peak of these unknown defects shift to lower wavelengths with increasing temperature (inset Fig. 8.3(c)). The $^5D_0 \rightarrow ^7F_J$ transitions of the 1 % doped nanoparticles were detected

for measurements at 10 K and 300 K. Their normalised intensities are higher than the PL intensity of the unknown defect centred at ~ 450 nm when compared to the 0.1 % doped sample.

Figure 8.2: (a) PL emission spectra for 0.1 %, (b) 0.5 %, (c) 1 % and (d) 5 % Eu doped RbMgF₃ at $\lambda_{ex} = 396$ nm at 10 K (solid curve) and at room temperature (dashed curve). Inset: PL excitation spectra detected at $\lambda_{em} = 450$ nm for the different Eu concentrations of RbMgF₃.

The nanoparticles doped with 5 % Eu show an emission from the unknown defect centred at ~ 450 nm and from 5D_0 transitions (Fig. 8.2(d)). The normalised PL intensity of the unknown defect decreases for measurements at room temperature resulting in an increase

of the normalised PL intensity of the 5D_0 transition. The inset in Fig. 8.2(d) shows the PL excitation with an emission wavelength of 450 nm. The peak at ~ 290 nm disappears for higher Eu concentrations. However, the peak centred at ~ 370 nm is broader for measurements at room temperature. For the NaMgF₃: Eu nanoparticles, a similar behaviour was observed. All of the samples show a double peak with maxima at ~ 290 nm and 370 nm at 10 K and the intensity of the peak centred at ~ 290 nm decreases for measurements at room temperature. The ratio I_{7F_2}/I_{7F_1} is 1.1:1 for the 0.1 % sample, 1.9:1 for the 0.5 % sample, 1:1 for the 1 % Eu doped sample, 1.1:1 for the 2 % doped sample and 1.6:1 for the 5 % sample. This means the higher this ratio the more distorted is the average crystal environment of the Eu³⁺ ion.

The PL lifetimes for the Eu²⁺ ions were measured with the Cary 50. For Eu³⁺ and the unknown defect average PL lifetimes were measured with the Jobin-Yvon FluoroLog[®] spectrometer. The PL decay can be fitted with multiple exponential components and the average lifetime was estimated as already explained in section 3.2.4. τ_{rad} was calculated with the corrected emission spectra of the Eu³⁺ emission where signal from the broad unknown defect centred at ~ 470 nm was subtracting. The temperature dependence of the PL lifetime is plotted in Fig. 8.3 for the 1 % Eu doped sample and in Fig. 8.4 for the 5 % Eu doped nanoparticles. Fig. 8.3(a) shows the PL lifetime calculated of the three components τ_1 , τ_2 and τ_3 . The first two components τ_1 and τ_2 seem to be less temperature dependent as τ_3 . Above 180 K, the values are bigger than the radiative lifetime, $\tau_{rad} = 7.47 \pm 0.75$ ms. The values get up to 11.3 ± 1.1 ms at 10K. Therefore, these values were not used for the calculation of $\tau_{12,ave}$ as already explained for the NaMgF₃: Eu nanoparticles. An average lifetime, $\tau_{12,ave}$, of 3.14 ± 0.31 ms was calculated at room temperature. The third component, τ_3 , might originate from the broad defect centred at 500 nm. Hence, the calculated average PL lifetime for all three components is higher than τ_{rad} for Eu³⁺.

Figure 8.3: (a) Temperature dependent average PL lifetime of 1 % Eu doped RbMgF₃ ($\lambda_{em} = 592$ nm; $\lambda_{ex} = 375$ nm) from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles), τ_3 (filled triangles) and the average lifetime, $\tau_{123,ave}$ (open squares). τ_3 was fitted using equation 8.1. (b) Temperature dependent average PL lifetime of 1 % Eu doped RbMgF₃ from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles) and the average lifetime, $\tau_{12,ave}$ (open squares) when only using the first and the second component.

It was already shown for the NaMgF₃ nanoparticles that the temperature dependence of τ_3 might occur from thermal quenching resulting in two decays: One radiative and one thermally active non-radiative. Therefore, τ_3 can be expressed with the following equation,

$$\frac{1}{\tau_3} = \frac{1}{\tau_{3,0}} + f \times e^{-\frac{E_A}{k_B T}} \quad (8.1)$$

with $\tau_{3,0}$ as the intrinsic effective decay time at 0 K, E_A the activation energy, k_B the Boltzmann's constant and f the attempt frequency [10]. At 592 nm $\tau_{3,0}$ is 10.5 ± 1.1 ms and E_A is 129 ± 42 meV.

Fig. 8.4(a) shows the three components of the average PL lifetime decay plotted with a multi-exponential fit for the 5 % doped nanoparticles. It is shown that the third component

is bigger than the radiative lifetime, $\tau_{rad} = 6.23 \pm 0.62$ ms. τ_3 is as high as 9.9 ± 1.0 ms at 10 K. τ_3 is also significant temperature dependent below 240 K. Therefore, the average lifetime, $\tau_{12,ave}$, was calculated with the first two components, τ_1 and τ_2 , leading to a $\tau_{12,ave}$ of 2.42 ± 0.24 ms at room temperature.

Figure 8.4: (a) Temperature dependent average PL lifetime of 5 % Eu doped RbMgF₃ ($\lambda_{em} = 592$ nm; $\lambda_{ex} = 375$ nm) from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles), τ_3 (filled triangles) and the average lifetime, $\tau_{123,ave}$ (open squares). τ_3 was fitted using equation 8.1. (b) Temperature dependent average PL lifetime of 5 % Eu doped RbMgF₃ from the three exponential fit of the data with only the τ_1 (filled squares), τ_2 (filled circles) and the average lifetime, $\tau_{12,ave}$ (open squares) when only using the first and the second component.

τ_3 was fitted applying equation 8.1. At an emission wavelength of 592 nm, $\tau_{3,0}$ is 9.7 ± 1.0 ms and the calculated E_A is 108 ± 44 meV (Fig. 8.4(a)). This value is within the experimental uncertainty as calculated for the 1 % doped sample (E_A is 129 ± 42 meV). For the NaMgF₃ nanoparticles, E_A was 104 ± 36 meV for the 1 % Eu doped samples and an activation energy E_A of 95 ± 40 meV was measured for the 5 % sample when exciting the sample at 592 nm. Williams et al. calculated for the unknown defect at 500 nm an E_A of 139 ± 20 meV. This

comparable with the calculated values in this chapter within the experimental uncertainty [10]. E_A is similar for the NaMgF₃:Eu and RbMgF₃:Eu nanoparticles. Therefore, the unknown defect has likely the same origin in all the investigated samples. In Fig. 8.5, the average PL lifetimes of Eu³⁺ (a) and the unknown defect (b) are plotted for different Eu concentrations.

Figure 8.5: (a) Average PL lifetime for Eu³⁺ ($\lambda_{em} = 592$ nm, $\lambda_{ex} = 375$ nm) doped RbMgF₃ nanoparticles against the rare earth concentration and (b) for the broad unknown peak $\lambda_{em} = 500$ nm and $\lambda_{ex} = 375$ nm.

The measurements were done at room temperature.

The Eu²⁺ lifetimes were measured with an emission wavelength of 360 nm for the ⁶P_{7/2} and ⁶P_{7/2} transitions and with an emission wavelength of 380 nm for the E_g transition ($\lambda_{ex} = 256$ nm). Eu³⁺ was measured with an emission wavelength of 592 nm while excited at 375 nm. For the 1 % Eu doped samples, the PL lifetimes the Eu ions were as high as 2.3 ± 0.2 ms at 360 nm, 0.97 ± 0.10 ms at 380 nm and 3.14 ± 0.31 ms at 592 nm [11].

Figure 8.6: (a) Average PL lifetime for Eu²⁺ ($\lambda_{em} = 360$ nm: open squares and $\lambda_{em} = 380$ nm: filled squares at $\lambda_{ex} = 256$ nm) doped RbMgF₃ nanoparticles against the rare earth concentration and (b) average PL lifetime for Eu²⁺ ($\lambda_{em} = 360$ nm: open squares and $\lambda_{em} = 380$ nm: filled squares at $\lambda_{ex} = 256$ nm) doped NaMgF₃ nanoparticles against the rare earth concentration. (c) PL lifetime for the Eu³⁺ ion with $\lambda_{em} = 590$ nm and $\lambda_{ex} = 375$ nm for the RbMgF₃ (circles) and NaMgF₃ (squares). (d) PL lifetime for the broad peak at $\lambda_{em} = 500$ nm and $\lambda_{ex} = 375$ nm for the RbMgF₃ (circles) and NaMgF₃ (squares). The measurements were done at room temperature.

The above Fig. 8.6 shows a summary of the average lifetimes for different ions in nanoparticles. Fig. 8.6(a+b) show the lifetimes for the Eu²⁺ ion in the nanoparticles and it was observed the lifetimes are not dependent of the Eu concentration. The lifetimes for the Eu³⁺ are plotted in Fig. 8.6(c) and the PL lifetime increases until it reaches a maximum after a concentration 1 % Eu. After this initial increase the PL lifetime starts to decrease until a concentration of 5 % Eu. The average PL lifetime decreases with increasing Eu concentration for the NaMgF₃ nanoparticles. For the 0.5 % sample, the highest I_{7F_2}/I_{7F_1} ratio was calculated and it was as high as 1.9:1. This indicates, the higher this ratio the more distorted is the average crystal environment of the Eu³⁺ ion. Due to the production of the nanoparticles the crystal environment of the 0.5 % sample could have changed and become more distorted. The PL lifetime of the broad defect centred around 470 nm increases for RbMgF₃ and decreases for NaMgF₃ with increasing Eu concentration. The radiative lifetimes and quantum efficiencies were calculated for the Eu³⁺ ions and are listed in Tab. 8.1.

Table 8.1: Summary of the different measured PL lifetimes, $\tau_{12,ave}$, the radiative lifetime, τ_{rad} , and the quantum efficiency, η , for RbMgF₃ doped with different concentrations of Eu [11].

Concentration (%)	$\tau_{12,ave}$ (ms)	τ_{rad} (ms)	η (%)
0.1	2.0±0.2 (em @ 360 nm)	6.73	38.5
	0.96±0.09 (em @ 380 nm)		
	54.6±5.5 (em @ 500nm)		
	2.59±0.26 (em @ 592 nm)		
0.5	1.9±0.2 (em @ 360 nm)	5.97	48.9
	0.8±0.1 (em @ 380 nm)		
	54.9±5.5 (em @ 500nm)		
	2.9±0.3 (em @ 592 nm)		
	2.3±0.2 (em @ 360 nm)		

Continued on next page

Table 8.1 – *Continued from previous page*

Concentration (%)	$\tau_{12,ave}$ (ms)	τ_{rad} (ms)	η (%)
1	0.97±0.1 (em @ 380 nm) 55.7±5.6 (em @ 500nm) 3.1±0.3 (em @ 592 nm)	7.47	42.0
2	1.9±0.2 (em @ 360 nm) 0.8±0.1 (em @ 380 nm) 56.2±5.6 (em @ 500nm) 2.7±0.3 (em @ 592 nm)	7.58	36.1
5	1.9±0.2 (em @ 360 nm) 0.8±0.1 (em @ 380 nm) 57.8±5.8 (em @ 500nm) 2.4±0.2 (em @ 592 nm)	6.23	38.9

All calculated τ_{rad} are greater than the measured PL lifetimes and this indicates there are non-radiative decays in the crystal. $\tau_{12,ave}$ slightly decreases with increasing Eu³⁺ concentration (for the 1 % Eu till 5 % Eu doped samples). This was also observed for the NaMgF₃:Eu nanoparticles, see chapter 6. But the lifetimes of the Eu³⁺ sites are lower than observed for the NaMgF₃ nanoparticles. Therefore, it can be assumed that the energy transfer with increasing concentration is already saturated. This is also illustrated in Fig. 8.7(b) where the PL lifetime decay curves are plotted for the different Eu concentrations.

Figure 8.7: (a) PL lifetime decay of 5 % Eu doped RbMgF₃ at $\lambda_{em} = 590$ nm (solid curve). The dashed curve is the exponential fit. The lifetime was measured at $\lambda_{ex} = 375$ nm. (b) The lifetime decay curves at $\lambda_{em} = 590$ nm emission for the different Eu concentrations in NaMgF₃.

τ_{rad} can also be used to calculate the quantum efficiency. The quantum efficiency for the 0.1 % doped sample was similar to the 5 % Eu sample. The quantum efficiency was as high as 48.9 % for the 0.5 % doped nanoparticles. The lifetime of the unknown defect was measured with an emission wavelength of 500 nm ($\lambda_{ex} = 375$ nm). The average lifetimes are listed in Tab. 8.1. It was observed that the lifetime increases with increasing Eu concentration. The average PL lifetime was as high as 57.8 ± 5.8 ms for the 5 % doped sample. The lifetimes of the RbMgF₃ and NaMgF₃ bulk materials are listed in Tab. 8.2. For the Eu²⁺ and Eu³⁺ ions in NaMgF₃ the PL lifetimes of the bulks and nanoparticles are comparable. An exception is the lifetime of the unknown defect centred at 470 nm. This PL lifetime is about 10 % higher for the bulk materials compared to the nanoparticles which might be due to the distribution of the traps in the samples. The nanoparticles show a shorter lifetime for the unknown defect. This might be due to the existence of more defects next to it. This makes this transition more likely which results in a shorter lifetime.

For the different RbMgF₃:Eu samples (nanoparticles and bulk materials), the calculated lifetime with an emission wavelength of 360 nm for the Eu²⁺ ion are similar. The lifetime of the transition from the 5d level is higher for the nanoparticles. This might be caused that the bulks were measured with an emission wavelength at 400 nm and the nanoparticles at 380 nm. This difference in the emission wavelength could cause a selection of a different inequivalent site of Eu²⁺. The lifetime of the unknown defect is also higher in the RbMgF₃ bulk materials, which might be due to the distribution of the traps in the samples.

Table 8.2: Summary of the measured PL lifetimes, τ_{ave} , for different Eu-ions and the broad peak around 470 nm for RbMgF₃ and NaMgF₃ bulk materials.

Compound	λ_{em} (nm)	τ_{ave} (ms)
NaMgF ₃	360	0.63±0.06
	390	0.42±0.04
	500	67±7
	592	11.1±1.1
RbMgF ₃	360	2.0±0.2
	400	0.51±0.05
	500	68±7

In Fig. 8.8, the quantum efficiencies for the RbMgF₃ and NaMgF₃ nanoparticles are plotted versus the Eu concentration. The overall quantum efficiencies for the RbMgF₃ samples are lower than the quantum efficiencies calculated for the NaMgF₃ nanoparticles. Both of the quantum efficiencies follow the same behaviour. The highest η was calculated for the 0.5 % samples which also shows the highest concentration of distorted defects near the Eu³⁺ sites.

Figure 8.8: Quantum efficiency, η , for RbMgF₃ and NaMgF₃ against the Eu concentration.

The Judd-Ofelt parameters, Ω_2 and Ω_4 , for the Eu³⁺ ions in RbMgF₃ nanoparticles were calculated [65, 66, 92]. The parameters were estimated from equation 3.4, where I_{0-J} are the values from the PL spectra in Fig. 8.2 at room temperature after subtracting the unknown defect observed at ~ 470 nm. The resulting Ω_2 and Ω_4 values are listed in Tab. 8.3. Ω_2 and Ω_4 are $8.81 \times 10^{-20} \text{ cm}^2$ and $32.7 \times 10^{-20} \text{ cm}^2$ for the 1 % doped Eu sample and $13.4 \times 10^{-20} \text{ cm}^2$ and $33.4 \times 10^{-20} \text{ cm}^2$ for 5 % Eu, respectively. For the NaMgF₃ sample the calculated values of Ω_2 and Ω_4 were $6.87 \times 10^{-20} \text{ cm}^2$ and $25 \times 10^{-20} \text{ cm}^2$ for 1 % Eu and $7.52 \times 10^{-20} \text{ cm}^2$ and $27.9 \times 10^{-20} \text{ cm}^2$ for 5 % Eu doped NaMgF₃ (see Tab. 6.2). As mentioned for the NaMgF₃:Eu nanoparticles, Ω_2 is found in ranges of $\sim 1 \times 10^{-20} \text{ cm}^2$ to $33 \times 10^{-20} \text{ cm}^2$ in other nanoparticle compounds, and the higher Ω_2 is the more Eu³⁺ is in a distorted site [22, 93, 94, 95]. Ω_4 is found in ranges from $(0.2 - 13) \times 10^{-20} \text{ cm}^2$ [93]. It is not clear why Ω_4 is higher for the RbMgF₃: Eu³⁺ as found in other compounds.

Table 8.3: The Judd-Ofelt parameters Ω_2 and Ω_4 for $^5D_0 \rightarrow ^7F_2$ transitions for different concentrations of Eu doped RbMgF₃ nanoparticles measured using the PL emission.

Concentration (%)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)
0.1	9.3 ± 0.9	40 ± 4
0.5	16.6 ± 1.7	27.5 ± 2.8
1	8.8 ± 0.9	32.7 ± 3.3
2	9.2 ± 0.9	29.4 ± 2.9
5	13.4 ± 1.3	33.4 ± 3.3

Fig. 8.9 shows the Judd-Ofelt parameters, Ω_2 and Ω_4 , for the Eu^{3+} ions for RbMgF₃ and NaMgF₃. Ω_2 has a comparable behaviour for the NaMgF₃ and RbMgF₃ nanoparticles. Ω_2 of the RbMgF₃ samples shows a maximum for the 0.5 % Eu sample. This sample has also the highest quantum efficiency, η , and the average crystal environment of the Eu^{3+} is more distorted compared to the other samples of RbMgF₃ with different Eu concentrations. Ω_4 does not show a dependence of the Eu concentration or the crystal environment.

Figure 8.9: The Judd-Ofelt parameters Ω_2 and Ω_4 for the Eu^{3+} ions for RbMgF₃ (a) and NaMgF₃ (b) against the Eu concentration.

8.1.2 Mn doped RbMgF₃ nanoparticles

Figure 8.10: (a) PL excitation spectra for 5 % Mn doped RbMgF₃ at $\lambda_{em}=500$ nm (dashed curve) and $\lambda_{em}=600$ nm (solid curve) for the distorted Mn²⁺ site [11].
 (b) PL emission spectrum for RbMgF₃ doped with 1 % Mn (red), 2 % (blue) and 5 % Mn (black) excited at 396 nm [11].

PL excitation and emission spectra for the RbMgF₃:Mn²⁺ nanoparticles are plotted in Fig. 8.10, where the PL excitation and emission peaks are consistent with Mn²⁺. Mn²⁺ substitutes for Mg, and RbMgF₃ has the P_{6₃/mmc} space group with two inequivalent Mg sites. Therefore, two Mn²⁺ sites where expected: one site, Mn1, has C_{3v} symmetry and the other site, Mn2, has D_{3d} symmetry [3]. This difference in the crystal field between the two sites is large enough to be detected in the PL excitation spectra (Fig. 8.10(a)), resulting in a shift in the PL excitation peaks, when detecting at 550 nm or 580 nm. The excited state levels of Mn²⁺ are indicated in Fig. 8.10(a) [11, 96, 97]. Fig. 8.10(b) shows the emission spectra of 1 % (red), 2 % (blue), and 5 % (black) Mn²⁺ doped RbMgF₃ nanoparticles. The emission spectra, when excited at 396 nm, contains one peak at 580 nm for 1 % Mn, and at 590 nm for 2 % and 5 % Mn. The small shift in the emission maximum to higher energies for the 1 % Mn²⁺ concentration might be due to a small change in the Mn1/Mn2

ratio, in the different distribution of traps or in the crystal field [11, 96, 97]. The transition wavelength of the ${}^6A_{1g}$ level was found at 580 nm for the RbMgF₃: 0.2% Mn doped bulk materials.

Figure 8.11: (a) PL lifetime decay of 5 % Mn doped RbMgF₃ at $\lambda_{em}=550$ nm (solid curve) and (b) at $\lambda_{em}=580$ nm (solid curve). The dashed curve is the exponential fit. The lifetime was measured at $\lambda_{ex}=465$ nm.

PL lifetime measurements were performed with the Jobin-Yvon FluoroLog[®]. The PL decay curves are illustrated in Fig. 8.11 for the 5 % Mn doped sample for an emission wavelength at (a) 550 nm (solid curve) and for an wavelength (b) at 580 nm (solid curve). The lifetimes for different concentrations of Mn are summarised in Tab. 8.4. The PL decay could be fitted with two - exponential components and the average PL lifetimes, τ_{ave} , were obtained from these components. PL lifetimes were measured at emission wavelengths of 550 nm and 580 nm for RbMgF₃ nanoparticles for the two inequivalent Mn²⁺ sites. τ_{ave} slightly shifts to higher lifetimes for the Mn²⁺ site measured at an emission wavelength at 580 nm with increasing Mn²⁺ concentrations. The two calculated lifetimes measured for the 1 % Mn sample are in the same range within the uncertainty (Tab. 8.4). τ_{ave} is as large as 55 ± 56 ms and comparable to the lifetimes observed in the RbMgF₃:Mn bulk materials (62.9 ± 6.3 ms) for the site observed at a emission wavelength at 580 nm, see also

chapter 7. The RbMgF₃ bulk materials show a higher lifetime for the Mn site measured at an emission wavelength of 550 nm (87.7 ± 9 ms). The difference in the lifetimes of the two Mn sites in the nanoparticles is not as significant as it is calculated in the bulks and it remains unchanged with increasing Mn²⁺ concentration [11]. The difference of the PL lifetimes of the Mn²⁺ in the nanoparticles compared to the bulk materials might be due to a higher concentration of distorted sites near Mn²⁺ in the nanoparticles resulting in a lower PL lifetime.

Figure 8.12: Average PL lifetime for the two inequivalent sites of Mn²⁺ ($\lambda_{em} = 550$ nm - circles and $\lambda_{em} = 580$ nm - squares) in RbMgF₃ nanoparticles against the rare earth concentration ($\lambda_{ex} = 465$ nm).

Table 8.4: Summary of different measured PL lifetimes, τ_{ave} , for RbMgF₃ doped with different concentrations of Mn, excited at 465 nm.

Concentration (%)	τ_{ave} (ms)
1	55.0±5.5 (em @ 550 nm)
	55.2±5.5 (em @ 580 nm)
2	58.6±5.9 (em @ 550 nm)
	54.4±5.4 (em @ 580 nm)
5	58.9±5.9 (em @ 550 nm)
	55.4±5.5 (em @ 580 nm)

8.2 Thermoluminescence measurements

Thermoluminescence measurements were performed on powdered samples immersed with isopropanol. All the measurements were performed after 20 minutes irradiation with an X-ray generator operating at 40 mA and 40 kV. The data was collected using a PMT at a heating rate of 1 K/s, heating up from 300 K until 630 K. The peaks were fitted with first order kinetics curve deconvolution.

8.2.1 Eu doped RbMgF₃ nanoparticles

The TL measurements for the Eu doped nanoparticles are shown for the 1 %, 2 % and 5 % Eu doped samples. There was no TL detected for the 0.1 % and 0.5 % doped samples (Fig. ??). The data from the glow curves are summarised in Tab. 8.5. The temperature peaks of the glow curves for the different compounds of RbMgF₃ are not comparable with each other. The normalised TL glow curves for the nanoparticles (1 % Eu doped RbMgF₃ and 0.5 % Eu doped NaMgF₃) and the bulk materials (0.2 % Eu doped RbMgF₃) are plotted in Fig. 8.13(d). RbMgF₃ bulk and nanoparticles seem have peaks at similar temperatures

but the activation energies for the TL peaks in the nanoparticles are smaller than observed in the bulk materials (Tab. 7.6). These values for the NaMgF_3 : Eu nanoparticles compare well with the values obtained for the RbMgF_3 : Eu nanoparticles. These traps seem to arise from the same defects.

Figure 8.13: TL glow curves for RbMgF_3 doped with 1 % (a), 2 % (b) and 5 % (c) Eu after 20 min irradiation with the X-ray generator operating at 40 kV and 40 mA (solid curves). The TL was detected with the PMT. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves). (d) Normalised TL glow curves for 1 % Eu doped RbMgF_3 nanoparticles (blue curve), 0.5 % Eu doped NaMgF_3 nanoparticles (green curve) and 0.2 % Eu doped RbMgF_3 bulks (red curve).

Table 8.5: The activation energies of the individual glow curve peaks for the RbMgF₃:1 %, 2 % and 5 % Eu sample obtained by first order kinetics glow curve deconvolution. The top line is the activation energy for the glow curve.

	0.50±0.05 eV	0.50±0.05 eV	0.52±0.05 eV
1 %	357 K	408 K	555 K
peak height	70	110	270
2 %	408 K	515 K	593 K
peak height	10	40	40
5 %	408 K	464 K	556 K
peak height	50	50	60

8.2.2 Mn doped RbMgF₃ nanoparticles

Fig. 8.14 shows the TL measurements on the Mn doped samples. The graph consist of low temperature peaks at ~ 357 K for the 1 %, and 2 % Mn sample and at ~ 359 K for the 5 % Mn sample. The activation energy for this low temperature peaks is 0.72 eV. The second TL peak with an activation energy of 0.58 eV was measured at 375 K for the 1 % doped sample and shifts to higher temperatures for the other Mn concentrations (379 K for the 2 % Mn and 378 K for the 5 % Mn sample). The activation energy of the peak centred at ~ 415 K is 0.56 eV. The last two temperature peaks have an activation energy of 0.5 eV and the peaks are centred at 459 K and 536 K for the 1 % sample and at higher temperatures for the 2 % sample (461 K and 539 K) shifting to lower temperatures for the 5 % sample (454 K and 523 K). Fig. 8.14(d) shows the normalised TL glow curves for the nanoparticles (5 % Mn doped RbMgF₃ and 5 % Mn doped NaMgF₃) and the bulk materials (0.2 % Mn doped RbMgF₃). The values of the glow curves are comparable to each other. The low temperature TL peaks for RbMgF₃ nanoparticles, at ~ 346 K and ~ 374 K, were also observed for the bulk materials but the activation energies were different

for the different compounds (see Tab. 7.4). However, the nanoparticles show mainly low temperature peaks.

Figure 8.14: TL glow curves for RbMgF_3 doped with 1% Mn (a), 2 % Mn (b), 5 % Mn (c) after 20 min irradiation with the X-ray generator operating at 40 kV and 40 mA (solid curves). The TL was detected with the PMT. The fitted peaks were obtained using first order kinetics glow curve deconvolution (dashed curves). (d) Normalised TL glow curves for 5 % Mn doped RbMgF_3 nanoparticles (blue curve), 5 % Mn doped NaMgF_3 nanoparticles (green curve) and 0.2 % Mn doped RbMgF_3 bulks (red curve).

These values for the NaMgF_3 Mn and Eu nanoparticles compare well with the values

obtained for the and RbMgF₃ nanoparticles (see Fig. 6.11 and Tab. 6.5).

Table 8.6: The activation energies of the individual glow curve peaks for RbMgF₃ doped with different concentration of Mn obtained by first order kinetics glow curve deconvolution. The top line is the activation energy for the different peaks for the glow curves.

	0.72±0.07 eV	0.58±0.06 eV	0.56±0.05 eV	0.50±0.05 eV	0.50±0.05 eV
1 % peak height	357 K 10	375 K 20	415 K 50	45 K 50	536 K 70
2 % peak height	357 K 220	379 K 530	415 K 330	461 K 190	539 K 130
5 % peak height	359 K 330000	378 K 8600	414 K 2100	454 K 1500	523 K 1500

8.3 Radioluminescence and temperature dependent RL measurements

Continuous radioluminescence measurements were performed on pressed pellets with an X-ray generator operating at 40 kV and 40 mA and collected using a CCD detector. The 5 % samples were additional irradiated with the ²⁴¹Am source to observe their low dose behaviour. During this irradiation the signal was collected using a PMT detector. The temperature dependent RL measurements were performed on pulverised samples immersed with isopropanol under the same conditions as the RL measurements. The temperature was changed in 10 K steps and 10 measurements with and integration time of 5 s were performed for each temperature step. After a certain temperature step, the sample was thermally bleached by heating it up until 350 °C.

8.3.1 Radioluminescence measurements

8.3.1.1 Eu doped RbMgF₃ nanoparticles

The following Fig. 8.15 - 8.17 show the RL spectra and the dependence of the integrated RL intensity on the dose for the RbMgF₃ doped with different concentrations of Eu. The RL spectra from the Eu RbMgF₃ doped samples show a strong Eu³⁺ component and a weaker Eu²⁺ component. The Eu²⁺ line emission centred at 360 nm arises from the Eu²⁺ 4f→4f transition and the broader peak centred at 450 nm is due to the unknown defect as observed in the PL spectra. The higher ratio of the Eu²⁺ component to the Eu³⁺ component for the 0.1 % sample indicates that this sample has a higher Eu²⁺ fraction. The ratio of Eu³⁺/Eu²⁺ increases with increasing Eu concentration. At 1.8 Gy, the ratio is 2:1 for the 0.1 % Eu doped sample (Fig. 8.16(a)) and 7:1 for the 5 % doped sample (Fig. 8.17(a)). The ratio changes after heavy irradiation (12.7 kGy) and it is 11:1 for 0.1 % doped sample, 25:1 for 0.5 % Eu doped sample, 5:1 for the 1 % sample and 38:1 for the 5 % sample. The difference in the ratio for the 1 % doped sample could be due to the preparation process. The Eu³⁺ RL emission wavelengths appear at the same wavelengths as observed in the PL emission spectra. The ratio I_{7F_2}/I_{7F_1} remains unchanged after irradiation. It was calculated with 1:1.6 for the 0.1 % Eu sample and decreases to 1:1.3 for the 5 % sample. This decrease may be caused by the crystal environment of the Eu³⁺ which gets more distorted with increasing Eu concentration. For the PL spectra, a ratio I_{7F_2}/I_{7F_1} of 1.1:1 for the 0.1 % sample, 1.9:1 for the 0.5 % sample, 1:1 for the 1 % Eu doped sample, 1.1:1 for the 2 % doped sample and 1.6:1 for the 5 % sample was calculated. In the PL spectra, the crystal environment of Eu³⁺ is more distorted for the 5 % sample than the 0.1 % sample but there was not a increase in the ratio for the 0.5 % sample observed. This might be caused by the effect that the PL is exciting directly in the band. The carriers generated by RL are more mobile and theses carriers might not recombine with the highly distorted site in the 0.5 % sample.

Figure 8.15: Radioluminescence spectra for RbMgF₃ nanoparticles doped with 0.1 % Eu (a) and 0.5 % Eu (c) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 0.1 % Eu (b) and 0.5 % Eu (d) doped samples (Eu²⁺ open squares and Eu³⁺ filled squares).

All samples show a decrease in the RL signal after heavy irradiation. I_{RL} of the 0.1 % Eu sample decreases by 9.9 % at 1 kGy and by 12.7 % at 12.7 kGy for the Eu³⁺ ion. The RL signal for the Eu²⁺ ion decreases by 39.9 % at 1 kGy and by 80.6 % at 12.7 kGy (Fig. 8.15(b)). At ~ 2 kGy, the RL intensity seems to be constant with increasing dose. The 0.5 % sample shows the highest decrease of the RL intensity. It decreases by 4.3 % at 1 kGy and by 15.5 % at 12.7 kGy for the Eu³⁺ ion. For the Eu²⁺ ion, the intensity decreases by

31.9 % at 1 kGy and by 89.3 % at 12.7 kGy (see Fig. 8.15(d)).

Figure 8.16: Radioluminescence spectra for RbMgF_3 nanoparticles doped with 1 % Eu (a) and 2 % Eu (c) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 1 % Eu (c) and 2 % Eu (d) doped samples (Eu^{2+} open squares and Eu^{3+} filled squares).

Fig. 8.16(a) shows the dose dependence of the RL signal for the 1 % sample. The Eu^{3+} RL intensity decreases by 3.9 % at 1 kGy and 11.2 % at 12.7 kGy. For the Eu^{2+} ion, the signal decreases by 31.7 % at 1 kGy and by 66.2 % at 12.7 kGy. The lowest decrease of I_{RL} was calculated for the 2 % Eu doped sample where the signal of the Eu^{3+} ion decreases

by 2.5 % at 1 kGy and by 6.7 % at 12.7 kGy. For the Eu²⁺ ion it decreases by 25.1 % at 1 kGy and by 61.0 % at 12.7 kGy (Fig. 8.16(d)).

Figure 8.17: Radioluminescence spectra for RbMgF₃ nanoparticles doped with 5 % Eu (a) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 5 % Eu (b) doped samples (Eu²⁺ open squares and Eu³⁺ filled squares, solid line ²⁴¹Am irradiation). The γ -ray RL was scaled to match the X-ray RL.

In Fig. 8.17(b), the I_{RL} of the 5 % doped sample is plotted. The RL intensity decreases by 9.2 % at 1 kGy and by 15.2 % at 12.7 kGy for the Eu³⁺ ion. For the Eu²⁺, the signal decreases by 51.3 % at 1 kGy and by 84.8 % at 12.7 kGy. Fig. 8.17(b) shows the measurements with the ²⁴¹Am source which emits monochrome γ -rays (solid line). It shows that the RL intensity is dose independent down to at least 10 mGy. The decrease of the RL signal at high doses might be due to the generation of defects that act as non-radiative decay centres. I_{RL} of the Eu²⁺ decreases in a faster rate than the RL signal of Eu³⁺ ion. As already mentioned for the NaMgF₃ nanoparticles, this might be caused by radiation induced defects that preferentially occur near the Eu²⁺ sites leading to more quenching of the Eu²⁺ RL compared to the RL signal of the Eu³⁺ ion [11, 12]. The 0.1 % sample (Fig. 8.15(a)) and 0.5 % sample (Fig. 8.15(c)) show the unknown defect centred around

470 nm in their RL emission spectra. The intensity of the unknown defect decreases with increasing Eu concentration. For higher Eu concentration above 1 %, the unknown defect will not be detected (Fig. 8.16(a+b) and Fig. 8.17(a)). This unknown defect was also detected in the PL spectra for all the different Eu concentrations (Fig. 8.2) and the PL intensity of this defect decreases with increasing Eu concentration. The RL emission for the unknown defect in the 0.1 % sample increases and reaches a maximum after a dose of 200 Gy. After this initial increase the RL intensity starts to decrease until 12.7 kGy (Fig. 8.15(a)). The RL intensity is initially low because some of the X-ray generated electrons and holes become trapped and hence the electrons and holes available for RL is low. For a high enough dose, all of the traps are filled and hence all of the X-ray generated electrons and holes are available for RL. Thus, the RL will increase with dose until all of the electron and hole traps are filled. This explains the initial increase in the RL until 200 Gy. The RL starts to decrease at high doses due to X-ray induced radiation damage that results in non-radiative recombination sites. Thus, some of the X-ray generated electrons and holes are not available for RL due to non-radiative recombination, which leads to a reduction in the RL for high doses. This non-radiative centre competes with unknown defect and the probability for mobile carriers to recombine in this centre is higher compared to unknown defect.

8.3.1.2 Mn doped RbMgF₃ nanoparticles

Fig. 8.18 and 8.19 show the RL emission spectra and dose dependence of the RL intensity of RbMgF₃ with different concentrations of Mn. The RL spectra can be completely attributed to the Mn²⁺ ion with RL emission centred at 580 nm for the 1 % and 590 nm for the 2 % and 5 % Mn sample. The RL and PL emission wavelengths remain unchanged after heavy irradiation. In Fig. 8.18(b), the I_{RL} is plotted against the X-ray dose for 1 % Mn and the RL increases by 31.9 % and reaches a maximum after a dose of 5.3 kGy. After this initial increase the RL intensity starts to decrease. After a dose of 12.7 kGy it has been decreased by 3.8 %. This results with a total difference of the RL signal of 26.9 %. The 1 % Mn

sample shows the biggest dependence for the RL signal on the dose. The RL intensity of the 2 % Mn doped sample increases by 8.3 % and reaches a maximum after a dose of 3.2 kGy. After this initial increase the RL intensity starts to decrease. After a dose of 12.7 kGy it has been decreased by 8.9 % (Fig. 8.18(d)). This results with a total difference of the RL signal of 1.5 %. The RL signal of the 2 % Mn sample is less dose dependent compared to the other two samples.

Figure 8.18: Radioluminescence spectra for RbMgF_3 nanoparticles doped with 1 % Mn (a) and 2 % Mn (c) for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 1 % Mn (b) and 2 % Mn (d) doped samples.

For the 5 % Mn doped sample, the RL intensity increases by 20.4 % and reaches a maximum after a dose of 5.3 kGy. After this initial increase the RL intensity starts to decrease. After a dose of 12.7 kGy it has been decreased by 5.3 %. This results with a total difference of the RL signal of 14.0 % (Fig. 8.19(b)). Similar measurements of the RL intensity could not be performed for lower doses because the sensitivity of the CCD detector was not high enough. Therefore, additional low dose measurements were performed with the ^{241}Am source for the 5 % doped sample. It was observed the RL signal is dose independent down to 10 mGy (solid line in Fig. 8.19(b)) [11].

Figure 8.19: Radioluminescence spectra for RbMgF_3 nanoparticles doped with 5 % Mn (a), for different doses and the integrated RL spectra as a function of dose during continuous X-ray irradiation for 5 % Mn (b) doped samples, solid line ^{241}Am irradiation. The γ -ray RL was scaled to match the X-ray RL.

For the RbMgF_3 bulk materials, a similar behaviour of dose dependence of the RL signal was observed. The RL intensity for the bulk materials increases until it reaches a maximum after a dose of ~ 1 kGy. After this initial increase the RL intensity starts to decrease as observed for the nanoparticles (see Fig. 7.10(b)). The behaviour of the RL signal can be explained with the same model, which was used for the RbMgF_3 : Eu doped bulk materials (see Fig. 7.8(c+d)). The RL intensity is initially low because some of the X-ray generated

electrons and holes become trapped and hence electrons and holes available for RL are low. For a high enough dose, all of the traps are filled and hence all of the X-ray generated electrons and holes are available for RL. Thus, the RL will increase with dose until all of the electron and hole traps are filled. This explains the initial increase in the RL until 3.2 kGy for the 2 % Mn and 5.3 kGy for the 1 % and 5 % Mn sample (Fig. 7.8(c)). The decrease of the RL signal for doses above 3.2 kGy for the 2 % Mn and 5.3 kGy for the 1 % and 5 % Mn is due to X-ray induced radiation damage that results in non-radiative recombination sites. Thus, as shown in Fig. 7.8(d), some of the X-ray generated electrons and holes are not available for RL due to non-radiative recombination, which leads to a reduction in the RL for high doses. Additionally, there could be a conversion of $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$. However, there was no Mn^{3+} in the PL spectra. This could be due to the PL of Mn^{3+} being too low to be detected. The nanoparticles show a similar behaviour of dose dependence in the RL compared to the bulk materials. However, the overall dose dependence of the RL is smaller for the nanoparticles. The RL intensity changed up to 104 % for the RbMgF_3 bulk materials and only up to 26.9 % for the 1 % doped nanoparticles. This leads to the conclusion that there is less generation of defects in the nanoparticles compared to the bulk materials. An initial increase of the RL signal is an indication that the nanoparticles should show OSL but no OSL was observed.

8.3.2 Temperature dependent RL measurements

8.3.2.1 Eu doped RbMgF_3 nanoparticles

Fig. 8.20 and 8.21 show the temperature dependent RL measurements for the 0.1 %, 1 % and 5 % RbMgF_3 nanoparticles. The integrated RL intensity of the Eu^{3+} ion increases by 0.9 % compared to room temperature when the temperature is increased to 100 °C and decreases by 0.02 % compared to 100 °C when the temperature is decreased to 40 °C. The difference between the first value measured at 40 °C and the last one is 0.9 % (Fig. 8.20(a) top graph). The RL signal of Eu^{2+} decreases by 31.8 % compared to room

temperature when the temperature is increased to 100 °C and the RL intensity decreases by 9.6 % compared to 100 °C when the temperature is decreased to 40 °C, resulting in a total difference for the RL intensity of 38.3 % (Fig. 8.20(a) lower graph).

Figure 8.20: Temperature dependent RL spectra for RbMgF₃ nanoparticles doped with 0.1 % Eu (a) for different temperatures up to 100 °C and the respective RL spectra versus the wavelength for different temperatures ((b) for 0.1 % Eu). Eu²⁺ is indicated by the red colour and Eu³⁺ by the blue colour.

Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature. Black curves show the trend of the temperature dependent RL.

The Eu³⁺ integrated intensity increases by 16.8 % compared to room temperature when the temperature is increased to 100 °C and decreases by 15.9 % compared to 100 °C when the temperature is decreased to 40 °C, with a total decrease of the RL intensity by 2.1 % for the 1 % Eu sample (Fig. 8.21(c)). I_{RL} of the Eu²⁺ RL signal decreases by 14.5 % compared to room temperature when the temperature is increased to 100 °C and decreases by 7.7 % compared to 100 °C when the temperature is decreased to 40 °C. A total decrease by 21.1 % was calculated (see also Fig. 8.21(c)). The biggest change of the RL signal with temperature increasing was observed with the 5 % Eu sample (Fig. 8.21(c)). The

RL of Eu³⁺ increases by 101.7 % compared to room temperature when the temperature is increased to 100 °C and decreases by 18 % compared to 100 °C when the temperature is decreased to 40 °C, resulting in a total difference of 65.3 %. The Eu²⁺ signal decreases by 14.2 % at 100 °C and further decreases by 8.6 % at 40 °C, with a total difference of the RL signal of 21.6 %.

For the Eu²⁺ and Eu³⁺ ions, the change of the RL signal with the temperature shows a similar behaviour for all of the different concentrations of Eu in the nanoparticles. The Eu³⁺ signal increases with increasing temperature and the Eu²⁺ signal is slightly decreasing with increasing temperature. In section 5.3.1, the increase for the RL signal with increasing temperature was explained with a model, which explained the same effect in NaMgF₃: Eu bulk materials. (Fig. 5.16(d)). The model shows the RL signal depends on the normal RL trapping and the trapping of deep traps, τ_{dt} . The probability of this trapping, τ_{dt} , can be estimated from the following equation,

$$\tau_{dt} = \tau_o e^{-\frac{\Delta_1}{kT}} \quad (8.2)$$

where Δ_1 is the energy of the level, k the Boltzmann's constant and T the temperature. It means, the probability, τ_{dt} , of filling these deep traps increases with increasing temperature. Thus, the RL signal increases with increasing temperature, which was observed for the Eu³⁺ site in the RbMgF₃ (Fig. 8.20 and 8.21). The decrease of the RL intensity with increasing temperature for the Eu²⁺ can be explained with an energy transfer to deep TL traps. These traps are filled during irradiation, but they show a non-radiative recombination. With temperature decreasing until 40 °C, the RL intensity further decreases at a slower rate. The nanoparticles are irradiated for 5 s and ten measurements are performed at each temperature step. It was already mentioned in the previous chapter thermal bleaching is not enough to empty the deep traps. Therefore, the decrease in the RL intensity with decreasing temperature can be caused by the normal dose dependence of I_{RL} . This was also observed for the NaMgF₃: Eu nanoparticles.

Figure 8.21: Temperature dependent RL spectra for RbMgF₃ nanoparticles doped with 1 % Eu (a) and 5 % Eu (c) for different temperatures up to 100 °C and the respective RL spectra versus the wavelength for different temperatures ((b) for 1 % Eu and (d) for 5 % Eu). Eu²⁺ is indicated by the red colour and Eu³⁺ by the blue colour.

Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature. Black curves show the trend of the temperature dependent RL.

There was no observable shift in the RL emission wavelengths of Eu²⁺ and Eu³⁺ transitions with increasing temperature because the temperature change was too low. The ratio of

I_{7F_2}/I_{7F_1} changes with increasing temperature for the 5 % sample. It is around 1.3:1 at 40 °C and it increases with increasing temperature to 1.5:1 at 100 °C and decreases again to 1.4:1 at 40 °C. The increasing ratio I_{7F_2}/I_{7F_1} means the crystal environment of the Eu³⁺ gets more distorted when increasing the temperature. It decreases with decreasing temperature until it reaches the initial ratio of the first measurement at 40 °C.

Tab. 8.7 summarises the thermal coefficient of the RL signal for different Eu-ions in the crystal. The thermal coefficient of the RL signal for the Eu²⁺ ion decreases with increasing temperature and is as high as 0.27 ± 0.2 %/K for the 0.1 % Eu doped sample. It is as low as 0.07 ± 0.1 %/K for the 5 % sample. The opposite was observed for the Eu³⁺ ion. The thermal coefficient of the RL signal increases with increasing concentration of Eu. It is as low as 0.01 ± 0.1 %/K for the 0.1 % sample and as high as 0.24 ± 0.05 %/K for 1 % Eu in the nanoparticles. The thermal coefficient could not be calculated for the 5 % Eu doped sample because the oscillations in the measured RL intensity was too large. The RbMgF₃ bulk materials showed a thermal coefficient of the RL of 0.13 ± 0.1 %/K for the 0.2 % Eu²⁺ samples, which is comparable to the value as was calculated for the 0.1 % Eu doped nanoparticles.

Table 8.7: Summary of thermal coefficients of the RL signal for different doped samples and the Eu²⁺ and Eu³⁺ ions in RbMgF₃ nanoparticles.

Concentration (%)	Eu ²⁺ (%/K)	Eu ³⁺ (%/K)
0.1	0.27 ± 0.2	0.01 ± 0.1
1	0.08 ± 0.1	0.24 ± 0.05
5	0.07 ± 0.1	

8.3.2.2 Mn doped RbMgF₃ nanoparticles

Fig. 8.22 shows the temperature dependence of the RL signal for the 1 % Mn (a+b) and 5 % Mn (c+d) doped nanoparticles. The RL signal for the 1 % Mn doped sample increases

by 10.7 % compared to room temperature when the temperature is increased to 100 °C and increases by 6.9 % compared to 100 °C when the temperature is decreased to 40 °C, leading to a total discrepancy of 16.8 % (Fig. 8.22(a)). For the 5 % Mn doped sample, the RL signal increases by 14.4 % compared to room temperature when the temperature is increased to 100 °C and decreases by 6.7 % compared to 100 °C when the temperature is decreased to 40 °C, resulting in a discrepancy of 8.7 % (Fig. 8.22(c)). The increase of the RL signal with increasing temperature for both Mn concentrations might be due to the normal RL trapping and the trapping of deep traps, which was already explained for the Eu doped RbMgF₃ nanoparticles. It can be estimated from equation 8.2. The probability of the trapping, τ_{dt} , of deep traps increases with increasing temperature as shown in Fig. 5.16(d).

The further increase of the RL for the 1 % Mn sample compared to 100 °C when the temperature is decreased to 40 °C was at a slower rate. This could be due to a redistribution of the carriers, which causes a further increase of the trapping rate if shallow traps will be filled during this redistribution and emptied during irradiation at low temperature. Tab. 8.8 summarises the thermal coefficient of the RL signal for the different Mn concentrations in RbMgF₃. The thermal coefficient of the RL signal increases with increasing concentration of Mn. It is as low as 0.01 ± 0.1 %/K for the 1 % sample, and as high as 0.05 ± 0.05 %/K for 5 % Mn in the nanoparticles. The RbMgF₃ bulk materials show a thermal coefficient of the RL of 0.06 ± 0.1 % for 0.2 % Mn, which is comparable to the values calculated for the nanoparticles.

Table 8.8: Summary of the thermal coefficient of the RL signal for the different doped samples and the Mn²⁺ ion in RbMgF₃ nanoparticles.

Concentration (%)	Mn ²⁺ (%/K)
1	0.01 ± 0.1
5	0.05 ± 0.05

Figure 8.22: Temperature dependent RL spectra for RbMgF_3 nanoparticles doped with 1 % Mn (a) and 5 % Mn (c) for different temperatures up to 100 $^{\circ}\text{C}$ and the respective RL spectra versus the wavelength for different temperatures ((b) for 1 % Mn and (d) for 5 % Mn).

Arrows facing up signal an increase of temperature, and arrows facing down signal a decrease in temperature. Blue curves show the trend of the temperature dependent RL.

8.4 Conclusion

Eu^{2+} , Eu^{3+} and a unknown defect centred around 470 nm were observed in the PL spectra of the nanoparticles. Temperature dependent PL measurements for the Eu doped samples show that the PL intensity of the unknown defect centred around 470 nm increases with decreasing temperature. The emission of the unknown defect in the excitation spectra broadens for measurements at low temperature. The intensity of the unknown defect is also dependent of the concentration of the dopant, which means it increases with decreasing Eu concentration. The PL lifetimes of the Eu doped nanoparticles are similar to the bulk materials. $\tau_{12,ave}$ of the Eu^{3+} ion increases up to a Eu concentration of 1 % and then decreases again for the 5 % Eu sample. The quantum efficiency was as high as 48.9 %. Temperature dependent PL lifetime measurements show $\tau_{12,ave}$ is nearly constant for decreasing temperature. The PL lifetime of the unknown defect is long and has a value of 57.8 ms for the 5 % sample and the average lifetime decreases to 54.6 ms for the 0.1 % Eu doped sample. It shows thermally activated behaviour with an activation energy of 129 ± 42 meV for the 1 % doped sample and 108 ± 44 meV for the 5 % one. The Judd-Ofelt parameters have been calculated as well and Ω_2 is in the range found in other nanoparticle compounds. Ω_4 is higher than Ω_2 and also higher than observed in other compounds. The $\text{RbMgF}_3:\text{Eu}$ nanoparticles show comparable TL peaks to the Eu doped bulk materials. The activation energies for these TL peaks measured for the nanoparticles were higher for the bulk materials. Eu^{2+} and Eu^{3+} were measured in the RL spectra. The unknown defect centred at ~ 470 nm was only observed for the 0.1 % and 0.5 % Eu samples. I_{RL} is independent of dose from 10 mGy to ~ 100 Gy. The RL intensity decreases for high doses. The integrated RL intensity of the Eu^{3+} decreases at a slower rate than the Eu^{2+} RL intensity which might be due that radiation induced defects preferentially occur near the Eu^{2+} sites leading to more quenching of the Eu^{2+} RL, when compared with the Eu^{3+} RL. The RL intensity shows a higher dependence of the temperature than the bulk materials. For the 0.1 % Eu doped nanoparticles, a thermal coefficient for the RL of 0.01 ± 0.1 %/K for the Eu^{3+} ion and of 0.27 ± 0.2 %/K for the Eu^{2+} ion was calculated, which is similar to the

value calculated for the 0.2 % Eu doped bulk materials (0.13 ± 0.1 %/K). For the 1 % doped sample, the thermal coefficient of the RL is 0.24 ± 0.05 %/K for the for the Eu^{3+} ion and 0.07 ± 0.1 %/K for the Eu^{2+} ion. The thermal coefficient of the RL for the Eu^{2+} decreases with increasing concentration of Eu and increases with increasing Eu^{3+} concentration.

PL measurements of the Mn^{2+} doped samples show two inequivalent sites of the Mn^{2+} , which were expected from the crystal structure. The two Mn sites were also observed in the RbMgF_3 bulk materials. The PL decay of the Mn^{2+} nanoparticles could be fitted two-exponential for the two regular sites of Mn^{2+} . The Mn site centred at 550 nm had a slightly higher lifetime than the Mn centred at higher wavelength, which means this site has a lower concentration of non-radiative sites. TL measurements for the Mn doped RbMgF_3 nanoparticles show similar peaks and activation energies as the NaMgF_3 : Mn nanoparticles. Mn^{2+} is also observed in the RL spectra and the integrated intensity has the same dose dependence as observed for the bulk materials. It increases until ~ 1 kGy for 5 % Mn^{2+} . Above 1 kGy, the RL signal decreases. For the Mn samples doped with 1 % and 2 %, the integrated RL intensity decreases also for low doses. The RL intensity is less dependent on the dose as it was observed for the bulk samples, which means that there are different defect distributions in the polycrystalline samples and nanoparticles. This means the nanoparticles show defects on the surface and the bulk materials show non-radiative recombination centres near the RE ion. For the 1 % Mn doped nanoparticles, the value for the thermal coefficient of the RL was 0.01 ± 0.1 %/K. For the 5 % Mn doped sample, the coefficient was as high as 0.05 ± 0.05 %/K. The thermal coefficient increases with increasing concentration and is comparable to the value, which was observed for the Mn doped bulk materials (0.06 ± 0.1 %/K). Next to the luminescent ion there exist additional electron-hole-traps. These electrons and holes, which are mobile after irradiation, will more likely recombine on the electron and hole traps and therefore, fewer electrons get trapped in the luminescent ion. The electron and hole traps saturate after an irradiation with a finite dose. Thus, for future temperature dependent RL measurements a finite dose should be

applied before the measurements.

9 Other polycrystalline nanoparticles

The following chapter gives an overview over measurements performed on other nanoparticles, which have potential to be employed in radiation dosimetry. Fluoride nanoparticles are being actively investigated, because of their wide range of potential applications that include scintillation detectors of ionizing radiation [23, 36] and optical amplifiers [22, 99]. In this case, the particular interest is in radiation detectors that are optical transparent, which takes advantage of the reduced scattering that is seen in composites containing nanoparticles [22, 100, 101]. Other advantages of transparent radiation detectors include the potential to detect over a larger volume, when compared with detectors made from bulk compounds, which can result in the ability to detect significantly lower radiation doses. Nanoparticle composites also have the advantage that they can be pressed into arbitrary shapes. Recently, fluoride nanoparticles have been researched for optical amplifiers [22, 99], but reports of the dosimeter properties of these nanoparticles is very limited [23, 24, 36]. In this chapter, the results of the concentration of the dopant on the PL spectra, PL lifetime and RL measurements of fluoride nanoparticles will be discussed.

9.1 Photoluminescence and PL lifetime measurements of LaF_3

The LaF_3 nanoparticles doped with Sm^{3+} and Eu^{3+} were prepared using high purity LaCl_3 , $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, NaF , OA, chloroform and ethanol. The nanoparticles capped

with oleic acid (OA) were prepared with a modified procedure described by Wang et al. [102]. NaF was dissolved in de-ionised water (90 ml) and ethanol (60 ml) and OA (20 ml) were added to it. The mixture was then stirred and heated up to 75 °C under an inert atmosphere. LaCl_3 and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ in an aqueous solution was added drop wise to the mixture and stirred at 75 °C for 5 h. The resultant solution was diluted with ethanol to precipitate the nanoparticles during centrifugation the whole solution at 4 000 rpm to wash the nanoparticles to remove the residual OA. After repeating this for 5 times the nanoparticles were then dispersed in hexane or chloroform for storage [22].

From XRD measurements, the space group of LaF_3 and with the Scherrer formula, the crystal size was obtained. The space group was P_{-3c1} with a crystal size of ~ 11 nm [19]. The appearance of the pressed pellets was transparent and the photos of the nanoparticles was already published by Janssens et al. [22, 99]. The powders were pressed into pellets that were ~ 1 mm thick where the diameters were ~ 9 mm for Eu^{3+} and ~ 6 mm for Sm^{3+} doped samples [12]. PL spectra and the PL lifetimes were measured using a Varian Cary Eclipse spectrofluorometer, which has a pulsed light source.

9.1.1 Eu doped LaF_3 nanoparticles

Fig. 9.1 shows the PL excitation spectra (a) and emission spectra (b) for LaF_3 doped with Eu^{3+} . The PL excitation spectra shows the PL excitation from the $\lambda_{em} = 590$ nm emission of the Eu^{3+} ions of the 5 % Eu doped nanoparticles, which corresponds to the ${}^7\text{F}_1$ level (Fig. 9.1(a)). In Fig. 9.1, the emission spectra for the Eu^{3+} spectra of the 5 % (b) doped sample and for all of the different Eu^{3+} concentrations (c) are plotted. The PL emission was excited at 395 nm and into the intense ${}^5\text{G}_6$ and ${}^5\text{L}_6$ levels. It originates mainly from the transitions from the ${}^5\text{D}_0$ level, and the transitions from the ${}^5\text{D}_1$ become weaker with increasing Eu^{3+} concentration, which is shown in Fig. 9.1(c), and can be related to the Eu^{3+} cross relaxation [84]. The ratio of I_{7F_2}/I_{7F_1} is 0.9:1 in the 5 % doped sample. There was no evidence from PL emission measurements for any Eu^{2+} transitions when excited in

the ultraviolet [12, 22].

Figure 9.1: (a) PL excitation ($\lambda_{em} = 590$ nm) and (b) PL emission ($\lambda_{ex} = 395$ nm) spectra for LaF_3 : 5 % Eu^{3+} nanoparticles.

(c) PL emission ($\lambda_{ex} = 395$ nm) spectra for all the different Eu^{3+} concentrations in LaF_3 nanoparticles [12].

Fig. 9.2 shows the average PL lifetime of LaF_3 doped with different concentrations of Eu^{3+} and a lifetime decay curve for 5 % Eu . The PL decay could be fitted to two PL lifetimes, and τ_{ave} was obtained from $\tau_{ave} = [\int t \times I(t) dt] / \int I(t) dt$. Fig. 9.2 shows the average PL lifetimes, τ_{ave} , for the LaF_3 nanoparticles doped with different concentrations of Eu^{3+} . The average PL lifetime decreases with increasing Eu^{3+} concentration [12]. The

decrease in τ_{ave} with increasing Eu^{3+} concentration has been previously reported for the other nanoparticles (RbMgF_3 and NaMgF_3), and can be attributed to energy transfer from Eu^{3+} sites away from the surface to Eu^{3+} sites near the surface followed by non-radiative decay at unidentified surface non-radiative recombination sites [10, 11, 12, 22]. This energy transfer process can occur via a dipole-dipole or a dipole-quadrupole interaction [91], and hence it will increase with increasing Eu^{3+} concentration. The Eu^{3+} PL lifetime will decrease until it reaches the PL lifetime of Eu^{3+} near the surface [12]. The radiative lifetime was calculated with a different method than explained for the NaMgF_3 : Eu and RbMgF_3 nanoparticles. In the method which was used for the other nanoparticles the radiative lifetime was estimated from [68],

$$\tau_{rad} = \frac{1}{\sum_J A_{0-J}} \quad (9.1)$$

where A_{0-J} are the 0-J transition rates calculated with the Judd-Ofelt theory. In this method the radiative lifetime, τ_{rad} , was estimated from [103],

$$\frac{1}{\tau_{rad}} = A_{MD} n^3 \frac{I_{tot}}{I_{MD}} \quad (9.2)$$

where n is the effective refractive index of the pressed nanoparticles. In this case it is the average of the refractive indices of the nanocrystalline material n_{LaF_3} ($=1.59$) and the surrounding media n_{OA} ($=1.459$), which leads to

$$n = x \times n_{LaF_3} + (1 - x)n_{OA} \quad (9.3)$$

where x ($=0.4$) is the nanoparticle volume fraction. A_{MD} ($=14.65 \text{ s}^{-1}$) is the spontaneous emission probability for the magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition in vacuo. I_{tot} and I_{MD} are the total and the $^5D_0 \rightarrow ^7F_1$ integrated emission intensity of the corrected Eu^{3+} emission spectra, respectively. It is relatively easy to calculate the Eu^{3+} quantum efficiency,

$$\eta = \frac{\tau_{ave}}{\tau_{rad}} \quad (9.4)$$

with the known radiative lifetime, τ_{rad} . It was calculated that τ_{rad} is (7.2 ± 0.7) ms, which is greater than the measured PL lifetimes. The resultant quantum efficiencies are listed in Tab. 9.1 and the quantum efficiency was as high as 79% [19].

Figure 9.2: (a) Average PL lifetime for Eu^{3+} ($\lambda_{em} = 590$ nm, $\lambda_{ex} = 400$ nm) doped LaF_3 samples against the rare earth concentration.

The line is guided to the eye [12].

(b) PL lifetime decay of 5 % Eu doped LaF_3 at $\lambda_{em} = 590$ nm (black curve). The red curve is the exponential fit. The lifetime was measured at $\lambda_{em} = 400$ nm.

Janssens et al. reported in a recent paper PL and PL lifetime studies of Eu doped LaF_3 nanoparticles. Their average PL lifetime was calculated with a method described in chapter 3.2.4 but the PL lifetimes were the same as calculated with this method. Janssens et al. already showed extensive studies of the PL decay curves in their paper as well as in his Ph.D. thesis. Hence, no further PL lifetime curves will be discussed as it was already published [19, 22].

Table 9.1: Summary of different measured PL lifetimes, τ_{ave} and the quantum efficiency, η , for LaF_3 doped with different concentrations of Eu^{3+} [12].

Concentration (%)	τ_{ave} (ms)	η (%)
1	5.7 ± 0.6	79
2	5.1 ± 0.5	71
5	4.2 ± 0.4	58
15	2.9 ± 0.3	40
20	2.6 ± 0.3	36

Janssens et al. reported in their paper similar quantum efficiencies. The quantum efficiency was as high as 83.8 % and their calculated Ω_2 and Ω_4 were in the range of $(1.6 - 1.9) \times 10^{-20} \text{cm}^2$ and $(2.5 - 3.6) \times 10^{-20} \text{cm}^2$, respectively [22]. It was observed that Ω_2 is larger than Ω_4 , which was also reported for the NaMgF_3 and RbMgF_3 nanoparticles in this thesis. There was no dependence of Ω_2 and Ω_4 on the concentration of the rare earth observed. Higher values for Ω_2 and Ω_4 for the TTA/OA (TTA=thenoyltrifluoroacetone) capped nanoparticles were reported by Janssens et al.. Ω_2 and Ω_4 were in ranges of $(4.1-8.7) \times 10^{-20} \text{cm}^2$ and $(3.0-4.7) \times 10^{-20} \text{cm}^2$, respectively. A decrease of Ω_2 and Ω_4 with increasing Eu^{3+} concentration was investigated [22]. As already mentioned in the previous chapters, Ω_2 is higher for more distorted sites, which means that low concentrations of Eu^{3+} in the TTA/OA capped materials show a higher distorted site of Eu^{3+} [10, 93].

9.1.2 Sm doped LaF_3 nanoparticles

The PL emission and excitation spectra for LaF_3 nanoparticles doped with 5 % Sm^{3+} are shown in Fig. 9.3(a) and Fig. 9.3(b). The PL emission was excited into the $\text{Sm}^{3+} {}^7\text{F}_{5/2}$ level (400 nm) and the emission for the excitation spectra was detected at 600 nm, which

corresponds to the Sm^{3+} ${}^6\text{H}_{7/2}$ level. The PL emission occurs via initial non-radiative decay to the ${}^4\text{G}_{5/2}$ level. Sm^{2+} can sometimes occur in nanoparticles even when Sm^{3+} is in the starting compounds [19, 104]. For this reason, PL measurements were also done by exciting in the ultraviolet and there was no evidence for any Sm^{2+} .

Figure 9.3: (a) PL excitation ($\lambda_{em}=600$ nm) and (b) PL emission ($\lambda_{ex}=400$ nm) spectra for LaF_3 : 5 % Sm^{3+} nanoparticles [12].

For the Eu^{3+} doped LaF_3 , it was shown that the decrease in τ_{ave} with increasing Eu^{3+} concentration can be attributed to energy transfer from Eu^{3+} sites away from the surface to Eu^{3+} sites near the surface followed by non-radiative decay at unidentified surface non-radiative recombination sites [10, 11, 12, 22]. A similar energy transfer process is also likely for Sm^{3+} . However, cross-relaxation to neighbouring Sm^{3+} sites can also occur [105]. For example, excitation followed by non-radiative decay to the ${}^4\text{G}_{5/2}$ level can result in a ${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{5/2}$ transition on one Sm^{3+} site, and a ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{11/2}$ transition on the neighbouring Sm^{3+} (Fig. 9.4).

Figure 9.4: Cross relaxation process between Sm^{3+} ion [13].

This leaves one Sm^{3+} ion in the $^6\text{F}_{5/2}$ level and the other Sm^{3+} ion in the $^6\text{F}_{11/2}$ level followed by non-radiative decay. This leads to two possible mechanisms that can cause the Sm^{3+} PL lifetime to decrease. The first energy transfer mechanism to Sm^{3+} sites near the surface followed by non-radiative decay should result in a PL lifetime that decreases and reaches a constant value for high concentrations. This is observed in Fig. 9.5(a). The second mechanism where there is cross relaxation and non-radiative decay might be expected to continually decrease with increasing Sm^{3+} concentration. This appears to be inconsistent with the data plotted in Fig. 9.5(a), and hence the first mechanism is probably the main process. Tab. 9.2 shows the summary of the measured average PL lifetimes, τ_{ave} , for LaF_3 doped with different concentrations of Sm^{3+} [12].

Figure 9.5: (a) Average PL lifetimes for Sm^{3+} ($\lambda_{em}=600$ nm, $\lambda_{ex}=400$ nm) doped LaF_3 samples against the rare earth concentration. The line is guided to the eye [12]. (b) PL lifetime decay of 5 % Sm doped LaF_3 at $\lambda_{em}=600$ nm (black curve). The red curve is the exponential fit. The lifetime was measured at $\lambda_{em}=400$ nm.

A detailed study of the PL and PL lifetime measurements including the PL decay curves was already published in the Ph.D. thesis of Stefaan Janssens and will not be repeated in this thesis [19].

Table 9.2: Summary of the different measured PL lifetimes, τ_{ave} , for LaF_3 doped with different concentrations of Sm^{3+} .

Concentration (%)	τ_{ave} (ms)
1	2.3 ± 0.2
5	0.9 ± 0.1
10	0.6 ± 0.1
15	0.30 ± 0.03
20	0.5 ± 0.1

9.2 Radioluminescence measurements of LaF_3

The RL measurements were performed during continuous 60 keV γ -ray irradiation using a ^{241}Am source or during exposure with X-rays generated by a cobalt X-ray tube (40 kV and 40 mA) with an Aluminium filter. The ^{241}Am RL measurements were performed using a custom-built system, where the ^{241}Am was placed on top of the sample that was located on top of a photomultiplier tube. Higher dose measurements were constructed employing a custom-built system attached to an X-ray set where the sample was located ~ 3 cm from the exit port. This system was also used to collect the RL spectra where an optical fibre was connected to an Ocean Optics USB 4000 spectrometer that had a CCD detector array.

9.2.1 Eu doped LaF_3 nanoparticles

Figure 9.6: (a) Radioluminescence spectra for LaF_3 : 5 % Eu^{3+} nanoparticles during continuous X-ray irradiation.

(b) The integrated RL spectra as a function of irradiation time for LaF_3 : 5 % Eu^{3+} nanoparticles during continuous X-ray irradiation (filled squares) or 60 keV γ -ray irradiation (solid line).

The dashed line is a guide to the eye.

Fig. 9.6(a) shows the RL spectra during continuous X-ray excitation for a 5 % Eu^{3+} sample. The RL can be completely attributed to Eu^{3+} and there are no Eu^{2+} emissions. The energies of the Eu^{3+} emissions are the same as those observed in the PL spectra. The integrated RL intensity is plotted in Fig. 9.6(b) (filled squares), and it can be observed that it is independent of dose up to ~ 10 kGy. It was not possible to perform similar measurements at lower doses, because the sensitivity of the CCD detector was not high enough. For this reason low dose measurements were performed with a ^{241}Am source. The resultant RL intensity is plotted in Fig. 9.6(b) (solid line), and scaled to match the data obtained from X-ray irradiation. It is apparent that the RL is linear even for low doses where a dose dependence might be expected if there exists electron and hole traps that become filled during irradiation [73]. Thus, it was found that the RL signal is linear from 0.1 Gy to 10 kGy and spanning 5 orders of magnitude. This is advantageous for real time dose monitoring, because other compounds can be damaged when exposed to doses in the kGy region and they can also display a dose-dependent RL. The RL signal decreases by 2.3 % at 1 kGy and by 3.0 % at 10 kGy. The ratio I_{7F_2}/I_{7F_1} is 0.9:1 in the 5 % doped sample, which was the same as observed in the PL spectra.

9.2.2 Sm doped LaF_3 nanoparticles

The RL spectra for the 5 % Sm^{3+} sample is plotted in Fig. 9.7(a), and it contains only Sm^{3+} emissions where the energy of the emissions are the same as those observed in the PL spectra. Figure 9.7(b) shows the integrated RL intensity plotted against the X-ray dose. It is apparent that the RL is independent of the dose up to ~ 5 kGy, and there is only a very small increase by 5.3 % in the RL intensity at 10 kGy [12].

Figure 9.7: (a) Radioluminescence spectra for (a) LaF₃: 5 % Sm³⁺ nanoparticles.

(b) The integrated RL spectra as a function of irradiation time for LaF₃: 5 % Sm³⁺ nanoparticles. The radioluminescence data were recorded during continuous X-ray irradiation.

9.3 Photoluminescence measurements of BaF₂

BaF₂ nanoparticles doped with 5 % Eu³⁺ were produced with a reverse micro-emulsion method similar to producing the NaMgF₃ and RbMgF₃ nanoparticles. The precursors were high purity BaNO₃, Eu(NO₃)₃, NH₄F and CTAB. BaF₂ has a cubic crystal structure and the crystal size was measured from the XRD data with the Scherrer formula and the nanoparticles had an average diameter of ~ 12 nm [26]. PL measurements were performed with the Cary50. BaF₂ were doped with 5 % Eu and the PL excitation and emission spectra is plotted in Fig. 9.8. The PL excitation spectra was measured at an emission wavelength of 590 nm and it consists only the Eu³⁺ emission from the ⁷F₁ level. The PL emission spectra was excited at 395 nm, which are into the intense ⁵G₆ and ⁵L₆ levels. The PL emission originates mainly from the ⁵D₀ transitions. The ⁵D₁ transitions are very weak (Fig. 9.8(b)).

Figure 9.8: (a) PL excitation ($\lambda_{em} = 590$ nm) and (b) PL emission ($\lambda_{ex} = 395$ nm) spectra for BaF₂: 5 % Eu³⁺ nanoparticles.

9.4 Radioluminescence measurements of BaF₂

RL measurements were performed with X-rays generated by a cobalt X-ray tube (40 kV and 40 mA) with an Aluminium filter, and RL was detected with a CCD detector. In Fig. 9.9(a), the RL spectra for BaF₂: 5 % Eu³⁺ nanoparticles during continuous X-ray irradiation, is plotted. Fig. 9.9(b) shows the integrated RL spectra as a function of irradiation time during continual X-ray irradiation. The RL emission can be completely contributed to the Eu³⁺ ⁵D₀ and ⁵D₁ transitions with RL emissions being the same as observed in the PL spectra (Fig. 9.9(a)). There is no shift in the RL or PL emission wavelength after heavily irradiation. Fig. 9.9(b) shows the integrated RL intensity plotted against the X-ray dose for 5 % Eu³⁺ and the RL is nearly independent of dose up to ~10 kGy. The RL intensity increases by 3.9 % at ~1 kGy and decreases by 1.3 % at ~7 kGy.

Figure 9.9: (a) Radioluminescence spectra for BaF₂: 5 % Eu³⁺ nanoparticles during continuous X-ray irradiation after 68 Gy (black line) and 6.5 kGy (blue line). (b) The integrated RL spectra as a function of irradiation time for BaF₂: 5 % Eu³⁺ nanoparticles during continuous X-ray irradiation.

9.5 Photoluminescence measurements of BaMgF₄

BaMgF₄ doped with 5 % Mn²⁺ were produced with a reverse micro-emulsion method similar to that used to the method to produce the other nanoparticles, i.e. NaMgF₃, RbMgF₃ and BaMgF₄ nanoparticles. The precursors were high purity BaNO₃, MgNO₃, Mn(NO₃)₃, NH₄F and CTAB. BaMgF₄ has a orthorhombic crystal structure and the crystal size was measured from the XRD data with the Scherrer formula and the nanoparticles had an average diameter of ~ 11 nm [19, 77]. PL measurements were performed with the Jobin-Yvon FluoroLog[®]. Mn²⁺ can substitute for two lattice sites in BaMgF₄, the Ba²⁺ and the Mg²⁺ site. An emission at 630 nm was detected which corresponds to the Mg²⁺ site [81]. BaMgF₄ were doped with 5 % Mn²⁺ and the PL excitation and emission spectra is plotted in Fig. 9.10. The PL excitation spectra were measured at an emission wavelength of 630 nm and it shows only the Mn²⁺ emission of the ⁶A_{1g} level, which are indicated in Fig. 9.10(a). The PL emission spectra was excited at 396 nm, which are into the intense

4E_g and $^4A_{1g}$ levels (Fig. 9.10(b)). The PL emission consists of one peak at 630 nm. There are no additional peaks from a highly distorted Mn^{2+} site detected in the PL emission spectrum as it was observed for the $NaMgF_3:Mn$ bulk and nanoparticles.

Figure 9.10: (a) PL excitation ($\lambda_{em} = 630$ nm) and (b) PL emission ($\lambda_{ex} = 396$ nm) spectra for $BaMgF_4: 5\% Mn^{2+}$ nanoparticles.

9.6 Radioluminescence measurements of $BaMgF_4$

RL measurements were performed with X-rays generated by a cobalt X-ray tube (40 kV and 40 mA) with an Aluminium filter and RL was detected with a CCD detector. In Fig. 9.11(a), the RL spectra for $BaMgF_4: 5\% Mn^{2+}$ nanoparticles during X-ray irradiation is plotted. Fig. 9.11(b) shows the integrated RL spectra as a function of irradiation time during continuous X-ray irradiation. The RL emission can be completely contributed to the Mn^{2+} emission at ~ 630 nm with RL emissions being the same as observed in the PL spectra (Fig. 9.11(a)). There is no shift in the RL or PL emission wavelength after heavily irradiation. Fig. 9.11(b) shows the integrated RL intensity plotted against the X-ray dose for $5\% Mn^{3+}$ and the RL increases by 7.3 % at 1 kGy and increases by 17.4 % at ~ 10 kGy.

Figure 9.11: (a) Radioluminescence spectra for BaMgF₄: 5 % Mn²⁺ nanoparticles during continuous X-ray irradiation after 68 Gy (black line) and 6.5 kGy (blue line). (b) The integrated RL spectra as a function of irradiation time for BaMgF₄: 5 % Mn²⁺ nanoparticles during continuous X-ray irradiation.

9.7 Conclusion

Fluoride nanoparticles show PL and RL. There were no distorted sites of Mn observed in the Mn²⁺ doped BaMgF₃ as it was performed for the NaMgF₃ nanoparticles and bulk materials. Eu³⁺ emission was detected in the RL spectra for the fluoride nanoparticles, which is different to the RL emission of Eu²⁺ and Eu³⁺ in NaMgF₃ and RbMgF₃ nanoparticles, which was reported in the previous chapters. The PL lifetimes for the LaF₃ decreases with increasing rare earth concentrations that can be attributed to energy transfer from luminescence ions in the core to luminescence ion near the surface followed by non-radiative decay. In comparison with RbMgF₃ and NaMgF₃, the decrease of the PL lifetimes was more due to non-radiative recombination centres inside the crystal.

The RL spectrum for LaF₃ shows only Eu³⁺ and Sm³⁺ occur. The integrated RL intensity is independent of dose for up to 5 orders of magnitude and for doses as high as 10 kGy. In

the range of ~ 100 Gy to ~ 10 kGy the RL signal of the other fluoride nanoparticles is nearly independent of dose which are summarised in Tab. 9.3. The Eu doped LaF_3 and BaF_2 samples show that there have very little dose dependence of the RL signal. The NaMgF_3 samples doped with 1 % Eu showed a constant RL signal after receiving a pre-dose of 15 kGy and the 1 % Mn doped sample show a constant RL signal after a pre-dose of ~ 1 kGy.

Table 9.3: Summary of the dose dependence of the RL signal for different fluoride compounds after receiving a dose of ~ 10 kGy.

Compound	Dose dependence of RL (%)
LaF_3 : 5 % Eu	3.0
LaF_3 : 5 % Sm	5.3
BaF_2 : 5 % Eu	1.3
BaMgF_3 : 5 % Mn	17.4

The dose independence of the RL of LaF_3 is a desirable property for real time radiation dosimeters that can detect low doses as well as very high doses without being damaged. Therefore LaF_3 has potential as a dosimeter for non-tissue equivalent applications or radiation imaging materials. Further work should be performed on the dependency of the dose for the RL after longterm irradiation. PL measurements before and after heavy irradiation should also be performed to observe the change of the PL emission and the excitation spectra as a function of dose.

10 Summary and Conclusion

In this thesis, fluoroperovskite materials have been investigated for their potential use in dosimetric applications. Both polycrystalline bulk materials and nanoparticles were researched and their behaviour in photoluminescence (PL), radioluminescence (RL), temperature dependent RL and thermoluminescence (TL) were compared. The main focus was on the RL and TL properties of these materials. These materials have the advantage that they can be employed as real-time dosimeters due to their good response to RL. The bulk materials and nanoparticles can be produced transparent, and therefore the incident light will not be scattered during stimulation of the sample. The nanoparticles are radiation hard for high doses. This means the RL is dose independent after heavy irradiation. NaMgF₃ doped with Mn is nearly tissue equivalent, which means that the material responds to radiation in a similar way as tissue. This is a desirable property of dosimeters employed in personal dosimetry.

It was observed that the bulk materials show optically stimulated luminescence (OSL) in addition to RL and TL [3]. Therefore, their use would be for OSL dosimeters, because they show a high sensitivity in PL, TL, RL and OSL. Their RL is dose history dependent and hence not favourable in real-time applications. With Mn being the best material for dosimeter applications for the polycrystalline samples because it shows less dose history dependence. Their thermal coefficient of the RL was smaller than observed for other materials. The Eu doped bulk materials show additional unidentified defects at around 470 nm. It shows a large PL lifetime for all of the different compounds. Hence, it can be assumed that the unknown defect is the same for the Rb and Na samples and needs to be

further investigated. Therefore, further work should be performed to find the origin of the unknown peak and distinguish if it originates is a result of F-centres or other defects. One possibility could be, to measure the sample with EPR. If the unknown peak is dominated by F-centres, it would be possible to detect this with EPR [98]. Another possibility would be, to powder the sample and heat it up. The mean free path will increase and oxygen can diffuse inside the crystal. By performing PL after this, an increase of the peak would mean the defects in the peak are caused by oxygen. Oxygen can also be detected by performing vacuum UV-PL on the peak. Future work should also be performed to measure TL after heavy irradiation for the NaMgF₃: Eu and RbMgF₃ samples.

The fluoroperovskite nanoparticles were produced with the reverse micro-emulsion method [76]. The nanoparticles can be pressed into pellets, which can be made transparent as it was shown for the LaF₃ nanoparticles [22] depending on the thickness of the pressed sample and if they are capped with oleic acid. The NaMgF₃ and RbMgF₃ fluoroperovskite nanoparticles, which were observed in this thesis, were not capped with any organics and hence, their appearance was not transparent. None of the nanoparticles show any OSL. The generation of defects is less compared to the bulk materials. Therefore, the RL is less dependent on the dose. After a pre-dose of a few kGy, the nanoparticles with a larger particle size show a constant RL signal with increasing dose. This is a desirable property for real-time radiation dosimeters that can detect high doses without being damaged. Hence, the nanoparticles are suitable for applications as a real-time dosimeter. Mn or Eu doped nanoparticles are favourable for this application since both dopants show a dose history independent RL. However, a dosimeter with two detectors, Mn and Eu, can be produced with the nanoparticles. The thermal coefficient of the RL for the nanoparticles has a high uncertainty.

The Mn and Eu doped nanoparticles show a different trap distribution compared to the bulk materials, which is shown in the lower PL lifetimes. The bulk materials show radiation damage and trapping of charged carriers in non-radiative recombination centres and the nanoparticles show an energy transfer to the surface of the crystal. The

crystal environment of the Eu^{3+} in the nanoparticles is less distorted compared to the bulk materials, which results in a lower ratio of $I_{7F_2}:I_{7F_1}$. The TL glow curves of $\text{RbMgF}_3:\text{Mn}$ and $\text{NaMgF}_3:\text{Mn}$ bulk materials all show high temperature peaks, whereas the $\text{RbMgF}_3:\text{Mn}$ and $\text{NaMgF}_3:\text{Mn}$ nanoparticles show low temperature peaks. It was mentioned that for the determination of the thermal coefficient of the RL, deep traps might not be completely emptied after heating the sample up to 620 K. Hence, further measurements should be performed with optical bleaching after each RL measurement.

For the fluoride nanoparticles, it was observed that the PL lifetimes for the LaF_3 decreases with increasing rare earth concentrations. This can be attributed to energy transfer from luminescence ions in the core to luminescence ions near the surface followed by non-radiative decay. In comparison, the decrease of the PL lifetimes of RbMgF_3 and NaMgF_3 is predominantly due to non-radiative recombination centres inside the crystal. The RL spectra for LaF_3 shows that only Eu^{3+} and Sm^{3+} was detected. The integrated RL intensity is independent of the dose for up to 5 orders of magnitude and for doses as high as 10 kGy. Therefore, LaF_3 can be employed as a real-time dosimeter that can detect low doses as well as high doses without being damaged for non-tissue equivalent applications or radiation imaging materials. Further work should be performed on the dependency of the dose for the RL after long-term irradiation. PL measurements before and after heavy irradiation should also be performed to observe the change of the PL emission and the excitation spectra as a function of dose.

11 Bibliography

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12 List of publications

1. C. Gaedtke, G.V.M. Williams, "Photoluminescence and radioluminescence study of NaMgF₃:Eu nanoparticles", *Radiation Measurements*, in press.
2. C. Gaedtke, G.V.M. Williams, D. Clarke, "Thermoluminescence studies of nanoparticle and bulk NaMgF₃:Mn", *International Journal of Nanotechnology*, in press.
3. C. Gaedtke, G.V.M. Williams, S. Janssens, S. Raymond, D. Clarke, "Photoluminescence and radioluminescence study of Eu and Mn doped RbMgF₃ nanoparticles", *Radiation Measurements* 56, 187-191, (2013).
4. G.V.M. Williams, S. Janssens, C. Gaedtke, S.G. Raymond, D. Clarke, "Observation of photoluminescence and radioluminescence in Eu and Mn doped NaMgF₃ nanoparticles", *Journal of Luminescence*, 143, 219-225 (2013).
5. C. Gaedtke, G. V. M. Williams, S. Janssens, S. G. Raymond, D. J. Clarke, "The effect of ionizing radiation on the luminescence properties of Eu³⁺ and Sm³⁺ doped LaF₃ nanoparticles", *Phys. Status Solidi (c)* 9, No. 12, 2247-2250 (2012).
6. G.V.M. Williams, S.G. Raymond, N. Denton, C. Gaedtke, "Development and characterization of a portable fibre optic dosimeter", *Materials Science Forum* 700, 174 (2011).