# Aligned Nanorods of AlPO<sub>4</sub>-5 Within the Pores of Anodic

## Alumina

by

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A thesis

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### Abstract

Anodic aluminium oxide has been identified as a versatile porous template material having high pore density, (up to  $10^{10}$  cm<sup>-2</sup>), controllable channel length and monodisperse pore diameter within the range 20-250 nm. A number of studies have demonstrated the concept of utilizing the porous structure for directing the growth of various nanostructures. An example of this is the growth of crystals of the aluminophosphate AlPO<sub>4</sub>-5 within the anodic nanochannels. The high aspect ratio of the template pores encourages growth of the crystals in the preferred c-axis orientation. We have produced membranes of this material and investigated the degree of crystal alignment using X-ray diffraction. The relative degree of preferred orientation is over 200 for a typical membrane. Field emission SEM micrographs clearly show the aligned crystals within the pores. The inclusion of luminescent guest molecules within the pores of the zeolite has also been achieved. This work describes the synthesis, characterization and potential application of these membranes. ii

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## List of Abbreviations

$\mu$ m	micrometre
Å	Angstrom
AFI	Aluminophosphate 5, also referred to as AlPO <sub>4</sub> -5
AlPO <sub>4</sub> -5	Aluminophosphate 5, also referred to by the three letter code AFI
BEA	the Zeolite Beta
CHA	The zeolite chabazite
cm	Centimetre
DCM	4-dicyanomethylene-2-methyl-6-(p(dimethylamino)styryl)-4H-pyran
DDR	the zeolite Deca-dodecasil 3R
EDS	Energy dispersive spectroscopy
FAU	The zeolite Faujasite
FER	The zeolite Ferrierite
IRL	Industrial Research Limited
LTA	The zeolite with the Linde Type A framework type
MAPO <sub>4</sub> -5	AlPO <sub>4</sub> -5 in which some of the aluminium in the framework has
	been replaced by other metal ions
MEL	The Zeolite ZSM-11
MFI	This abbreviation refers to 'mobil composition of matter 5' and
	refers to the aluminosilicate ZSM-5, which was patented by
	Mobil Oil Company
MOR	The zeolite Mordenite
NaA	The Linde type A sodium form of zeolite A
nm	Nanometre

PAA	Porous Anodic	Alumina

- SAPO<sub>4</sub>-34 the aluminophosphate 34, in which some of the aluminium in the framework has been replaced by silicon
- PEEK polyetheretherketone, an engineering plastic
- PTFE Polytetrafluoroethylene, more commonly known as Teflon
- SEM Scanning Electron Microscopy
- SHG Second harmonic generation, a nonlinear optical process, in which photons interacting with a nonlinear material are effectively "combined" to form new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons.
- UV Ultraviolet light
- XRD X-ray diffraction
- ZSM-5 an aluminosilicate with the structural type MFI

## Chapter 1

## Introduction

### **1.1** Nanomaterials

Nanotechnology is the engineering of functional systems at the molecular scale. Generally, nanotechnology deals with structures of the size 100 nanometres or smaller, and involves developing novel materials or molecular devices within that size range. Nanotechnology is very diverse, ranging from extensions of conventional synthethic techniques and macro-scale materials, to completely new approaches based upon molecular self-assembly, to developing new materials with dimensions on the nanoscale. The field of nanotechnology has the potential to create new materials that are not only faster, cleaner and cheaper to produce than conventional materials, but also display novel properties not available on the macro-scale [1].

A number of physical phenomena become pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the quantum size effect where the electronic properties of solids are altered as particle size decreases into the nano region [2, p.23]. This effect does not come into play by going from macro to micro dimensions, however, it becomes dominant when the nanometer size range is reached. Additionally, a number of physical (mechanical, electrical, optical, etc.) properties change when compared to macroscopic systems. One example is the increase in the ratio of surface area to volume, altering mechanical, thermal and catalytic properties of materials [2, p.29]. Nanotechnology exploits these phenomena to create materials with startlingly different properties to their macro scale counterparts.

This project seeks to investigate the potential of forming aligned nanocrystallites with specific properties in order to access functionality not available at larger scales. The project examines two functionalities derived from the use of zeolitic crystal, both resulting from the presence of open channels through the zeolite crystal structure. The first is the use of aligned arrays of the crystals arranged on the macro scale to act as a size exclusion molecular filter. The second function is to use the channels as cages in which to trap functional molecules, (in this case a 2<sup>nd</sup> order non-linear photonic molecule) in order to provide a macro scale material containing fully aligned molecules. As most zeolites form crystalline powders rather than films or membranes, it is necessary to utilise a template to produce crystallographically aligned arrays of zeolite crystals. In order to force this alignment a porous anodic alumina membrane is used as the template, the pores of which orient the zeolite crystals with their c-axis perpendicular to the membrane surface.

### **1.2** Porous Anodic Alumina

In recent years, nanoporous porous anodic alumina (PAA) membranes have become popular and attractive materials for a diverse range of applications including molecular separation [3], catalysis [4], drug delivery [5], biosensing [3], and template synthesis [6] [7]. This profound interest is due to the salient features of this nanostructured material. Firstly, PAA membranes can be easily fabricated with monodisperse, geometrically regular and self-organised pore diameters within the range 20-250 nm. Furthermore, such membranes have a high surface area ( $180-250 \text{ m}^2\text{g}^{-1}$ ), high pore density, (up to  $10^{10} \text{ cm}^{-2}$ ), controllable channel length, and are robust and biocompatible.

A number of studies have demonstrated the concept of utilizing PAA as a template for directing the growth of various nanostructures. Various composite materials with metals have been reported, including platinum [8] or palladium [9] membranes supported on PAA, composites of PAA with nanogold [10] and zinc, cobalt or iron nanotubes within PAA [11]. Other nanotube composites include carbon nanotubes grown within PAA [12] and nanocarbon networks [13]. Composites have also been made with the ionic conductor AgI within PAA [14]. These materials show an enhancement in conductivity over AgI powders. Composites of PAA with photoluminescent materials including liquid crystalline azo dyes [15], photoluminescent polymers [16] and Tb<sup>3+</sup> [17] show the diverse range of materials that can be supported on or contained within PAA.

Several different ceramic-based composites have also been reported, including aluminium titanate/PAA composites [18], zirconia-zircon com-

posites with PAA [19] and the zeolites MFI [20, 21, 22, 23, 24, 25, 26], FAU [23, 27] and the aluminophosphate AFI [28, 29], also known as AlPO<sub>4</sub>-5, which is discussed in this work. The naming schemes for zeolites and aluminophosphates from which these three letter codes are derived can be found in sections 1.3 and 1.4, and further detail on zeolite and aluminophosphates membranes is found in sections 1.3.2 and 1.5.4. This list shows the extreme versatility of PAA as a support for or template to direct the growth of different composite materials.

Porous anodic alumina is made by anodizing pure aluminium foil in an acidic electrolyte (typically, dilute solutions of various acids - sulfuric, phosphoric or oxalic for example - are used) [30]. The anode of the electrochemical cell is composed of aluminium while the cathode is an inert conductor such as carbon or platinum. The aluminium is oxidized to give a film of alumina, which grows in a hexagonal porous structure (see Fig 1.1), due to the preferential growth of oxide in nanosized pits on the surface of the aluminium, which are a result of polishing the aluminium foil. These pits grow into cells of alumina, each with a central pore [31].

The size of these pores and their interpore distance is dependent on the electrolyte used [30], and is approx 50 nm for the locally made anodic alumina membranes used in this study, which are shown in Fig 1.2. The residual Aluminium metal is removed and the ends of the pores are opened by immersion in an acidic solution [32].

Although anodizing highly pure aluminium can produce regular periodic arrays of pores, less regular porous alumina discs with pore diameters of 100 - 200 nm are commercially produced for microfiltration applica-



Figure 1.1: Idealized structure of Porous Anodic Aluminium Oxide [31].

tions. The synthetic procedure discussed in this work is suitable for both highly ordered and commercially available PAA membranes, demonstrating a high degree of flexibility with regards to the purity and pore size of the substrates that may be used.

## 1.3 Zeolites

Zeolites are a class of microporous molecular sieve based mostly on porous aluminosilicates, but also encompass a wider range of materials including the aluminophosphates, which are studied in this work. The name zeolite (from zeo, "to boil"; lithos, "a stone" [33]) was bestowed by the



Figure 1.2: A side view of porous anodic alumina made by the method in Kirchner et al. at 33000 magnification [32].

Swedish mineralogist Axel Fredrik Cronstedt. In 1756 he discovered a zeolite now widely used for water softening, upon observation that when heated rapidly, the stones began to dance about as the water evaporated [34].

Zeolites are three-dimensional, crystalline compounds with an open porous framework structure composed of alternating  $AlO_4$  and  $SiO_4$  tetrahedra [35]. According to the diameter of the largest pore, porous materials can be classified as microporous (aperture diameter of less than 2 nm), mesoporous (aperture diameter of 2-50 nm) or macroporous (aperture diameter of greater than 50 nm) [36]. The pore diameters for zeolites are generally in the microporous region, of the order of 0.5 to 1.5 nm.

The basic zeolite formula is  $M_2/_nO.Al_2O_3.xSiO_2.yH_2O$ , with M defining the compensating cation, valence n indicating the ratio of atoms of Si:Al and y indicating the ratio of  $H_2O:Al$  [37]. A number of different cations can provide the counter charge. An example of a common zeolite (ZSM-5) is shown in figure 1.3.



Figure 1.3: The zeolite ZSM-5 showing the pores along which molecular sieving is achieved [38].

Zeolites are synthesised hydrothermally, from an aqueous solution of the aluminate, silicate and a template around which the porous framework is formed. The precise zeolite formed during synthesis is dependent on the reactants and synthetic conditions used. Zeolites are categorized by their framework type and as of July 2009, 179 unique zeolite frameworks have been identified [39].

Zeolite framework types are categorized by a unique 3 letter identifi-

cation code, which is designated according to the laboratory in which it was synthesised, and the order in which it was discovered. This can be a confusing scheme for researchers to follow as it is in no way descriptive of the structure of the zeolite in question. For example the zeolite ZSM-5 was so named because it was discovered by the researchers at Zeolite Secony Mobil, and was the 5<sup>th</sup> such zeolite to be discovered. It is given the three letter code MFI, the M refers to Mobil, and the letters FI refers to the first two letters in the number five.

#### **1.3.1** Applications of Zeolites

Over the past few decades, interest in zeolites has increased due to their many potential applications in catalysis, molecular sieving, separations and water purification. Zeolites have many interesting properties. They are able to act as catalysts for various reactions which take place within their cavities [40, p.327-328]. Their very regular pore structure allows them to behave as molecular sieves, to selectively sort molecules based primarily on a size exclusion process, and furthermore, the cations which provide counter charge in zeolites are labile, and can undergo ion exchange with other cations [40, p.81].

One of the most important uses of zeolites is in catalysis, for the cracking of heavier petroleum fractions into their lighter and more valuable constituents. The zeolite holds the long alkyl chain molecules within its pores, and acidic sites help break them into smaller chains [40, p.388]. After introduction of metal ions (e.g. titanium or copper) into the framework, zeolites can also function as oxidation or reduction catalysts [40,

#### p.415-416].

Zeolites are extensively used in the separation of gases and liquids, both by simple size exclusion, based on the pore sizes relative to the material to be separated, and by the speed with which molecules of different polarity diffuse through the pores.

The ability of zeolites to ion exchange leads to application in water purification, both for domestic and commercial uses. Zeolites are extensively used in water softening, by removing  $Ca^{2+}$  and  $Mg^{2+}$ , which form insoluble deposits and precipitates with soap [41]. An example of this is the use of zeolite A, as shown in Figure 1.4. The sodium ions in the framework are replaced by the hard ions  $Mg^{2+}$  and  $Ca^{2+}$ . When the zeolite has become saturated with hard ions it can be regenerated by passing a saturated solution of NaCl through it, exchanging  $Na^+$  for  $Mg^{2+}$  and  $Ca^{2+}$ .



Figure 1.4: A schematic showing the role of NaA in water softening [42].

An important environmental application of zeolites which exploits their ability to ion exchange is in the processing of commercial waste water streams where zeolites can be used to remove heavy metals or radioactive residues from the waste stream [43].

#### **1.3.2** Zeolite Membranes

Many of the separative applications of zeolites rely on the use of their nonlinear porosity, where pores pass through only one crystal plane. This can only be fully utilized if the orientation of the zeolite crystals can be controlled relative to the material to be separated. As most zeolites form crystalline powders, a support or template is needed in order to manufacture zeolite films and membranes. Zeolite films and membranes promise far superior performance to their conventional polymeric counterparts, due to their relative thermal and chemical stability, and tunable, nanometer sized pores.

Membranes composed of a zeolite layer on a support material have the potential to replace energy-intensive thermally driven separation processes with membrane based ones, which can provide a reduction in energy usage of up to an order of magnitude [44]. Different types of zeolite membrane that have been reported include LTA [45, 46, 47, 48, 49], FAU [50, 51, 52, 53], MOR [54, 55], FER [56], MEL [57], CHA [58], SAPO-34 [59, 60, 61, 62], DDR [63], and AFI [64, 65, 29, 48, 21, 28].

Potential applications of zeolites membranes include separative processes such as the de-watering of ethanol by LTA membranes [66, 67, 68, 69], for which a pilot plant is in operation. These membranes have a separation factor (water/ethanol) of 10,000 for 90 wt% ethanol solution. Zeolite membranes have also been use in hydrogen separation, carbon dioxide separation and separation of xylene isomers [44].

Another novel application of zeolites films and membranes is their use in reactors to enhance a particular chemical reaction. There are numerous examples of their use in membrane reactors by equilibrium displacement or by selectively removing reaction rate inhibitors [70]. In addition to these applications zeolite membranes may be used in chemical sensors, as electrodes, as opto-electronic devices or low dielectric constant materials, as protective or insulating layers, as corrosion-resistant coatings [71] or as hydrophilic antimicrobial coatings [72]. Sulfonated zeolite BEA may also be used for proton exchange [73].

Although there has been much research in the field of zeolite membranes over the last decade this technology is very much in its infancy, and there are only a few pilot plants in operation. Initial successes however mean that many more are planned. The range of possible applications has also increased greatly over the past few years with the possibility of generating new structures via inclusion of guest molecules into the pores of the zeolite.

### 1.4 Aluminophosphates

It has been more than 25 years since the first reported synthesis of aluminophosphates by Wilson and Flanigan [74]. Before that time the field of zeolites was restricted to those containing silica [75]. The work of Wilson and Flanigan in reporting on the aluminophosphate molecular sieves opened the field to a whole new variety of different zeolite based materials.

More than 53 different aluminophosphate structures have now been synthesised, with 18 analogues of natural or synthetic zeolites [39]. Their naming scheme, though somewhat less confusing than that of the silica based zeolites, still makes no reference to the structure of the material. Each aluminophosphate has a three letter code, the first letter of which is A (for aluminophosphate), and the second two letters of which refer to the order in which it was discovered. For example  $AlPO_4$ -18 is given the three letter code AEI, for Aluminophosphate Eighteen.

The aluminophosphates are mostly microporous molecular sieves with pores with diameters ranging from 4 to 12 depending on the structure [76], which are used for many of the same applications as the original silica based zeolites. The subject of the present study is  $AIPO_4$ -5, a medium pore size (0.78 nm) aluminophosphate, which is one of the more widely studied in the field. It is referred to by the three letter code AFI, for Aluminophosphate Five.

## **1.5** AlPO<sub>4</sub>-5

#### 1.5.1 Structure

AlPO<sub>4</sub>-5 has a hexagonal open framework structure with a=13.827 Å, b=13.827 Å, c=8.580 Å and  $\alpha = 90^{\circ}$ ,  $\beta = 90^{\circ}$ ,  $\gamma = 120^{\circ}$ . The structure is composed of alternating alumina and phosphate tetrahedra with the main porosity along the [001] plane as seen in Figures 1.5 and 1.6. The pore size of AlPO<sub>4</sub>-5 is 7.3 Å. The space group is P6/mcc (mass centred cubic), and the largest ring size is 12 atoms. Bulk AlPO<sub>4</sub>-5 has the powder X-ray diffraction pattern shown in Fig. 1.7, which is taken from the database of zeolite structures at the International Zeolite Association [39].



Figure 1.5: AFI viewed along the 001 axis [77].

### 1.5.2 Synthesis

 $AIPO_4$ -5 is usually synthesised hydrothermally from a solution of the aluminium source and phosphoric acid, with an amine structure directing agent [78]. A number of different amine structure directing agents can be used. One of the commonly used organic templating molecules is triethy-lamine (TEA), which is used in the syntheses discussed in chapters three and four.

Other commonly used templating molecules include tetrapropylammonium hydroxide and tripropylamine.

Various aluminium sources may also be employed, the most common of which are pseudoboehmite and aluminium isopropoxide, although many others have been used. The original synthesis proposed by Wilson and



Figure 1.6: AFI viewed channel normal to the 001 axis [77].

Flanigen over 20 years ago used an aqueous slurry of orthophosphoric acid and pseudoboehmite, with tetrapropylammonium hydroxide as the templating agent. This synthesis involved a slow crystallisation at 150 °C over a period of 43 hours [74]. Guth et al. introduced the use of HF as a mineraliser in 1986 [79], which, combined with the introduction of microwave heating [80, 81] greatly reduced the crystallisation time needed. Advantages of microwave heating include speed, increased phase purity, narrow particle size distribution and the fact that heating is not disturbed by convection [75]. A typical microwave synthesis involves a crystallisation time of between 10 and 30 minutes and may be as short as 60 seconds [82, 83].



Figure 1.7: The powder XRD pattern of the zeolite AFI, taken from the website of the International Zeolite Association [39].

### 1.5.3 Applications

The two main applications for which AlPO<sub>4</sub>-5 has historically been studied are catalysis and molecular sieving [74]. MAPO<sub>4</sub>-5 (AlPO<sub>4</sub>-5 in which other metal ions have been introduced into the framework) has been demonstrated to be a recyclable catalyst for various oxidation reactions of alkanes, cycloalkanes or phenols [84]. Examples of this include the use of Fe-AlPO<sub>4</sub>-5 for the oxidation of cyclohexane [85], Cr-AlPO<sub>4</sub>-5 for the autoxidation of cyclohexane, tetralin, indane and ethylbenzene [86], Cr-AlPO<sub>4</sub>-5 synthesised from aluminium dross (a byproduct of aluminium smelting) for the liquid phase oxidation of tetralin [52], Mn, Zn, Co and Mg substituted AlPO<sub>4</sub>-5 for the dehydration and dehydrogenation of cyclohexanol [87]and Co-AlPO<sub>4</sub>-5 for oxidation of cyclohexane [88].

AlPO<sub>4</sub>-5 has also been shown to be of potential utility for gas separa-

tions, including the separation from air of  $O_2/N_2$  [89], the separation of  $C_8$  aromatics including benzene and o-xylene [90] and the separation from  $N_2$  of  $CH_2Cl_2$  [91].

### **1.5.4** AlPO<sub>4</sub>-5 Membranes

AlPO<sub>4</sub>-5 membranes promise the same potential benefits as membranes of other zeolite-based materials. In the past few years, due to their molecular sieving action, potential value as catalytic membranes in membrane reactors, and value as chemical sensors or low dielectric constant materials [78], a number of papers have been published on the growth of such membranes [28, 78, 92, 93, 94, 85, 29, 95, 96]. Growth of oriented crystals in such a membrane can effectively enhance the mass transport and control the thermal stress applied during chemical separations [97].

Another possible use of such membranes is as a way to induce preferential orientation of the zeolite allowing controlled host-guest interaction. This opens up a wide range of potential applications for composites as molecular wire, quantum electronic and non-linear optical devices [29].

Several different types of substrate have been used to synthesise oriented films or membranes of AlPO<sub>4</sub>-5, including gold coated quartz crystal microbalances, Ni grids, and anodized alumina. All of these membranes were synthesized using microwave heating as the energy source [98].

Bein et al. [99] prepared ultrathin films of AlPO<sub>4</sub>-5 using pretreated, gold-coated quartz crystal microbalances as a substrate. These membranes were not crystallographically aligned. Caro et al. [92] prepared large AlPO<sub>4</sub>-5 single crystals via microwave heating which were then c-axis oriented

within a nickel grid in an electric field, i.e. with the porosity perpendicular to the substrate. Voids in the membrane were sealed by deposition of nickel. Tsapatsis et al. [93, 94] prepared AlPO<sub>4</sub>-5 membranes on a seeded, pretreated silicon substrate. These were prepared via two methods. The first method published by this group yielded a highly oriented but poorly intergrown film, the gaps in which were subsequently filled by a second round of in-plane AlPO<sub>4</sub>-5 growth, and the second a poorly aligned yet highly intergrown film without the second step. Shih et al. [29] prepared an aligned AlPO<sub>4</sub>-5 membrane crystallised on anodised alumina via a microwave heating method that suspended the anodised alumina at the liquid/air interface. These membranes showed a high degree of alignment; however in the SEM micrographs shown in the paper, they do not appear to fully cover the surface of the anodized alumina substrate [29]. This work has also been extended to the synthesis of SAPO-5 membranes [95]. All of the AlPO<sub>4</sub>-5 membranes prepared on anodic alumina thus far have used highly ordered anodic alumina membranes synthesized in a laboratory setting as the substrate. These membranes are expensive and not readily available on a larger scale.

Qiu et al. [97] have taken the preparation of  $AIPO_4$ -5 membranes one step further, preparing a single crystal  $AIPO_4$ -5 substrate by gluing large  $AIPO_4$ -5 crystals onto a glass slide with their *c*-axes aligned perpendicular to the surface of the slide, and then growing a highly oriented molecular sieve film on top of this via epitaxial growth. The  $AIPO_4$ -5 film prepared has been doped with the laser dye Rhodamine B for potential application as a microlaser system.

#### **1.5.5** AlPO<sub>4</sub>-5 as a host for other materials

Much of the recent research into  $AIPO_4$ -5 has utilised the open pore structure of  $AIPO_4$ -5 as a template to fabricate host-guest composite materials for a range of novel applications.

AlPO<sub>4</sub>-5 crystals are electrically insulating, optically transparent from ultraviolet to infrared, and thermally stable to 900 °C [100]. These properties, combined with their uniaxial open pore structure, make them an excellent starting point for the fabrication of host-guest nanostructured composites. A number of different materials have been encapsulated within the pores of AlPO<sub>4</sub>-5 to generate novel materials with interesting properties on the nanoscale.

One example of this is the encapsulation of p-nitroaniline within the pores of  $AIPO_4$ -5. It was discovered by Stucky et al. [101, 102] in 1988 that p-nitroaniline-loaded  $AIPO_4$ -5 was an efficient second harmonic generator. Second harmonic generation (SHG, also called frequency doubling) is a nonlinear optical process, in which photons interacting with a nonlinear material are effectively "combined" to form new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons.

This discovery led the way for the inclusion of a number of different types of organic molecule within AlPO<sub>4</sub>-5, for potential applications in optical data storage or optical frequency doubling [82], laser frequency conversion, and as microcavity lasers [100]. Dyes introduced into the pores of AlPO<sub>4</sub>-5 to date include pyridine 2 [103], coumarin 466, coumarin 7, and DCM [104]. Laser emission has been demonstrated from these com-
posites [103]. These composites will be discussed in more depth in the following section.

Another example of use of  $AIPO_4$ -5 for the preparation of a novel material is single walled carbon nanotubes (CNTs), which can be grown within the pores of  $AIPO_4$ -5 via chemical vapour deposition. Confining the growth of the CNTs within the pores of the zeolite allows control of the nanotube diameter and growth direction. These nanotubes may be useful in carbon nanotube based electronics [105, 106].

#### 1.5.6 Microlaser Introduction

A laser (short for light amplification by stimulated emission of radiation) consists of a gain medium inside a highly reflective optical cavity, as well as a means to supply energy to the gain medium [107]. The gain medium is a material with properties that allow it to amplify light by stimulated emission. Stimulated emission is the process by which an electron, perturbed by a photon having the correct energy, may drop to a lower energy level resulting in the creation of another photon. The perturbing photon is seemingly unchanged in the process, and a second photon is created with the same phase, frequency, polarization, and direction of travel as the original [107].

In its simplest form, a cavity consists of two mirrors arranged such that light bounces back and forth, each time passing through the gain medium. Typically one of the two mirrors, the output coupler, is partially transparent. The output laser beam is emitted through this mirror.

A dye laser is a laser in which an organic dye is used as the gain



Figure 1.8: Simple laser. Principal components: 1. Gain medium, 2. Pump, 3. High reflector, 4. Output coupler, 5. Laser beam [108].

medium. The gain medium is the source of optical gain within a laser. Usually the dye is in solution, however the same dyes may be utilised in  $AIPO_4$ -5/dye microlasers, in which the optically transparent  $AIPO_4$ -5 single crystals act as the optical cavity, with the hexagonal plate-like faces of the crystal behaving as the mirrors, and the gain medium provided by organic dye molecules occluded within defects in the crystal. It is proposed that these micro sized lasers will have a greatly reduced lasing threshold due to the nanometre size of the laser [109].

#### 1.5.7 AlPO<sub>4</sub>-5/dye Microlasers

There are several methods by which an AlPO<sub>4</sub>-5/laser dye composite may be synthesized. One method by which these microlaser systems are synthesized is hydrothermal synthesis of the zeolite according to the usual synthetic procedure, followed by removal of the organic structure directing agent and loading of the dye molecule either from solution or from the vapor phase by insertion (for neutral molecules) or ion exchange (for cationic molecules) [110]. This type of synthesis can lead to high dye loadings, but requires several steps. The more elegant synthetic method involves synthesis of the composite in one step, in which the dye molecule is introduced into the framework of the zeolite *in-situ* during synthesis. This requires that the organic dye be adapted to the (relatively harsh) conditions of hydrothermal synthesis, but does give more flexibility than may initially be assumed, as it has been shown that a guest molecule may reside in an enlarged defect pore that it has created during its occlusion, as well as directly within the pores of the host [110].

Examples of the first type of synthesis include the vapor phase diffusion of disperse red 1 (2-[4-(4-nitrophenylazo)-phenyl]- ethylamino-ethanol) molecules into the channels of AlPO<sub>4</sub>-5 single crystals. The composite material generated by this synthesis shows second harmonic generation when irradiated by a laser, meaning that the dye is well aligned within the pores of the zeolite [100]. Another similar example involves the diffusion of the laser dye Styryl 7 into AlPO<sub>4</sub>-5. These composites have also demonstrated laser activity [59].

Examples of the second type of synthesis include the *in-situ* inclusion of pyridine 2 and rhodamine BE50 dyes into AlPO<sub>4</sub>-5. Laser activity was observed from pyridine 2 loaded single crystals as the dye molecules in these crystals were highly aligned, although at higher dye loadings crystal growth was disturbed, and a bundle-like morphology was observed. Crystals with this morphology did not exhibit laser activity [83]. Fluo-

rescence emission from the rhodamine BE50 doped crystals was partially polarized, meaning that the guest molecules were only weakly aligned within the host crystals.

Schuth et al. [111] prepared AlPO<sub>4</sub>-5 based composites via in situ inclusion of the laser dyes coumarin 466, coumarin 7, pyridine 2 and DCM within AlPO<sub>4</sub>-5 single crystals. An image of the composites fluorescing under UV is shown in Fig. 1.9. Laser activity was demonstrated from the DCM/AlPO<sub>4</sub>-5 composites when a single crystal was attached to a glass slide and irradiated with a Nd/YAG laser.

Because of the nanometre size of the resonator for these  $AIPO_4$ -5 based single crystals the lasing threshold is much lower than that of conventional millimetre sized lasers [109]. One potential difficulty of these materials, however, is aligning the microlasers relative to the pump. One potential way to overcome this is to force alignment of the  $AIPO_4$ -5 crystals within a membrane in which the individual zeolite crystals are held in a particular orientation. It is this aspect of the technology that this work explores.

## **1.6 Project Aims/Summary**

The aim of this project was to demonstrate the ability to produce a composite material incorporating crystallographically aligned crystals of a zeolite. In turn, the zeolite should contain molecular sized channels aligned such that the composite material could contain molecules with non-linear optical properties highly preferentially aligned within the channels of the zeolite.

The present study investigates the *in-situ* growth of the aluminophos-

phate AlPO<sub>4</sub>-5 within the nanochannels of a porous anodic alumina host. This host material may be locally fabricated, highly ordered anodic alumina membranes, or inexpensive commercially available Whatman Anodisc membrane filters. The high aspect ratio of the template pores compels the aluminophosphate crystals to grow in the preferred c-axis orientation. This material is then used as a host for the laser dye 4-dicyanomethylene-2-methyl-6-(p(dimethylamino)styryl)-4H-pyran (DCM).

The work described in this thesis provides a method for reproducibly forming the highly aligned arrays of  $AIPO_4$ -5 within porous anodic alumina membranes, which are then doped with the laser dye DCM. DCM is a highly stable molecule with excellent 2<sup>nd</sup> order non-linear optical properties, which was chosen as it has previously been incorporated into  $AIPO_4$ -5 single crystals via an *in-situ* synthesis [104]. In order to be successfully incorporated into  $AIPO_4$ -5 a laser dye needs to be stable, uncharged (as protonated groups can interfere with crystal grain growth), and relatively long and linear. Although DCM is larger than the channel width of  $AIPO_4$ -5, it has been shown to be incorporated into defect sites within the crystal structure during crystal growth [104].

The approach used in this work involves crystallization of the zeolite  $AIPO_4$ -5 within the pores of a porous anodic alumina template via a pore plugging synthesis. The  $AIPO_4$ -5 membranes are synthesized hydrothermally, using microwave heating as the energy source, and the dye DCM is incorporated into the membrane during crystallization.

The highly aligned arrays of DCM-doped AlPO<sub>4</sub>-5 produced as a result of this work may then be suitable for non-linear optical applications.



Figure 1.9: AlPO<sub>4</sub>-5/laser dye composites fluorescing under UV [104].

# Chapter 2

# **Materials And Methods**

## 2.1 Introduction

This chapter outlines the materials and methods used in the fabrication of  $AIPO_4$ -5 using PAA as a structure directing agent. Also included are details of the analytical techniques and instruments used to investigate the properties of these materials. Each subsection outlines a method or instrument employed during this research.

## 2.2 Materials

#### 2.2.1 Reagents

The chemicals used in these syntheses, and their purities as assayed by the manufacturer, are given in Table 2.1. The laser dye 4-dicyanomethylene-2-methyl-6-(p(dimethylamino)styryl)-4H-pyran (DCM) and the other laser dyes used in this work were synthesised by Andrew Kay of Industrial

Research Ltd. DCM was synthesised via the method in Hammond et al., 1979 [112]. Alphabond 300 is a material used by the cementing industry composed of  $\rho$  alumina. The manufacturer's information sheet is included in appendix D.

Chemical Purity Manufacturer HF 48% in aqueous solution BDH 98% Aluminium isopropoxide Acros Alphabond 300 N/A Almatis GmbH Triethylamine 99% Unilab Orthophosphoric acid AR Park Scientific Ltd. 98%

Table 2.1: Chemicals used and their respective purities and manufacturers.

#### 2.2.2 Porous Anodic Alumina

Both commercial porous anodic alumina membranes (Anodisc 13  $0.2 \,\mu$ m membrane discs by Whatman) and porous anodic alumina membranes synthesized locally were used [32].

Due to the higher stability of the Kirchner PAA, these syntheses were carried out using only 200 eq. H<sub>2</sub>O and a 1:1 ratio of Al:P (as the membrane was not corroded during synthesis in the way that the anodiscs were). PAA membranes prepared using two different acidic electrolytes were trialed. PAA anodised in sulphuric acid (pore size of  $\sim 30$  nm) was found to give poor samples. The pores of these membranes may be too small to allow the AlPO<sub>4</sub>-5 crystallites to penetrate during crystallisation, however PAA membranes prepared using oxalic acid (pore size of  $\sim 50$  nm) gave high quality AlPO<sub>4</sub>-5 membranes, without damage to the PAA substrate.

The PAA membranes prepared using oxalic acid as the electrolyte were

anodised at a constant 150.0 V potential versus a platinum cathode for at least 12 hours. They were then pore opened in 5%  $H_3PO_4$  for at 30 °C for 60 minutes [32]. Table 2.2 A discusses differences between the properties of the two types of membrane successfully used, while figure 2.1 shows a comparison between the physical appearance.

	Anodiscs	IRL PAA
Electrolyte	$H_3PO_4$	(COOH) <sub>2</sub>
Pore Size	$\sim 0.2 \mu { m m}$	${\sim}0.05\mu$ m (depending on electrolyte)
Chemical/thermal resistance	Stable over a pH range of 5-8, curls and cracks at ~600 °C	Much higher resis- tance to extreme pH values, stable to above 1000 °C
Pore Structure	Disordered	Highly ordered through pores

Table 2.2: Comparison of Whatman Anodisc membrane filters and highly ordered periodic PAA.



Figure 2.1: Commercially prepared Whatman Anodisc membrane (left) compared with PAA made by Kirchner et al. [32] (right).

#### 2.2.3 Equipment

Furnaces - 90 °C pre-treatment and 180 °C crystallisation were performed in a Contherm digital oven, model number CAT 2150.

Microwave - a Kenwood Galaxy microwave (RM-1390) modified by the addition of a Shinho Microcomputer based programmable temperature controller (PC635-A/E) such that the synthesis temperature and time could be accurately controlled. More details of the modification of the microwave and its use are included in Appendix A.

## 2.3 Preparation

Firstly, a method was devised for the synthesis of bulk  $AIPO_4$ -5 without the use of HF. This method is outlined in 2.3.1. Two different syntheses were used, the first a route to highly aligned  $AIPO_4$ -5 membranes using a conventional oven as the heating source, and the second a quicker microwave route. The second route allows the laser dye DCM to be incorporated into the zeolite during crystallisation. This organic dye decomposes when subjected to long periods at the elevated temperature and pressure required for the conventional oven synthesis.

The first synthesis employs aspects of various published routes to AlPO<sub>4</sub>-5 adjusted to optimise the required features of the crystallites and synthetic conditions. The second technique is similar, with variations in the heating and the addition of HF as a mineraliser as proposed by Qui et al. [79]. The design of these procedures is discussed in more detail in chapters 3 and 4.

#### 2.3.1 Conventional Hydrothermal Synthesis of bulk AlPO<sub>4</sub>-5

A reaction mixture was prepared by combining alphabond 300 ( $\rho$ -alumina), orthophosphoric acid, triethylamine and distilled water in the ratio

$$Al_2O_3 : P_2O_5 : 1.6TEA : 400H_2O$$

via the following method: Alphabond 300 (1.040 g, 0.01 mol) was suspended in  $H_2O$  (5.45 g, 0.3 mol) in a beaker with vigorous magnetic stirring. Orthophosphoric acid (2.352 g, 0.02 mol) then triethylamine (1.651 g, 0.016 mol) were added dropwise while continuing to stir. The sample was then stirred vigorously for 30 minutes before being transferred to a Teflon lined steel autoclave and pre-treated at autogeneous pressure and without stirring at 90 °C for 24 hours. The temperature was then increased to 180 °C for hydrothermal crystallization for a further 24 hours.

After crystallization the autoclave containing the sample was quenched under flowing water and the crystals were recovered using a Buchner funnel and flask. The crystals were then washed with distilled water and dried at 70 °C in an oven overnight.

# 2.3.2 AlPO<sub>4</sub>-5 within the pores of PAA - Conventional Hydrothermal Synthesis

A reaction mixture was prepared by combining alphabond 300 ( $\rho$ -alumina), orthophosphoric acid, triethylamine and distilled water in the ratio

$$Al_2O_3 : P_2O_5 : 1.6TEA : 400H_2O$$

via the following method: Alphabond 300 (0.459 g, 0.0045 mol) was suspended in H<sub>2</sub>O (36.0 g, 2 mol) in a beaker with vigorous magnetic stirring. Orthophosphoric acid (1.152 g, 0.01 mol) then triethylamine (0.810 g, 0.008 mol) were added dropwise while continuing to stir. The sample was then stirred vigorously for 30 minutes before being transferred to a Teflon lined steel autoclave and pre-treated at autogeneous pressure and without stirring at 90 °C for 24 hours. The autoclave containing the pretreated gel was quenched under flowing water, opened, and an anodic alumina template was floated at the surface of the liquid on a doughnut-shaped Teflon ring (see figures 2.2 and 2.3). The sample was then re-sealed in the autoclave for hydrothermal crystallisation for 24 hours at 180 °C.



Figure 2.2: A Whatman Anodisc membrane (left) next to the Teflon ring (right) used in this synthesis.

After crystallization the sample was quenched again under flowing water and the composite membrane removed carefully with tweezers. The membrane was then washed with distilled water under ultrasonic vibration for 2 minutes three times to remove any loose material on the surface, and dried at 70 °C in an oven overnight.



Figure 2.3: A Whatman anodisc membrane floating on the surface of water in a glass beaker, demonstrating how the Teflon ring is used during the synthesis.

# 2.3.3 AlPO<sub>4</sub>-5 Within the Pores of PAA - Attempts to Dope AlPO<sub>4</sub>-5 with Laser Dyes during Conventional Oven Synthesis

The reaction mixture was prepared as in section 2.3.2, however before pre-treatment at 90 °C an ethanolic solution of the laser dye in question (0.00025 mol of dye dissolved in 0.138 mol/6.36 g ethanol) was added to the synthesis liquor. The synthesis was then carried out as detailed above. After washing the membrane in distilled water, it was washed well in ethanol and then refluxed in ethanol for 4 hours to remove all trace of

material adsorbed onto the crystal surface [83]. Samples were then dried at 70 °C in an oven overnight. In some of the syntheses the procedure discussed above was modified slightly in attempts to increase the chance of successfully incorporating the dyes into the membrane. The dyes used and changes made to the standard synthesis are detailed in Table 2.3. None of these syntheses were successful.



Table 2.3: Laser dyes trialed during conventional oven syntheses, and the results of these syntheses.





# 2.3.4 AlPO<sub>4</sub>-5 Within the Pores of PAA - Microwave Synthesis

The reaction mixture was prepared as for the first synthesis, and the 90 °C pre-treatment was carried out in the Contherm oven as detailed above. After the pre-treatment 0.007 mol/0.3 g hydrofluoric acid was added with stirring and the sample was transferred from the steel autoclave to the microwave-safe pressure vessel. An anodic alumina template was floated on the surface as shown in Fig. 2.3. The autoclave was then sealed for crystallisation at 180 °C for 10 minutes via microwave heating. The heating program involved heating to 180 °C over 1 minute 40 seconds (using full power on the microwave) and holding at temperature for a further 10 minutes (using a program in which the solenoid of the microwave was controlled by the Shinho temperature controller to maintain a constant temperature of 180 °C).

After crystallization the sample was quenched again under flowing water and the membrane removed carefully with tweezers. The membrane was then washed with distilled water under ultrasonic vibration for 2 minutes three times to remove any loose material on the surface. Samples were then dried at 70 °C in an oven overnight.

# 2.3.5 AlPO<sub>4</sub>-5 Within the Pores of PAA doped with DCM -Microwave Synthesis

The reaction mixture was prepared as in section 2.3.4, however before pretreatment at 90  $^{\circ}$ C an ethanolic solution of DCM (0.00025 mol / 0.08 g of DCM dissolved in 0.138 mol/6.36 g ethanol) was added to the synthesis liquor. The synthesis was then carried out as detailed in 2.3.4. After washing the membrane in distilled water, it was washed well in ethanol and then refluxed in ethanol for 4 hours to remove all trace of material adsorbed onto the crystal surface [83]. During this refluxing no dye was observed to be extracted. Samples were then dried at 70 °C in an oven overnight.

### 2.4 Template Removal

Template removal was performed by heating samples in a tube furnace under vacuum for 24 hours. Samples were heated from room temperature to 300 °C over a period of 3 hours and then held at temperature for 24 hours before being furnace cooled. The vacuum pump used was a Speedivac high vacuum pump. Section 3.5.1 discusses the reasons for choosing this method.

# 2.5 Analysis

#### 2.5.1 Scanning Electron Microscopy

Scanning electron microscopy was carried out on a Jeol JSM 6500-F. The DES unit is a Jeol JED 23003 BU. Samples were coated with carbon (2 coatings, 8 nm) or platinum (3 coatings, 12 nm) before analysis.

#### 2.5.2 X-Ray Diffraction

Crystallization of the AlPO<sub>4</sub>-5 was monitored via X-ray diffraction (XRD) using a Bruker D8 advance diffractometer with an incident beam Goebel mirror and 0.23 degree parallel plate diffracted beam collimator using Co K radiation. XRD measurements were performed on the final AlPO<sub>4</sub>-5/PAA membrane samples, which were laid in an aluminium XRD holder standard to this diffractometer. A 2 $\theta$  scan from 4° to 80° at a rate of 0.5° per minute was used.

AlPO<sub>4</sub>-5 was identified by matching with pattern number 00-039-0216 for AlPO<sub>4</sub>-5 in the database maintained by the International Centre for Diffraction Data using the software program EVA, a module of Diffrac-Plus (Bruker AXS).

#### 2.5.3 Fluorescence Spectra

These spectra were recorded on an Ocean Optics Fibre Optics UV/VIS/IR spectrometer, with the 489 nm Line from an Argon Ion Laser as the excitation source. No preparation was required, as the composite membranes were placed in the beam lying on a glass slide.

# Chapter 3

# Conventional Oven Synthesis of AlPO<sub>4</sub>-5 within PAA

## 3.1 Introduction

This chapter provides a method for reproducibly forming highly aligned arrays of  $AIPO_4$ -5 within the nanochannels of an anodic alumina host via a hydrothermal synthesis. This synthesis was carried out via the method described in section 2.3.2, and uses a conventional oven as the heating source. Crystallization of the  $AIPO_4$ -5 was monitored via X-ray diffraction. XRD shows a high degree of crystal alignment, with the ratio of preferential alignment being over 300 for a typical membrane.

SEM shows that the  $AIPO_4$ -5 is incorporated into the pores of the membrane, with a high degree of pore filling.

#### 3.2 Synthesis

Various different methods have been reported for the synthesis of  $AIPO_4$ -5 [82, 113, 114, 115, 116, 117, 104, 74, 75, 100], employing different templates, aluminium sources and reaction conditions. An important consideration in this study is the reactivity of the anodic alumina membranes used, which are not stable to prolonged exposure to extreme pH values. A number of different synthetic routes were tested for this thesis before a method was developed involving relatively mild conditions and a pre-treatment to facilitate crystallisation of  $AIPO_4$ -5 within the pores of the anodic alumina membrane. Initially the focus of this research was to synthesise  $AIPO_4$ -5 membranes using a conventional hydrothermal synthesis, and Whatman Anodisc membranes as the template, and to then incorporate a non-linear photonic molecule into the pores of the zeolite via in-situ inclusion.

Firstly, bulk AlPO<sub>4</sub>-5, was synthesised, using a combination of techniques published by Girnus et al. [82] and Wilson and Flanigen [74], in order to avoid the use of HF which is typically used in such syntheses as a mineraliser [79], and which is extremely dangerous as it is both highly corrosive to human flesh and may cause decalcification of the bones.

The first several attempts were unsuccessful, either forming a clear solution or a thick viscous gel, despite extended crystallisation periods. Several steps were taken in order to prevent this viscous gel from forming, as it appeared to hinder crystallisation. Firstly, the amine template around which the micelles of  $AlPO_4$ -5 were formed was changed to triethylamine, used in a 1.6 ratio. This was in place of the more reactive tetramethylammonium hydroxide used by Girnus et al. [82], as tetramethylammonium hydroxide was found to cause formation of a highly viscous gel through which the crystallites could not move freely.

Secondly, the aluminium source used was changed to alphabond 300. Alphabond is a commercial product used by the cement industry which contains  $\rho$  alumina - a reactive form of amorphous alumina. This product is less reactive than pseudoboehmite or aluminium isopropoxide, the most common aluminium sources used for synthesis of AlPO<sub>4</sub>-5, and therefore helps prevent formation of a highly viscous gel when used for this synthesis.

As the synthesis liquor was now less reactive, a 90 °C pre-treatment step was incorporated into the synthesis [118, 119, 120, 121, 122] in order to facilitate crystallisation by production of a precursor to the microporous aluminophosphates known as metavariscite [122]. This intermediate may then be easily transformed to AlPO<sub>4</sub>-5 during the subsequent crystallisation [118].

These changes produced a successful, reproducible synthesis for bulk AlPO<sub>4</sub>-5, which is described in section 2.3.1.

Once this synthetic procedure had been developed, attempts were made to add a Whatman Anodisc membrane to the synthesis liquor to try to force  $AIPO_4$ -5 to crystallise within the membrane. As porous anodic alumina is susceptible to acidic media, these attempts were unsuccessful, as the anodiscs dissolved, even if added after the 90 °C pre-treatment step.

In order to overcome this, the water content for the synthesis was hugely increased, as in the work of Chao et al. [28] in order to reduce the damage done to the porous anodic alumina by exposure to the acidic solution. The water content was increased from 30 equivalents to 200, and finally 400 equivalents. Although immersion of the PAA membrane in this dilute synthesis liquor also resulted in dissolution of the membrane, if the PAA membrane was floated on the surface of the synthesis liquor the membrane largely survived.

This technique was adopted as it may facilitate *c-axis* crystallisation, by forcing the crystal nuclei into the pores of the substrate with the *c-axis* normal to the plane of the substrate. This is due to upward vapour pressure at the water/vapour interface, as crystallites are presumed to behave in solution like logs floating in a river, and pack in order [29]. This procedure also serves to prevent excessive attack of the PAA membrane by the acidic synthesis liquor.

In order to suspend the PAA membrane at the vapour/solution interface during crystallisation, the porous anodic alumina substrate was floated on a Teflon doughnut. The PAA membrane was not added to the autoclave until after the 90 °C pre-treatment step as the pH was lower at this point (before any heating the pH=1, after pre-treatment the pH=7, after crystallisation the pH=7), which minimised damage caused to the PAA membrane by the acidic synthesis liquor. This synthetic procedure produced a well aligned AlPO<sub>4</sub>-5 membrane.

Other techniques which were trialed included adjusting the pH of the solution to  $\sim 6$  with NaOH or NH<sub>4</sub>OH before addition of the PAA membrane. Samples made in this manner were found to be completely amorphous. A step in which the pretreated solution was introduced into the pores of the anodisc by vacuum infiltration was trialed, to attempt to force

the AlPO<sub>4</sub>-5 to penetrate (and grow) all the way through the pores of the membrane, rather than just penetrating a short distance. This step was abandoned as membranes produced in this manner were mostly amorphous. Attempts were also made to design a more sophisticated Teflon float, however using Teflon of more than an 0.3 mm thickness caused the float to sink during synthesis.

Despite these measures taken to protect the porous anodic alumina from dissolution, when Whatman Anodiscs membranes were used as the PAA substrate they were somewhat degraded during crystallisation. To compensate for this samples were made using a 10% deficit of Al giving the synthetic ratios

 $0.9Al_2O_3 : P_2O_5 : 1.6TEA : 400H_2O$ 

as dissolution of the anodisc during synthesis may cause a higher local concentration of Aluminium at the membrane surface. This reduction in aluminium proved to produce highly aligned, highly crystalline membranes.

At this point a number of samples were made to test the reproducibility of this technique. The final procedure used for conventional oven synthesis of AlPO<sub>4</sub>-5/PAA membranes is discussed in section 2.3.2.

#### 3.3 Crystallisation within Anodisc PAA membranes

#### 3.3.1 XRD

X-ray diffraction data were collected on the surface of the membrane samples. The degree of penetration of the X-rays varies between approximately 4  $\mu$ m at 4 degrees 2 $\theta$  and 90  $\mu$ m at 80 degrees 2 $\theta$ , indicating that the diffraction patterns represent a combination of material on the surface and material occluded in the pores of the substrate. The XRD trace for a membrane made using a Whatman Anodisc porous anodic alumina membrane as the template, and the synthetic ratios

 $Al_2O_3 : P_2O_5 : 1.6TEA : 400H_2O$ 

is shown in Fig. 3.1. This membrane was made via the method in section 2.3.2.

The peak intensities are clearly different from the reference pattern shown below the scan data, with the measured [002] and [004] reflections much larger than expected. This is due the preferred orientation of AlPO<sub>4</sub>-5 crystals in the sample. In the  $\theta$  - 2 $\theta$  scans used, diffraction is only measured from lattice planes which lie parallel to the sample surface. The reference pattern assumes a random distribution of crystallites so that all lattice planes align with the sample surface with equal probability. However, our pattern shows that the [001] planes lie parallel to the surface with a far greater frequency than random orientation would predict. This is equivalent to saying that most of the AlPO<sub>4</sub>-5 crystals have their crystallographic *c-axis* normal to the sample surface. A quantitative measure of the degree of preferred orientation has been given by Tsai et al. [29], using the ratios of XRD peaks that are similar intensity in a powder sample to give a measure of the degree of preferred orientation in an aligned sample. The measures used in this study were:

$$Dp = \frac{\text{Intensity of } [002] \text{ peak}}{\text{Intensity of } [100] \text{ peak}}$$
$$Dp' = \frac{\text{Intensity of } [002] \text{ peak}}{\text{Intensity of } [210] \text{ peak}}$$

Perfect alignment would give a value of  $\infty$ , random alignment would give a value of 1. For the sample shown in Fig. 3.1, this gives values of Dp = 105 and Dp' = 130. Averaging the above values gives a degree of preferred orientation is for this sample of approximately 118.

The XRD trace in Fig. 3.2 shows a sample made in the same manner, but with the ratios

$$0.9Al_2O_3 : P_2O_5 : 1.6TEA : 400H_2O$$

Reducing the amount of  $Al_2O_3$  relative to the phosphate gave good quality membranes on Whatman anodiscs, possibly due to a higher local concentration of aluminium at the membrane surface due to dissolution of the membrane. Again, this membrane shows a high degree of preferential orientation, with Dp = 115 and Dp' = 168, giving an average degree of preferred orientation of approximately 142.



Figure 3.1: XRD trace for a membrane made via the method in section 2.3.2 using a Whatman anodisc.

#### 3.3.2 SEM

SEM images of a  $AIPO_4$ -5 membrane made via the method in section 2.3.2 and with the synthetic ratios

$$Al_2O_3 : P_2O_5 : 1.6TEA : 400H_2O$$

are shown in Figs. 3.3, 3.4, and 3.5. Fig. 3.3 shows a view of a broken membrane edge, in which the  $AIPO_4$ -5 coating has broken away from the surface of the substrate, showing the crystals of  $AIPO_4$ -5 as they grow out



Figure 3.2: XRD trace for a membrane made via the method in section 2.3.2 using a higly ordered, periodic PAA membrane.

of the pores of the membrane. This confirms that the porous anodic alumina directs the growth of the zeolite layer. As this is a broken edge there is not complete pore filling, but images of the top face of the substrate in Figs. 3.4 and 3.5 confirm that the  $AIPO_4$ -5 layer is continuous, an important trait for molecular sieving applications.

Figs. 3.4 and 3.5 show the surface of this membrane. The hexagonal plate morphology of the top faces of the crystals can also be observed in Fig. 3.5, confirming the *c-axis* alignment of the membrane. These membranes were difficult to view under SEM due to charging, and the proper



Figure 3.3: A broken edge of an AlPO<sub>4</sub>-5 membrane at 20000 magnification, showing crystal growth as it appears at the surface of the membrane.

coating protocol had not been devised at the time these images were taken, hence the poor quality if the image in Fig. 3.5. The morphology of membranes made with a 10% deficit of Aluminium was very similar to that of those made without the deficit.



Figure 3.4: The surface of an AlPO<sub>4</sub>-5 membrane at 800 times magnification.

# 3.4 Crystallisation within Highly Periodic PAA

#### 3.4.1 XRD

The XRD trace in Fig. 3.6 shows a sample made via the method in section 2.3.2, with the ratios

$$Al_2O_3 : P_2O_5 : 1.6TEA : 200H_2O$$

and using a locally made periodic PAA membrane anodised with oxalic acid by Kirchner et al. [32] as the template. These membranes had an average pore size of  $\sim 50$  nm. The AlPO<sub>4</sub>-5 membranes made with locally



Figure 3.5: The surface of an  $AlPO_4$ -5 membrane at 8000 times magnification.

fabricated PAA were similar in quality to those in 3.3.1, but due to the higher stability of the PAA used the resultant membrane had much higher mechanical strength, and the PAA was not damaged during the synthesis. As above, the highly increased [002] and [004] peaks can be seen, with Dp = 303 and Dp' = 275, giving an average degree of preferred orientation of approximately 289.

The XRD trace in Fig. 3.7 shows another membrane prepared in the same manner on periodic PAA, in order to show the high degree of reproducibility of this technique, despite subtle variations in the PAA membranes used as templates for these syntheses. This membrane is even more highly aligned, with Dp = 1133 and Dp' = 565, giving an average of 849,



Figure 3.6: XRD trace for a membrane made via the method in section 2.3.2 using highly ordered, periodic PAA

much higher than that of similar membranes prepared by Tsai et al. [29], where the degree of preferred alignment was approximately 250.

#### 3.4.2 SEM

SEM images of an AlPO<sub>4</sub>-5 membrane made via the method in section 2.3.2 on highly ordered PAA are shown in Figs. 3.8, 3.9, 3.10 and 3.11. Figs. 3.8 and 3.9 show cross-sectional views of a broken membrane edge. From these images the *c*-axis alignment of the crystals can be clearly seen, along



Figure 3.7: XRD trace for another membrane made via the method in section 2.3.2 using highly ordered, periodic PAA.

with the high degree of pore filling. Figs. 3.10 and 3.11 show the top surface of the same membrane, showing the hexagonal plate morphology of the top face of the crystals. Some randomly oriented crystals can also be observed on the surface of the membrane, but the side views of the membrane confirm that the bulk of the AlPO<sub>4</sub>-5 crystals are *c-axis* aligned, as supported by the XRD data.



Figure 3.8: A broken edge of an  $AIPO_4$ -5 membrane at 43000 magnification, showing  $AIPO_4$ -5 crystals growing out of the pores of the PAA membrane. The crystals join on the surface to form a continuous layer.

## 3.5 Template Removal

#### 3.5.1 Introduction

A number of different methods have been used for the removal of templates from zeolite powders [123, 124, 125, 126, 127, 128, 129, 130], the most common of which is calcination. This is usually performed in air or oxygen at between 550-700 °C. The disadvantages of this technique are the fact that expensive organic templates cannot be recycled and that the fine structure of the material may be damaged during calcination. Recycling of the template is not an issue for this synthesis as such a small amount of



Figure 3.9: Another view of a broken edge of the  $AIPO_4$ -5 membrane at 45000 magnification. In this view the crystalline nature of the  $AIPO_4$ -5 within the membrane pores can be more clearly seen

material is used, but as the porous anodic alumina templates used in this synthesis cannot withstand such high temperatures without curling [131] calcination is not an option. Appendix C details papers that use milder methods of template removal that may be suitable for the samples used in this study. Due to ease and availability of the technology the method used in this thesis is vacuum template removal, as discussed by Goworek et al. [130] This method involves heating the sample under vacuum at low temperatures (up to 250 °C) for several hours in order to force the degradation of the template and evaporation of the fragments.

In this study these limits were increased somewhat in order to com-


Figure 3.10: The surface of an  $AlPO_4$ -5 membrane at 300 times magnification

pensate for the hindrance to evaporation caused by the confinement of the zeolite within the anodic alumina membrane, which may increase the difficulty of removal. To this end the samples were exposed to vacuum using a Speedivac high vacuum pump in a tube furnace at 300 °C for 24 hours as discussed in 2.4.

#### 3.5.2 XRD

X-ray diffraction data for a membrane made via the method in section 2.3.2 before and after vacuum template removal via the method discussed in 2.4 are shown in Fig. 3.12. These data confirm that the template removal method used does not destroy the fine structure of the  $AIPO_4$ -5. The two



Figure 3.11: The surface of an  $AIPO_4$ -5 membrane at 3000 times magnification, showing the hexagonal plate structure of the top face of the membrane

traces are almost identical, with very similar peak intensities.

The successful removal of the amine template occluded in the pores of the zeolite was confirmed by testing the gas permeability of the membrane after vacuum template removal. Before template removal the amine template in the zeolite layer completely blocked the membrane pores, hence no gas was able to pass through the membrane. After template removal the sample was gas permeable, showing that the amine template had been removed.

These membranes showed a modest gas seperative ability, but far below that of conventional membrane filters. AlPO<sub>4</sub>-5 is not however the



Figure 3.12: A comparison of the XRD traces of an  $AlPO_4$ -5 membrane pre-and-post template removal via the method discussed in 3.5.1.

optimum zeolite for a gas seperative membrane, and this work focuses more on potential utility of these membranes after doping with the laser dye DCM.

#### 3.5.3 SEM

As SEM is a destructive method for these membranes due to the coating process, it was not possible to take SEM images of the same membrane both before and after template removal. Fig. 3.13 shows an  $AlPO_4$ -5



Figure 3.13: SEM of the top face of an  $AIPO_4$ -5 composite membrane after vacuum template removal.

membrane made on Kirchner PAA [32] following template removal via the method discussed in 2.4. This image shows the same hexagonal plate-like morphology seen in similar membranes prior to template removal, confirming that the structure of the zeolite is intact after the template removal process.

### 3.6 Discussion

Although the method discussed in this chapter allows the formation of highly aligned AlPO<sub>4</sub>-5 membranes, there are some drawbacks to this technique. When Whatman Anodisc membrane filters are used as the porous anodic alumina template for this synthesis they are degraded to the point where they lack mechanical stability and are therefore unable to be used in any application where any degree of mechanical strength is required. Secondly, the synthesis conditions are too hostile to allow incorporation of organic dyes into the membranes during synthesis. This significantly reduces the potential usefulness of this technique.

In order to overcome these challenges the crystallisation time needed to be greatly decreased, requiring that the method of heating for synthesis be changed to microwave heating. As a microwave safe pressure vessel and a microwave in which the temperature, time and heating rate could be controlled were not available it became necessary to design a microwave autoclave and modify an existing laboratory microwave in order to carry out a microwave synthesis. The design of the Teflon lined microwave autoclave is discussed in Appendix A, and its usage is discussed in Chapter 4.

### Chapter 4

# Microwave Crystallisation of AlPO<sub>4</sub>-5 doped with DCM within Porous Anodic Alumina

### 4.1 Introduction

Many of the traditional routes to  $AIPO_4$ -5 involve exposing the PAA membrane to highly acidic conditions for extended periods of time, rendering it brittle and unworkable, or dissolving it entirely. The synthetic procedure discussed in chapter 3 was designed with this in mind, and although it was successful, it required a 24 hour crystallisation at 453 K in which the membrane was suspended in an acidic solution. When using Whatman Anodiscs as the PAA membrane this synthesis caused the PAA to become brittle and difficult to handle.

The second aim of this work was to enclose an organic laser dye, DCM, within the framework of the AlPO<sub>4</sub>-5, adding another element of diffi-

#### Microwave Crystallisation of AlPO<sub>4</sub>-5 doped with DCM within Porous 70 Anodic Alumina

culty. This dye is also susceptible to acidic media, particularly at the elevated temperatures at which this synthesis was carried out. The 24 hour crystallisation used in the first synthesis caused the dye to almost fully degrade.

One way to speed the crystallisation of AlPO<sub>4</sub>-5 is to employ microwave heating as the energy source. Microwave syntheses of AlPO<sub>4</sub>-5 typically involved a crystallisation time of between 10 and 30 minutes [82, 83] which greatly reduces the exposure of the PAA and DCM to the corrosive synthesis liquor. In order to carry out a hydrothermal synthesis in the microwave however a microwave pressure vessel is necessary. To this end a Teflon lined microwave autoclave in which the temperature, time, and heating rate could be controlled was designed (see appendix A for details). Although using microwave heating greatly reduced the crystallisation time, this synthesis did require the addition of a small amount of HF as a mineraliser as discussed by Guth et al. [79] to facilitate crystallization. It was also found that using a conventional oven pre-treatment followed by a microwave crystallisation gave the optimum quality membranes. However, using this second synthetic procedure allowed crystallisation to occur in 10 minutes rather than 24 hours. This meant that Whatman Anodiscs could be used as the substrate rather than the highly ordered PAA, and also allowed the possibility of including organic dyes within the AlPO $_4$ -5.

### 4.2 Initial Microwave Synthesis

The design of the microwave autoclave and the modifications made to the microwave with which it was used are discussed in appendix A. In order to use this autoclave the synthetic procedure needed to be modified to be suitable for microwave crystallization. The experiments in which this microwave autoclave was used are discussed below.

Firstly, the 90 °C conventional-oven pre-treatment was kept in order to minimise the crystallisation time needed. Despite this it was discovered that in order to achieve crystallisation in the microwave it was necessary to add a small amount of HF (0.007 mol/0.3 g), to the synthesis liquor before crystallisation, as discussed by Guth et al. [79].

It was found that a 10 minute crystallisation at 180 °C gave the highest quality samples, with maximum material occluded in the pores of the PAA substrate while minimising the amount of randomly oriented material on the surface of the membrane. Full details of the synthesis used can be found in section 2.3.4.

#### 4.2.1 XRD of AlPO<sub>4</sub>-5 prepared in the Microwave

The XRD trace for a membrane made using a Whatman Anodisc membrane as the template, and the synthetic ratios

$$Al_2O_3 : P_2O_5 : 1.6TEA : 400H_2O : 1.4HF$$

is shown in Fig. 4.1. This membrane was made via the method in section 2.3.4 with a 10 minute crystallisation in the microwave.



Figure 4.1: XRD trace for a membrane made via the method in section 2.3.4 using a Whatman anodisc.

For this sample Dp = 214 and Dp' = 51. Averaging the above values gives a degree of preferred orientation is for this sample of approximately 133. Although this is lower than that seen for conventional oven synthesis, this still represents a high degree of alignment. At this point it was decided to try *in-situ* encapsulation of the laser dye DCM (4-dicyanomethylene-2-methyl-6-(p(dimethylamino)styryl)-4H-pyran) within the AlPO<sub>4</sub>-5/PAA membrane.

### 4.3 Synthesis of DCM@AlPO<sub>4</sub>-5

#### 4.3.1 Introduction

One aim of this research was to encapsulate a laser dye within the pores of an AlPO<sub>4</sub>-5 membrane via an *in-situ* synthesis. Various laser dyes have previously been encapsulated within AlPO<sub>4</sub>-5 including coumarin 7, coumarin 466, pyridine 2, Styryl 7 and DCM [103, 104, 82, 59, 83]. These dyes were selected to be uncharged (as protonated groups can interfere with crystal growth), and relatively long and linear (the unit cell of AlPO<sub>4</sub>-5 has a=13.8 Å, c=8.6 Å and channel width 7.3 Å). The laser dye DCM is, however, larger than the channel size, but has been successfully incorporated into defect sites in the crystal structure of AlPO<sub>4</sub>-5.



Figure 4.2: The laser dye DCM (4-dicyanomethylene-2- methyl - 6 - (p(dimethylamino)styryl)-4H-pyran).

DCM was chosen, as it is an highly stable molecule with excellent 2<sup>nd</sup> order non-linear optical properties, which has previously been shown to

be incorporated into AlPO<sub>4</sub>-5 single crystals via an *in-situ* synthesis without disturbing the crystal morphology, as some of the other laser dyes previously used had done [83]. Additionally, laser action had been demonstrated from single crystal DCM/AlPO<sub>4</sub>-5 laser composites [104]. The structure of DCM is shown in Fig. 4.2.

#### 4.3.2 Synthesis

Once the microwave synthesis had been designed attempts were made to incorporate DCM into the synthesis. The DCM was initially dissolved in ethanol, as it is relatively insoluble in water, and added to the synthesis liquor prior to the 90 °C pre-treatment step. Varying amounts of DCM and ethanol were trialed, in order to find the optimum with respect to amount of DCM incorporated and crystallinity of the final membrane. The synthetic procedure used is given in section 2.3.5. After the synthesis the membrane was first washed well with distilled water, and then refluxed in ethanol for several hours to remove any DCM that was physically adsorbed on the surface of the membrane. During this refluxing no DCM was observed to be extracted, suggesting that the DCM that remained was incorporated into the crystal structure of the AlPO<sub>4</sub>-5 crystals, rather than simply adsorbed onto the surface of the membrane. Further evidence for this can been found in section 4.3.6.

#### 4.3.3 XRD

The XRD trace for a sample made via the method in 2.3.5 is shown in Fig. 4.3. This sample has a slightly lower degree of alignment, which may



Figure 4.3: An XRD trace for a composite membrane made via the method in 2.3.5 with the laser dye DCM incorporated into the membrane during crystallisation.

be due to the effect of the DCM on the crystal structure of the zeolite. For this sample Dp = 36 and Dp' = 66. Averaging the above values gives a degree of preferred orientation for this sample of approximately 51. While this is lower than in previous samples it is still a significant degree of alignment, and (as supported by SEM). Most of this decrease can be attributed to randomly oriented AlPO<sub>4</sub>-5 that formed on the surface of the membrane during the microwave crystallization.

Microwave Crystallisation of AlPO<sub>4</sub>-5 doped with DCM within Porous 76 Anodic Alumina

#### 4.3.4 SEM



Figure 4.4: DCM/AlPO<sub>4</sub>-5 membrane at 2300 magnification.

SEM images of a DCM/AlPO<sub>4</sub>-5 membrane made via the method in section 2.3.5 are shown in Figs. 4.4, 4.5, and 4.6. Figs. 4.4 and 4.5 show cross-sectional views of a broken edge of the membrane. From these images it can be seen that the AlPO<sub>4</sub>-5 layer is an highly intergrown, columnar layer of approximately 16  $\mu$ m thickness, with the *c-axis* of the crystals aligned perpendicular to the substrate surface. The orientation of the AlPO<sub>4</sub>-5 layer appears to decrease with distance from the substrate surface, with the outermost 3  $\mu$ m of the film appearing to be somewhat randomly ordered relative to the inner 13  $\mu$ m. As there is no separation between the zeolite layer and the PAA substrate it is difficult to determine



Figure 4.5: SEM image of a broken edge of a DCM/AlPO<sub>4</sub>-5 membrane at 3700 magnification.

the penetration depth of the  $AIPO_4$ -5 into the PAA. It appears, however, from the SEM images that the channel structure of the PAA directs the growth of the  $AIPO_4$ -5, due to the highly ordered nature of the  $AIPO_4$ -5 layer at the substrate surface.

Fig. 4.6 shows a view of the surface of the same membrane, showing the poorly aligned layer at the surface.

#### 4.3.5 Luminescence Measurements

Many studies have discussed the use of  $AIPO_4$ -5 as a host for optically active materials, which can be oriented within the nanochannels [102, 82, 100, 103, 104, 59, 83]. These composites, however, are not useful for appli-

Microwave Crystallisation of AlPO<sub>4</sub>-5 doped with DCM within Porous 78 Anodic Alumina



Figure 4.6: A view of the surface of a DCM/AlPO<sub>4</sub>-5 membrane at 2500 magnification.

cations without a method of aligning the host crystals relative to the incident laser light, in order to facilitate laser activity from the AlPO<sub>4</sub>-5 [107]. AlPO<sub>4</sub>-5/dye composites in which laser activity has been demonstrated so far have used a single crystal, glued to a substrate to force orientation with the c-axis of the crystal perpendicular to the Nd/YAG laser used as the pump [104, 83]. A much easier method, however, is to force the crystals to grow in a preferred orientation. Luminescence measurements on membranes of this type are shown in the following sections.

#### 4.3.5.1 Photographs

Fig. 4.7 compares an undoped  $AIPO_4$ -5 composite membrane (left) with an  $AIPO_4$ -5 membrane doped with the laser dye DCM (right) under UV light. Both samples were prepared using Whatman Anodiscs as the PAA template. The high degree of fluorescence of the doped membrane can clearly be seen in this image.



Figure 4.7: An undoped composite membrane (left) next to a composite membrane doped with DCM fluorescing under UV (right).

#### 4.3.5.2 Spectra

Fig. 4.8 shows the emission spectrum for a membrane prepared using a Whatman Anodisc via the method described in 2.3.5. This spectrum was recorded on an Ocean Optics Fibre Optics UV/VIS/IR spectrometer, with the 489 nm Line from an Argon Ion Laser as the excitation source. This spectrum correlates to that observed for DCM in solution [132] (see Fig. 4.9 for an image from this reference). While this spectrum does not prove laser activity, bleaching was not observed, suggesting that the laser dye is in fact incorporated into the pores of the zeolite (and was thus unable to

be destroyed by the laser), and previous research [104, 83] suggests that if this is the case, then the DCM molecules will be highly aligned within the AlPO<sub>4</sub>-5, and thus would exhibit laser activity.

Fluorescence Spectrum for AIPO<sub>4</sub>-5/DCM Composite Membrane



Figure 4.8: Emission Spectrum for a DCM/AlPO<sub>4</sub>-5 composite membrane at 298 K and  $\lambda_{exc}$  = 489 nm.

# 4.3.6 Procedure for determining incorporation of DCM into composite AlPO<sub>4</sub>-5/dye membranes

Once DCM/AlPO<sub>4</sub>-5 membranes had been successfully prepared, a sample was made to check whether the DCM was in fact incorporated into the crystal structure of the AlPO<sub>4</sub>-5 or whether it was just clinging to the surface of the membrane. First an AlPO<sub>4</sub>-5 membrane was prepared via the standard synthesis method described in 2.3.2. Following the normal washing and drying of the membrane DCM,  $H_2O$  and ethanol (0.00025 mol



Figure 4.9: Emission Spectra of DCM in various solvents, temperatures and wavelengths from Bondarev et al [132]. Spectrum 4 shows DCM in n-propanol at 298 K and  $\lambda_{exc}$  = 450 nm.

DCM, 0.138 mol ethanol, and 2 mol  $H_2O$ ) were combined to mimic the synthesis conditions in section 2.3.5. The sample was then floated on the surface of this solution and sealed within the Teflon lined autoclave for 'crystallisation' at 180 °C. The sample was then washed and refluxed in ethanol as per 2.3.5 until no more dye was observed to be removed.

Unlike the samples in which DCM was incorporated during the crystallisation, this sample showed no observable fluorescence under UV, supporting the idea that in the samples discussed above, DCM is actually incorporated into the AlPO<sub>4</sub>-5, rather than just physically adsorbed onto the surface of the membrane.

### 4.4 Discussion

The syntheses discussed in this chapter produces highly aligned membranes of AlPO<sub>4</sub>-5 within the pores of an anodic alumina substrate by combining a conventional hydrothermal pre-treatment with microwave crystallisation within a teflon lined microwave autoclave. This autoclave was designed and made expressly for this project, and allows easy control of the heating rate, time and synthesis temperature.

This synthesis avoids the problems associated with the synthesis discussed in chapter 3, namely the damage done to the PAA substrate by the 24 hour crystallisation, as the crystallisation can be achieved in 10 minutes, a more than 100 fold reduction in the crystallisation time. As crystallisation is so fast, incorporation into the zeolite composite membrane of the laser dye DCM (4-dicyanomethylene-2- methyl-6-(p(dimethylamino)styryl)-4H-pyran) is also made possible.

Testing shows that the fluorescence observed from these membranes is highly likely to be from DCM incorporated into the zeolite, rather than material physically adsorbed onto the surface of the membrane, and previous work by Schuth et al. [104] suggests that such composites should demonstrate laser activity, thus showing promise for use in non-linear optical applications. Further testing is required to fully test the non-linear optical activity of these composite membranes.

### Chapter 5

# **Conclusions and Future Work**

The aims of this project were to demonstrate the ability to produce a composite material incorporating crystallographically aligned crystals of a zeolite. In turn, the zeolite should contain molecular sized channels aligned such that the composite material could contain dye molecules with nonlinear optical properties highly preferentially aligned within the channels of the zeolite.

These aims were fully realised, as the syntheses discussed in this thesis allowed the formation of highly aligned AlPO<sub>4</sub>-5 membranes, which could then be doped with the laser dye DCM to produce DCM@AlPO<sub>4</sub>-5 membranes. The first synthesis discussed in chapter 3 used a conventional oven as the heating source and membranes produced in this manner, while highly aligned, have some drawbacks. When Whatman Anodisc membrane filters are used as the template for this synthesis they are degraded to the point where they lack mechanical stability and are therefore unable to be used in any application where any degree of mechanical strength is required. Secondly, the synthetic conditions are too hostile to allow incorporation of organic dyes into the membranes during synthesis. This made it necessary to design a synthetic procedure that would allow achievement of the second aim of this work, that of incorporating molecules with non-linear optical properties (in this case, the organic dye DCM) into the AlPO<sub>4</sub>-5 membrane, via an *in-situ* inclusion.

In order to overcome these challenges the crystallisation time needed to be greatly reduced, requiring that the method of heating used for crystallisation be changed to microwave heating. As a microwave safe pressure vessel and a microwave in which the temperature, time and heating rate could be controlled were not available it was necessary to design a microwave autoclave, and modify an existing laboratory microwave, in order to carry out a microwave synthesis. Once this microwave autoclave had been fabricated and the synthetic conditions required determined, highly aligned membranes of AlPO<sub>4</sub>-5 within the pores of an anodic alumina substrate were produced by combining a conventional hydrothermal pre-treatment with microwave crystallisation within the teflon lined microwave autoclave. This avoided the problems associated with the synthesis discussed in chapter 3, namely the damage done to the PAA substrate by the 24 hour crystallisation, as microwave crystallisation was achieved in 10 minutes, a more than 100 fold reduction in the crystallisation time. As crystallisation was so fast, incorporation into the zeolite composite membrane of the laser dye DCM (4-dicyanomethylene-2- methyl-6-(p(dimethylamino)styryl)-4H-pyran) was also made possible, realizing the second goal of this research.

Preliminary testing of the composite membranes prepared in this man-

ner shows that the fluorescence observed from these membranes is highly likely to be from DCM incorporated into the zeolite, rather than material physically adsorbed onto the surface of the membrane, and previous work by Schuth et al. [104] suggests that such composites should demonstrate laser activity, thus showing promise for use in non-linear optical applications. Further work is, however, required to fully test the properties of these membranes.

#### 5.1 **Recommendations for Future Work**

On the basis of results obtained during the research undertaken for this thesis, the following recommendations for future research can be made:

- Testing of the laser activity of the AlPO<sub>4</sub>-5/DCM composite membranes. This requires the ability to focus on a single AlPO<sub>4</sub>-5 crystal within the membrane, and ensure its alignment relative to both the Nd:YAG laser used as the pump, and the detector.
- Preparation of composite membranes containing aluminophosphates with smaller pore sizes which would be suitable for gas filtration. An example of a suitable aluminophosphate is AlPO<sub>4</sub>-18, which has a pore size of 3.8 Å. Attempts were made (see Table B.9) during this thesis to crystallise AlPO<sub>4</sub>-18 within a PAA substrate; however, although it was possible to synthesize bulk AlPO<sub>4</sub>-18 in a manner which was not hostile to the PAA membrane used, when the synthesis was applied to a PAA membrane, the product that crystallised within the membrane was the more stable aluminophosphate AlPO<sub>4</sub>-

5.

 Preparation of membranes which utilise other laser dyes, either those previously incorporated into bulk AlPO<sub>4</sub>-5 or similar long, linear, uncharged dyes, in order to produce tunable microlasers.

# Appendix A

## Microwave-Safe Pressure Vessel

The microwave-safe pressure vessel discussed in Chapter 4 has several specific requirements. The container must be sealed and able to with-stand the expected operating temperatures and pressures and must be sufficiently chemically resistant. Also, due to the powerful microwave field, any electrically conductive components must have a geometry free of inductive arc gaps.

The design methodology is to use a very strong outer jacket with a mechanically weaker but chemically more resistant inner sleeve. The outer jacket was fabricated from solid, interface free PEEK GF30 (polyetheretherketone reinforced with 30% glass fibre) from DOTMAR Engineering Plastics Limited. PEEK was chosen due to its good mechanical characteristics, temperature resistance (PEEK has a continuous operating temperature of 250 °C, significantly higher than the working temperature of 180 °C required for the crystallisation of AlPO<sub>4</sub>-5) and chemical resistance (although it is not directly exposed to the synthesis liquor it may come into contact with it, and thus must be able to withstand contact with the chemicals used during the synthesis. The liner of the bomb is PTFE, which has excellent chemical resistance and a maximum operating temperature of 260 °C.

Internal Volume of the Teflon liner is

$$V = \frac{\pi D^2 h}{4}$$
$$= 68.5 \,\mathrm{cm}^3$$

The working temperature is 180 °C and at this temperature the expected pressure within the chamber is

P = 7514 mmHg= 145.3 psi = 10.018 10<sup>6</sup> Nm<sup>-2</sup> = 9.884 atmospheres

The thermocouple used was a K-type thermocouple, attached to a Shinho temperature controller. This was inserted into the bomb via a hole in the top, which was sealed with 'gasketseal' silicone gasket sealant. This hole was counterbored in a conical fashion from the interior surface so that as the internal pressure of the bomb increased, the silicone sealant was forced further down the cone, increasing the strength of the seal. The hole was set slightly off centre, in order to allow the Teflon float to float in the centre of the bomb. The lid of the bomb was designed so that the PEEK exterior was flush with the lid of the Teflon liner, forming a tight seal. The silicone sealant formed a slight bulge where the temperature probe entered the liner, sealing the hole.

The bomb was held closed by 6 stainless steel bolts. Although these are metal, they do not introduce electrical arcing. The distance between bolts is sufficiently large that any induced potentials or needle point potentials are much smaller than the break down potential between the bolts. One other consideration is the possibility of arcing between the threads on any one of the bolts. However, the voltages induced within the semi-closed loop of the thread are small and are effectively shorted by the body of the bolt itself.



Figure A.1: Photograph of the Microwave-safe pressure vessel.

# Appendix **B**

# Summary of all samples made.

Conventional Oven synthesis of AlPO<sub>4</sub>-5 within Whatman Anodiscs

The initial objective of this research was to prepare membranes composed of  $AIPO_4$ -5 within the pores of Whatman PAA membranes via a conventional oven synthesis. Following this the intention was to incorporate laser dyes into the zeolite via *in-situ* inclusion. The initial goal of preparing  $AIPO_4$ -5 membranes was achieved, but this synthesis had several drawbacks.

Table B.1:	Samples	made	during	the	design	of a	synthesis	for	Alpo	<sub>4</sub> -5
membrane	s using a	conver	ntional o	oven	as the l	neati	ng source.			

Name	Synthetic Details	Results
LC1	Bulk AlPO <sub>4</sub> -5 by a method which uses a combination of the techniques in Girnus et. al [82] and Wilson and Flanigen [74] in order to avoid the use of HF and use the available amine templates. Uses tetraethylammonium hydroxide as the template	No crystals formed, formed a clear so- lution even after extended crystalliza- tion in the oven at 180 °C.
LC2	As for LC1 but using tetramethyam- monium hydroxide as the template.	Formed a clear viscous gel, de- spite extended crystallisation.
LC3	As for LC1 but using tetra(n-butyl) ammonium hydroxide as the template.	Formed a clear viscous gel, de- spite extended crystallisation.
LC6	Preparation with tetrabutylammo- nium fluoride (to try to combine template with source of fluoride to remove the need for HF)	Formed a non-porous aluminophosphate.
LC7	Sample made with alphabond. Added a 90 °C pretreatment step [118] to facilitate crystallization. Also changed order of addition of reac- tants, made a slurry of the aluminium source and added the phosphoric acid followed by the amine dropwise to that. This prevents a thick viscous gel from forming, which appears to hinder crystallization.	Bulk AlPO <sub>4</sub> -5
LC8	Same as LC7, but using using Alu- minium isopropoxide as the alu- minium source.	Bulk AlPO <sub>4</sub> -5
LC9	Same as LC7 but with an anodisc added.	Anodisc dissolved.
LC10	Same as LC9, but anodisc added after 90 °C step and using extra water (200 eq.) to try to prevent dissolution of the anodisc	Anodisc dissolved.

Table	B.1:	Continued
Incic	D.1.	Continued

Name	Synthetic Details	Results
LC11	Same as LC10, but using a dough- nut shaped piece of teflon to hold the anodisc at the liquid/vapor interface - this may facilitate <i>c-axis</i> crystalliza- tion. Because of upward fluid flow, the crystallites are presumed to be- have like logs floating in a river and pack in order. [29]	AlPO <sub>4</sub> -5, but poorly aligned. Tried to remove the template by calcination of the anodisc at 550 °C, but the anodisc black- ened and curled.
LC14	Same as LC11, but with anodisc 'right' way up(as taken from the box). The 'top' and 'bottom' of the an- odiscs look different under SEM, so this sample was made to see if this makes any difference to synthesis.	This sample and LC15 showed no discernable differ- ence. According to XRD the degree of alignment of these samples was approx. 60 (taken as the ratio of the [210]/[002] peak). SEM showed that the anodisc was badly degraded during synthesis.
LC15	Same as LC11 but with anodisc 'up-side down'.	See above.
LC17	Repeat of LC11	Same as LC11
LC18	The same asLC17, but withdoublethewaterStandard Synthesis	AlPO <sub>4</sub> -5 with a de- gree of alignment of $\sim$ 110.
LC19	The same as LC17, but with triple the water (600eq.)	Completely amorphous.
LC20	Repeat of LC11, but with a layered Teflon float designed to prevent the anodisc from slipping off when the bomb was moved.	This Teflon float was heavier than the sim- ple doughnut shaped one, and sank dur- ing synthesis. The $AIPO_4$ -5 membrane was poorly aligned.

	Table D.1: Continued	
Name	Synthetic Details	Results
LC23	Standard synthesis with the pH ad- justed to 6 after the 90 °C pretreat- ment with NH <sub>4</sub> OH in order to make the synthesis liquor less corrosive to the anodic alumina.	The product was alu- minium ammonium phosphate.
LC25	Standard synthesis with the pH ad- justed to 6 after the pretreatment with NaOH	Formed a con- densed phase aluminophosphate.
LC55	AlPO <sub>4</sub> -5 within an anodisc, but with a vacuum infiltration step before crystallization in order to try to force the AlPO <sub>4</sub> -5 to penetrate all the way through the pores of the PAA membrane.	Mostly amorphous.
LC56	As for LC55, but sample was dried in the oven at 70 °C after vacuum infil- tration and before crystallization.	Mostly amorphous.
LC62- LC66	Repeat of LC18 (standard AlPO <sub>4</sub> -5 prep.) to test reproducibility.	As for LC18
LC75	Standard AlPO <sub>4</sub> -5 prep. with reduced crystallization time (8 hours).	Basically amorphous - needs a longer crystallization.
LC76	Standard AlPO <sub>4</sub> -5 prep. with reduced crystallization time (16 hours).	Better than LC75, but still inferior to membranes made with a 24 hour crystallization.
LC77	Standard AlPO <sub>4</sub> -5 prep. with reduced ratio of $Al_2O_3$ (10% deficit), as dissolution of the anodisc may cause a higher local concentration of Al at the membrane surface.	Highly aligned, highly crystalline sample.
LC83	As for LC77 to test reproducibility.	As for LC77
LC84	As for LC77 to test reproducibility.	As for LC77

Table B.1: Continued

#### Attempts to synthesise AlPO<sub>4</sub>-5 microlaser membranes.

Various laser dyes prepared by Andrew Kay of Industrial Research Limited were trialed using the above synthesis as a starting point. None of these dyes proved to be suitable, either decomposing during the 180 °C crystallization or simply not being incorporated. These dyes were selected to fit the following criteria:

- Very stable
- Uncharged (protonated groups can interfere with crystal growth, although some charged dyes have successfully been incorporated into AlPO<sub>4</sub>-5)
- Relatively long and linear (the unit cell of AlPO<sub>4</sub>-5 has a=13.8 Å, c=8.6 Å and channel width 7.3 Å, but it is not necessary for the dye to conform to this as it can be encapsulated in defects in the crystal structure, c.f. DCM).
- Dyes which have been previously been incorporated into bulk AlPO<sub>4</sub> 5 are Coumarin 7, Coumarin 466, pyridine 2 and DCM.

Section 2.3.3 gives details of the structures of the laser dyes used.

Table B.2: Attempts to synthesise  $AlPO_4$ -5 microlaser membranes using conventional oven heating.

Name	Synthetic Details	Results
LC29	Standard AlPO <sub>4</sub> -5 syntheses but with laser dyes supplied by An- drew Kay added.	Dyes decomposed during crystallization.
LC30	Standard AlPO <sub>4</sub> -5 syntheses but with laser dyes supplied by An- drew Kay added.	Dyes decomposed during crystallization.
LC31	Standard AlPO <sub>4</sub> -5 synthesis but with DCM added.	DCM had partially decomposed during the synthesis, and the crystals formed were berlinite. (A condensed phase AlPO <sub>4</sub> )
LC32	Standard AlPO $_4$ -5 synthesis but with the Katritsky laser dye added.	The dye had partially de- composed during the syn- thesis, and the crystals formed were berlinite.
LC36	Standard AlPO <sub>4</sub> -5 prep. but with the Katritsky laser dye added. (twice the water of LC32)	Poor surface covering and poorly aligned, but crys- talline (AlPO <sub>4</sub> -5). Dye does not appear to be incorporated.
LC37	Standard AlPO <sub>4</sub> -5 prep. but with DCM added. (twice the water of LC31)	Poor surface covering and poorly aligned, but crys- talline (AlPO <sub>4</sub> -5). Dye does not appear to be incorporated.
LC42	As for LC40 (Katritsky dye) but with twice the dye (0.08 g)	Dye decomposed the anodisc was badly decomposed.
LC44	As for LC42, but using only a minimum of material in the bomb for crystallization to try to minimise the damage to the an- odisc.	Poorly crystalline, very lit- tle alignment. Dye not incorporated.
LC47	AlPO <sub>4</sub> -5 with DCM added and using aluminium isopropoxide.	Anodisc dissolved.
LC48	AlPO <sub>4</sub> -5 with a dye synthesized by Andrew Kay added.	Dye had completely decomposed.
LC49	AlPO <sub>4</sub> -5 with a dye synthesized by Andrew Kay added.	Dye had completely decomposed.

Attempts were also made to dope these ALPO<sub>4</sub>-5 membranes with Europium, to form photoluminescent membranes. This was not successful. These experiments are summarised below.

Name	Synthetic Details	Results
LC29	Standard AlPO <sub>4</sub> -5 syntheses but with laser dyes supplied by An- drew Kay added.	Dyes decomposed during crystallization.
LC68	AlPO <sub>4</sub> -5 in an anodisc doped with 1% europium nitrate	Good membrane, but sample did not lumi- nesce under UV and EDS was unconclusive as to whether europium was incorporated.
LC70	AlPO <sub>4</sub> -5 in an anodisc doped with 5% europium nitrate	Poorly crystalline and con- tained impurity phases, sample did not luminesce under UV.
LC78	Sample with 10% europium.	Very poor sample.
LC80	AlPO <sub>4</sub> -5 in an anodisc doped with 5% europium nitrate	Very poor sample.
LC81	Repeat of LC78	Europium did not appear to be incorporated.
LC86	AlPO <sub>4</sub> -5 doped with Europium via the method in Yan et al. [133] but crystallized in a conven- tional oven (not microwave).	Not AlPO <sub>4</sub> -5, other condensed phase aluminophosphates.

Table B.3: Attempts to dope AlPO<sub>4</sub>-5 membranes with europium.

Conventional Oven Synthesis of AlPO<sub>4</sub>-5 within Porous Anodic Alumina prepared by Alexander Kirchner of Industrial Research Limited.

Although the conventional oven syntheses using Whatman Anodiscs as the alignment template yielded highly aligned  $AIPO_4$ -5 membranes, the Anodisc was corroded during the synthesis so that the final product was very brittle and unlikely to be suitable for any gas filtration application. In order to overcome this, samples were crystallized using PAA prepared by Alexander Kirchner of Industrial Research, which was more ordered and thermally/chemically stable, as the template.

Due to the higher stability of the Kirchner PAA, these syntheses were carried out using only 200eq.  $H_2O$  and a 1:1 ratio of Al:P (as the membrane did not partially dissolve as the anodiscs did).
Name	Synthetic Details	Results
LC29	Standard AlPO <sub>4</sub> -5 syntheses but with laser dyes supplied by An- drew Kay added.	Dyes decomposed during crystallization.
LC 79	Sample prepared with PAA made via the method in Kirch- ner et al. [32] (anodized in sulfuric acid, pore size of 30nm). PAA membrane was poor quality.	Poor sample.
LC82	Repeat of LC79 with a slightly higher quality PAA membrane. (anodized in sulfuric acid, pore size of $\sim 30$ nm)	Almost x-ray amorphous. The pores of these mem- branes may be too small to allow the AlPO <sub>4</sub> -5 crystallites formed during the 90 °C pretreatment to enter.
LC91	Standard prep in PAA mem- brane anodized in oxalic acid (pore size 50nm) made by Kirchner [32].	Good sample.
LC93	Repeat of LC91	Good sample.
LC94	Repeat of LC91	Good sample.
LC95	Repeat of LC91	Good sample.
LC98	Repeat of LC91	Good sample. Template later removed at 300 °C un- der vacuum overnight. Af- ter this step XRD showed that the zeolite had not been damaged.
LC99	Repeat of LC91	Good sample.
LC100	Repeat of LC91	Good sample.

Table B.4: AlPO<sub>4</sub>-5 membranes prepared on highly ordered PAA.

# Microwave Crystallisation of AlPO<sub>4</sub>-5 within Porous Anodic Alumina

Although using the Kirchner PAA allowed the crystallisation of mechanically sound, highly aligned membranes of AlPO<sub>4</sub>-5 using a conventional oven as the heating source, the Kirchner PAA had the disadvantage of being costly and not easily available in larger quantities; therefore it is preferable that these membranes be made using Whatman anodiscs. Also, after the experiments with laser dyes it became apparent that in order to achieve my goal of creating AlPO<sub>4</sub>-5 microlaser membranes it would be necessary to crystallize my membranes in a microwave oven, to ensure that the laser dyes incorporated into the membranes did not decompose during synthesis.

At this point it was necessary to design a Teflon lined microwave autoclave in which the temperature, time, and heating rate could be controlled. The design of this autoclave (and modifications to the microwave with which it was used) are discussed in appendix A. The experiments in which this microwave autoclave was used are discussed below. Firstly, my standard synthetic procedure needed to be modified in order to be suitable for microwave crystallization.

Table B.5: AlPO <sub>4</sub> -5 membranes using a microwave as the heating source
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Name Synthetic Details	Results
LC101 Bulk AlPO <sub>4</sub> -5 microwave prep. With PEEK autoclave. Similar to the prep in Yan et al. [133]	Not a great sample, only moderately crystalline and con- tained impurity phases.
LC102 As for LC101 but with an anodisc floated on a Teflon float and a 20 minute crystallization	An OK sample.
LC103 As for LC101, but using more recently purchased HF, 130 eq. H <sub>2</sub> O and pseudoboehmite.	A moderately good sample.
LC104 As for LC101 but with less water.	Similar to LC103
LC105 2 step microwave heating, similar to the synthesis in Tsai et al. [29]	Lots of amorphous material on surface at the liquid inter- face, almost nothing on the top surface.
LC109 Sample crystallized in the microwave, same as the conventional oven crys- tallization but with the addition of HF and a pretreatment performed in the conventional oven. 20 minutes crys- tallization.	XRD showed good alignment
LC110 As for LC109 but with 10 min crystal- lization Standard Microwave Synthesis.	Similar results to LC109 using XRD, looks more crys- talline on SEM.

Once this method had been devised, further attempts were made to incorporate the laser dye DCM into the membranes. These attempts were successful.

Name	Synthetic Details	Results
LC114	Microwave sample with 0.05:1 DCM:Al. 10 minute crystallization.	Sample luminesces under UV. XRD shows well aligned AlPO <sub>4</sub> -5.
LC115	As for LC114, but with more ethanol to dissolve the DCM.	Very similar in qual- ity to LC114.
LC116	As for LC115	As for LC114/LC115

Table B.6: Microwave samples doped with DCM.

After synthesis of these  $AIPO_4$ -5 membranes doped with DCM, samples were made to check whether the DCM was in fact incorporated into the zeolite, or just physically adsorbed onto the surface of the membrane. These experiments are summarised below.

Table B.7: Samples prepared to check whether DCM was incorporated into the membranes in Table B6.

Name	Synthetic Details	Results
LC117	Standard conventional oven hydrothermal AlPO $_4$ -5 sample made with an anodisc.	Prepared to check whether dye is incor- porated into LC114 or just clinging to the surface of the membrane.
LC119	Experiment with LC117 to see if DCM will cling to the surface of an AlPO <sub>4</sub> -5/PAA membrane. Appropriate amounts of DCM, H <sub>2</sub> O and ethanol were combined to mimic the synthesis conditions in LC114. LC117 was sealed in a Teflon lined autoclave and left at 180 °C for 2 hours then quenched, opened, washed and refluxed in ethanol until no more dye was observed to be removed.	observable fluores- cence under UV, unlike LC114.

Attempts were also made to incorporate Europium into the microwave AlPO<sub>4</sub>-5 membranes. Initial attempts were unsuccessful, and further attempts were not made due to time constraints.

Name	Synthetic Details		Results
LC111	Europium doped sample, 20 minute tion.	microwave crystalliza-	X-ray amorphous. SEM showed amorphous mate- rial on the surface con- tained all the europium, i.e. it was not incorporated into the AlPO <sub>4</sub> -5 (and be- sides which, there wasn't much AlPO <sub>4</sub> -5).
LC113	As for LC111 but crystallization.	10 minute	As for LC111

Table B.8: Europium doped microwave samples.

# Attempts to Synthesize Zeolite Membranes containing other Aluminophosphates

Attempts were made to synthesize several smaller pore zeolite membranes. It was found that these zeolites were much more difficult to synthesize within PAA as

- AlPO<sub>4</sub>-5 is more stable, so often the syntheses would yield the zeolite in question for the bulk, but AlPO<sub>4</sub>-5 would crystallize within the membrane
- The synthetic conditions required for these syntheses proved to be very corrosive to the PAA membranes used, as these syntheses typically use higher Al<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub> ratios.

Name	Synthetic Details	Results
LC21	Synthesis to try to prepare AlPO <sub>4</sub> - 18. Used a published synthesis from Verified Syntheses of Zeolitic Materi- als [134]	Amorphous.
LC22	Experiment to try to prepare AlPO <sub>4</sub> - 18. As for LC21 but using pseu- doboehmite.	A non-porous aluminophosphate
LC24	AlPO <sub>4</sub> -18 following the procedure in Vilaseca et al. [135]	Mostly amorphous, a very small amount of $AlPO_4$ -18.
LC26	As for LC24, but using Aluminum sec-Butoxide as the aluminium source.	Mostly amorphous.
LC27	Repeat of LC26 with an anodisc added. Crystallized for 24 hours	Anodisc dissolved.
LC28	As for LC27, but crystallized for 48 hours	Anodisc dissolved.
LC43	An Anodisc coated in TiO <sub>2</sub> using a precursor provided by Tim Kemmitt of IRL. This was intended to protect the anodisc from the corrosive AlPO <sub>4</sub> -18 precursor. Attempts were then made to crystallize AlPO <sub>4</sub> -18 within the anodisc.	Anodisc completely dissolved
LC45	Anodisc prepared with TiO <sub>2</sub> coating for SEM	It was impossible to see using SEM whether there was a coating present or not, and if so whether it com- pletely coated the anodisc (including in the pores).
LC46	As for LC43 but with a thicker coating of $TiO_2$	Anodisc dissolved.
LC50	Precursor solution for $AlPO_4$ -18.	

Table B.9: Attempts to synthesise small pore Alpo<sub>4</sub>-5.

	Table B.9: Continued	
Name	Synthetic Details	Results
LC51	Anodisc crystallized in a minimum amount of LC50	Anodisc completely dissolved.
LC52	Anodisc into which LC50 had been incorporated, placed on a Teflon float in the vapour above water in a bomb.	Amorphous.
LC57	Attempt to crystallize $AIPO_4$ -11 in an anodisc using a published route.	Anodisc dissolved and product was not crystalline.
LC58	Attempt to crystallize AlPO <sub>4</sub> -18	Bulk powder was $AlPO_4$ -18, anodisc dissolved.
LC59	Attempt to crystallize AlPO <sub>4</sub> -52 via a published route	Actually crystallized as poorly aligned, poorly crystalline AlPO <sub>4</sub> -5
LC60	Modified attempt to crystallize AlPO <sub>4</sub> -52 using pseudoboehmite.	Anodisc dissolved.
LC61	Modified attempt to crystallize $AIPO_4$ -52 using aluminium isopropoxide.	Anodisc dissolved.

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# Appendix C

# Methods used for Template Removal from Zeolites

**Calcination** - This is the most common method used. The details below are given as an example of how this technique may be applied to AlPO<sub>4</sub>-5.

 Samples are calcined in O<sub>2</sub>, heating slowly (2 °C min<sup>-1</sup>) to 550 °C, held there for 30 hours and slowly cooled [136].

## Photochemical Template removal

- Materials are exposed to ultraviolet radiation between 260-180 nm in O<sub>2</sub> for 20-50 hr with the UV source approx. 2 cm from the sample. UV is produced by a low or med pressure Hg discharge lamp in a quartz envelope in a closed chamber under ambient conditions [124].
- ZSM-5 was treated for 30 mins in O<sub>2</sub> mixture with 50 g/m<sup>3</sup> of ozone at 200 °C. Longer times are needed for samples with higher Al contents [126].

## **Microwave Irradiation**

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• Sample is irradiated at low temperature but heating to 550 °C is still required [127].

# Vacuum Removal Method

• MCM-41 was heated @ 200-250 °C for several hours under vacuum [130].

# **Solvent Extraction**

- Template was removed from Al-MCM-41 by:
  - Solvent extraction with 0.75 M HCl in 1:1 ethanol:heptane for 40 hours
  - Solvent extraction with  $0.05 \text{ M H}_2\text{SO}_4$ /ethanol for 1 hour @ 0 °C [125].

# **Supercritical Fluid Extraction**

Template was removed from Al-MCM-41 via supercritical fluid extraction @ 100 bar @ 100 °C for 15 minutes using supercritical CO<sub>2</sub> modified with 20% MeOH [125].

Appendix D

Alphabond 300 Materials Safety Data Sheet



#### SAFETY DATA SHEET according to EC Directive 2001/58/EC ALPHABOND

Revision Number 3, January 26, 2006

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND THE COMPANY/UNDERTAKING			
Product code: 834			
Product name	Alphabond		
Synonyms	Alphabond 300		
Synonyms Manufacturer, importer, supplier Emergency telephone number	Alphabond 300 Almatis GmbH Olof-Palme-Strasse 37 60439 Frankfurt am Main Germany Almatis, Inc. 501 West Park Road Leetsdale, PA 15056 US/ Almatis GmbH Giulinistrasse 2 67065 Ludwigshafen Germany Almatis Limited 1815-2 Aza Nagano, Iwakuni Ci Yamaguchi Pref 740-004 Japan Qingdao Almatis Co., Ltd Box 150, Sunshine Towei 61 Hongkong Middle Roa Qingdao 266071 P.R. China CHEMTREC: +1-703-527	ty 5 d -3887 +1-800-424-9300	
	Almatis: 501-776-4677		
Use of the Substance/Preparation	Binder		
Additional information available from:	www.almatis.com		
2.0	COMPOSITION/INFORMA	TION ON INGREDIENTS	
CAS Chemical Name	% Weight	EINECS - European Union*	

 Instruction
 <thInstruction</th>
 <thInstruction</th>

#### 3. HAZARDS IDENTIFICATION

Emergency Overview		
<ul> <li>Non-combustible</li> </ul>		
Eye contact	<ul> <li>Contact with eyes may cause irritation</li> </ul>	
Skin contact	May cause eye/skin irritation	
Inhalation	May cause irritation of respiratory tract	
Ingestion	Ingestion may cause irritation to mucous membranes	
Aggravated Medical Conditions	asthma	
	Iung irritation	

	dermatitis
Classification	Not applicable

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Canadian Hazard Symbol:Not applicable

	4. FIRST AID	MEASURES		
General advice	<ul> <li>Show this safety d</li> </ul>	ata sheet to the doctor in attendance		
Skin contact	Wash off immediately with soap and plenty of water removing all			
	contaminated clothes and shoes			
	<ul> <li>If skin irritation per</li> </ul>	sists, call a physician		
Eye contact	<ul> <li>Immediately flush contact lenses and</li> </ul>	with plenty of water. After initial flushing, remove any continue flushing for at least 15 minutes		
	<ul> <li>If symptoms persis</li> </ul>	t, call a physician		
Inhalation	<ul> <li>Move to fresh air</li> </ul>			
	<ul> <li>If breathing is diffic</li> </ul>	ult, give oxygen		
	<ul> <li>If not breathing, given a second secon</li></ul>	e artificial respiration		
	<ul> <li>Consult a physicia</li> </ul>	n if necessary		
Ingestion	<ul> <li>Clean mouth with v</li> </ul>	vater and afterwards drink plenty of water		
	<ul> <li>Never give anythin</li> </ul>	g by mouth to an unconscious person		
	<ul> <li>Do not induce vom</li> </ul>	iting without medical advice		
	<ul> <li>Consult a physicia</li> </ul>	n		
	5. FIRE-FIGHTI	NG MEASURES		
Suitable extinguishing media   • The product itself does not burn				
		Use extinguishing measures that are appropriate to		
	local circumstances and the surrounding environment			
Special protective equipment for	firefighters	<ul> <li>Wear self-contained breathing apparatus and</li> </ul>		
protective suit				
	6. ACCIDENTAL RE	LEASE MEASURES		
Personal precautions	<ul> <li>Wear personal pro</li> </ul>	tective equipment		
	Avoid dust formation			
Environmental precautions	No special environmental precautions required			
Methods for cleaning up	Take up mechanically and collect in suitable container for disposal			
7. HANDLING AND STORAGE				
Handling				
Technical	No special handling advice required			
measures/Precautions				
Cofe handling adulas	A	in confined areas		

measures/Precautions					
Safe handling advice	Avoid dust formation in confined areas				
Storage					
Technical measures/Precautions	Keep in a dry place				
Incompatible products	No information available				
Specific use(s)	None				

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

#### Exposure Limit Values

CAS	Chemical Name	% Weight	OSHA*	ACGIH*	MEL*	GOEL*
1333-84-2	Aluminium oxide (Al2O3), hydrate	91.5-95.0	N/A	N/A	N/A	
* OSHA - Final	PELs - Time Weighted Averages (TWAs)					

OSHA - Final PELs - Time Weighted Averages (TWAs)
 ACGIH - Occupational Exposure Limits - TWAs
 MEL - United Kingdom - Maximum Exposure Limits - (STELs)
 GOEL - Germany - TRGS 900 - Occupational Exposure Limits – TWAs, (a) exempt facilities listed in 2.4(8) and (9)

#### Personal protective equipment

Respiratory protection	<ul> <li>In case of insufficient ventilation, wear suitable respiratory equipment</li> </ul>				
	<ul> <li>When workers are facing concentrations above the exposure limit they must use appropriate certified respirators</li> </ul>				
Hand protection	Wear suitable protective gloves				
Eye protection • tightly fitting safety goggles					
	<ul> <li>safety glasses with side-shields</li> </ul>				
Skin and body protection	No special protective equipment required				
Hygiene measures	When using, do not eat, drink or smoke				
	<ul> <li>Regular cleaning of equipment, work area and clothing</li> </ul>				
Environmental exposure controls	No information available				

#### 9. PHYSICAL AND CHEMICAL PROPERTIES

#### **General Information**

Form	• powder
Colour	• white
	off-white
Odour	None

#### Important Health Safety and Environmental Information

Melting point/range	-2,050°C
Boiling point/range	Not determined
Flash point	Not applicable
Autoignition temperature	does not ignite
Risk of explosion	Not applicable
Density 3.2 g/cm3	
Bulk density	0.32-1.09 g/cm3
Water solubility	insoluble
pH 10	
Solubility in other solvents	insoluble
Vapour density	No information available

10. STABILITY AND REACTIVITY				
Stability	Stable under normal conditions			
Conditions to avoid  • No decomposition if stored and applied as directed				
Interials to avoid <ul> <li>No information available</li> </ul>				
Hazardous decomposition products	Not applicable			
polymerization	olymerization    Hazardous polymerisation does not occur			
Reactions	None under normal processing			

Local effects					
Skin irritation	May cause skin irritation and/or dermatitis.				
Eye irritation	Contact with eyes may cause irritation.				
Inhalation	May cause irritation of respiratory tract.				
Ingestion	Ingestion may cause irritation to mucous membranes.				
Additional advice	The following toxicological data shown are those obtained from tests on products of similar composition (in accordance with EC-Directive 1999/45/EC) No information available				
Long term effects					
Skin contact	No information available				

Skin contact	No information available
Eye contact	No information available
Inhalation	No information available
Ingestion	No information available
Additional advice	

12. ECOLOGICAL INFORMATION						
Additional e	Additional ecological No information available.					
Ecotoxicity	effects	<ul> <li>not wate</li> </ul>	er endangering	]		
CAS	Chemical Name		% Weight	WGK		
1333-84-2	Aluminium oxide (Al20	03), hydrate	91.5-95.0	N/A		
		13. DIS	POSAL CON	SIDERATIONS		
Waste from products	Waste from residues / unused Dispose of in accordance with local regulations.					
Contaminat	ted packaging	Empty conta	iners should b	e taken for local recycling, recovery or waste disposal.		
Further info	ormation	Can be land	illed, when in	compliance with local regulations.		
		14. TF		IFORMATION		
DOT	DOT not regulated					
ADR/RID not regulated						
IATA-DGR not regulated						
ICAO	not regulate	ed				
Further infor	mation not regulate	ed				

### 15. REGULATORY INFORMATION

The preparation is non-dangerous in accordance with Directive 1999/45/EC

Contains	Not applicable
Labelling	Not applicable
Indication of danger	Not applicable
R-phrase(s)	Not applicable
S-phrase(s)	Not applicable

#### U.S. Inventories

CAS	Chemical Name	% Weight	TSCA*	CERCLA/S ARA*	NJRTK*	MRTKL*	PRTK*		
1333-84-2	Aluminium oxide (Al2O3), hydrate	91.5-95.0	N/A	N/A	N/A	N/A	N/A		
* TOCA Linites	TECA United States Castion 8 (b) Inventory (TECA)								

\* TSCA - United States - Section 8 (b) Inventory (TSCA)
 \* CERCLA/SARA - Hazardous Substances and their Reportable Quantities
 \* NJRTK - New Jersey - Department of Health RTK List
 \* MRTKL - Massachusetts - Right To Know List
 \* PRTK - Pennsylvania - RTK (Right to Know) List

International	Inventories								
CAS	Chemical Name	% Weight	AICS - Austral ia*	EINECS - Europe an Union*	ENCS*	TSCA*	DSL - Canada *	IECSC*	ECL*
1333-84-2	Aluminium oxide (Al2O3), hydrate	91.5-95.0	Present	N/A	1-23	N/A	Present	Present	N/A
* AICS - Austr * EINECS - Eur * ENCS - Japar * TSCA - (Toxic * DSL - Canad * IECSC - Chin * ECL - Korea -	1333-64-2 [Aluminium oxide (ALZO3), hydrate 91.5-95.0 Present N/A 1-23 N/A Present Present N/A ALCS - Australia - Inventory of Chemical Substances (AICS) 'EINECS - European Union - European Inventory of Existing Commercial Chemical Substances (EINECS) 'EINECS - Japan Existing and New Chemical Substances (ENCS) 'TSCA - (Toxic Substances Control Act) - Export Notification 'DSL - Canada - Domestic Substances List (DSL) 'ECL - Korea - Existing and Evaluated Chemical Substances (FCL)								

#### **16. OTHER INFORMATION**

#### Prepared By

Literary reference

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501-776-4677.

Literary reference	
Other information	ACGIH - American Conference of Governmental Industrial Hygienist AICS - Australian Inventory of Chemical Substances
	CAS - Chemical Abstract Services
	CERCLA - Comprehensive Environmental Response, Compensation, and Liability Act
	CFR - Code of Federal Regulation
	CPR - Cardio-pulmonary Resusitation
	DOT - Department of Transportation
	DSL - Domestic Substances List (Canada)
	ECL - Korea - Existing and Evaluated Chemical Substances
	EINECS - European Inventory of Existing Commercial Chemical Substances
	ENCS - Japan - Existing and New Chemical Substances
	EWC - European Waste Catalogue
	IARC - International Agency for Research on Cancer
	IECSC – China – Inventory of Existing Chemical Substances Manufactured or
	Imported in China
	LC - Lethal Concentration
	LD - Lethal Dose
	MAK - Maximum Workplace Concentration (Germany) "maximale Arbeitsplatz-
	Konzentration"
	N/A - Not Available or Not Applicable
	NDSL - Non - Domestic Substances List (Canada)
	NIOSH - National Institute for Occupational Safety and Health
	NTP - National Toxicology Program

OEL - Occupational Exposure Limit OSHA - Occupational Safety and Health Administration PIN - Product Identification Number RCRA - Resources Conservation and Recovery Act SARA - Superfund Amendments and Reauthorization Act STEL - Short Term Exposure Limit TCLP - Toxic Chemicals Leachate Program TDG - Transportation of Dangerous Goods TLV - Threshold Limit Value TSCA - Toxic Substances Control Act TWA - Time Weighted Average WGK - Water Hazard Class (Wasergefaehrungsklasse) WHMIS - Workplace Hazardous Materials Information System

End of Safety Data Sheet

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