

Carbothermal Reduction and Nitridation of Geopolymer-Carbon Composites:

A Study of Reaction Mechanisms

By

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Abstract

The mechanism of carbothermal reduction and nitridation of potassium-graphite and potassium-, sodium- and ammonium-carbon black geopolymer composite systems was studied by varying the reaction conditions of temperature, time and reaction atmosphere. The effects of different carbon and alkali types were examined and it was determined that the formation of β -sialon occurs by a series of complex reaction pathways with conventional and new pathways observed.

Potassium-graphite and ammonium-carbon black composites reacted mostly through the conventional mechanism understood for clay based systems while significant kinetic hindrance to the crystallisation or melting of potassium- and sodium-carbon black composites resulted in the observation of non-conventional pathways. These new reaction pathways were determined to be a consequence of eutectic formation in the samples resulting in silica-rich and alumina-rich phases. The silica-rich phases formed silicon oxynitride type materials, suggested to be K-O1-sialon and Na-O-sialon, which subsequently formed a low z -value β -sialon phase with further carbothermal reduction and nitridation. The alumina-rich phase reacted via X-phase sialon and through direct conversion to produce a high z -value phase resulting in overall diphasic β -sialon materials.

To explain these results, the reaction pathways were discussed in context of previously determined mechanisms and a schematic representation for the formation of β -sialon presented, having some implications for the design of reactive systems.

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Table of Contents

1	Introduction	1
1.1	Silicon Nitride Ceramics and Sialons	1
1.1.1	Structure and Phase Relationships	1
1.1.2	Physical, Mechanical, Chemical and Thermal Properties and Applications.....	5
1.1.3	Synthesis of Sialons	6
1.1.4	Reaction Mechanism of Carbothermal Reduction and Nitridation	7
1.2	Geopolymers.....	12
1.2.1	Synthesis, Structure and Physical and Chemical Properties	13
1.2.2	Thermal Evolution of Geopolymers	16
1.2.3	Ion Exchange of Geopolymers	17
1.3	Using Geopolymers as Precursors for the Synthesis of Sialons	18
1.4	Research Proposal.....	20
2	Materials and Methods	23
2.1	Synthetic Methods	23
2.1.1	Synthesis of Geopolymer-Carbon Precursors	23
2.1.2	Ammonium Ion Exchange	25
2.1.3	Firing of Samples	25
2.2	Analytical Methods	29
2.2.1	Powder X-Ray Diffraction Studies	29
2.2.2	Solid State Nuclear Magnetic Resonance	31
2.2.3	Fourier Transform Infrared Spectroscopy	31
2.2.4	Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy	32
3	Potassium Geopolymer-Graphite Composites	35
3.1	Introduction	35
3.2	Results	35
3.2.1	Synthesis of Potassium Geopolymer-Graphite Composites	35
3.2.2	Firing of Samples with Varying Graphite Content	39
3.2.3	Reaction Sequence of Potassium-Graphite Composites.....	43
3.3	Discussion	62

3.3.1	Carbothermal Reduction and Volatilisation	62
3.3.2	Mechanism of Sialon Formation from Potassium-Graphite Composites	63
3.4	Summary	64
4	Potassium Geopolymer-Carbon Black Composites	65
4.1	Introduction	65
4.2	Results	65
4.2.1	Synthesis of Potassium Geopolymer-Carbon Black Composites.....	65
4.2.2	Firing of Samples with Varying Carbon Black Content	69
4.2.3	Reaction Sequence of Potassium-Carbon Black Composites.....	72
4.3	Discussion	89
4.3.1	Mechanism of Sialon Formation from Potassium-Carbon Black Composites ..	89
4.3.2	Comparison to Potassium-Graphite Composites	92
4.4	Summary	94
5	Sodium Geopolymer-Carbon Black Composites	97
5.1	Introduction	97
5.2	Results	97
5.2.1	Synthesis of Sodium Geopolymer-Carbon Black Composites	97
5.2.2	Firing of Samples with Varying Carbon Black Content	101
5.2.3	Reaction Sequence of Sodium-Carbon Black Composites	105
5.3	Discussion	119
5.3.1	Mechanism of Sialon Formation from Sodium Carbon Black-Composites.....	119
5.3.2	Comparison to Potassium-Carbon Black Composites.....	121
5.4	Summary	122
6	Ammonium Geopolymer-Carbon Black Composites	125
6.1	Introduction	125
6.2	Results	125
6.2.1	Synthesis of Ammonium Geopolymer-Carbon Black Composites	125
6.2.2	Firing of Samples with Varying Carbon Black Content	130
6.2.3	Reaction Sequence of Ammonium-Composites.....	134
6.3	Discussion	147
6.3.1	Preparation of Ammonium-Exchanged Geopolymer Composites	147
6.3.2	Mechanism of Sialon Formation from Ammonium-Composites	148

6.3.3	Comparison to Alkali-Carbon Black Composites	149
6.4	Summary.....	150
7	Summary Discussion.....	151
7.1	Introduction	151
7.2	The Effect of Carbon Type	151
7.3	The Effect of Alkali	152
7.4	Fibre Formation	155
7.5	Reaction Pathways for β -Sialon Formation	155
7.6	Summary.....	159
8	Conclusions and Future Prospects	161
8.1	Conclusions	161
8.2	Future Prospects	164
	References	165
	Appendices	173

1 Introduction

1.1 Silicon Nitride Ceramics and Sialons

The class of materials known as silicon nitride ceramics is one of most well known and most extensively studied non-oxide ceramic systems.² The backbone of this system is the parent phase, Si_3N_4 , which has the ability to form ceramic alloys with a number of other elements to form a wide variety of compounds.

1.1.1 Structure and Phase Relationships

Silicon nitride is a covalent solid and exists in 3 crystallographic forms; α -, β - and γ - Si_3N_4 ,^{2,3} the atomic arrangements of which are shown in Figure 1.1. Both the α - and β - forms of Si_3N_4 have hexagonal crystal structures which are comprised of interconnected, corner-sharing SiN_4 tetrahedra. β - Si_3N_4 has a phenacite (Be_2SiO_4) type structure with an ABAB... stacking arrangement while the α - Si_3N_4 modification has an ABCDABCD... arrangement due to a c -axis glide plane. As a consequence, β - Si_3N_4 contains long continuous channels running parallel to the c -axis and forms uniaxial grains while the α - Si_3N_4 phase contains interstices and forms equiaxial grains. Thus, α - Si_3N_4 is the harder of the two phases due to its longer Burgers vector whereas β - Si_3N_4 is tougher due to the reinforcing nature of its elongated microstructure.⁴ The γ - Si_3N_4 modification is a fairly recent discovery and relatively unstudied. It is formed under higher pressures and temperatures than the other modifications and is described as a spinel phase with a cubic crystal structure comprised of silicon in both 4- and 6-fold coordination in a 1:2 ratio.³ It is theorised to be the hardest of the 3 phases with a hardness on par with SiO_2 -stishovite. Although α - Si_3N_4 is the prevalent phase at lower temperatures, it transforms irreversibly to β - Si_3N_4 at temperatures above 1400 °C and during sintering.^{2,5}

Of the multi-component mixtures and ceramic alloys of Si_3N_4 which make up the family of silicon nitride ceramics, the class known as silicon aluminium oxynitrides (Si-Al-O-N or sialons) is arguably the most extensively researched.⁵ These materials, independently reported by Oyama in 1971^{6,7} and Jack and Wilson in 1972,⁸ are the product of the

incorporation of aluminium and oxygen into the structure of Si_3N_4 , replacing silicon and nitrogen respectively, to form solid solutions.

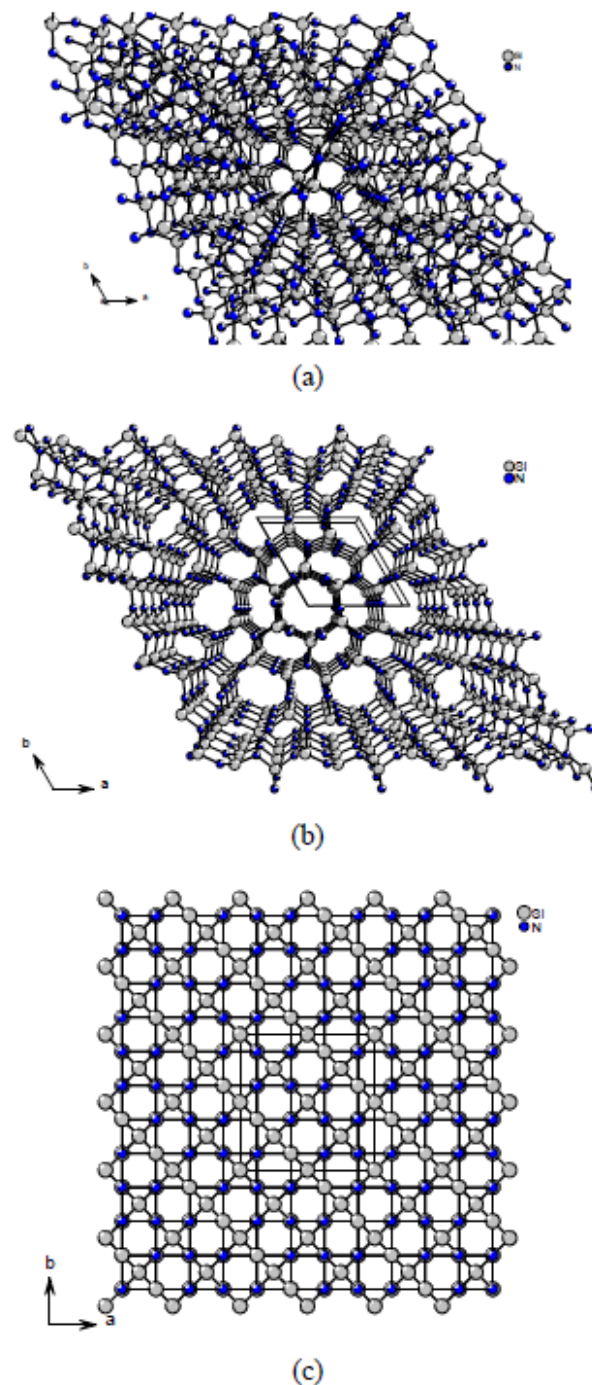


Figure 1.1: Cell projections for the different modifications of Si_3N_4 projected along the c -axis:
a) α -, b) β - and c) γ - Si_3N_4 , after Peng.⁹

The major product of the reaction between Si_3N_4 and Al_2O_3 is β -sialon. This material has the formula $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, where the “ z -value” represents the amount of Al substituted

into the phase. The β -sialon phase extends along the Si_3N_4 - Al_2O_3 :AlN tie line between $z = 0$ (Si_3N_4) to $z = \sim 4.2^{10,11}$ in the SiO_2 - Si_3N_4 -AlN- Al_2O_3 system, as seen in the sialon behaviour diagram in Figure 1.2. It is isostructural with β - Si_3N_4 and as such shares its hexagonal crystal structure, albeit slightly enlarged due to the longer bond length of Al-N of 187 pm (versus 175 pm for Al-O and Si-N).⁵ The coordination environment of Al in β -sialon is tetrahedral like Si.

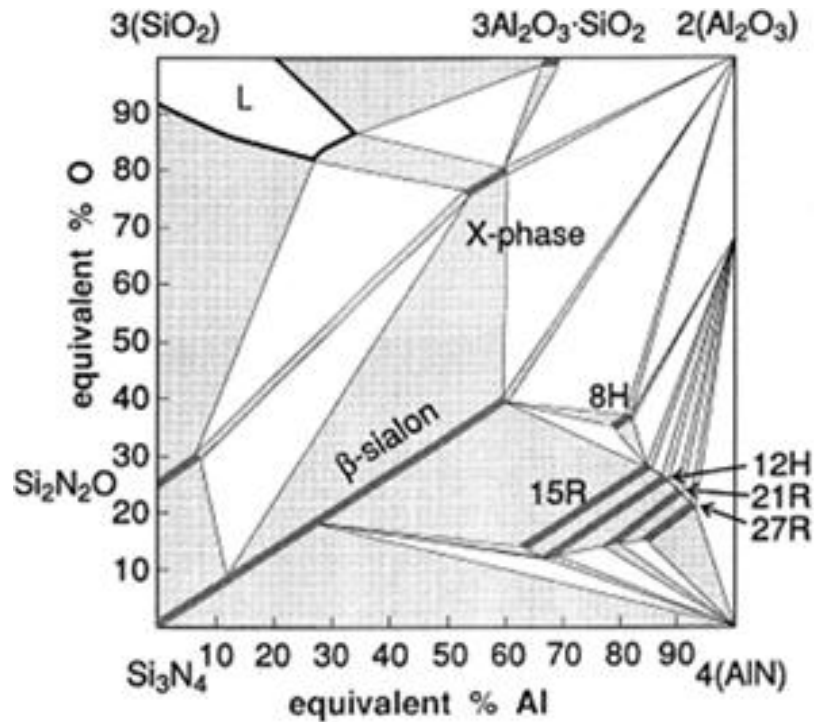


Figure 1.2: A behaviour diagram in the SiO_2 - Si_3N_4 -AlN- Al_2O_3 subsystem at approximately 1700 °C.¹¹ Although these diagrams do not necessarily show true thermodynamic equilibrium, they help illustrated the idealised relationships between the various compositions of sialon phases.^{10,11}

While α - Si_3N_4 is the predominant form of silicon nitride at lower temperatures, it is not a normally occurring phase in sialons unless a source of alternative cations is introduced, such as Li^+ , Ca^{2+} , Mg^{2+} , Y^{3+} or lanthanides with $Z > 58$.^{2,5} The inclusion of these soluble, stabilising cations forces the resulting materials to adopt an α - Si_3N_4 type structure such that the cations fill the resulting interstitial cavities. These “modifying cations” in the sialon form what is known as an interstitial solid solution or stuffed derivative.¹¹ Due to the extra positive charge provided by the modifying cation, α -sialon contains less Al and has a formula of $\text{M}_x^{v+}\text{Si}_{12-(m+n)}\text{Al}_{(m+n)}\text{O}_n\text{N}_{(16-n)}$, where M is the modifying cation, v its valency and $x = m/v < 2$.

Another phase of significance is O-sialon. Whereas α - and β -sialon have crystal structures based on Si_3N_4 , O-sialon has a unit cell which is isostructural with silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) and has a formula of $\text{Si}_{2-x}\text{Al}_x\text{O}_{1+x}\text{N}_{2-x}$. The “x-value” normally varies between 0 – 0.2,¹² but this value may be increased to ~0.4 by the use of sintering aids.¹³ The structure of silicon oxynitride is orthorhombic and is shown in Figure 1.3b. It consists of SiN_3O tetrahedra which are arranged in parallel puckered layers of Si_3N_3 rings joined by bridging Si-O-Si bonds.^{14,15} O-sialon also has a low temperature polymorph phase which is designated O1-sialon (Figure 1.3c). This polymorph is comprised of the same tetrahedral units but the Si_3N_3 layers are distorted allowing altered stacking and resulting in a slightly smaller unit cell of greater density.¹ Like α -sialon, O-sialon has been reported to form stuffed derivative phases with the alkali cations of Li^+ and Na^+ .^{14,16} These materials remain particularly unstudied however.

Although it was one of the sialon phases reported and has been relatively extensively studied,^{8,10,14,17-23} X-phase sialon continues to provide a challenge to ceramicists. While an

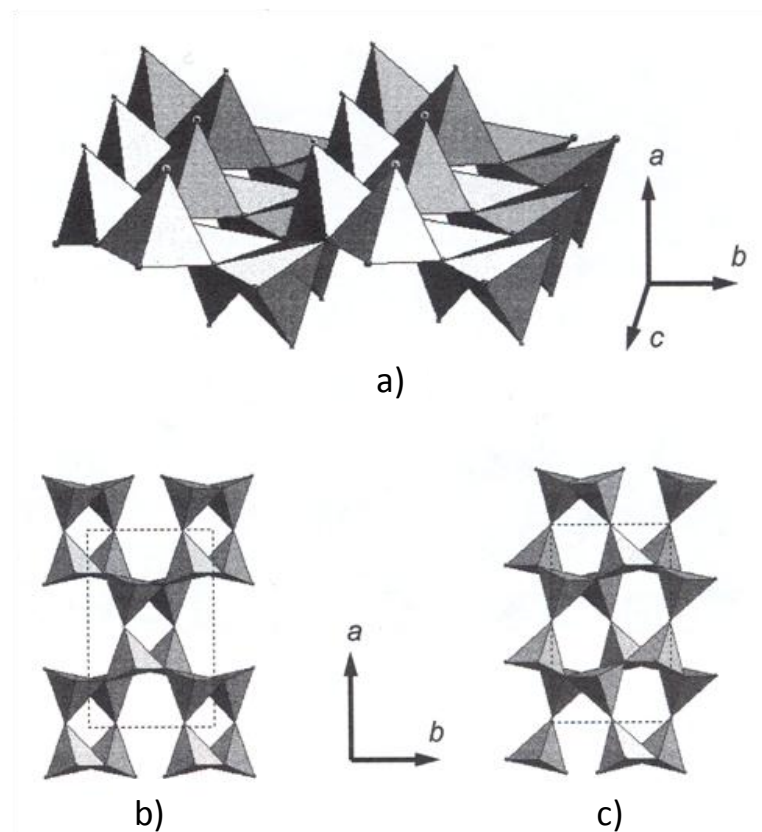


Figure 1.3: Polyhedral representations of the structures of O-sialon and O1-sialon. a) shows a single layer of O-sialon, whereas b) and c) are equivalent projections of O-sialon and O1-sialon respectively, looking down the c-axis showing the comparatively distorted tetrahedra of O1-sialon, after Bowden et al.¹

absolute determination of its crystal structure is still unavailable, it has been reported that X-phase exists in two crystallographic modifications, a low and a high form. The low form is a superlattice of the high form and both have a triclinic crystal structure.^{18,19,24} Its crystal structure resembles that of mullite with columns of AlO_6 octahedra cross-linked by SiO_4 and AlO_4 tetrahedra.^{22,25} The nitrogen present in the structure is thought to bridge the Si and Al tetrahedra.²⁶ X-phase can be found on the $\text{Si}_2\text{N}_2\text{O}-\text{Al}_2\text{O}_3$ tie-line (the same tie-line as O-sialon) and displays a short solubility range of between $\text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8$ and $\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_2$, representing an Al equivalence of 52.9 eq% and 60 eq% respectively.¹⁹ Although the best point representation of its stoichiometry is $\text{Si}_4\text{Al}_6\text{O}_{11}\text{N}_4$,²⁰ this thesis will instead use $\text{Si}_3\text{Al}_6\text{O}_{12}\text{N}_2$ to represent X-phase due to its ease of use in complex chemical equations.

Also of note are the many polytypoid sialon phases that are found in the bottom-right corner of the sialon diagram of states. These materials are polymorphs of AlN and have hexagonal or orthorhombic wurtzite-type structures which are described using their Ramsdell notation, i.e. 2H, 8H, 12H, 15R, 21R and 27R.¹⁸ Ramsdell notation gives the number of stacked layers in the repeating sequence along with the overall unit cell symmetry, where C, H and R indicate cubic, hexagonal and rhombohedral structures.²⁷ The most commonly encountered polytype by-product when synthesising β -sialon is 15R-sialon.

1.1.2 Physical, Mechanical, Chemical and Thermal Properties and

Applications

Silicon nitride is an ideal high performance ceramic and displays an impressive array of physical, chemical and thermal properties.^{10,28} Its physical and mechanical properties include high strength, good fracture toughness, high hardness, excellent wear resistance and low density.^{10,29} It retains many of these features at high temperatures with good creep resistance, high thermal conductivity and low coefficient of thermal expansion combined with good thermal shock resistance.^{29,30} Chemically, silicon nitrides are extremely corrosion resistant, non-wetting in non-ferrous molten metals and have good oxidation resistance.^{10,30}

For high performance ceramics, where optimisation of mechanical performance is critical, achieving a defect free or fully dense solid material is crucial. However, being a covalently bonded solid with inherently low self-diffusivity, it is difficult to fire silicon nitride

to full density without the use of high pressures or sintering aids.^{8,31} Comparatively, alloying with aluminium and oxygen to form sialons helps to ameliorate this difficulty, and provide improved oxidation resistance while sacrificing little in the way of physical and mechanical properties.⁵ In addition, their resistance to oxidation and corrosion is seen to improve.⁸ Jack said of β -sialon, *“Because of its structure, its physical and mechanical properties are similar to that of β -silicon nitride, but chemically it is closer to aluminium oxide”*.¹⁰

A further benefit of sialons is that there exists an exploitable transformation between α -sialon and β -sialon which is essentially reversible by the inclusion or exclusion of an intergranular glassy phase. This reversible behaviour, when coupled with an appropriate sintering aid (such as Y_2O_3 or Ln_2O_3), permits the tailoring and optimisation of component phases and microstructure by varying the heat treatment of the reaction mixture. This allows a range of hardness, strength and toughness values to be obtained for the same starting composition.^{4,11}

It is the combination of these properties that allows silicon nitride ceramics to be used in a number of diverse applications. They are especially useful in situations requiring hardness and/or high wear resistance such as cutting tools,^{5,29} bearings,⁵ spray nozzles,³² hydrocyclones for the extraction of sand from oil³² and have potential as bulletproof armour plating.³³ Their excellent thermal and chemical properties have found them wide usage as car engine parts³⁴ and as refractory materials,²⁸ especially in the smelting of aluminium.³⁵

1.1.3 Synthesis of Sialons

Sialon ceramics can be synthesised in a variety of ways which generally fall into three broad categories:³⁶ direct reaction, carbo-, alumino- or silico-thermal reduction and nitridation methods and vapour-phase synthesis (not discussed here).

Direct reaction is a synthetic method whereby a number of starting powder components, typically Si_3N_4 , Si_2N_2O , SiO_2 , Al_2O_3 and AlN , are combined intimately and fired at temperatures high enough to allow reactive sintering of the powders into a new sialon phase.¹⁰ Often, the Si_3N_4 component is synthesised by direct nitridation of Si metal before reactive sintering takes place, helping to reduce the costs of firing.³⁷ This direct nitridation process is typically referred to as a reaction bonding process.^{2,31} Self propagating high

temperature synthesis (also known as combustion synthesis) and spark plasma synthesis also fall into this category.^{2,38}

Simultaneous carbothermal reduction and nitridation (CRN) is a versatile method for the production of many non-oxide ceramics, including borides, nitrides and carbides. In the case of sialons, this technique uses carbon to reduce siliceous or aluminosiliceous materials such as silicates,³⁹ clays,^{30,40-42} fly-ash⁴³ and zeolites⁴⁴⁻⁴⁶ in the presence of flowing nitrogen to produce sialon containing materials at moderate temperatures of ~1350 °C. While CRN is a very cost-effective technique due to the low cost of the starting materials, the complexity of the reaction mechanism and exacting firing conditions have limited its commercial application.^{2,47} Despite this, it remains a popular technique in the literature. Due to its pertinence to this thesis, the mechanism of CRN is discussed in depth later in this introduction.

Analogous to CRN is aluminothermal or silicothermal reduction and nitridation whereby sialons are synthesised from aluminosiliceous materials by the use of excess quantities elemental aluminium³⁹ or silicon.^{22,47} These reactions may be carried out at slightly lower temperatures than CRN and reduction of the starting materials occurs concurrently with reaction bonding of the matrix.

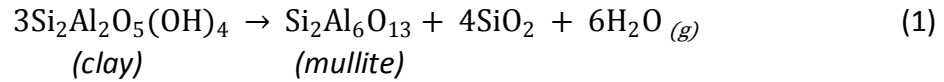
In general, sialons are conventionally fabricated from powders at ambient pressures in one of two ways; either the reaction bonding process mentioned above or with the use of additional pressure in a regime called hot isothermal pressing (HIP). The HIP process has the advantages of allowing good control of the final stoichiometry of the materials, loss due to decomposition being suppressed and little or no residual porosity in the final products. Its main drawbacks are that it is expensive,⁴⁸ very homogeneous mixtures are required⁴⁹ and complex shapes are difficult to fabricate.¹⁴

1.1.4 Reaction Mechanism of Carbothermal Reduction and Nitridation

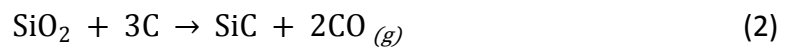
With its versatility and promise of reduced cost, simultaneous carbothermal reduction and nitridation (CRN) synthesis of aluminosilicates with powdered carbon has been extensively explored in the literature.^{30,42,48,50} The first direct synthesis of β -sialon via CRN is attributed to Lee and Cutler who used kaolinite clays as a starting material with coal

at temperatures of >1450 °C.³⁰ The mechanism of this conversion was studied in detail by Higgins and Hendry⁵⁰ and also by Bowden *et al.*⁴² and was found to involve a number of complex steps and intermediates, the most important of which are:

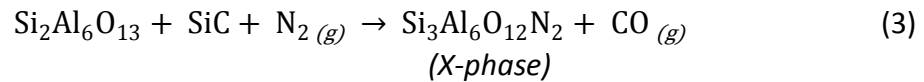
The dehydroxylation and dissociation to form mullite and silica



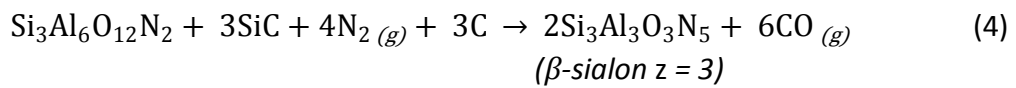
The reaction of silica with carbon to form silicon carbide and carbon monoxide



The reaction of mullite with silicon carbide to form X-phase sialon



The reaction of X-phase sialon and silicon carbide with more carbon producing β -sialon



For the purposes of this thesis, this reaction mechanism will be referred to as the “conventional mechanism”.

The SiO_2 produced by the decomposition of the kaolinite may be either amorphous or crystalline.⁴⁸ Thermodynamic calculations have shown that an appreciable partial pressure of SiO vapour can be formed at temperatures above 1400 °C due to the decomposition of SiO_2 . This is especially true in the presence of carbon, which provides a driving force for the decomposition.⁵¹

The evaporation of SiO is seen as an important determining factor in the phase assemblage of the resulting material as it is a potential means of decreasing the Si/Al ratio of products. SiO can be reincorporated into the reaction mixture by one of two means however, the formation of Si_3N_4 ,⁵¹ typically in its α -form, or the formation of silicon oxynitrides.⁴¹ These products are observed as long, columnar grains for Si_3N_4 ^{48,51,52} and as woolly fibres for $\text{Si}_2\text{N}_2\text{O}$,⁵¹ when examined using a scanning electron microscope (SEM) (Figure 1.4). Silicon monoxide vapour may also react with carbon to form silicon carbide.

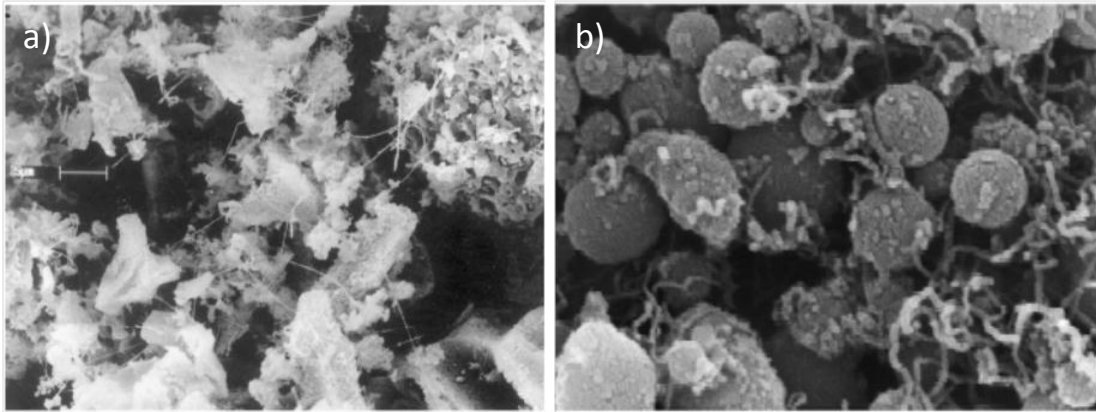


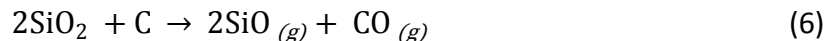
Figure 1.4: SEM images of the growth of a) α - Si_3N_4 whiskers in a sample prepared via CRN from kaolinite⁵² and b) woolly fibres of $\text{Si}_2\text{N}_2\text{O}$ in a zeolite CRN system.⁵¹

As flowing nitrogen is used as an atmosphere to allow nitridation and remove resulting CO, it also acts as a carrier gas for SiO vapour and control over its loss is related to the flow rate.⁴⁸ Therefore, precise control over the nitrogen flow rate is required to form β -sialon with the desired z-value. Other factors which influence SiO formation and loss are reaction temperature and reaction time.^{48,53} Reactions to form SiO and its subsequent reaction products are shown in Equations (5) – (10) below. The reaction for $\text{Si}_2\text{N}_2\text{O}$ is shown originating solely from SiO_2 but invariably contains small quantities of aluminium resulting in O-sialon.⁴¹

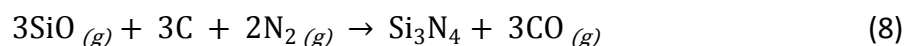
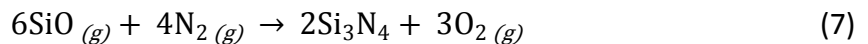
Decomposition of silica to form silicon monoxide



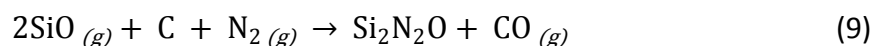
Carbothermal reduction of silica to silicon monoxide

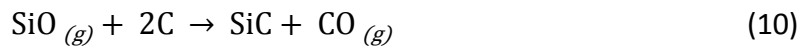


Formation of silicon nitride from silicon monoxide

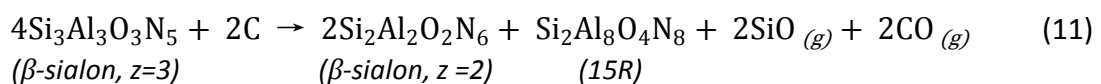


Formation of silicon oxynitride from silicon monoxide



Formation of silicon carbide from silicon monoxide

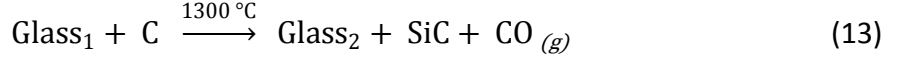
Additionally, the quantity of carbon required must be strictly controlled in order to achieve single phase β -sialon.⁴⁸ Sub-stoichiometric quantities of carbon tend to result in under-reaction and results in the formation of O-sialon, X-phase, SiC, corundum (α -Al₂O₃) and ALON by-products. Too much carbon, on the other hand, results in the over-reaction and the formation of AlN and its polytypes, particularly 15R-sialon.^{48,54} This is ostensibly due to the loss of vaporous SiO from fully reacted phases which may be exemplified by the reaction below whereby a high z-value β -sialon is decomposes to form a β -sialon of lower z-value and 15R-sialon and AlN, given sufficient excess carbon.⁴⁸ Varying the carbon content also has the effect of altering the reaction rate of β -sialon synthesis but does affect the reaction mechanism.^{40,52,55}



The type and size of carbon is also known to have an effect on the synthesis of sialon materials via CRN.⁵⁶ Studies have shown that the rate of reaction is dependent on the type of carbon used with carbon blacks and activated charcoals being more reactive than graphite.⁵⁶ The surface area of carbon is generally seen to be determined by their size and it has been shown that carbons of smaller particle size tend to significantly increase the rate of reaction.

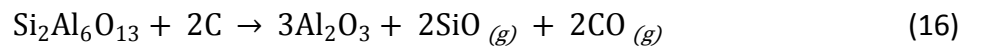
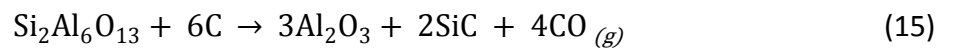
Impurities present in the starting clays may also have a significant effect on the reaction mechanism, typically by favouring the formation of various intermediate components. Iron oxide (Fe₂O₃) impurities have been found to be catalytic to the formation of sialon.⁵⁷ The presence of calcium oxide was observed by Narciso *et al.* to favour the formation of O-sialon whereas potassium increased the quantity of X-phase present during reaction.⁵⁶ However, this is in contrast to studies done by Ekström in which potassium favoured the formation of O-sialon.⁵⁸ At present, the role of impurities is not well understood but they are thought to enhance the reaction process by the formation of eutectic melts in the reaction mixture.⁵⁹ Mazzoni and Aglietti have suggested that in mixtures with high sodium and potassium content (i.e. bentonite clays), the mechanism may

involve the carbothermal reduction and nitridation of glassy phases.^{60,61} These glassy phases were suggested to be the results of vitreous melts rather than temperature stable, non-crystalline amorphous phases. The non-stoichiometric equations below represent this reaction pathway.

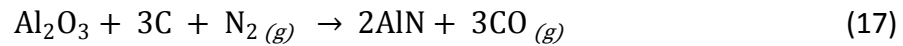


Another class of aluminosilicate materials which has been studied are zeolites. Initially described by Sugahara⁴⁴ and studied extensively by Wakihara and colleges,^{45,46,51,62-64} when compared to clays, zeolites are very pure systems and have the advantage of a variable Si/Al ratio during initial synthesis. Unlike the clay and SiO₂ systems commonly used in clay-based CRN, the Si and Al homogenously distributed throughout the zeolites prevents the formation of SiO vapour, suppressing α -Si₃N₄ and silicon oxynitride formation favouring the formation of monophasic β -sialon.⁴⁶ These studies have indicated the formation of β -sialon may occur via carbothermal reduction and nitridation of non-melted, amorphous phases.

The CRN processes also compete with the parallel, strictly carbothermal reduction processes of clays and aluminosilicate firing intermediates producing corundum and SiC. These reactions, examples of which are shown below by the carbothermal reduction of mullite, compete with CRN processes for carbon and produce SiO and SiC by-products. As they react to form CO gas their reaction rate is a function of the partial pressure of CO and as such these processes are strongly affected by the nitrogen flow rate. For the purposes of this thesis, these processes are designated CR.



The corundum formed by these reactions may also undergo carbothermal reduction and nitridation causing the formation of AlON and AlN by-products.



Thus, it can be seen that the formation of β -sialon by the CRN process occurs via a complex series of complimentary and competing reactions and through a variety of mechanistic pathways. This leads to the formation of multiple by-products and intermediates and requires exacting control over the composition of samples as well as firing conditions in order to produce a solely β -sialon final product.

1.2 Geopolymers

Geopolymers are the generic names given to a class of inorganic, cementitious materials formed via the reaction of aluminosiliceous materials, commonly clays or fly-ash, with an aqueous alkali mixture.^{65,66} They are also sometimes referred to as “inorganic polymers”,⁶⁶ despite this being an ambiguously used term with diverse application throughout chemistry. Due to their compositional similarities, geopolymers are often considered to be the amorphous analogues of zeolites.⁶⁷⁻⁶⁹ To differentiate geopolymers from other aluminosilicate systems (i.e. zeolites, clays, etc.), a stricter working definition comprising of four essential features has been proposed^{70,71}:

1. They are formed by alkali activation of an aluminosilicate source.
2. They set at temperatures between ambient and $\sim 90^\circ\text{C}$.
3. They are comprised of cross-linked tetrahedral Si and Al units ($\text{Si Q}^4(\text{mAl})$ centres) with charge compensation provided by the alkali ions.
4. They are X-ray amorphous materials which display a lack of long range ordering.

Geopolymers have attracted considerable attention as a new, low CO_2 emission replacement for Portland cements. Other potential low technology applications have included fire-proof insulation and as a binder for the immobilisation of hazardous heavy metals and radioactive wastes.⁷²

1.2.1 Synthesis, Structure and Physical and Chemical Properties

In general, geopolymers are synthesised by the activation of aluminosilicates such as clay or fly-ash with a strong alkali base. The process of geopolymerisation, represented schematically in Figure 1.5, is proposed to occur by a complex series of concurrent and coupled reactions, the mechanism of which is thought to involve several key processes.^{66,73}

- Dissolution of the aluminosilicate by the alkali to form separate, mainly monomeric silicate and aluminate species.
- Equilibrium of the dissolved species and the development of a supersaturated solution.
- Nucleation and condensation of monomers into oligomers forming a gel.
- Reorganisation and cross-linking to form a three dimensional network.
- Continued condensation and cross-linking causing hardening to form a monolith.

The resulting monolithic solids consist of cross-linked polymeric silicate chains of tetrahedrally coordinated Si and Al units bridged by O. These tetrahedral SiO_4 and AlO_4 units have well defined coordination geometries but form a highly disordered network, shown in Figure 1.6.⁷⁴ Furthermore, indications from ion-probe analysis suggest that geopolymers lack the regular aluminosilicate six-membered rings or hexagonal prisms typical of some crystalline zeolites.⁷⁵

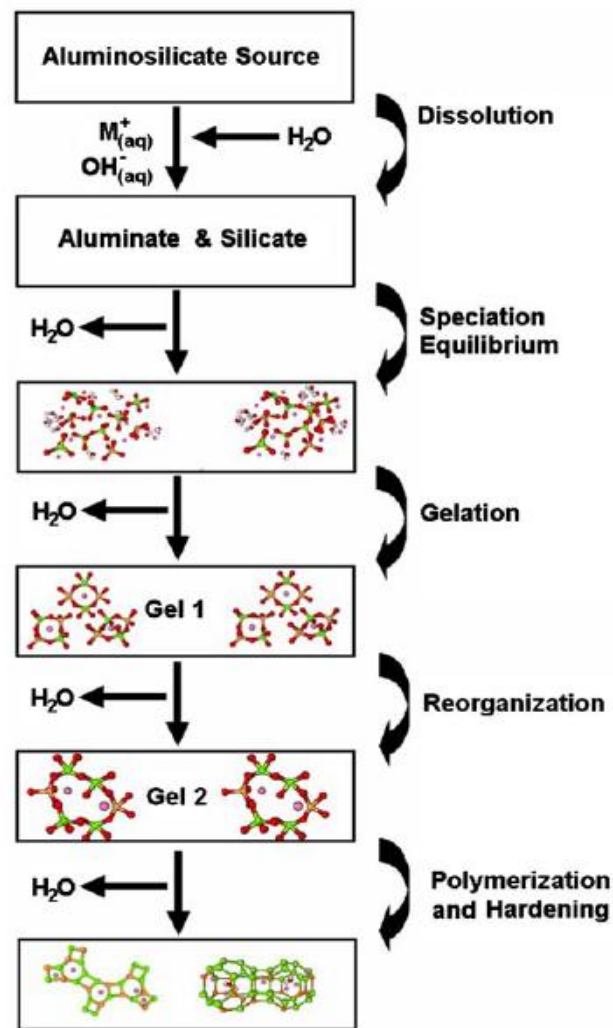


Figure 1.5: Conceptual model of geopolymerisation as proposed by Duxson et al.⁶⁶

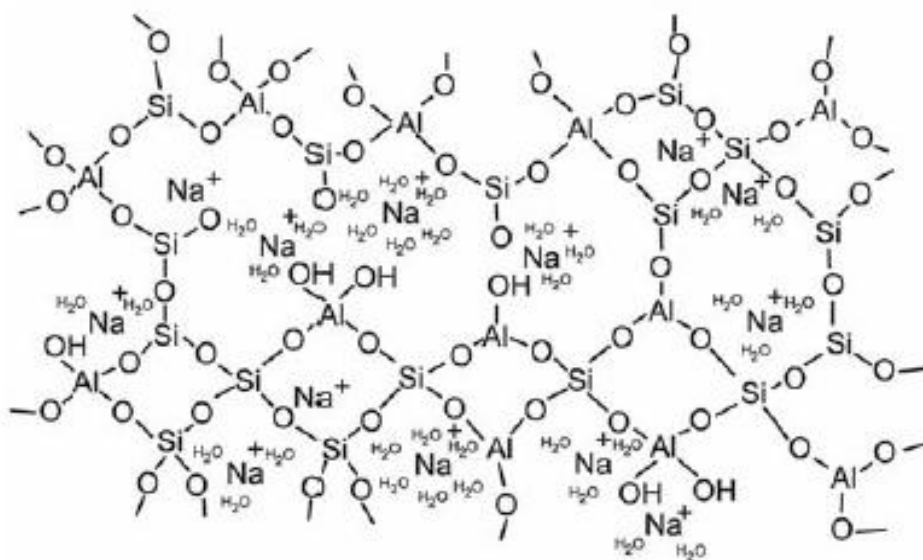


Figure 1.6: Semi-schematic structural model of the geopolymer network as proposed by Rowles et al.⁷⁴

The dissolving alkali cation remains in the structure in irregular sites within the networks cavities. They take a range of hydrated states and provide charge balance to the AlO_4^- moieties or Si-O-Si bridges depending on the amount of free OH in the geopolymer structure.⁷⁴ Although a significant amount of the initial water content is lost during gelation and hardening due to evaporation, large amounts are also retained as free and exchangeable water within the porous microstructure of the monolith.⁶⁶

The microstructure and morphology of geopolymers varies depending on the aluminosilicate source used to produce them (Figure 1.7) but geopolymers typically appear as amorphous solids with an open macroporous structure.^{66,76} On a smaller scale (Figure 1.8), the nanostructure is built up of small clusters of precipitate particles with micropores and mesopores dispersed throughout.⁶⁶ Total void content varies between <1 – 40% and although the average pore size varies too, it is generally below 10 nm.⁷³ These features are however dependent on reaction conditions and composition, with pore size shown to be significantly affected by initial water content.⁷³ Their large inherent porosity has seen them suggested as possible absorbent materials, filters and catalytic supports.⁷⁷

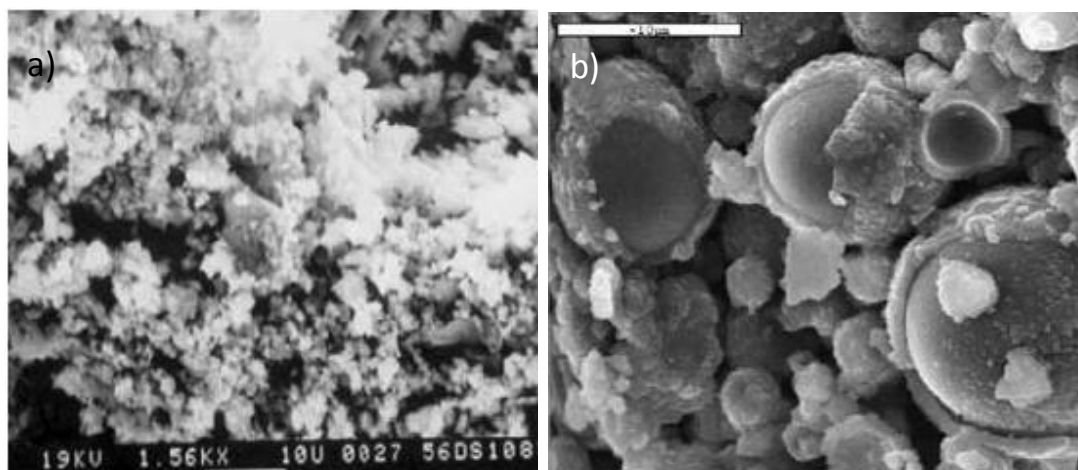


Figure 1.7: SEM images of a) geopolymer derived from clay and b) SEM image of fly-ash derived geopolymer produced under similar conditions.⁶⁶

The mechanical properties that are often of interest for geopolymeric materials are related to their potential use as building materials. As such, compressive and tensile strengths are commonly measured but results vary depending on aluminosilicate source, overall composition, network density and reaction conditions.⁶⁶ Typical compressive strengths range from 45 – 70 MPa and the majority of this strength is achieved rapidly,

within 4 hr of setting.^{66,70,72} Chemically, geopolymers are resistant to acid and alkali corrosion,^{65,78} are heat resistant⁷⁹ and their high absorbance,⁷⁸ exchangeable free water and cations have found emerging applications as ion-exchange materials.^{69,80}

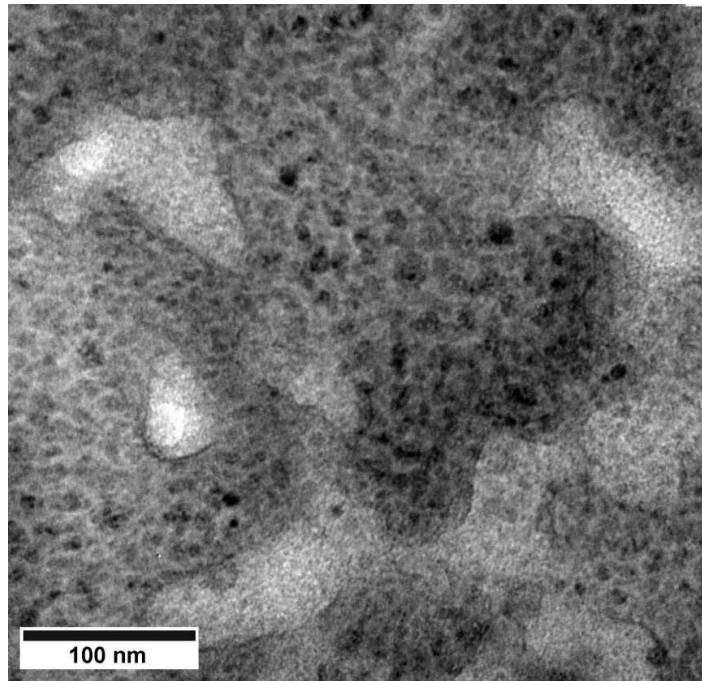


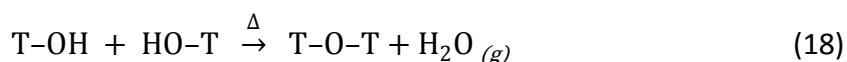
Figure 1.8: TEM image of geopolymer nanostructure showing micro- and meso-porosity.⁷⁶

1.2.2 Thermal Evolution of Geopolymers

Due to their potential application as building materials, fire retardants and as potential precursors for the synthesis of other ceramics, the thermal evolution of geopolymers has been studied by a number of researchers. Most studies are carried out between ambient temperatures and 1000 °C with a few providing data to 1300 °C.

Duxson *et al.* studied the evolution of metakaolin derived geopolymers up to 1000 °C^{79,81,82} and determined that their behaviour could be divided into four distinct regions; resilience, dehydration, dehydroxylation and sintering (labelled I-IV). Region I extends from ambient temperatures to ~100 °C, covering the initial dehydration of excess water from samples. Region II begins with the onset of initial shrinkage, lasting until the evaporation of all free water is complete at ~300 °C. Above these temperatures, in Region III, shrinkage and

weight loss is gradual and slow, likely due to the dehydroxylation of aluminol and silanol groups (both represented by T-OH below) within the geopolymer gels.

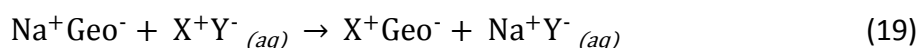


Region IV begins with the onset of a renewed dramatic increase in densification, attributed to viscous sintering. This sintering allows the bulk rearrangement Si and Al units allowing for crystallisation of new phases to occur. The onset temperatures of all regions were related to sample composition, with the onset of all regions being generally higher with increasing Si/Al ratio. K-derived geopolymers were found to be more thermally stable than NaK- and Na-derived gels with lower deformation at higher temperatures.⁸¹

Heating of geopolymers to 1000 °C and above results in phase transformations from amorphous to crystalline materials. The onset temperature and phases formed depend on the Si/Al ratio and alkali present in the geopolymer with Na-geopolymers forming nepheline, Cs-geopolymers forming pollucite⁸³ and K-geopolymer forming kaliophite, leucite and kalsilite.^{82,84} Interestingly, NaK-geopolymer systems formed zeolitic phases including faujasite and Zeolite V.⁸² At higher temperatures, non-alkali containing phases including mullite and $\alpha\text{-Al}_2\text{O}_3$ have been observed, possibly suggesting potential decomposition at high temperature.⁸⁵

1.2.3 Ion Exchange of Geopolymers

An area of emerging interest is the ion-exchange of geopolymers. Like their zeolites analogues, geopolymers contain cations which may be replaced with other incoming cations as long as charge balance is maintained.



Bortnovsky *et al.*⁷⁵ first reported the ion-exchange of geopolymers in an attempt to characterise the channel/ring structure of geopolymers by exploiting the dimensional differences of introduced Cs^+ and Co^{2+} cations. Following this work, ion-exchange has been explored as a technique for the synthesis and functionalisation of new types of

geopolymers, ceramics and catalytic support materials. To date, Na^+ , K^+ , Li^+ , NH_4^+ , Ag^+ , Pb^{2+} , Cd^{2+} , Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Pt^{2+} and Ti^{4+} have all been exchanged with varying degrees of success into the geopolymer matrix.^{69,77,80} Often these materials are achieved by the pre-exchange of the activating alkali for NH_4^+ before exchange for the desired final cation in a two-step method. Functionalised materials fabricated by this technique have included new catalytic supports for the reduction of NO_x by NH_3 , oxidation of decane as a volatile organic compound (VOC),⁸⁰ inclusion of TiO_2 for the photocatalytic bleaching of methylene blue⁷⁷ and using Ag^+ as an antimicrobial agent.⁶⁹ Ceramics fabricated by this method include nepheline, leucite, spodumene and mullite.⁶⁹

1.3 Using Geopolymers as Precursors for the Synthesis of Sialons

Due to their similarities to zeolites and their ability to form solid monoliths, geopolymers have been studied as potential precursors for the fabrication of sialon containing materials.⁸⁶ Previous studies by the author⁸⁷ have investigated the carbothermal reduction and nitridation of geopolymer-graphite composites treated in flowing nitrogen at 1400 °C for 10 hr and found the formation of multiphasic materials with β -sialon as a dominant component. These studies looked at a variety of factors affecting the fabrication of geopolymer-graphite precursors and their influence on the fired products. A focus was placed on potassium geopolymer-composites and the effect of the geopolymer composition (silicon, alkali and water content) and temperature. It was found that:

- Yields of β -sialon were affected by the overall alkali content with an optimum found to exist at $\text{K}_2\text{O}/\text{SiO}_2 = 0.20 - 0.30$.
- The structural integrity of the precursor monoliths was significantly affected by the water content and samples with higher water content, and therefore greater porosity, had lower β -sialon content and increased formation of α - Si_3N_4 .
- The effect of varying the silicon content could not reliably be established due to the incomplete reaction of the samples, but this may have been an issue associated with the reaction conditions.
- The dry milling of dehydroxylated halloysite and graphite caused a significant increase in the quantity of β -sialon obtained.

- The carbon content, which was included as a 1.2x stoichiometric quantity based on the assumption of the loss of alkali as an oxide rather than pure vapour, was found to be insufficient to allow complete nitridation.
- The activating alkali was not associated with any crystalline phases and no α -sialon phases were observed.

It was theorised that the mechanism for transformation from geopolymer to sialon might take place through simultaneous pathways; the conventional pathway for clay based systems (Equations (1) – (4)) and also through a second pathway as similar to those proposed by Mazzoni and Aglietti⁶⁰ for alkali-containing systems shown in Equations (12) – (14).

1.4 Research Proposal

The objective of this research was to continue the investigation of the potential of geopolymers as a precursor material for the fabrication of silicon nitride based ceramics, more specifically β -sialon. In particular, the effect of alkali on the reaction mechanism of transformation was studied. To achieve this, powdered geopolymer composites were subjected to various elevated temperatures and held at synthesis temperature for various times. Ion-exchange techniques from the literature were employed to synthesise non-alkali containing precursors to explore alkali-free geopolymers for comparison.

Geopolymers were synthesised by similar means to previous studies with the exception that conclusions drawn from our experiences to help improve homogeneity (dry milling) and simplify fabrication (two-pot mixture). The nominal composition of all geopolymers is $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.00$, $\text{M}_2\text{O}/\text{SiO}_2 = 0.25$ and $\text{H}_2\text{O}/\text{M}_2\text{O} = 10.00$ or 12.00 for potassium and sodium derived samples, respectively. This effectively means a $\text{M}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 1.00, which is considered as optimal in studies involving ion-exchange of zeolites.⁸⁸

It should be noted that, in the case of the potassium geopolymers, the composition is designed to reflect the composition of stoichiometric leucite. This was done intentionally as leucite is particularly thermally stable with a melting point of $\sim 1693^\circ\text{C}$. This thermal stability should prevent melting of potassium samples during firing and allowing samples to undergo full nitridation. The corresponding melting point of sodium geopolymers of the same composition is $\sim 1150^\circ\text{C}$. Relevant $\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ ternary phase diagrams with the relevant composition marked are provided in Appendix B. The intended z-value of all samples, if nitrided to completion without loss of silicon through volatilisation of SiO vapour is $z = 2.00$.

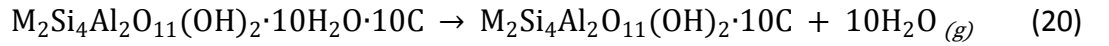
In determining the quantity of carbon required for full reaction of alkali-composites to form β -sialon of the intended z-value, three assumptions were made:

- Carbon does not react with the geopolymer slurry but forms a composite material comprised of a geopolymer matrix encapsulating the carbon.
- The hydroxyl groups will condense according to Equation (18) and that all water, either initially present as free water or resulting from condensation, will evaporate without affecting the amount of carbon required.

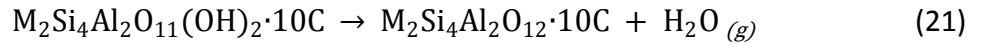
- Importantly, and in contrast to our previous studies, the alkali present in samples will volatilise, not as the oxide ($M_2O_{(g)}$), but as a metallic vapour ($M_{(g)}$) as part of a carbothermal reduction reaction.

The following sequence of reactions (Equations (20) – (24)) are based on a 1.0x stoichiometric sample and describe these assumptions with respect to several processes that are expected to take place based on the information provided by the literature and previous studies.

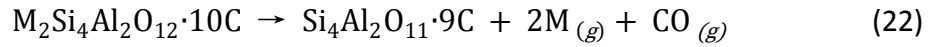
Dehydration



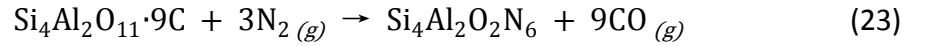
Dehydroxylation



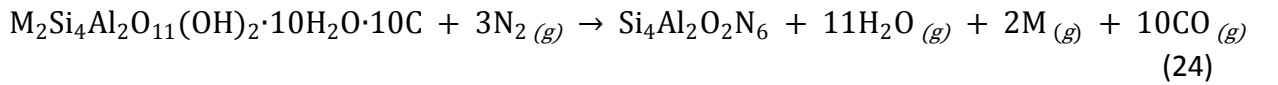
Decomposition



Carbothermal reduction and nitridation



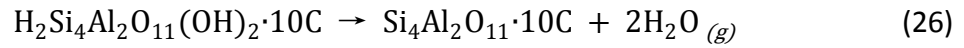
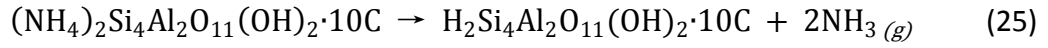
Overall Reaction



For alkali-composites, the carbon content was varied in 0.10 increments between 1.00 – 1.30 times the stoichiometric quantity as required by Equation (24) and analysed by powder X-ray diffraction and infrared spectrometry to determine an optimal composition for further study under varying holding temperatures and times.

With respect to ammonium-composites one further assumption was made. Ammonium has been determined to gradually decompose from ammonium-exchanged geopolymers above 100 °C and is completely lost upon heating to 600 °C.⁶⁹ It is therefore assumed that the results in the formation of new hydroxyl groups and that either after or

concurrent with this decomposition, samples undergo subsequent dehydroxylation at elevated temperatures in a similar manner to conventional geopolymers leaving an aluminosilicate phase for CRN. These processes are represented by Equations (25) and (26) after the initial dehydration:



This implies that the ammonium-samples will be oxygen deficient leading to a different carbon content requirement. As samples were prepared directly from the sodium composites, no adjustment for this deficiency was made and consequently the ammonium-composites will be carbon-rich compared to the alkali-composites. Consideration of Equations (26) indicates that samples will effectively have stoichiometric carbon contents of between 1.1 – 1.4 times the quantity required.

2 Materials and Methods

2.1 Synthetic Methods

2.1.1 Synthesis of Geopolymer-Carbon Precursors

To prepare the geopolymer-carbon composites, halloysite clay (New Zealand China Clays, 105 microns, sieved) was first dehydroxylated at 600 °C for 12 hr before being dry-milled with a predetermined stoichiometric quantity of graphite (British Drug Houses) or carbon black (Degussa Lampblack 101) for 24 hr with Si₃N₄ milling balls. The purpose of dry milling is to increase homogeneity between the two powders. It is not done with the express purpose of decreasing particle size; although this may be an advantageous side effect. The relevant properties of both carbon sources are outline in Table 2.1.

Table 2.1. Physiochemical Properties of Carbon Materials

Carbon Type	Particle Size / μm	Specific Surface Area (BET) / $\text{m}^2 \text{g}^{-1}$	Ash Content (wt%)
Graphite	40.6	4.87	0
Carbon Black	0.095 [†]	19.0	0.05

[†]Supplier's specifications

The resulting clay-carbon mixture was then passed through a 105 μm sieve to reduce the size of aggregates before being activated by an alkali silicate solution, prepared from potassium hydroxide (Pure Science, Ltd.), silica fume (BDH supplied Carbosil M5) and distilled water, and which had been aged for at least one week prior to mixing. The nominal composition of this potassium silicate solution was 24.61 wt% SiO₂, 24.29 wt% K₂O and 51.10 wt% H₂O.

The resulting pastes were placed in cylindrical moulds (25 mm x 25 mm deep), vibrated for 10 minutes to remove entrained air bubbles, sealed with plastic and cured at 40 °C for 24 hr to form solid, monolithic geopolymer-carbon composites. Non-composite control samples without carbon were also fabricated in a similar fashion but with the milling

step excluded. The molar ratio of the reaction gels are $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$, $\text{K}_2\text{O}/\text{SiO}_2 = 0.25$, $\text{K}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$ and $\text{H}_2\text{O}/\text{K}_2\text{O} = 10.0$.

Sodium containing samples were prepared as above with the exception that the sodium silicate solution used was prepared from sodium hydroxide (Panreac), Carbosil M5 silica fume (BDH supplied) and distilled water. Its nominal composition was 26.84 wt% SiO_2 , 17.44 wt% Na_2O and H_2O 55.72 wt%. The molar ratio of the reaction gels are $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.25$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 12.00$.

The absolute composition of the prepared samples and their stoichiometric ratio of carbon (based on Equation (21)) and its weight percentage in the uncured slurry are shown in Table 2.2 and Table 2.3. Samples containing graphite and carbon black are denoted -G and -CB, respectively. The intended fired z-value of all samples in this study is $z = 2.0$.

Table 2.2. Composition of Potassium Geopolymer & Geopolymer-Carbon Composites

Sample code	Absolute Composition of Geopolymer/Composite	Carbon (w/w %)	Stoichiometric Ratio of carbon
K0	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$	0	0
K1.0-G	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 10\text{C}$	15.9	1.0
K1.1-G	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 11\text{C}$	17.2	1.1
K1.2-G	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 12\text{C}$	18.4	1.2
K1.3-G	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 13\text{C}$	19.7	1.3
K1.0-CB	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 10\text{C}$	15.9	1.0
K1.1-CB	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 11\text{C}$	17.2	1.1
K1.2-CB	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 12\text{C}$	18.4	1.2
K1.3-CB	$\text{K}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 13\text{C}$	19.7	1.3

Table 2.3. Composition of Sodium Geopolymer & Geopolymer-Carbon Composites

Sample code	Absolute Composition of Geopolymer/Composite	Carbon (w/w %)	Stoichiometric Ratio of Carbon
Na0	$\text{Na}_2\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$	0	0
Na1.0-CB	$\text{Na}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 10\text{C}$	15.8	1.0
Na1.1-CB	$\text{Na}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 11\text{C}$	17.1	1.1
Na1.2-CB	$\text{Na}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 12\text{C}$	18.4	1.2
Na1.3-CB	$\text{Na}_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{H}_2\text{O} \cdot 13\text{C}$	19.6	1.3

2.1.2 Ammonium Ion Exchange

To synthesise precursors free of alkali, 5.000 g of powdered sodium or sodium-carbon black geopolymers (N0-N4) were placed in cylindrical plastic bottles and exchanged with 500 ml of 0.50 mol dm^{-3} NH_4Cl solutions, as per the method set out by Samaza *et al.*⁸⁰ Containers were placed on a rotating milling apparatus and stirred for 4 hr before being filtered over vacuum and washed with distilled water and small quantities of isopropanol to settle any flocculated carbon black. During this washing process, very minor quantities of carbon black were lost. Samples were then dried at 60°C for several hr or overnight to remove any exchanged solvent. This exchange process was repeated twice more. Table 2.4 shows the absolute compositions and stoichiometric carbon ratios intended for the ammonium-exchanged samples. The carbon weight percentages and water contents of the resulting samples are not shown as samples were not prepared directly from slurries and these variables were not determined after preparation.

Table 2.4. Composition of Ammonium Geopolymer & Geopolymer-Carbon Composites

Sample code	Absolute Composition of Geopolymer/Composite	Stoichiometric Ratio of Carbon
A0	$(\text{NH}_4)_2\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$	0
A1.1-CB	$(\text{NH}_4)_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 10\text{C}$	1.1
A1.2-CB	$(\text{NH}_4)_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 11\text{C}$	1.2
A1.3-CB	$(\text{NH}_4)_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 12\text{C}$	1.3
A1.4-CB	$(\text{NH}_4)_2\text{Si}_4\text{Al}_2\text{O}_{11}(\text{OH})_2 \cdot 13\text{C}$	1.4

2.1.3 Firing of Samples

Between 0.400 – 2.200 g of selected powdered geopolymer-carbon composites was weighed into an alumina boat and placed into a horizontal tube furnace inside of its hot-zone (Figure 2.1). These powders were then fired at various elevated temperatures in a flowing oxygen-free nitrogen (99.99%) atmosphere using a flow rate of 50 mL min^{-1} .

To determine the behaviour and development of samples before CRN processes began, samples were fired under pre-synthesis temperatures of 1200°C , 1300°C and 1400°C without isothermal holds. In order to monitor the CRN reaction mechanism of the geopolymer composites as a function of time, samples were also fired at 1400°C with

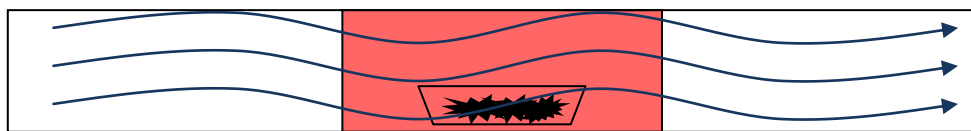


Figure 2.1: Schematic of horizontal tube furnace set-up showing sample, hot-zone and flow direction of the inert atmosphere.

isothermal holding durations between 1 – 24 hr. Prior to each firing at elevated temperature, a drying step of 200 °C for 3 hr was employed to remove entrained water from the powders. The heating rate between each step was 5 °C min⁻¹ while a cooling rate of -10 °C min⁻¹ was used until the cooling rate dropped below -10 °C min⁻¹ whereby the furnace cooled freely. Samples were removed between 200 °C and room temperature. A representative schematic for a 10 hr firing is shown in Figure 2.2, indicating pre-synthesis (blue) and CRN synthesis (red) conditions.

A selection of samples were also fired for 10 hr at 1400 °C in flowing argon to determine the effect of carbon on geopolymers heated under non-nitriding conditions. The different firings, their various hold duration and gaseous atmosphere are detailed in Table 2.5.

Table 2.5. Hold Temperature, Durations and Atmosphere of Firings

Hold Temperature / °C	Hold Duration / hr	Flowing Gas Atmosphere
1200	0	Nitrogen
1300	0	Nitrogen
1400	0	Nitrogen
1400	1	Nitrogen
1400	2	Nitrogen
1400	4	Nitrogen
1400	8	Nitrogen
1400	10	Nitrogen
1400	16	Nitrogen
1400	24	Nitrogen
1400	10	Argon

The weight loss during firing was determined by weighing samples before and after firing and calculated as a percentage using the following formula:

$$\text{Weight Loss percentage} = \frac{W_f - W_i}{W_i} \times 100\% \quad (27)$$

Where W_i and W_f are the initial and final weights of samples, respectively.

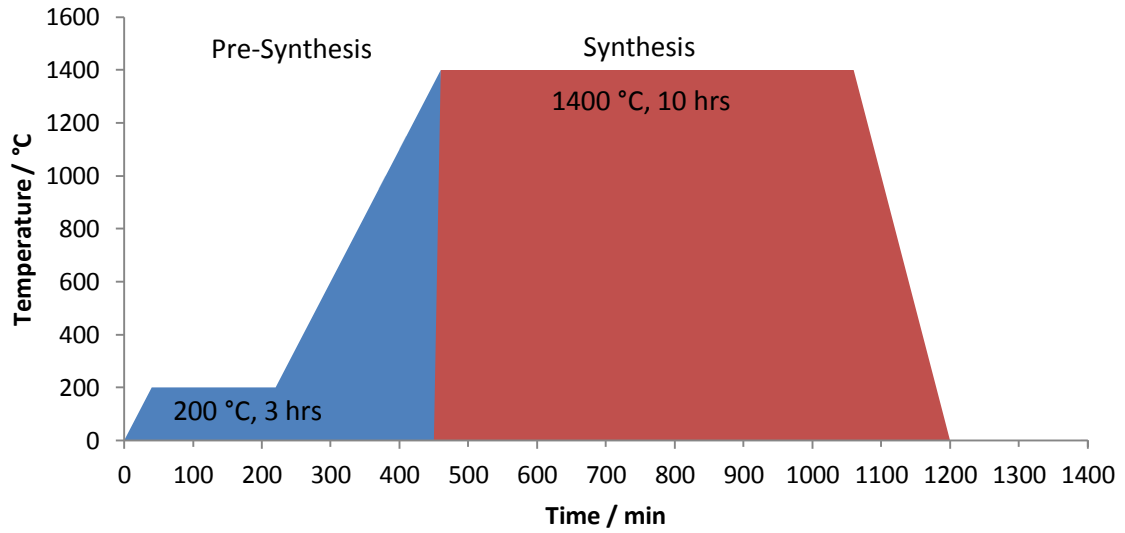


Figure 2.2. An example of a firing pattern (1400 °C, 10 hr) used to synthesis samples.

A schematic for the overall process is shown in Figure 2.3.

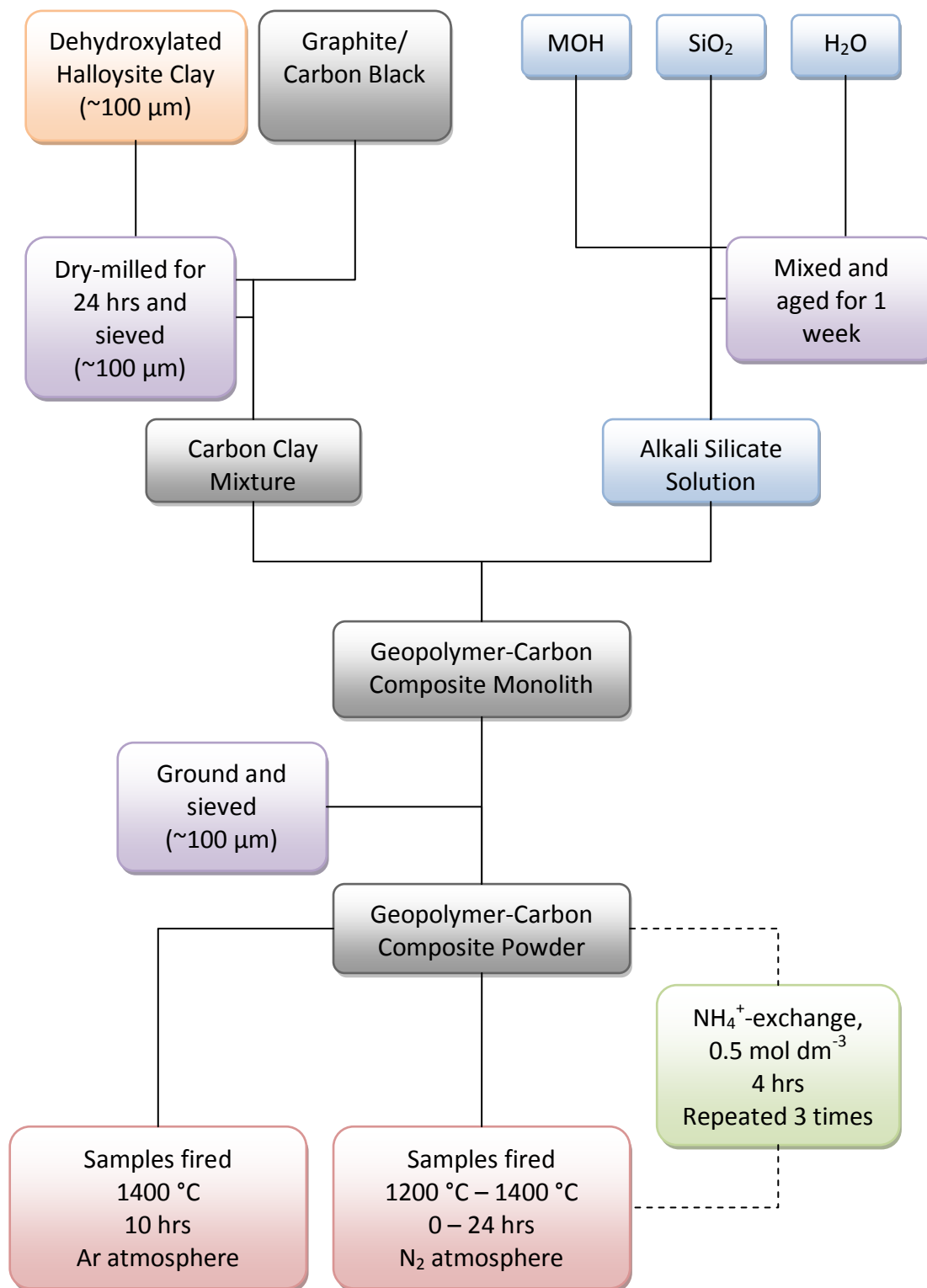


Figure 2.3: Schematic showing the process of geopolymer-carbon composite fabrication and sialon synthesis.

2.2 Analytical Methods

2.2.1 Powder X-Ray Diffraction Studies

X-ray diffraction (XRD) of powders was used to identify occurring component crystalline phases of fired and unfired samples and raw materials. Data were collected on a PANalytical X'Pert PRO MPD diffractometer using CuK α -radiation ($\lambda = 1.5418 \text{ \AA}$) with a PIXcel detector. Powders were placed and levelled in an acrylic sample holder ($\varnothing 17 \text{ mm}$) and patterns collected using an automatic divergence slit of 10 mm in conjunction with a 5 mm mask to limit the irradiated area to a 10 mm x 10 mm square. Scans were conducted between 8 - 80° (2 θ) with a resolution of 0.02° and a count time of 500 counts per step.

Resulting diffraction patterns were analysed qualitatively using PANalytical Highscore Software to determine the component crystalline phases of both fired and unfired materials. Patterns were converted from automatic divergence slit data to 1° fixed divergence slit data using the function provided in Highscore, creating pseudo-fixed slit patterns. All background and scattering from non-crystalline materials was removed using the background subtraction function of the program and a manual subtraction using point picking with automatic linear interpolation.

Using these patterns, semi-quantitative estimates of the relative concentration of major phases were made from their peak height measured at selected 2 θ angles. Due to the multiphasic nature of most materials and overlapping peak intensities, the chosen peak height may not be the most intense reflection for a specific phase. As such, the peak height has been scaled to reflect the height of the major reflection for the assigned phase for consistency. The details of the assigned phases and reflection data are shown in Table 2.6 in no particular order. In the case of β -sialon, with its wide range of solid solubility and varying unit cell dimensions, the (100) reflection has been used due to its narrow width and ability to represent all z-values including 0 (β -Si₃N₄) with its intensity. It should be made clear that the resulting data does not make use of any reference intensity ratios (RIR) and as such any particular phase can only be compared quantitatively to the same phase in other samples and phases within the same sample cannot be compared quantitatively. Essentially, this

method tracks the growth or decline of a particular phase with varying reaction conditions and is not an indication of absolute concentration.

Table 2.6. Assigned crystalline phases, measured reflections with Miller indices in parenthesis and scaling factors

Crystalline Phase	JCPDS File No.	Measured Reflection / degrees 2 Θ	Major Reflection / degrees 2 Θ	Scale Factor
Graphite	00-056-0159	34.7 (004)	26.5 (002)	14.29
Cristobalite	00-039-1425	22.0 (101)	-	-
Quartz	01-075-8322	20.8 (100)	26.6 (011)	4.69
Leucite	01-071-1147	27.2 (400)	-	-
Mullite	00-015-0776	31.0 (001)	26.3 (210)	5.00
Corundum	00-010-0173	43.4 (113)	-	-
γ-alumina	01-074-4629	45.3 (220)	-	-
β-SiC	00-029-1129	60.2 (110)	35.7 (102)	2.86
6H-SiC	00-029-1131	60.2 (110)	35.7 (102)	2.86
β-Si₃N₄	00-33-1160	13.4 (100)	27.1 (200)	2.94
β-sialon				
z = 1	00-048-1615	13.4 (100)	26.9 (200)	2.94
z = 2	00-048-1616	13.4 (100)	26.9 (200)	2.94
z = 3	00-036-1333	13.4 (100)	26.9 (200)	2.94
z = 4	00-048-1617	13.4 (100)	26.9 (200)	2.94
X-Phase	00-048-0637	24.4 (1,0,-3)	24.6 (2,0,-3)	1.25
O-sialon				
x = 0.15	04-010-4832	19.9 (200)	-	-
x = 0.4	00-042-1492	19.9 (200)	-	-
O1-sialon	00-052-1477	20.0 (200)	26.7 (111)	1.15
15R-polytype	00-042-0160	32.0 (0,0,15)	34.4 (101)	1.11
AlN	00-025-1133	66.1 (103)	33.2 (100)	3.33

Qualitative Rietveld analysis was also carried on samples of interest using the software package Maud (Materials Analysis Using Diffraction).⁸⁹ Modelling of the diffractions pattern allowed the determination of the lattice cell parameters of several phases. From the values obtained, estimations of unit cell volumes of observed O-sialon and O1-sialon phases were made. Calculation of the z-values of the β -sialon phases was achieved using the modelled a - and c -axis cell lengths utilising the Ekström formula seen below.⁹⁰

$$a = 7.603 + 0.0296z \text{ \AA} \quad (28)$$

$$c = 2.907 + 0.0255z \text{ \AA} \quad (29)$$

Despite its use in our previous work, Rietveld analysis could not be effectively used to quantitatively model the diffraction patterns of materials due to the presence of X-phase sialon in many samples. Presently, the atomic positions of X-phase remain uncharacterised and this precludes the modelling of its diffraction pattern and the intensity of reflections. Despite this, quantification of X-phase can and has been achieved by determination of intensity scaling factor by comparing it to a known quantity of a standard material (corundum, Si, etc.). At the time of this study, this resource was not available to us.

2.2.2 Solid State Nuclear Magnetic Resonance

In order to characterise any amorphous phases present in fired potassium samples, powders were analysed using ^{27}Al and ^{29}Si magic angle spinning solid state nuclear magnetic resonance (MAS NMR). A Bruker Avance 500 Spectrometer (11.7 T) was used with the following conditions:

^{27}Al : Powders were packed into a 4 mm Doty MAS probe which was spun at 10-12 kHz in a Si_3N_4 rotor. The spectrometer frequency was 130.224 MHz, using a 1 s pulse ($\pi/10$ for solutions) and a 1 s delay. Spectra are referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

^{29}Si : Powders were packed into a 5 mm Doty MAS NMR probe and spun at 5-6 kHz in a ZrO_2 rotor. The spectrometer frequency was 99.926 MHz, using a 6 μs pulse and a 30 s delay. Spectra are referenced to tetramethylsilane (TMS).

NMR spectra were only obtained for the potassium-graphite and potassium-carbon black samples fired in nitrogen for up to 10 hr.

2.2.3 Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FTIR) spectra presented in this thesis were measured using a Perkin-Elmer Spectrum One spectrometer. Samples were suspended in 1.000 ± 0.003 g window of KBr in approximately 0.1 – 0.3 wt%. Spectra were collected in two ranges; $4000 - 400 \text{ cm}^{-1}$ and $1250 - 400 \text{ cm}^{-1}$ in absorbance mode. The former range was used to determine the presence of NH_4^+ vibrational modes, while the latter range is used to

characterise the major vibrational modes associated with aluminosilicates, carbides and nitrides.

Spectra were analysed using the Perkin-Elmer Spectrum program with positions marked at peaks and points of inflection to distinguish potential absorption bands. Spectra were auto-background corrected using the function supplied and deconvolution of spectra was not carried out.

As the characterisation of the reaction mechanism of sialons is not commonly undertaken using IR techniques, a series of reference spectra were also obtained for comparison. The reference materials examined include: dehydroxylated halloysite (150# mesh sieved), mullite crystallised from kaolinite (HF treated but contains quartz and cristobalite impurities), a nepheline-syenite sample (Industrial Research Limited (IRL)), SiC (Navarro, 1000# sieved, mixture of α - and β -SiC), corundum (IRL secondary XRD standard, 88% crystalline) and O-sialon (IRL reference material, $x = 0.2$, trace of X-Phase and β -sialon). These reference spectra are provided in Appendix A.

The z -values of Si_3N_4 materials were determined by comparison to data taken from Wild *et al.*⁹¹ and examination of two Si-N-Si bending vibrational modes which occur between $580 - 480 \text{ cm}^{-1}$ and between $440 - 360 \text{ cm}^{-1}$ (labelled ν_3 and ν_2 respectively). The resulting z -values are the averaged value calculated using the following derived formulas:

Using the ν_3 vibrational mode

$$z = \frac{\nu_3 - 585.1}{-21.965 \text{ cm}^{-1}} \quad (30)$$

Using the ν_2 vibrational mode

$$z = \frac{\nu_2 - 451.71}{-19.118 \text{ cm}^{-1}} \quad (31)$$

2.2.4 Scanning Electron Microscopy and Energy Dispersive X-Ray

Spectroscopy

In order to investigate the microstructural evolution of samples during firing, a JEOL 6500F scanning electron microscope (SEM) with a field emission gun was used. Unfired samples and samples fired at 1400°C for between 0 – 10 hr were prepared by mounting

their powders on a 10 mm diameter x 10 mm high aluminium stub with a strip of conducting carbon tape to earth samples. They were then sputtered coated with either carbon (14 nm) or platinum (12 nm) and placed in a desiccator for a minimum of 24 hr.

Secondary electron and back-scattered electron images were obtained and to investigate the elemental composition of samples, energy dispersive X-ray spectroscopy (EDS) was employed. All samples were examined under EDS conditions using an accelerating voltage of 15 kV with both spot and bulk EDS data acquired.

EDS was also used to determine the extent of exchange in NH_4^+ -treated samples. This is an appropriate technique for the investigation of ion-exchange for the materials discussed as EDS is not a surface analysis technique; penetration depth and width in samples of density 2.5 g cm^{-3} is at least $2 \text{ }\mu\text{m}$ under an accelerating voltage of 15 kV. As such, it has found use with various authors in the literature.^{69,75,92}

For the purposes of comparison with other phases and determination of the growth or loss of any particular element, the aluminium peak serves as an internal standard. The loss of aluminium for samples is assumed to be very minimal as the vapour pressure of aluminium containing gases ($\text{Al}_2\text{O}_{2(g)}$, $\text{AlO}_{2(g)}$, $\text{Al}_{(g)}$, $\text{Al}_2(g)$) is either low or thermodynamically unfavourable under the reaction conditions used.^{48,51,93} As such, all raw counting data of all elements has been normalised to Al by scaling the data so that the Al count of a sample is the same as the greatest Al count in a set of samples.

Compositional data related to carbon in samples was not determined as most samples were coated in carbon and anchored and earthed to the SEM stub using carbon tape. Averaged EDS data presented in this thesis was determined using the mean of the results of at least 5 different spot analyses.

3 Potassium Geopolymer-Graphite Composites

3.1 Introduction

Graphite was chosen as a source of carbon for the carbothermal reduction and nitridation process in a continuation of the previous work.⁸⁷ The original goal was to utilise the conclusions from the previous study to synthesise a geopolymer-composite capable of forming a product with a high yield of β -sialon. Using the proposed reaction scheme (Equation (24)), several mixtures were formulated with the express purpose of ascertaining the stoichiometric amount of carbon necessary to achieve between 95 – 100% conversion to β -sialon. These samples were fired at 1400 °C for 10 hr and analysed.

From these experiments, one composition was subsequently chosen to explore the reaction mechanism by firing the composite mixture at 1200 °C, 1300 °C and at 1400 °C for between 0 – 24 hr in flowing nitrogen. A sample was also fired in flowing argon to ascertain the effect of carbon in a non-nitriding atmosphere. Finally, a control sample prepared without the addition of carbon was also fired at 1400 °C to determine the effect, if any that a lack of carbon would have.

3.2 Results

3.2.1 Synthesis of Potassium Geopolymer-Graphite Composites

Potassium geopolymers including graphite (hereafter called potassium-graphite composites) and a non-graphite containing control were readily synthesised using graphite-clay mixtures and the prepared potassium silicate solution without the use of any additional water or additives. The resulting potassium-graphite composite pastes were more viscous than the control sample but retained good workability. Vibration of samples caused the release of entrained air bubbles from the control sample but had little effect on composite pastes, likely due to their greater viscosity.

Upon treatment at 40 °C for 24 hr, all samples were observed to set and harden to form monolithic solid materials. Weight loss during this process was not monitored. Control samples were chalk white in appearance whereas the potassium-graphite composites could be distinguished by their lustrous grey colour. All samples appeared both internally and externally homogeneous on visual inspection.

All monoliths were hard and strong and could not be broken or scratched by hand. While measurements were not made on the differences in density between samples, it is known from previous work that the inclusion of graphite causes composites to have a lower density than geopolymer controls and reduces the compressive strength.⁸⁷ All samples were pulverised using a concussion mortar before being ground by hand and passed through a 150# mesh with openings of $\sim 105\ \mu\text{m}$. No appreciable difference between the hardnesses of the control and the composites were noted during grinding.

In all, five samples were prepared for study; a control sample lacking graphite and four composites with varying graphite contents of 1.0, 1.1, 1.2 and 1.3 times the stoichiometric quantity of carbon as required by Equation (24). The non-carbon containing control sample was designated K0 while the graphite composites were designated K1.0-G, K1.1-G, K1.2-G and K1.3-G with increasing carbon content.

When analysed by X-ray diffraction (XRD), the only observed difference between the patterns (Figure 3.1) of the composites and the control was the appearance of reflections corresponding to graphite at 26.6, 54.7 and 77.5°. Reflections due to cristobalite and quartz stem from unreacted materials present in the halloysite clay starting material.

The addition of graphite into the geopolymer pastes was seen to have no effect on samples when analysed by infrared (IR) spectroscopy. The resulting spectra (Figure 3.2) show vibrational bands characteristic of geopolymeric materials⁹⁴⁻⁹⁷ which included a dominant, broad band comprising the Si-O-T asymmetric stretches between 1250 and 900 cm^{-1} , T-OH bends (873 cm^{-1}), Si-O-T bends (696 cm^{-1}), Si-O-T symmetric stretches (588 cm^{-1}) and Si-O-T rocking modes (444 cm^{-1}). The small, sharp peaks at 797 and 779 cm^{-1} are bands also observed in the reference spectrum of the dehydroxylated halloysite and indicate the presence of a small amount of unreacted clay in the geopolymer. Here, T represents either Si or Al in a tetrahedral environment. The Si-O-T asymmetric stretch band had a maximum at 1020 cm^{-1} which can be associated SiQ^2 environments. Shoulders at 1081 and 873 cm^{-1} were assigned to SiQ^3 and SiQ^1 (silanol (Si-OH) terminal groups), respectively.

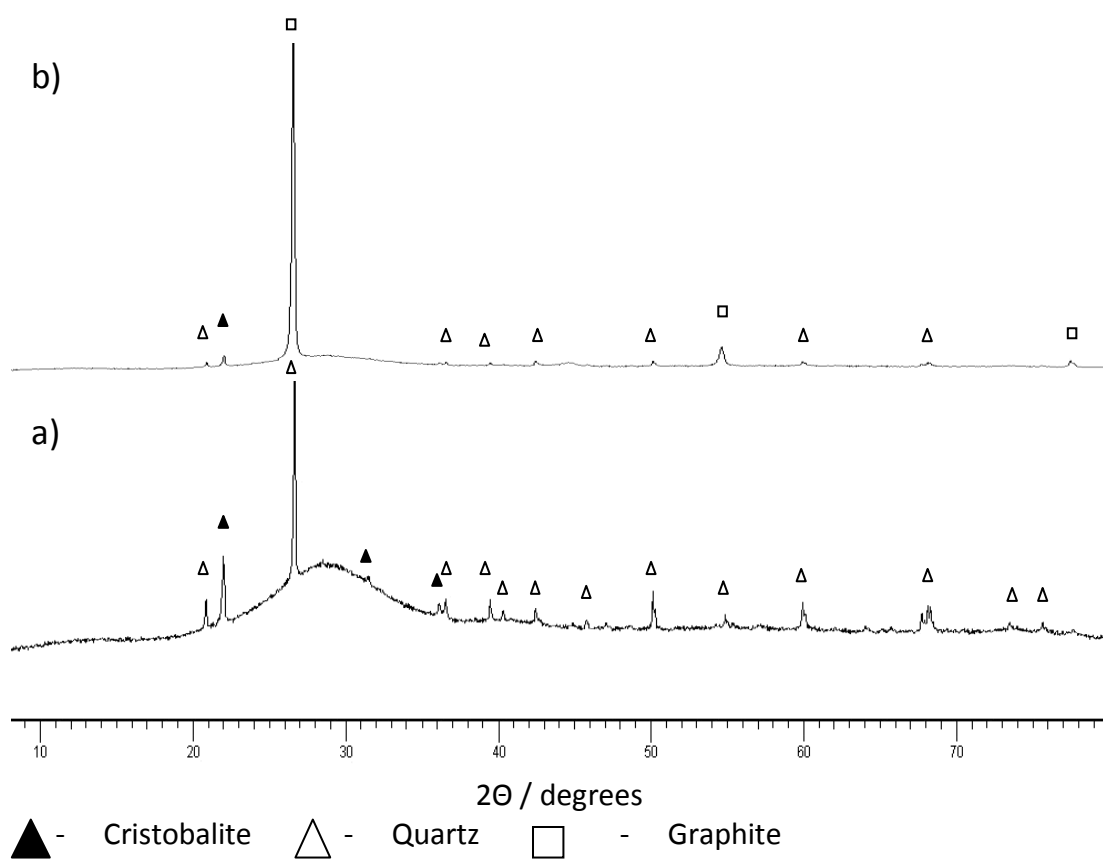


Figure 3.1: XRD patterns of a) K0, the control sample and b) the K1.0-G potassium-graphite composite.

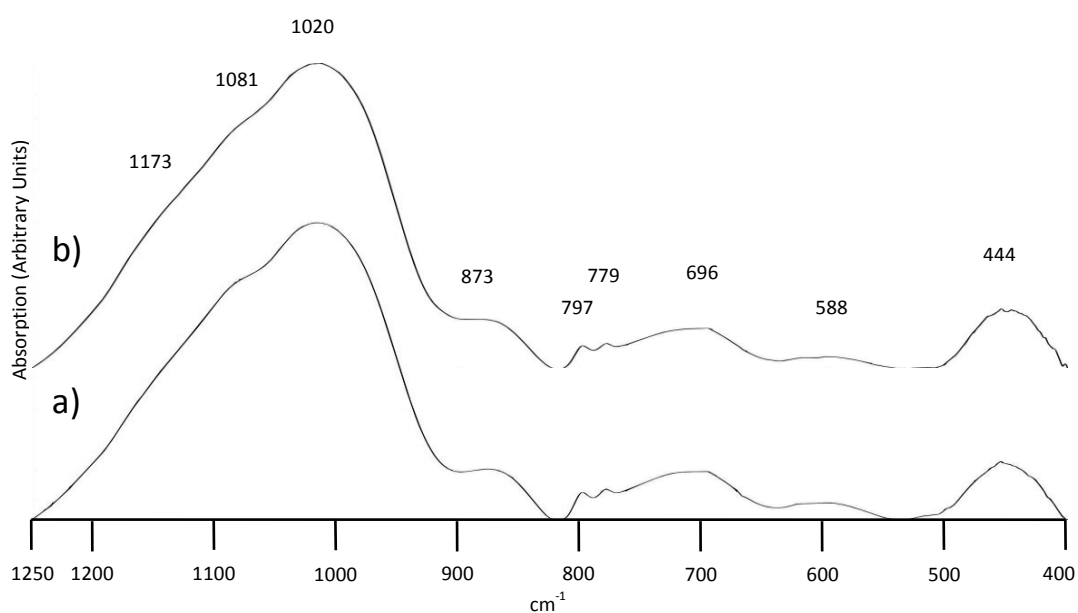


Figure 3.2: IR spectra of a) the unfired K0 control sample and b) the K1.0-G potassium-graphite composite.

This broad band shows the large degree of cross-linking with-in the geopolymer and indicates a heterogeneous system with a mixture of bonding environments.⁹⁶ The presence of the unreacted silica phases was seen by the observation of an absorption shoulder at $\sim 1170\text{ cm}^{-1}$.

Backscattered images and energy dispersive X-ray spectroscopy (EDS) maps of ground, unfired K1-G (Figure 3.3) show that the intimacy of mixing between the geopolymer matrix (brighter particles) and graphite (darker particles) is relatively poor and only small quantities of graphite remain encased in the matrix after grinding. The graphite was not homogeneously dispersed throughout the sample and tended to sit between larger geopolymer particles. The geopolymer matrix on the other hand appeared very homogeneous and silicon- or aluminium-rich regions were not observed. The results of an EDS spectrum taken at 100x magnification indicates that the compositional ratios of K1.0-G were very close to the expected values (Table 3.1).

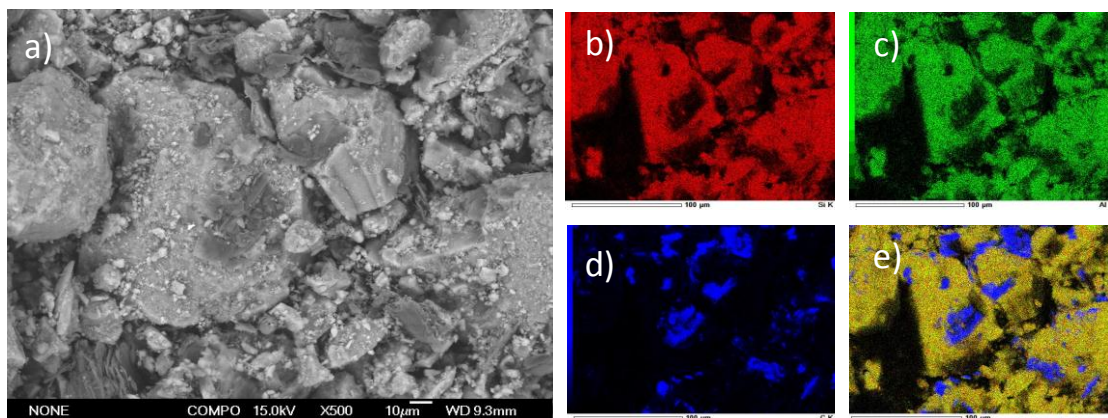


Figure 3.3: a) Backscattered SEM image of ground, unfired K1.0-G with b) silicon, c) aluminium and d) carbon EDS maps and e) their overlay.

Table 3.1: EDS elemental analysis of unfired K1.0-G at 100x magnification

Sample	Atom %				Si/Al Ratio	K/Al Ratio
	K	Si	Al	O		
K1.0-G	15.12	31.43	15.58	37.87	2.02	0.97

3.2.2 Firing of Samples with Varying Graphite Content

To determine the effect of carbon on the potassium geopolymers, the K0 control sample was fired at 1400 °C in flowing nitrogen to establish a baseline for comparison. Figure 3.4 shows the resulting XRD pattern which indicates that, as intended, upon firing to elevated temperatures, the potassium geopolymer formed well crystallised leucite with no apparent residual amorphousity.

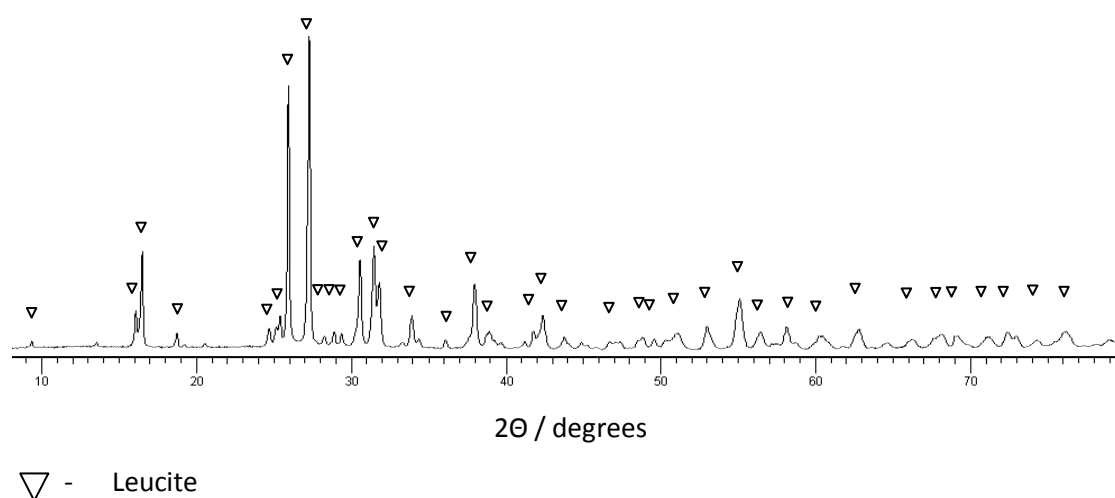


Figure 3.4: XRD pattern of the K0 control sample fired in flowing nitrogen at 1400 °C for 10 hr.

The IR spectrum of the resulting crystalline leucite is shown in Figure 3.5. When compared with its unfired precursor (Figure 3.2a), the main Si-O-T asymmetric band is observed to broaden and shift to lower wavenumbers. This is caused by the change in the potassium from a charge balancing cation in the geopolymer matrix to a network modifier as the potassium is incorporated into the atomic structure of leucite. Further changes observed are the disappearance of the T-OH band (873 cm^{-1}) and small peaks at 797 and 779 cm^{-1} . These differences indicated that dehydroxylation had occurred that the unreacted halloysite had been incorporated into the new phase, respectively. The growth of the Si-O-T bending modes ($800 - 650\text{ cm}^{-1}$) and rocking bands (433 cm^{-1}) was also observed. The formation of peaks at 635 , 605 , 540 , 519 and 482 cm^{-1} is attributed to four- and six-membered rings of tetrahedra in the leucite structure and to lattice vibrations,^{98,99} indicating that a crystalline phase has been produced.

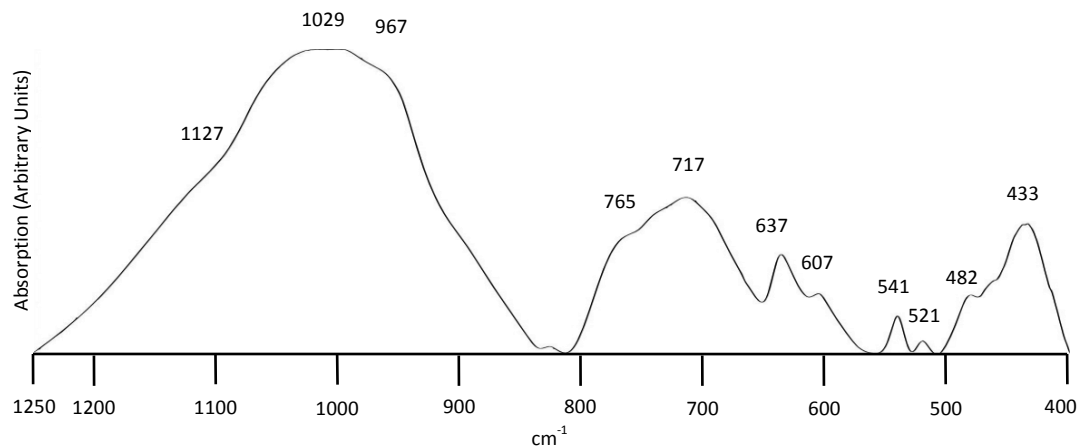


Figure 3.5: IR spectrum of the K0 control sample fired at 1400 °C for 10 hr in flowing nitrogen.

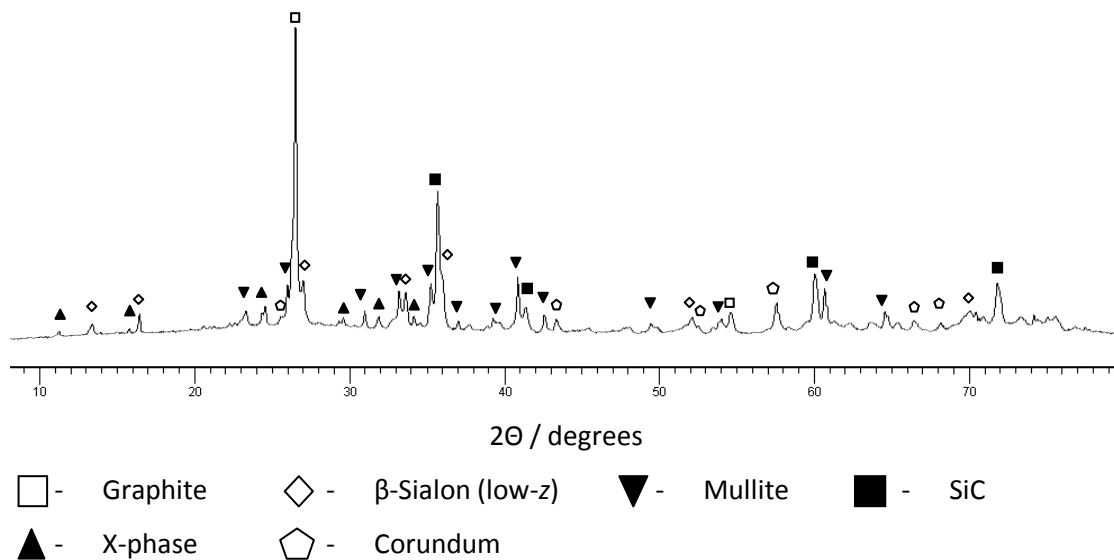


Figure 3.6: XRD pattern of the K1.0-G sample fired in nitrogen at 1400 °C for 10 hrs.

To explore the effect of varying the carbon content, samples were fired at 1400 °C for 10 hr in flowing nitrogen. The XRD results of these firings, represented in Figure 3.6, show that after firing, the graphite-composites were composed of varying quantities of mullite, X-phase sialon, β-Sialon, SiC, corundum (α -Al₂O₃) and graphite. A small amount of amorphous phases were also observed by a broad hump centred at ~28°. Rietveld modelling indicated that the z-values of the β-sialon phases formed were very low, with all samples having calculated z-values of between 0.1 – 0.2. However, the observation of a broad shoulder at ~32.7° suggests a distribution of z-values and that some high aluminium content

β -sialon phases were also being present. These phases could not be modelled due to their low abundance and diffuse nature.

Figure 3.7 is a semi-quantitative representation of the constituent phases of fired composites and shows that despite the increasing graphite content, the phase assemblage of samples was very similar.

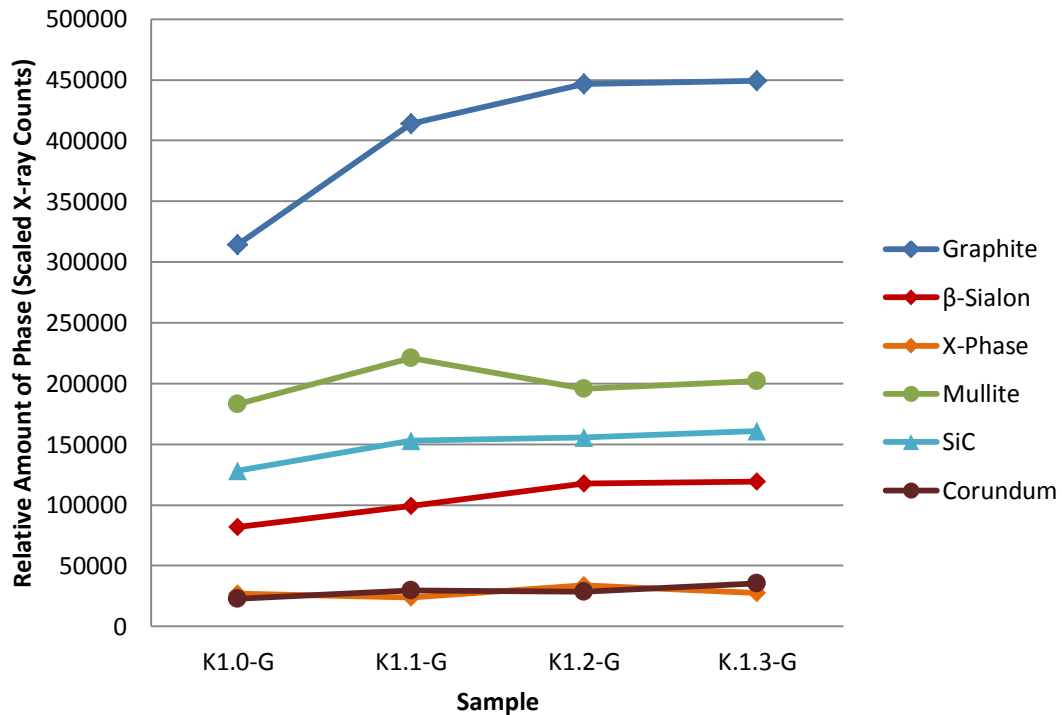


Figure 3.7: Semi-quantitative representation of the phases detected by XRD in potassium-graphite composites with varying carbon content fired in nitrogen at 1400 °C for 10 hr.

The IR spectrum of K1.0-G (Figure 3.8) shows that fired composites sample form broad, diffuse spectra due to the large number of overlapping absorption bands from the various vibrational modes of the components of the multiphasic product. Nevertheless, comparison the XRD results, use of reference spectra and examination of the literature provides sufficient detail for reasonable assignment of major observed absorbance bands.

Silicon nitride phases can be distinguished using IR by the presence of 6 distinct vibrational modes, labelled $\nu_6 - \nu_1$ with decreasing wavenumber. The $\nu_6 - \nu_4$ modes are Si-N stretching modes whereas the $\nu_3 - \nu_1$ absorbance bands are associated with Si-N-Si and N-Si-N bending modes. Only 5 modes are present in the 1250 – 400 cm^{-1} range with the ν_1 mode occurring at $<400 \text{ cm}^{-1}$.^{91,100} The substitution of Al into the Si_3N_4 phase causes all

modes to shift to decreasing wavenumbers with increasing z -value.^{91,101} Added complexity arises when silicon oxynitride phases or X-phase are present as they display similar vibrational modes. However, the different symmetries and compositions of the phases results in the shifting, convergence or disappearance of these vibrational modes with additional modes also being observed.¹⁰²⁻¹⁰⁴

In the spectrum below, the peaks at 1036, 944 and 898 cm^{-1} are attributed to the ν_6 , ν_5 and ν_4 stretching modes of β -sialon, respectively. The shoulder at 1170 cm^{-1} indicates the presence of a siliceous phase, presumed to be amorphous silica due to the lack of crystalline SiO_2 in the corresponding XRD pattern. The peaks at 995, 740, and 460 cm^{-1} are likely a combination of the Si-O-T asymmetric stretching and bending modes of mullite and the amorphous phase while the peak 439 cm^{-1} may be a combination of the Si-O-T and Si-O-Si rocking modes of mullite, silica and the amorphous phase with the ν_2 mode of β -sialon. The small peak at 635 cm^{-1} is thought to be an octahedral Al-O stretch of corundum from comparison to the reference spectrum. As this stretch occurs at the same location as one of the ring/lattice vibrations of leucite, it could also indicate the presence of some unreacted leucite not detected by XRD. The sharp peak at 570 cm^{-1} is attributed to octahedral Al-O stretches from mullite¹⁰⁵ which obscures the ν_2 Si-N mode.

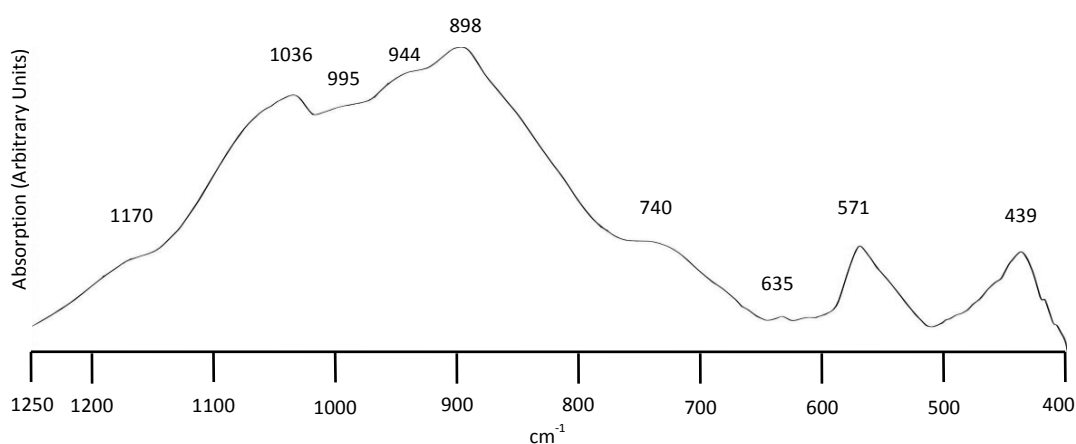


Figure 3.8: IR spectrum of K1.0-G fired at 1400 °C for 10 hr in flowing nitrogen.

These results indicated that the reaction to synthesise β -sialon was only partially complete and additional time was required for full reaction. To explore the reaction mechanism and improve β -sialon yields, the sample K1.0-G was chosen for further investigation using firings with varying temperature, duration and flowing gas atmosphere.

Despite having the lowest yield of nitrogenous phases, K1.0-G was chosen as a lower stoichiometric quantity of carbon would help avoid complications due to the formation of over-reacted phases such as 15R-sialon, AlON and AlN in firings of longer duration.

3.2.3 Reaction Sequence of Potassium-Graphite Composites

The development and reaction mechanism of potassium-graphite composites was investigated in a series of firings of K1.0-G samples in flowing nitrogen. The pre-synthesis behaviour was determined by firing samples at progressively greater temperatures of 1200, 1300 and 1400 °C for without isothermal holds while the CRN reaction mechanism was investigated by firings of varying duration between 1 – 24 hr at the synthesis temperature of 1400 °C. For comparison, a sample was also fired in flowing argon at 1400 °C for 10 hr. The resulting fired products were characterised by of XRD, IR spectroscopy, ^{27}Al and ^{29}Si solid state nuclear magnetic resonance (NMR) and also examined using SEM with complimentary EDS analysis.

3.2.3.1 Observations and Weight Loss

Upon firing, all samples were observed to sinter and densify regardless of firing temperature, with samples fired at higher temperatures for longer durations being the most sintered and hardest to grind. In many cases, large cracks were observed in the densified powder compacts but no consistency in this behaviour was established. Samples changed from the initial charcoal grey colour to a pale grey colour, becoming progressively lighter in colour with increased reaction time. This change in colour was more pronounced in samples fired for 4 hr or more at 1400 °C. Most firings at 1400 °C saw the formation of small deposits of white whiskers on samples, firing boats and at the downstream end of the firing tube outside the hot-zone. These observations suggest the liberation of SiO due to the decomposition of samples during firing. The formation of glassy rings either side of the hot-zone of the firing tube was also observed.

Weight losses during firing were recorded for all samples and the results are shown in Figure 3.9. Initial weight loss in the pre-synthesis region was low, at about 12%, and is

attributed to the loss of free water in the composite powder and subsequent dehydroxylation. Weight loss increased dramatically once synthesis temperature of 1400 °C was reached but the rate of loss decreased with increased holding time, resulting in an overall loss of 58.0% after 24 hr. Weight loss in this region is attributed to the loss of CO, SiO and K vapour.

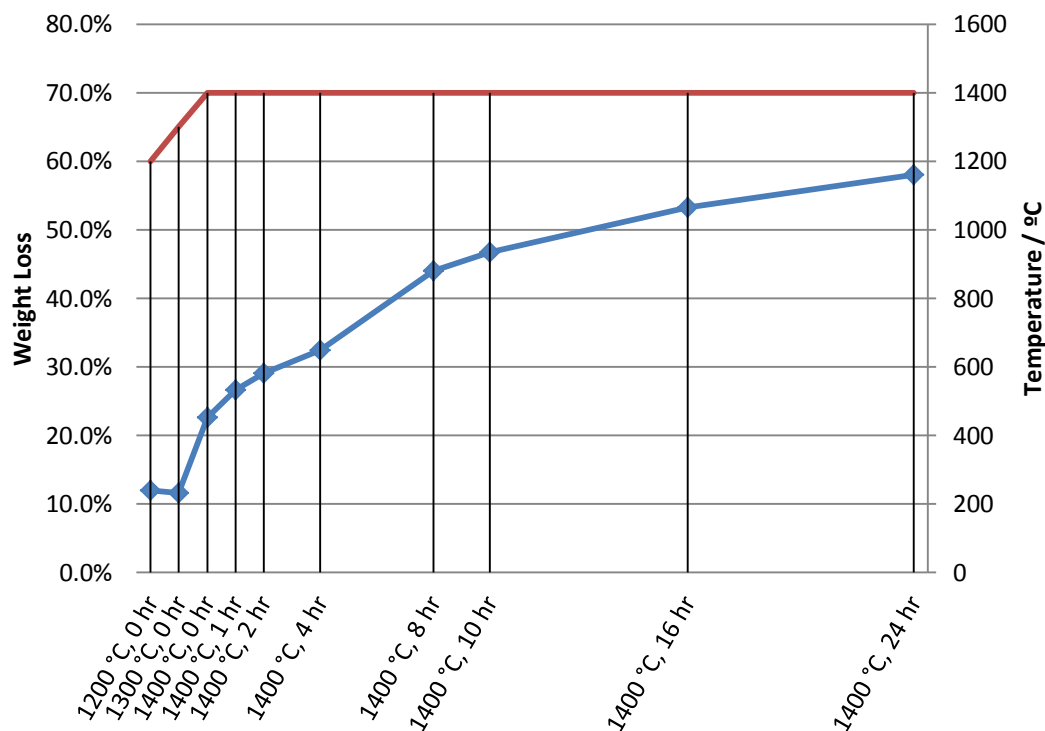


Figure 3.9: Weight loss of K1.0-G samples fired at progressively higher temperatures for varying durations. The red line indicates the temperature.

3.2.3.2 X-Ray Diffraction Studies

The appearance and disappearance of crystalline phases was monitored using X-ray diffraction studies. The pre-synthesis XRD results are shown in Figure 3.10. Upon firing to 1200 °C, the amorphous geopolymer crystallised, having incorporated the unreacted quartz and cristobalite phases to form a leucite-graphite composite. This leucite composite remained stable up to the sialon synthesis temperature of 1400 °C, where a trace amount of SiC was observed.

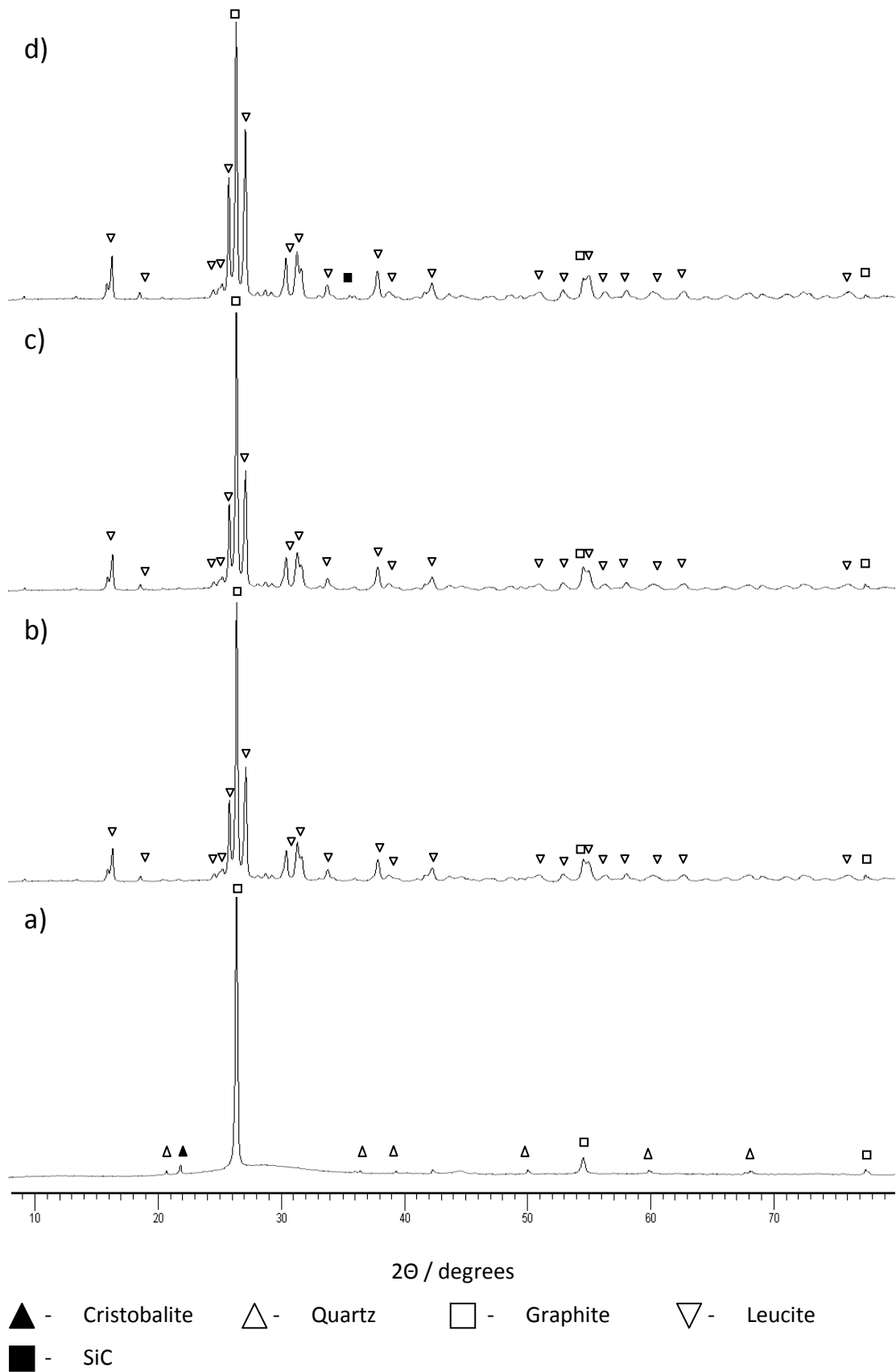


Figure 3.10: XRD patterns of K1-G: a) Unfired, b) 1200 °C, 0 hr, c) 1300 °C, 0 hr and d) 1400 °C, 0 hr.

The XRD results of the CRN synthesis firings are shown in Figure 3.11 while the semi-quantitative analysis is shown in Figure 3.12. It can be seen that after 1 hr of firing, the quantity of leucite declined with the formation of mullite and trace quantities of X-phase and corundum. Of these new phases, SiC and mullite grew with the continued decline of leucite after 2 hr while the quantity of X-phase and corundum stabilised. The formation of a low z-value β -sialon phase was detected after 4 hr of firing and after 8 hr, leucite had completely disappeared with the reappearance of an amorphous phase with a small, broad hump centred at 25° observed. Little difference is seen after 10 hr with a slight growth of the β -sialon phase, mullite and SiC. After 16 hr, mullite and SiC had achieved their relative maximum contents, with a significant decrease in graphite and increase in the quantity of β -sialon. The longest firing carried out had an isothermal hold duration of 24 hr and showed the further decline of graphite, SiC and mullite with a dramatic increase in the intensity of corundum. A small quantity of another phase, assigned as γ -alumina, was detected after 4 hr of firing and remained present in near constant quantity throughout the reaction.

Despite the decline in mullite after 24 hr of firing, the peak at 33.3° grows in intensity and broad peaks are noted at 51.5 and 69.5° (indicated by the red arrows). The changes in these three diffuse peaks indicate the formation of higher z-value β -sialon phases, most likely a result of the conversion of X-phase. Rietveld modelling of the most intense β -sialon peak indicates phases with z-values between 0.1 – 0.2, similar to the samples with varying carbon content.

The presence of new phase was also detected at 16 hr of firing, with additional peaks observed at 20.6 , 34.5 and 39.0° . With the exception of the peak at 34.5° , a tentative assignment of β -quartz is proposed, due in part to the uncharacteristic height of the peak at 26.2° where the major peak of β -quartz would overlap with the most intense peak of mullite. The presence of SiO_2 in the system is not unexpected, however, the crystallisation of SiO_2 as β -quartz is. This is due to two reasons; firstly, SiO_2 is usually observed in the literature as either amorphous silica or, if crystallised, as cristobalite, and secondly, β -quartz is the meta-stable, high temperature form of quartz which typically converts to α -quartz below 573°C .¹⁰⁶ This may therefore indicate that of some aluminium or potassium has been dissolved into the silica allowing the retention of the meta-stable β -quartz structure.

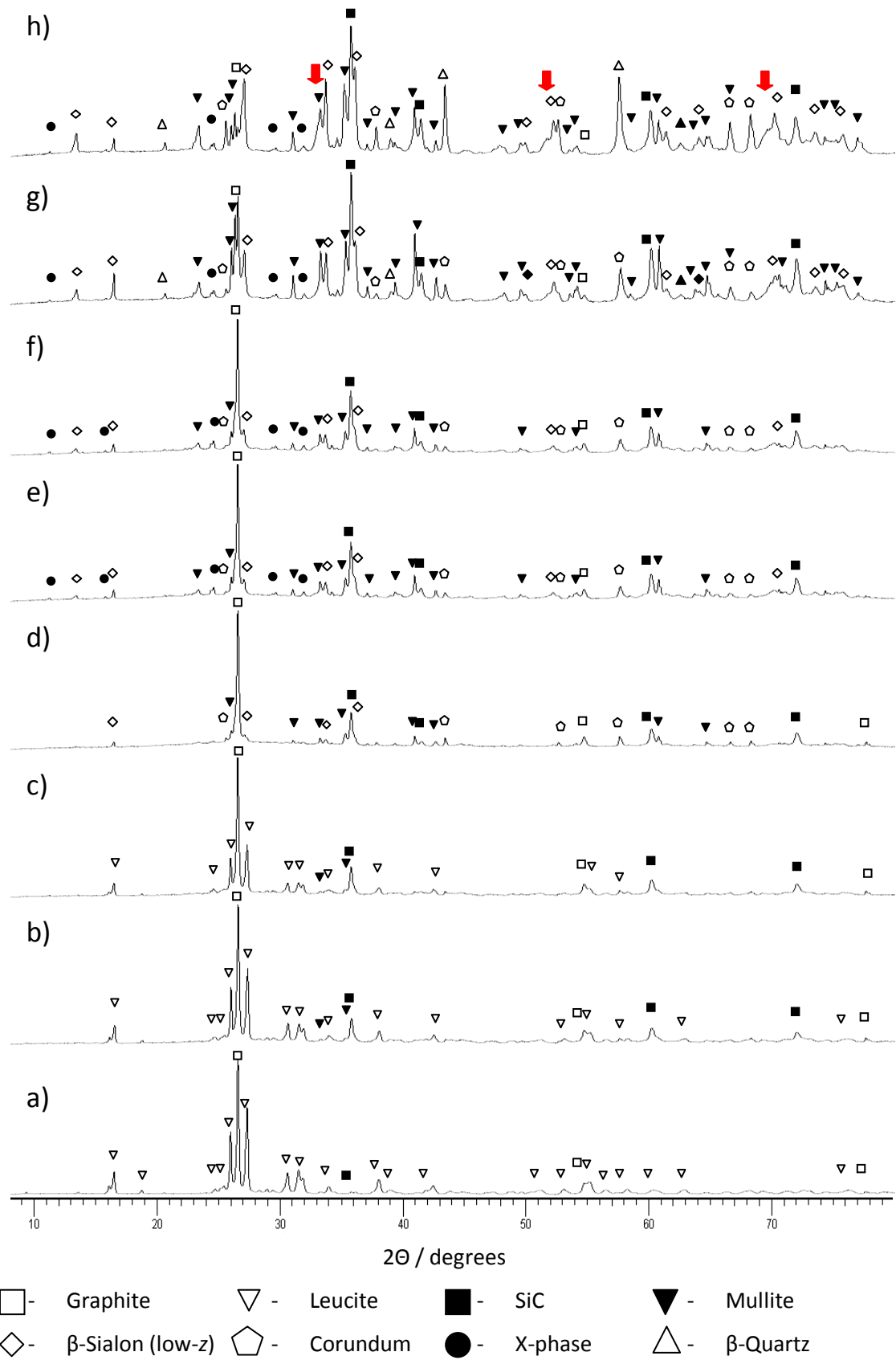


Figure 3.11: XRD patterns of K1-G samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr, f) 10 hr, g) 16 hr and h) 24 hr. The red arrows indicate a broadening of peaks caused by a distribution of higher z-value β -sialon.

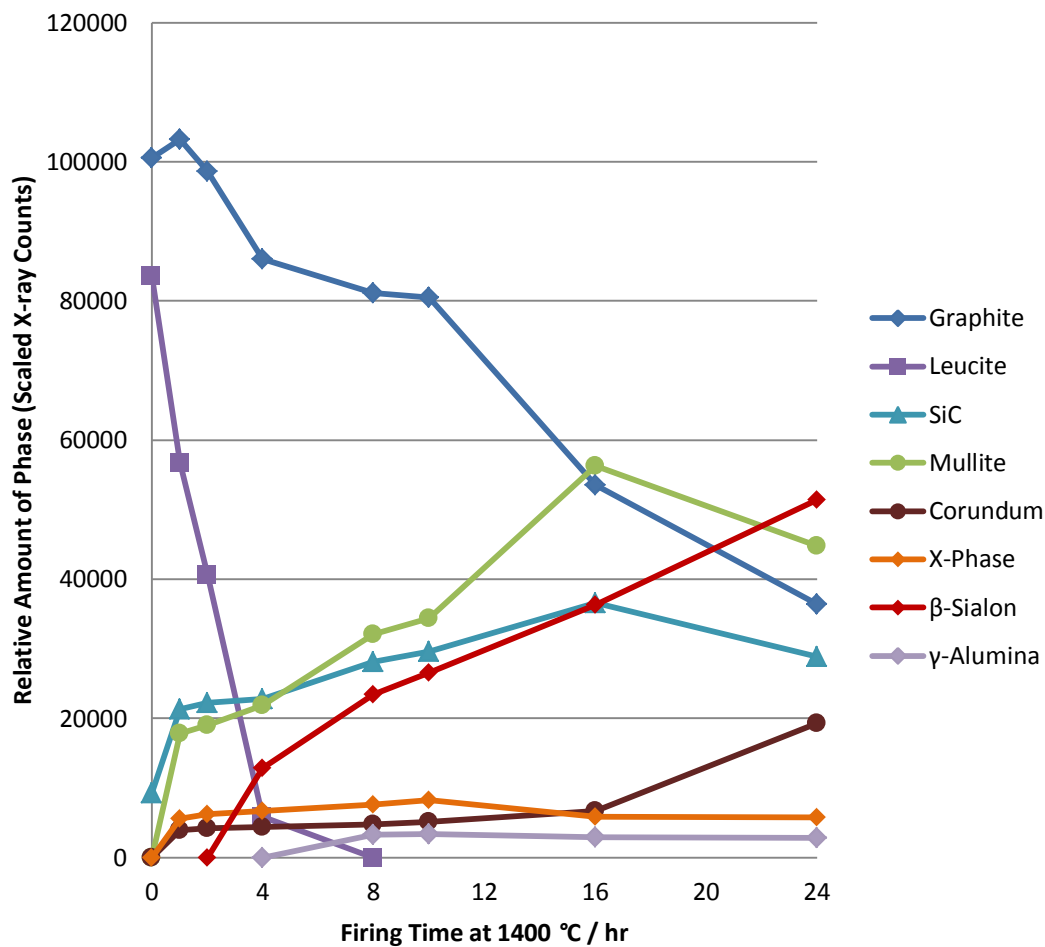


Figure 3.12: Semi-quantitative representation of the phases detected by XRD in K1.0-G samples fired in nitrogen at 1400 °C for various times.

It can be seen from the diffraction pattern at 24 hr (Figure 3.11h) that the reaction to synthesise β -sialon is incomplete with many intermediaries still present in the fired product. When considered against examples in the literature, incomplete reaction after this length of firing is indicative of a very slow reaction rate and it is unlikely that full reaction would be achieved for some time yet. This is further evidenced by the slow weight loss and the semi-quantitative analysis which suggests that the quantity of graphite is only about two-thirds reacted. Additional evidence of incomplete reaction is the lack of any decomposition phases such as AlON, 15R-polytype or AlN, although they would not necessarily be expected in a 1.0 stoichiometric mixture.

3.2.3.3 Infrared Spectroscopy

As with the XRD patterns, the IR spectra are presented in two figures. Figure 3.13 shows the spectra from the pre-synthesis firings compared to the unfired potassium-graphite composite while Figure 3.14 shows the firings carried out at 1400 °C.

Upon heating to 1200 °C, the main asymmetric Si-O-T band broadened with the disappearance of the T-OH shoulder, indicating that dehydroxylation had occurred. A significant growth in the Si-O-T bends (764 and 714 cm^{-1}) and Si-O-T rocking modes (432 cm^{-1}) was also seen. The formation of peaks at 635 , 605 , 540 and 519 cm^{-1} are attributed to the four- and six-membered rings of tetrahedra in the leucite structure or to lattice vibrations.^{98,99} The disappearance of the peaks at 797 and 779 cm^{-1} suggests that the unreacted halloysite was incorporated in to the leucite structure before reaching pre-synthesis temperatures. The spectra of samples heated to 1300 and 1400 °C showed little difference from the sample heated to 1200 °C indicating good thermal stability and suggest near complete crystallisation of the leucite phase.

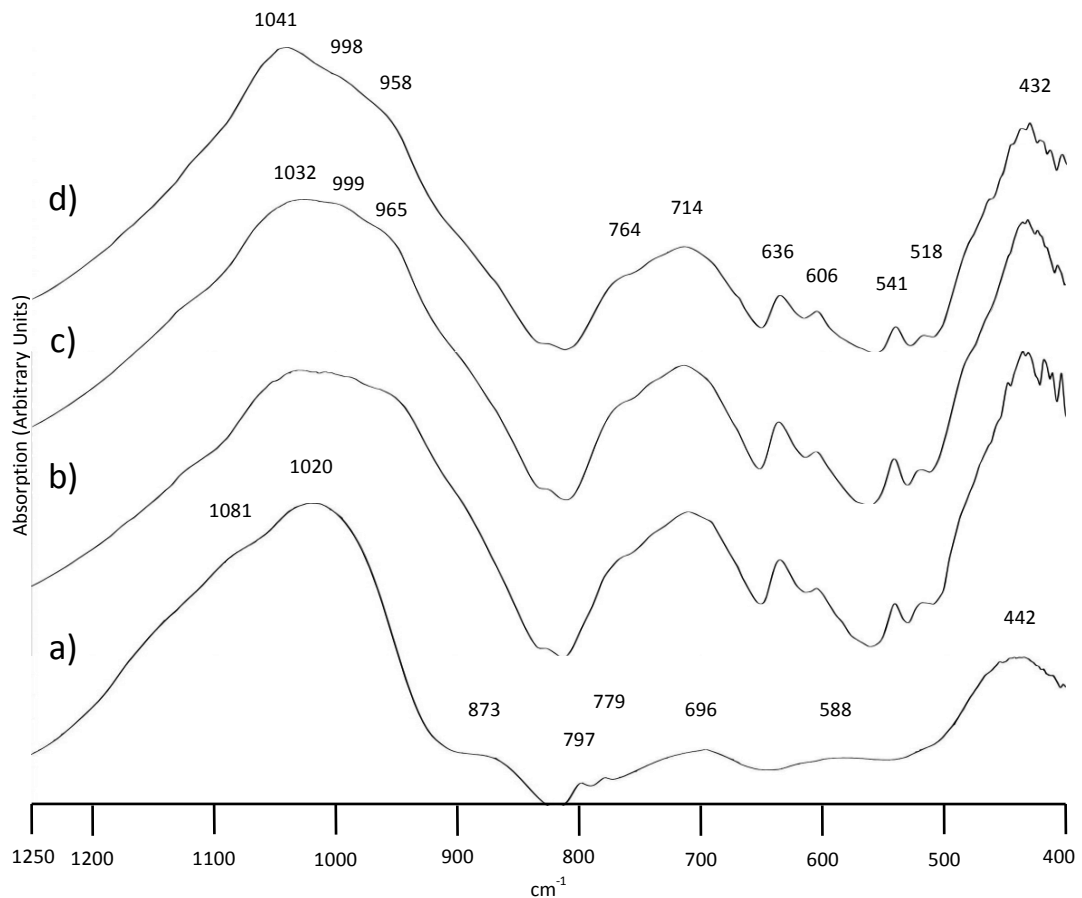


Figure 3.13: IR spectra of K1.0-G sample: a) Unfired, b) 1200 °C, 0 hr, c) 1300 °C, 0 hr and d) 1400 °C, 0 hr.

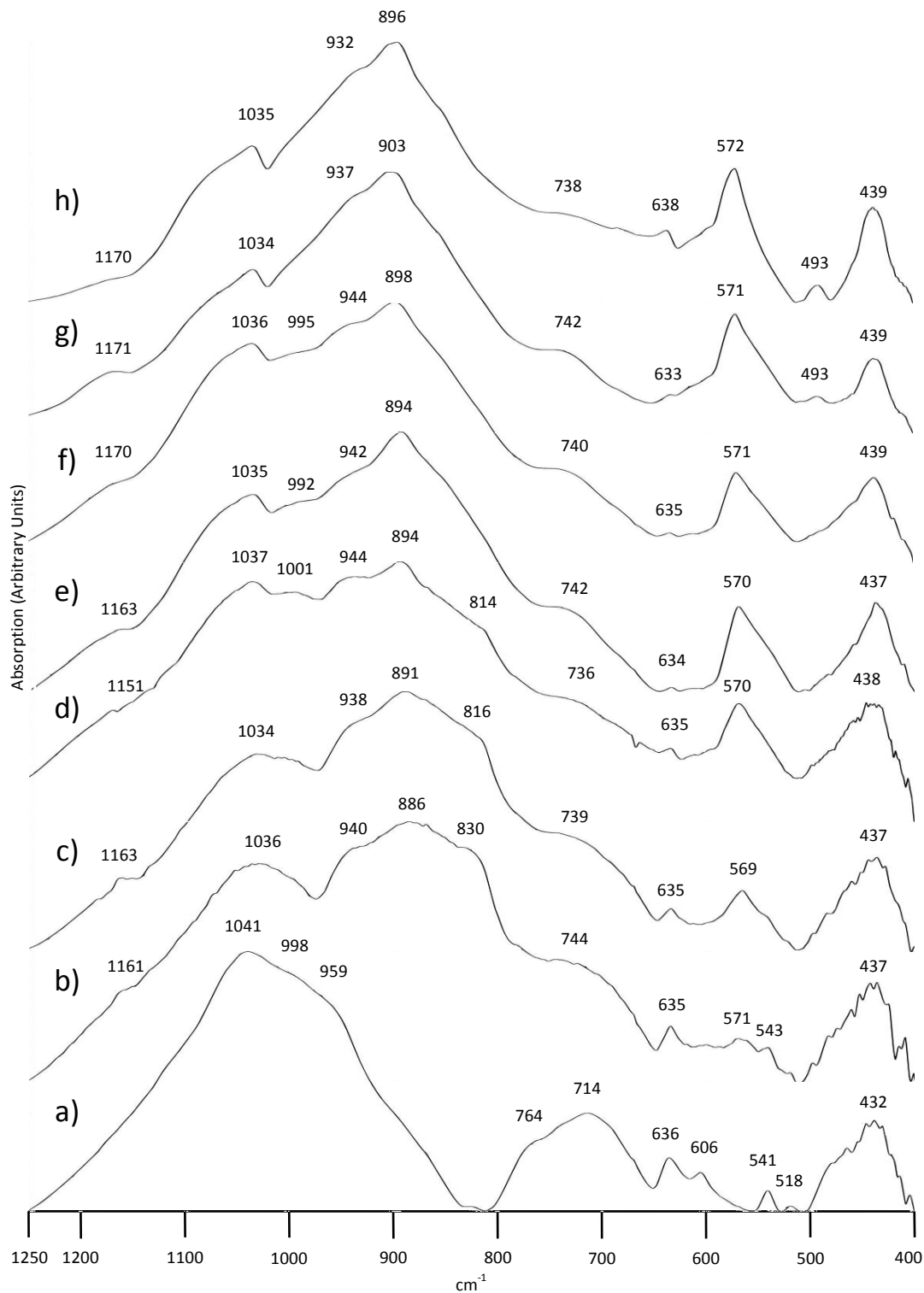


Figure 3.14: IR spectra of K1-G samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr, f) 10 hr, g) 16 hr and h) 24 hr.

Significant changes in the spectra were observed during firing at the synthesis temperature of 1400 °C. After 1 hr, the presence of three new bands between 950 and 800 cm^{-1} was observed with a shoulder at 743 cm^{-1} . These bands were broad and occurred in an

ambiguous region and may indicate a range of new vibrational modes but are most likely tetrahedral Al-O out-of-plane stretches, tetrahedral Al-O in-plane stretches and Si-C stretches, based on the presence of SiC and mullite in the corresponding diffraction pattern. The shoulder at 743 cm^{-1} was assigned to tetrahedral T-O-T in-plane bending modes.¹⁰⁵ The main Si-O-T band was observed to narrow and shift to a slightly higher frequency of 1036 cm^{-1} . A new peak at 1163 cm^{-1} was observed indicating the formation silica while a reduction of intensity of the ring/lattice peaks at 635, 606 and 543 indicated the loss of leucite. The emerging peak at 570 cm^{-1} was attributed to the octahedral Al-O stretches of mullite.

After 2 hr, little difference was noted with the exception of the shift of the Si-C stretching band to 816 cm^{-1} and the growth of the silica Si-O stretching band with the further decline of the peaks associated with leucite. The formation of β -sialon was observed after 4 hr of firing with the emergence of the ν_6 , ν_5 and ν_4 bands at 1037, 944 and 891 cm^{-1} , respectively. These assignments are ambiguous due to these bands occurring in the same locations as the Si-O-T asymmetric stretches and the tetrahedral Al-O in- and out-of-plane stretches and as such are likely a combination of overlapping bands. As leucite was no longer detected by XRD, it is thought that the peak at 635 cm^{-1} was caused by the formation of corundum in the material.

The bands corresponding with mullite and β -sialon were seen to intensify with longer isothermal holds of 8 and 10 hr. Firings of samples to 16 and 24 hr saw the disappearance of the peak at 995 cm^{-1} , relative decrease in intensity of the shoulder at 740 cm^{-1} and narrowing of the peak at 570 cm^{-1} . These subtle changes may indicate the decline of mullite with the further emergence the ν_3 and ν_2 modes of β -sialon also located around 570 and 439 cm^{-1} . A new peak at 493 cm^{-1} could not be assigned to any phase and is therefore thought to be a result of the β -quartz observed in the XRD patterns of these firings. The flattening of the section between $700 - 630\text{ cm}^{-1}$ in the sample fired for 24 hr is thought to be caused by the growth of a broad octahedral Al-O stretch from corundum. Despite the overlapping bands, estimations from the ν_3 and ν_2 bands at 572 and 439 cm^{-1} were in good agreement and indicated a β -sialon material with a low z-value of ~ 0.6 , slightly higher than the XRD result.

3.2.3.4 Solid State Nuclear Magnetic Resonance

To follow the changes and formation of new bond types and investigate the presence of any non-crystalline phases, magic angle spinning solid state nuclear magnetic resonance was carried out on samples fired at pre-synthesis temperatures and also those fired at 1400 °C for up to 10 hr.

The ^{27}Al spectra of the sample fired to 1200 °C (Figure 3.15a) showed a resonance at 58.1 ppm and a trace resonance at 2.9 ppm, corresponding to tetrahedral and octahedral Al-O bonding environments, respectively. The tetrahedral resonance at 58.1 ppm is typical of conventional geopolymers, leucite and mullite, all of which occur between 53 – 59 ppm meaning that these phases cannot be distinguished by ^{27}Al NMR.^{107,108} The AlO_6 resonance at 2.9 ppm may stem from unreacted halloysite in the geopolymer. As the temperature

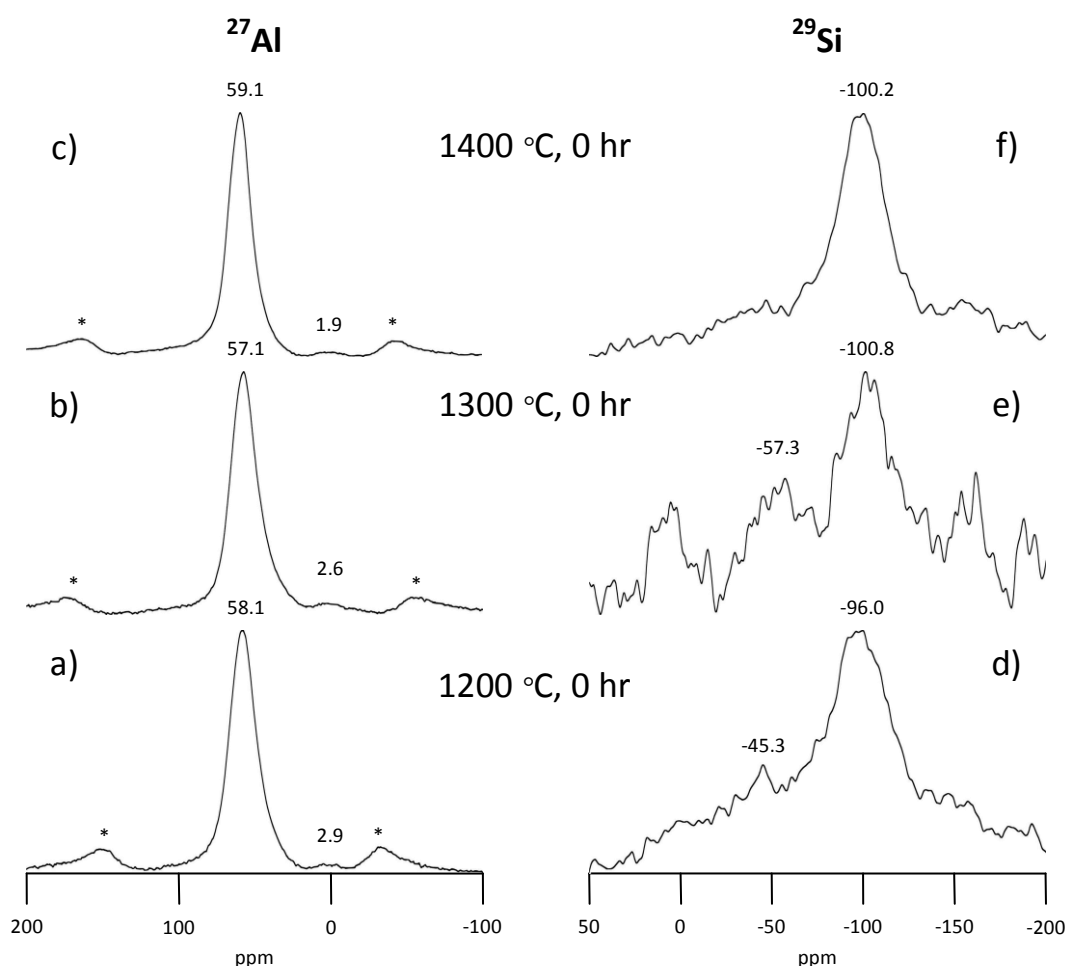


Figure 3.15: ^{27}Al and ^{29}Si NMR spectra of K1.0-G samples fired at varying temperatures without isothermal holds. *Denotes spinning side bands.

increased to 1400 °C, no change was observed in the location of either of the tetrahedral or octahedral resonances (Figure 3.15c) indicating good thermal stability of the material.

Firings at 1400 °C show that after 1 hr (Figure 3.16b), the octahedral resonance grew slightly and shifted downfield to 7.0 ppm. This value is slightly outside the 0 – 5 ppm range where mullite is typically observed but is concordant with other studies of halloysite and kaolinite clays undergoing CRN to form sialon.⁴¹ Between 2 and 4 hr, the octahedral resonance grew and shifted gradually to 11.5 ppm with a small upfield shift in the tetrahedral resonance to 53.0 ppm (Figure 3.16c and Figure 3.16d). This shift in the octahedral peak is attributed to the formation of corundum, the intensity of which may overlap the mullite peak. A third resonance at -1.0 ppm was also noted at 8 hr and is tentatively assigned as the AlO_6 resonance of X-phase despite being slightly outside the reported range of 0.05 – 2.8 ppm.^{21,22} At no stage were Al-N bonds detected, the resonances of which are expected at ~60 ppm.¹⁰⁸

The ^{29}Si spectra of fired samples are generally of poor quality, owing to the difficulty in obtaining good NMR data due the characteristic broadening of silicon materials and the long and greatly varying relaxation time of ^{29}Si . After firing to 1200 °C, the SiO_4 resonance centred about -93 ppm had broadened and showed multiple peaks, behaviour typical of leucite which may show up to 8 spectral features.¹⁰⁷ With further firing, the spectra continued to contain a similar SiO_4 resonance but the other observed features could be assigned with much confidence until the spectra of the sample fired at 1400 °C for 10 hr. The spectra of this sample showed distinct resonances at -12.6 ppm, -47.9 ppm and -101.7 ppm which can be assigned to SiC, Si_3N_4 materials and SiO_4 environments, respectively.^{41,108}

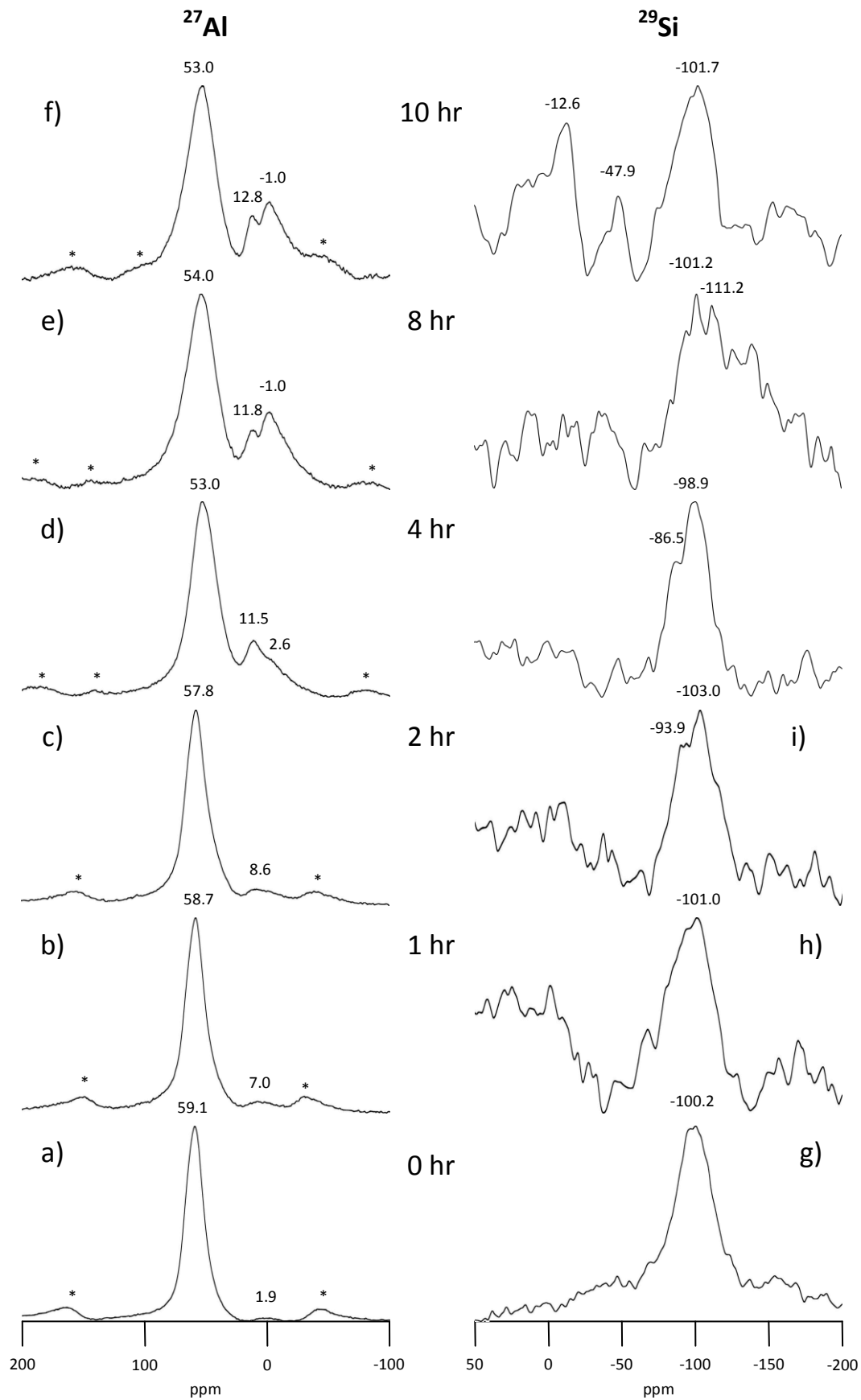


Figure 3.16: ^{27}Al and ^{29}Si NMR spectra of K1.0-G samples fired in nitrogen at 1400 °C for varying durations. *Denotes spinning side bands.

3.2.3.5 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Scanning electron microscopy (SEM) was utilised in the present study to investigate a number of features of geopolymer-composites during sialon synthesis (1400 °C, 0 – 24 hr) including: the intimacy and homogeneity of carbon distribution throughout the composite, microstructural morphology before and during reaction, the evolution of fibrous materials during reaction. Both backscatter and secondary electron imaging were used. Energy-dispersive X-ray spectroscopy (EDS) was also carried out to characterise the elemental make-up of materials. Due to its use as a coating and earthing material, the quantity of carbon was not analysed except for relative abundances in limited cases. The elemental compositions of samples were determined by EDS carried on samples at either 100 or 200x magnification.

Figure 3.17 shows the results normalised to Al, tracking the relative changes in the abundances of K, Si, O and N between samples. During the first hour a significant reduction in the amount of potassium and oxygen is observed, showing the volatilisation of potassium via carbothermal reduction of leucite. After this initial loss, the loss of both elements stabilises and decreases at a steadier rate across the rest of the firings. Potassium was no longer detected after 24 hr of firing. Nitrogen is only positively detected after 10 hr of firing,

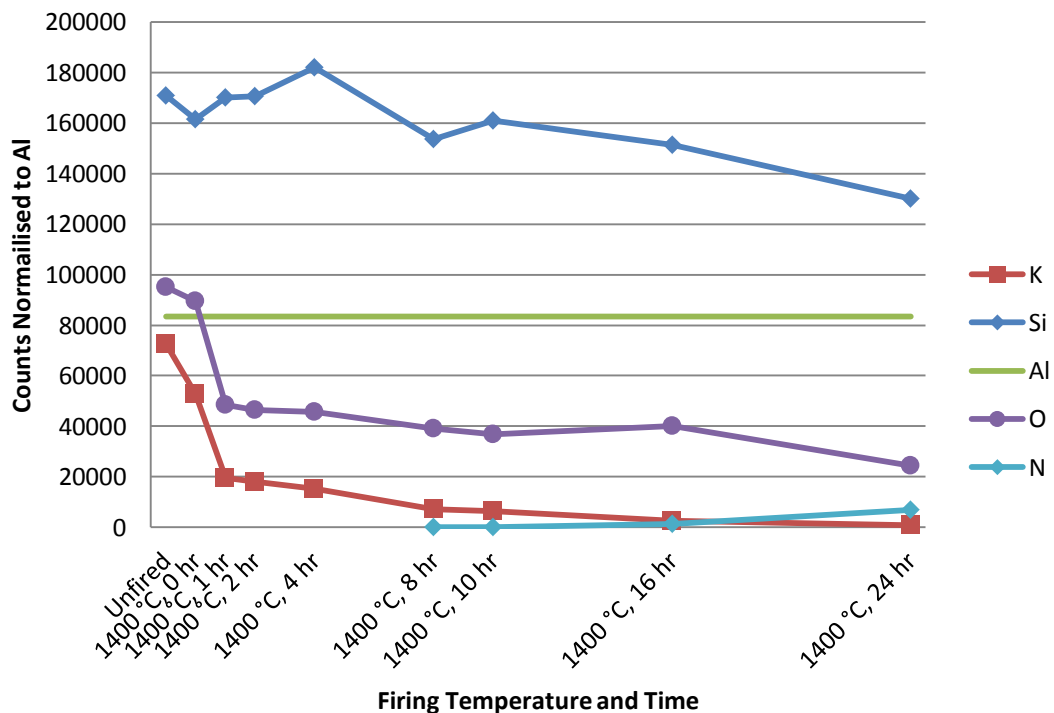


Figure 3.17. Normalised elemental counts of K1.0-G samples fired at 1400 °C between 0 – 24 hr compared to the unfired sample.

despite the presence of β -Sialon according to XRD after 8 hr. This is likely caused by the much stronger overlapping peaks of carbon and oxygen either side of the nitrogen peak limiting its detection.

Figure 3.18 shows a backscattered image of a K1.0-G composite fired to 1400 °C without an isothermal hold. The presence of both the aluminosiliceous and graphite phases are apparent as lighter and darker particles respectively. These images reveal that the intimacy of mixing is reasonably poor, with the two phases appearing rather separate. Graphite is mostly excluded from the aluminosiliceous phases and very little graphite is bound inside the matrix.

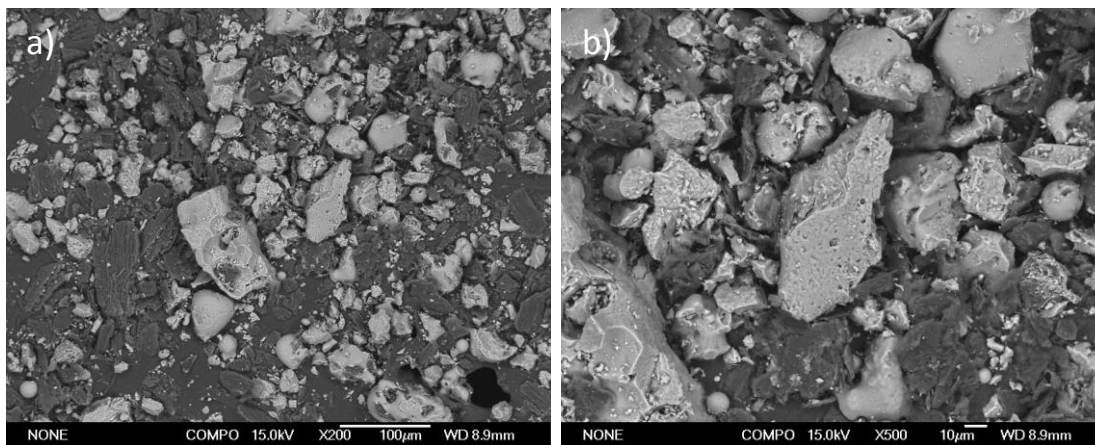


Figure 3.18: Backscattered SEM images of K1.0-G fired at 1400 °C of 0 hr at a) 100x and b) 500x magnifications. Lighter particles are the potassium aluminosilicate phase whereas the darker particles are graphite.

Also apparent was the presence of particles with rounded morphologies and smooth surfaces (Figure 3.19a and b), indicating sintering of the aluminosiliceous phase. Fractured particles revealed internal structures containing residual closed porosity and rougher surfaces (Figure 3.19c and d). The averaged results of 6 spot EDS spectra taken of the rounded and fractured particles in Figure 3.19 are shown in Table 3.2. It can be seen from these results that there are differences in the elemental make-up of the two-particles, with the rounded particle being SiO_2 rich compared to the fractured, rougher particle. This compositional variation is the likely cause of the different morphologies as SiO_2 rich potassium aluminosilicates are predicted to be less thermal stable than aluminium rich compositions from the phase diagram (Appendix B) and will sinter at lower temperatures. The theoretical Si/Al ratio of stoichiometric leucite is 2.

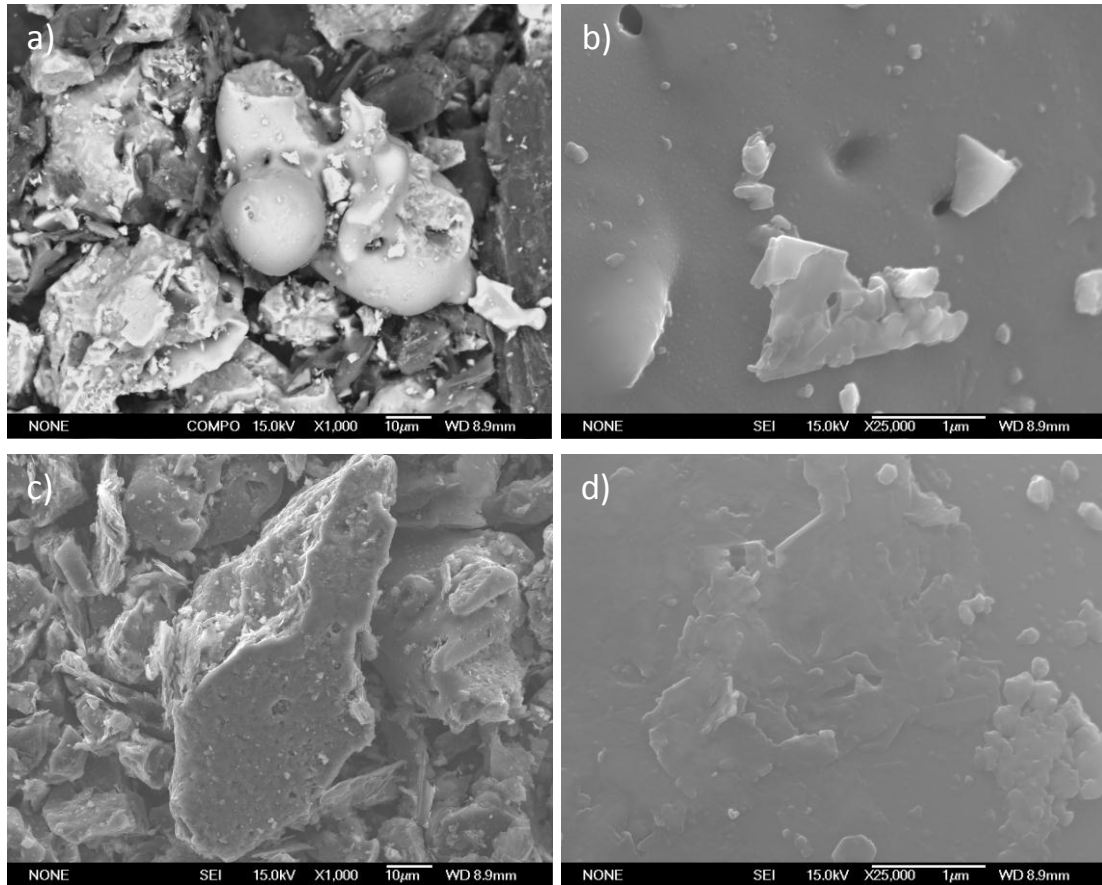


Figure 3.19: SEI images of a) a sintered, spherical particle with b) its smooth, non-porous surface and c) a porous, fractured particle with d) its rougher surface topography.

Table 3.2: Averaged spot EDS elemental analysis of certain particles compared to overall value of sample

Particle	Atom %				Si/Al Ratio
	K	Si	Al	O	
Fractured	14.36	32.84	25.02	37.78	1.55
Spherical	9.66	34.52	13.47	42.35	2.56
Overall	11.98	32.28	16.95	38.79	1.90

As the reaction proceeded, the morphology of particles was observed to change subtly with the porosity of particles increasing and the development of rougher surfaces covered in small debris. This transformation is shown in Figure 3.20. Smooth, sintered particles were noted in all samples but a gradual decrease in their presence was observed with increasing firing duration.

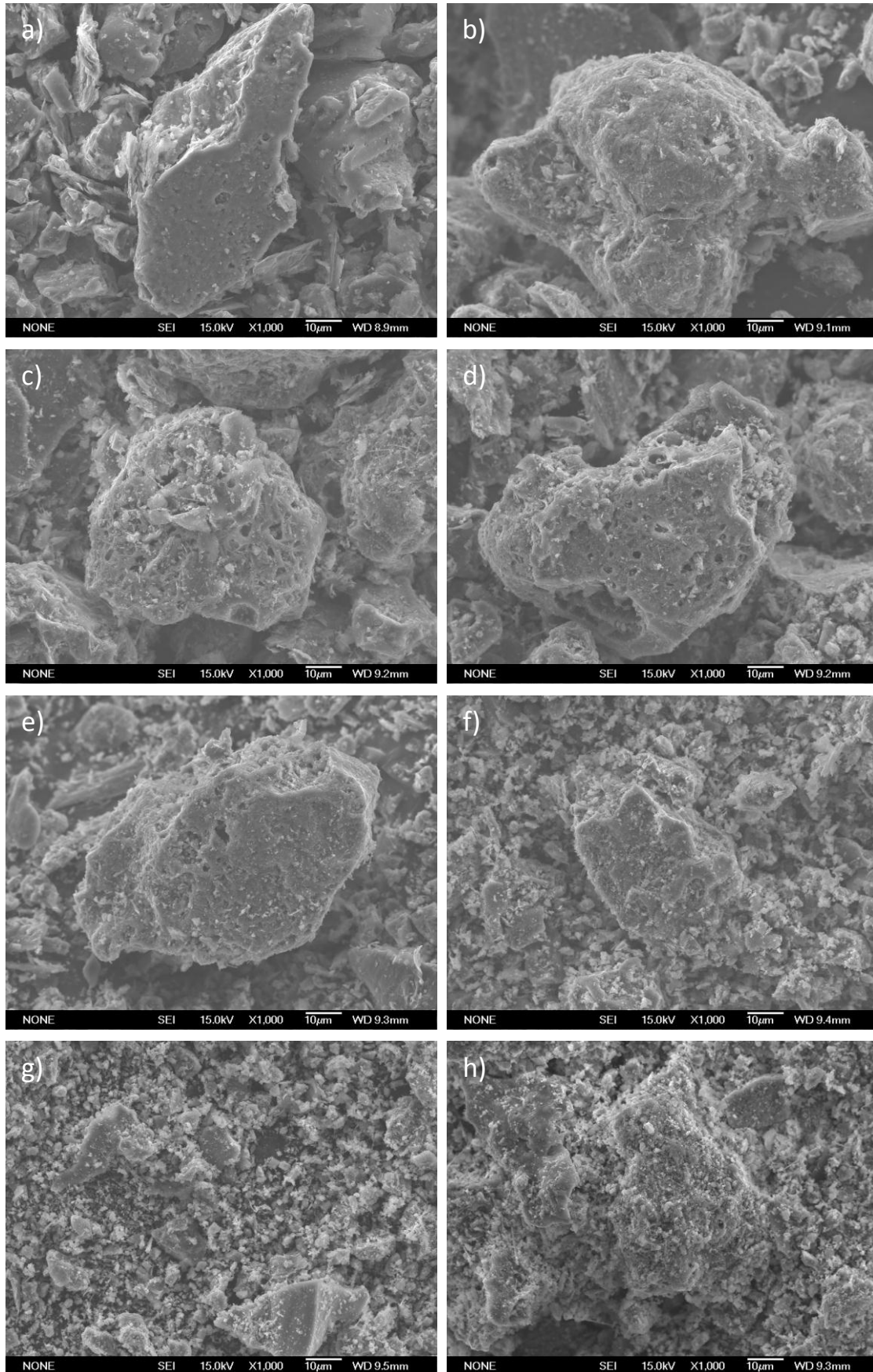


Figure 3.20: Selected SEI images for K1.0-G samples fired at 1400 °C for a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr, f) 10 hr, g) 16 hr and h) 24 hr. Magnification is 1000x.

The presence of significant quantities of nano-scale whiskers and fibres was observed in samples fired for 1 hr or more (Figure 3.21). These elongated particles had widths ranging from several hundred nanometres to $\sim 1.5 \mu\text{m}$ and considerable aspect ratios with many examples having lengths in the 1 – 10 μm range. The literature identifies these fibres as either α - or β - Si_3N_4 depending on reaction conditions.^{48,51} These fibres were generally observed to grow in length and abundance with increasing time. Spot EDS analysis and elemental mapping (Figure 3.22) show the whiskers to be β -sialon with calculated z-value of almost 1, which is greater than the XRD and IR results.

Examination of the tips of these fibres did not reveal the presence of melted agglomerates. This suggests that despite the presence of potassium vapour during firing, these were fibres formed via a vapour-solid (VS) mechanism rather a vapour-liquid-solid (VLS) mechanism.

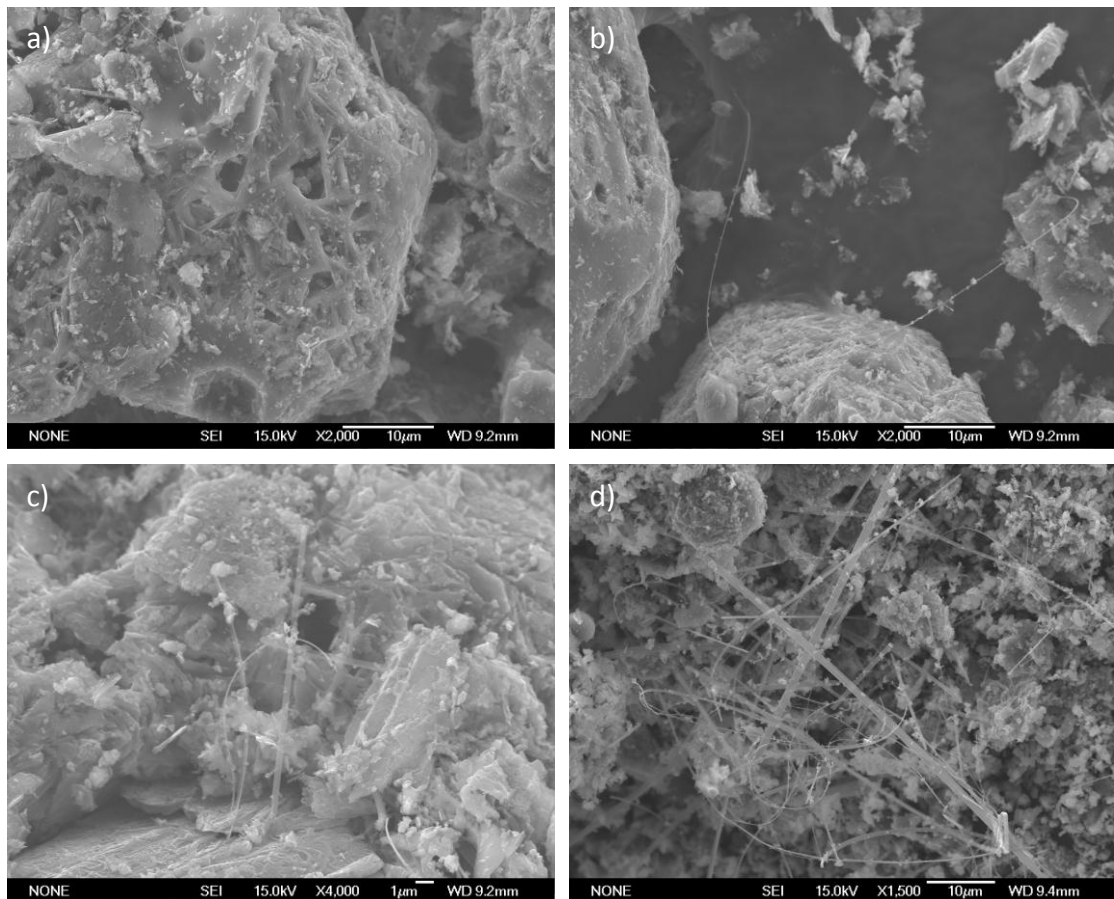


Figure 3.21: Selected SEI images of porous structures and nano- and micro-sized whiskers from various firings, a) and b) 1400 °C, 2hrs, c) 1400 °C, 4hrs, d) 1400 °C, 24hrs.

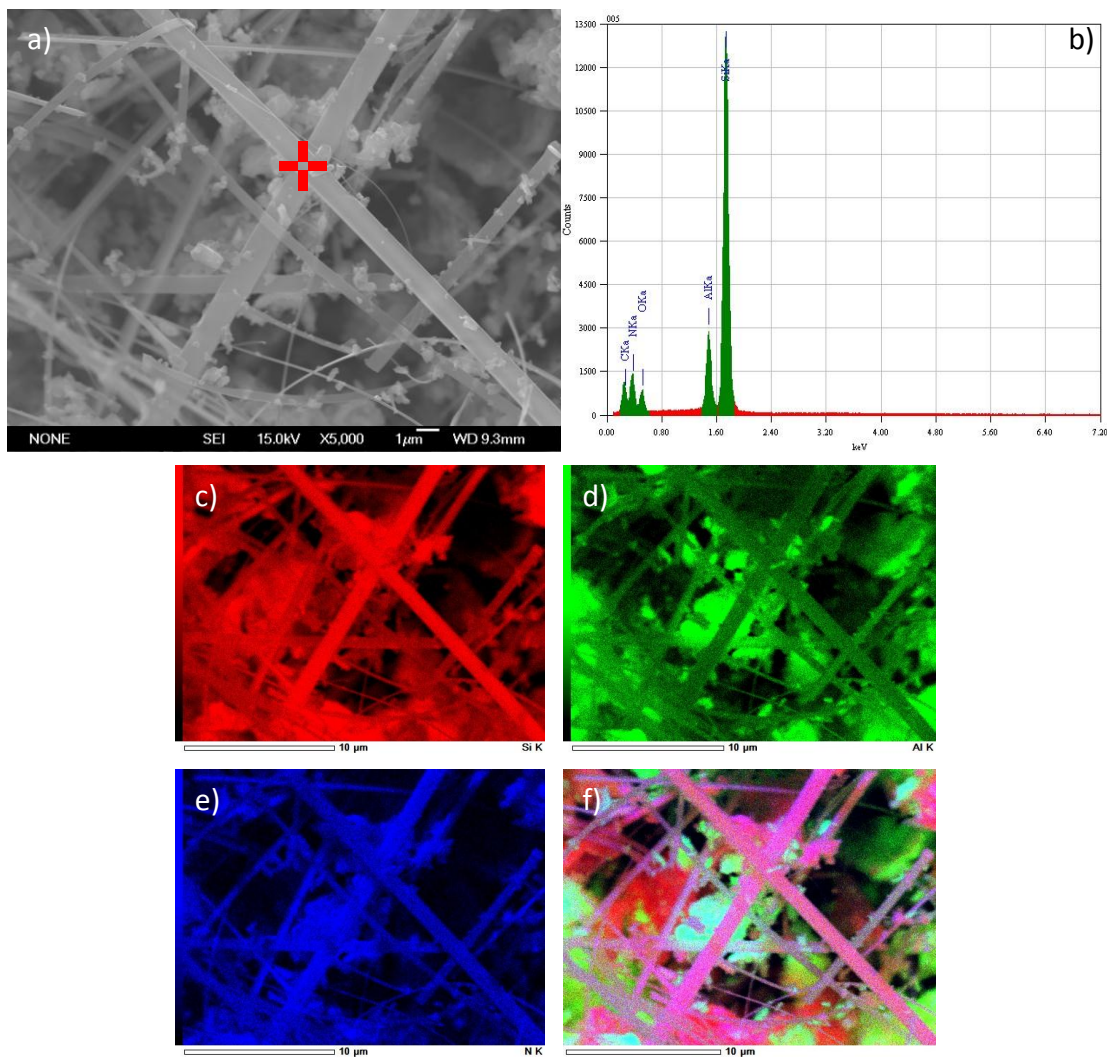


Figure 3.22: a) SEI image of nano- and micro-sized whiskers with EDS spot marked in red. b) Spot EDS results showing the elements Si, Al, O and N with the c) silicon, d) aluminium and e) nitrogen EDS maps and f) their overlay shown below.

3.2.3.6 Firing under Argon

From the results of the EDS compositional analysis, it can be seen that progressive firing of the potassium-graphite samples in nitrogen caused the gradual loss of potassium. To ascertain whether simultaneous nitridation of the materials was required to cause this loss, a K1.0-G sample was fired in a flowing argon atmosphere at 1400 °C for 10 hr.

The XRD pattern (Figure 3.23) was comprised of a mixture of SiC, corundum, graphite and mullite, with a trace amount of γ -alumina but no crystalline potassium bearing phase. The IR spectrum, shown in Figure 3.24, contained a dominant peak at 808 cm^{-1} which was attributed to SiC stretches and several peaks from corundum, with octahedral Al-O observed

at 637 and 588 cm^{-1} and octahedral Al-O bends observed at 490 and 447 cm^{-1} . The presence of mullite was determined by the Si-O-T asymmetric stretching band at 1043 cm^{-1} and the Si-O stretching band at 924 cm^{-1} .¹⁰⁵ The octahedral Al-O stretches and Si-O-T bending band overlap with the Al-O stretches and bends of corundum.

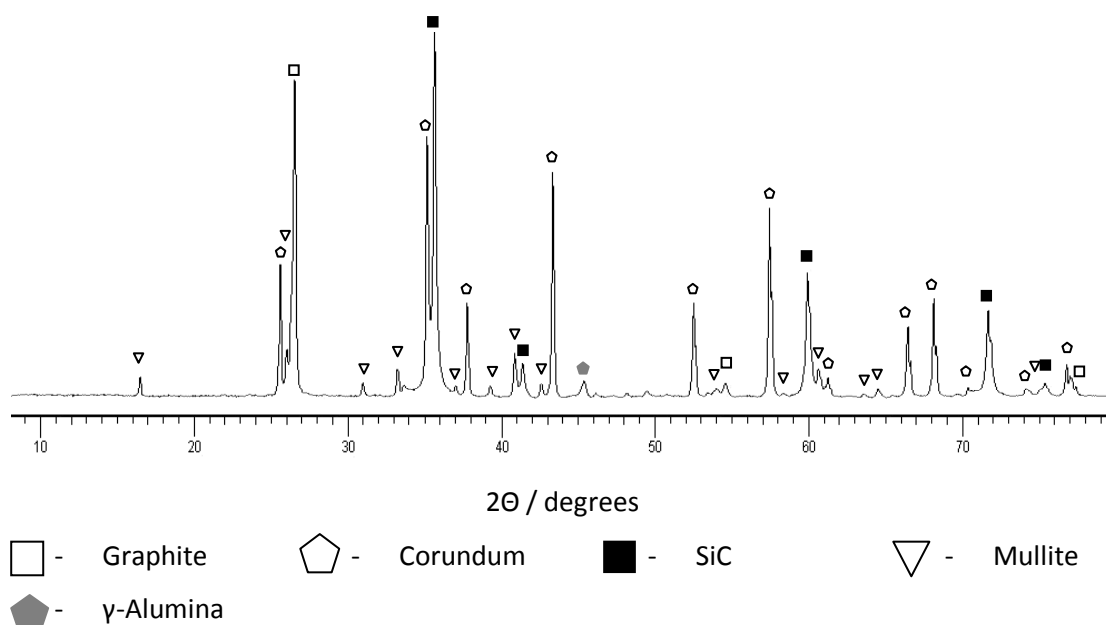


Figure 3.23: XRD pattern of K1.0-G sample fired at 1400 °C for 10 hr in flowing argon.

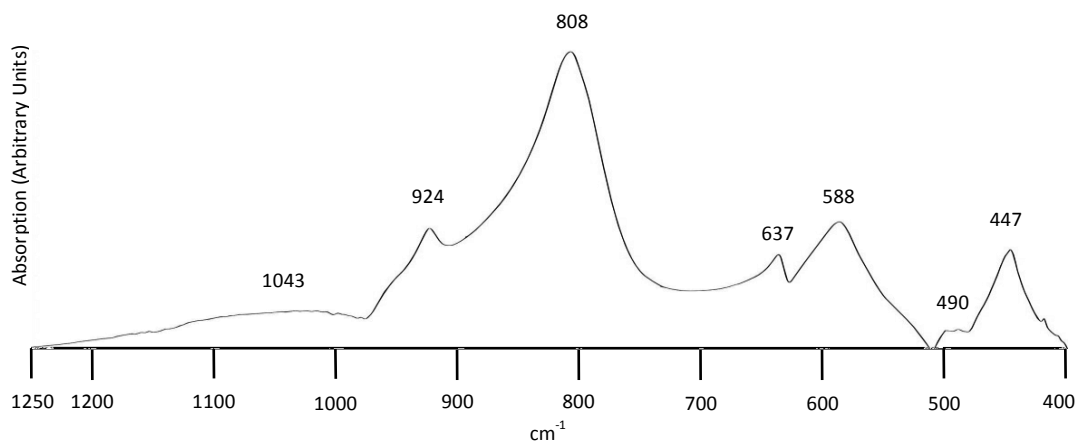


Figure 3.24: IR spectrum of K1.0-G sample fired at 1400 °C for 10 hr in flowing argon.

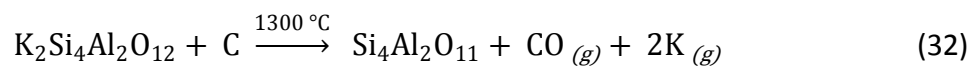
These results indicate that the loss of potassium is driven by the carbothermal reduction of the potassium-graphite composite and may occur independently of any nitridation processes. Both of these processes occur however, in the same temperature regions and will occur simultaneously.

3.3 Discussion

3.3.1 Carbothermal Reduction and Volatilisation

When fired at 1400 °C for 10 hr, the geopolymer control sample dehydroxylated and crystallised into leucite showing that the composition used was thermally stable and does not normally spontaneously decompose under the firing temperatures used in these experiments. Upon firing to temperatures below 1400 °C, potassium geopolymer-graphite composites were observed to form materials comprised solely of leucite and graphite. These materials were thermally stable up to at least 1300 °C, after which they begin to react with the loss of potassium. This reaction was determined to occur in the absence of nitrogen and is therefore a product of strictly carbothermal reduction (CR) processes and may occur independently from CRN reactions. As these processes cause the loss of potassium however, they are distinct from aforementioned CR processes (Equations (15) and (16)) and for ease of differentiation will be referred to as carbothermal reduction and volatilisation, abbreviated to CRV.

It can be seen from the EDS compositional data (Figure 3.17) and the semi-quantitative XRD analysis (Figure 3.12) that CRV occurs in the same temperature range as CRN. Comparison of the loss of potassium to the growth of nitrogen content indicates that these processes occur at different rates with CRV occurring at a faster rate than CRN. This suggests that the leucite that forms first undergoes CRV before CRN occurs. This would cause the formation of an aluminosilicate phase which could then dissociate and explains the almost complete disappearance of leucite before the observation of mullite in the XRD patterns. This aluminosilicate is presumed to be amorphous due to a lack of new crystalline phases and possibly reacts with the formation of silica, observed in IR spectra. It is thought that CRV processes begin around 1300 °C due to the observation of a significant mass loss between 1300 °C and 1400 °C. These reactions may be represented by the below reaction which confirms the assumed process shown in Equation (22).



3.3.2 Mechanism of Sialon Formation from Potassium-Graphite

Composites

The aluminosilicate phase which forms after CRV and the loss of potassium is not thought to be phase stable at these temperatures due to the observation of silica stretches in the IR spectra during the early stages of the firing sequence. The carbothermal reduction of this silica would explain the presence of SiC which is observed at 1400 °C after 0 hr and indicates that CR processes are also occurring simultaneously to the CRV processes. The observation of mullite and silica suggests that the amorphous phase dissociates in a similar fashion to clays.

These newly formed phases appear to react via the conventional mechanism described in Equations (2) – (4) through intermediates of X-phase and SiC. The expected product of this mechanism is a high z-value β -sialon phase which is only observed late in the reaction sequence after 16 – 24 hr of firing. This suggests that the low z-value β -sialon phase observed is formed by as a side-product of the formation of SiO vapour during firing and not by reaction of the amorphous aluminosilicate phase. This also explains the large abundance of fibres observed under SEM. XRD, IR and EDS analysis all show the presence of aluminium in this low z-value β -sialon phase which suggests that some amount of Al containing vapour is also formed.

The reaction was incomplete after 24 hr of firing and, as evidenced by the low rate of weight loss, proceeding slowly, significant time was still required to achieve complete reaction. The reason for this slow rate of reaction is attributed to the graphite used as the reducing agent. Its large particle size of ~40 μm caused an inhomogeneous and non-intimate mixture to form, reducing the surface contact and slowing the reaction. Also, as noted by various authors,^{56,109} graphite is a more thermally stable form of carbon and is naturally less reactive than amorphous carbon.

3.4 Summary

In this chapter, the CRN synthesis of β -sialon from powdered potassium-derived geopolymer-graphite composites was examined by exploring the effect of varying the quantity of graphite used, flowing gas atmosphere and firing temperature and time.

It was found that composites containing graphite in a 1.0 – 1.3x stoichiometric quantity reacted after 10 hr at 1400 °C to form a mixture of intermediate phases consistent with β -sialon synthesis while a non-graphite containing control formed only leucite. The intermediary products included mullite, SiC and X-phase. Reaction by-products of elongated β -sialon whiskers and corundum were observed and are thought to result from the *in-situ* formation of SiO and decomposition of mullite, respectively.

Of these reaction mixtures, the sample containing a 1.0x stoichiometric quantity of graphite was selected to investigate the reaction mechanism and further development of β -sialon by firing samples at 1200 °C and 1300 °C without isothermal holds and at a synthesis temperature of 1400 °C for between 0 – 24 hr. Pre-synthesis firings indicated the dehydration and dehydroxylation of the geopolymer matrix occurs with sample crystallising to form a leucite-graphite mixture. The leucite subsequently reacted to form a mixture of mullite and SiC through the loss of potassium upon firing above 1300 °C. Firings under argon indicated that the volatilisation of potassium from the system is a result of carbothermal reduction. Extended firing of samples showed the formation of X-phase and eventual formation of a high z-value β -sialon in a low yield, with its positive identification after 24 hr of firing. A low z-value phase, detected after 4 hr of firing at 1400 °C, is thought to be the result of the elongated β -sialon fibres observed by SEM

Overall, the mechanism of β -sialon formation from potassium geopolymer graphite-composites is consistent with the conventional mechanism proposed for the CRN synthesis of aluminosiliceous materials, with the exception of the intermediate formation and reaction of leucite.

The incompleteness of the reaction after 24 hr at 1400 °C indicated a very slow reaction rate which was attributed to the use of a coarse graphite powder and its poor integration into the geopolymer mixture. This resulted in inhomogeneous, non-intimate composite powders with low reactivity.

4 Potassium Geopolymer-Carbon Black Composites

4.1 Introduction

It can be seen from the results of the experiments on geopolymer-graphite composites that geopolymers have the potential to form sialon containing materials via carbothermal reduction and nitridation. However, the use of coarse grained graphite resulted in an inhomogeneous and poorly intimate mixture which remained incompletely reacted even after 24 hr at 1400 °C.

Examination of the reaction sequence suggests that β -sialon could be formed if the rate of reaction was increased. This could be achieved by the use of a carbon reducing agent with a smaller particle size and of a more reactive type, such as carbon black.^{48,56} For this purpose, a series of potassium derived geopolymer-carbon black composites were fabricated using Degussa Lamp Black 101, a commercial carbon black which has been successfully used to synthesise sialons in several previous studies.^{41,58,110,111}

These carbon black composites have the same compositional formula as the graphite composites and have been prepared using the same reaction conditions. The formation of β -sialon was explored in the same way as graphite based samples. Samples of varying carbon content were first fired at 1400 °C for 10 hr in flowing under nitrogen and a sample then chosen to explore the reaction sequence in firings at 1200 °C, 1300 °C and 1400 °C without isothermal holds before a series of firings at 1400 °C with the duration varying between 1 – 10 hr. Samples were analysed using the range of analytical techniques, namely, XRD, IR spectroscopy, NMR and SEM microscopy with EDS.

4.2 Results

4.2.1 Synthesis of Potassium Geopolymer-Carbon Black Composites

As was the case with graphite-composites, carbon black-composites were readily synthesised from carbon-clay mixtures and a potassium silicate solution without the need

for additional water or additives. In comparison however, the resulting carbon-black composite pastes were considerably more viscous and more difficult to mix by hand. Vibration could not remove the entrained air bubbles. Treatment at 40 °C for 24 hr caused samples to harden and set into monolithic solids. No appreciable differences in strength or hardness were noted when compared to the control and graphite-composites. All samples were pulverised using a concussion mortar before being ground by hand and passed through a 150# mesh with openings of $\sim 105\ \mu\text{m}$.

In all, four potassium-carbon black composites were prepared with varying carbon contents of 1.0, 1.1, 1.2 and 1.3 times the stoichiometric quantity of carbon as required by Equation (24). These samples were designated K1.0-CB, K1.1-CB, K1.2-CB and K1.3-CB with increasing carbon content.

XRD analysis (Figure 4.1) showed patterns with typical geopolymer features including a broad, amorphous hump centred at 28° and reflections from the unreacted quartz and cristobalite originally present in the halloysite clay. The slight shift in the centre of the major amorphous hump from 28.5° to 28° and a new hump at 43.6° are the result of the overlapping amorphous peaks of the geopolymer and the carbon black which has three amorphous peaks in the region examined, centred at 25.1 , 43.6 and $\sim 79.6^\circ$; the hump at 43.6° being especially broad and stretching to $\sim 60^\circ$.

Unfired carbon black-composites analysed with IR spectroscopy showed no significant differences in their resulting spectra (Figure 4.2). This indicates that the addition of carbon black had no effect on the short range bonding or coordination environments of materials after geopolymerisation. The spectra can be characterised by the dominant Si-O-T asymmetric stretching band centred at $1031\ \text{cm}^{-1}$, T-OH stretches ($889\ \text{cm}^{-1}$), Si-O-T symmetric stretches ($697\ \text{cm}^{-1}$) and Si-O bending band at $453\ \text{cm}^{-1}$. The $10\ \text{cm}^{-1}$ shift of the Si-O-T asymmetric stretch and Si-O-T bending modes to higher wavelengths indicates a shorter bond average bond length and increased tetrahedral bond angle.¹¹² This, along with the broadening of the T-OH stretch, now centred at $873\ \text{cm}^{-1}$, suggests the inclusion of less Al into the geopolymer network and a greater proportion of aluminol groups in the carbon black-composites.

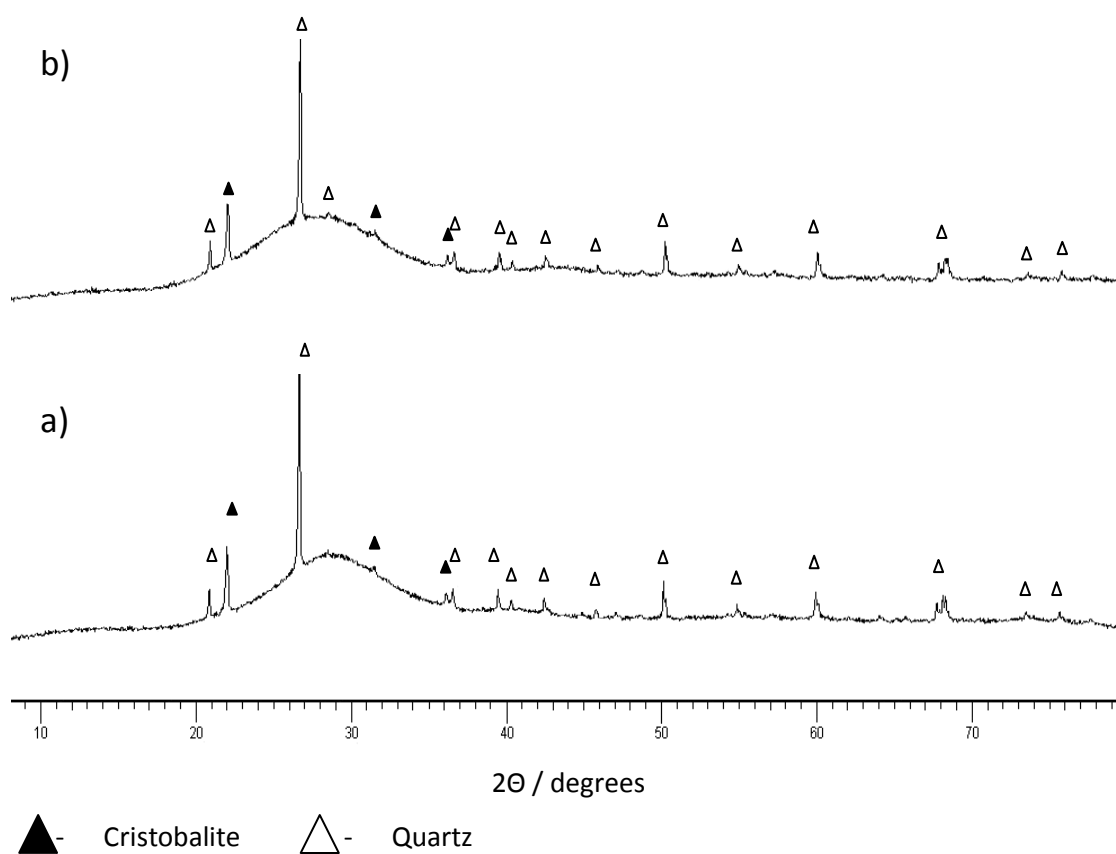


Figure 4.1: XRD patterns of a) K0, the control sample and b) an unfired K1.3-CB sample.

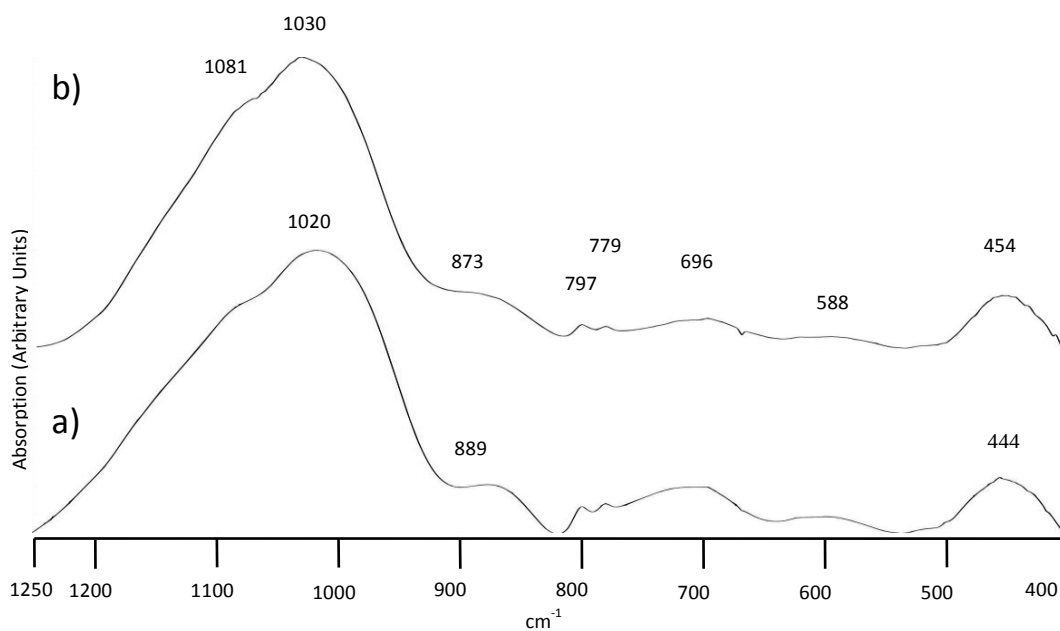


Figure 4.2: IR Spectra of a) potassium-derived geopolymer control (K0) and b) geopolymer-carbon black composite (K1.3-CB)

When examined by SEM under backscattering conditions (Figure 4.3a), the distribution of carbon throughout samples appeared well dispersed; the sample was homogeneous in colour and the presence of individual particles of carbon black were not observed. Interestingly, an atypical morphology was observed in carbon black-composites with the appearance of nodule-like features being apparent (Figure 4.3b). These, small, spherical particles were interconnected and associated by EDS with the presence of carbon (Figure 4.4). This suggests that the carbon black present in samples may act as nucleation sites for condensing species during geopolymerisation. This would be ideal behaviour as it would result in a very intimate mixture of good homogeneity.

The powdered geopolymer-carbon black samples were subsequently fired in flowing nitrogen at 1400 °C for 10 hr.

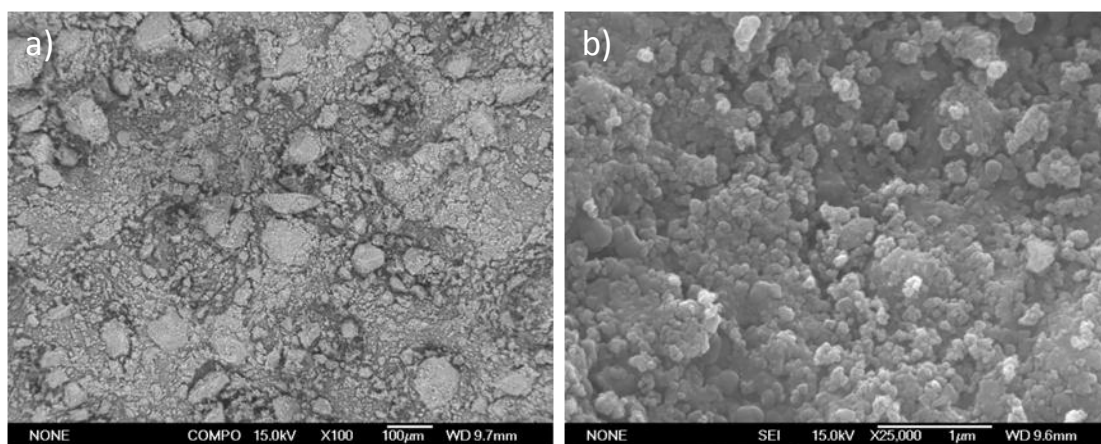


Figure 4.3: a) Backscatter image of ground, unfired K1.3-CB sample (100x) and b) a close up SEI image showing its small, spherical, nodular morphology (25000x).

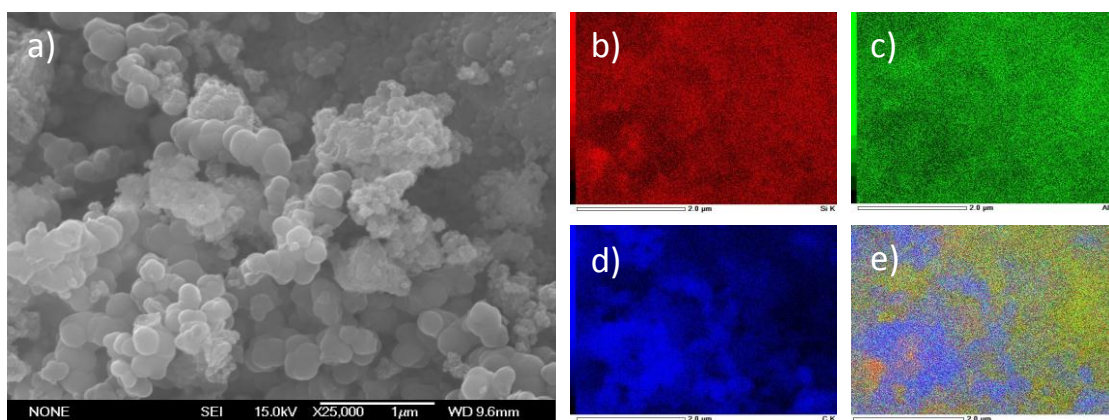


Figure 4.4: a) SEI image of ground, unfired K1.3-CB with b) silicon, c) aluminium and d) carbon EDS maps and e) their overlay.

4.2.2 Firing of Samples with Varying Carbon Black Content

The four prepared geopolymer-carbon black compositions were fired at 1400 °C for 10 hr to determine the effect of varying the amount of carbon in samples. After firing, the presence of small quantities of fibres was observed on boats and deposited on the firing tube outside of the hot-zone. Glassy rings were also visible at the edges of the hot-zone.

Analysis of the resulting XRD patterns (Figure 4.5) showed a range of reaction products between fired samples with β -sialon being the major component phase in all cases. Figure 4.5a shows that K1.0-CB was incompletely reacted with significant amounts of O1-sialon, X-phase, SiC and corundum present. While X-phase and SiC are expected products based on the reaction sequence of clays, the presence of O1-sialon as a by-product is a novel finding. O1-sialon has only been sparingly reported in the literature and only as a product of silicothermal reduction methods.^{1,15,47} In addition, the synthesis temperature of 1400 °C is above the reported transition temperature of O1-sialon (~1350 °C) and of the silicon oxynitrides, O-sialon is the expected phase.¹⁵

Increasing the carbon content in samples resulted in the disappearance of O1-sialon and decline of X-phase, which were not observed in the fired K1.2-CB or K1.3-CB samples. AlN is observed in both K1.2-CB and K1.3-CB, indicating some over-reaction. Small quantities of corundum and γ -alumina were also present in all samples except K1.0-CB, where the presence of γ -alumina was indeterminable due to overlapping O1-sialon peaks. Semi-quantitative XRD analysis of samples shows these reactions trends (Figure 4.6).

Infrared spectroscopy of samples between 1250 – 400 cm^{-1} (Figure 4.7) showed a large number of bands indicating polyphasic aluminosiliceous and nitrogenous materials. The major band of all samples was located between approximately 1100 – 900 cm^{-1} and is comprised of various Si-(O,N)-T asymmetric stretches. The peaks at ~1030, ~945, and ~900 cm^{-1} are the $\nu_6 - \nu_4$ Si-N vibrational modes, respectively, while the higher wavenumber shoulders at 1175 cm^{-1} and 1092 cm^{-1} in K1.0-CB are Si-O-Si stretches from silica and O1-sialon respectively. The broad, flat absorption band between 800 – 600 cm^{-1} are a combination of a number of vibrational modes including the Si-(O,N)-T bending modes and the Al-O and Al-N stretches which have peaks at 788 cm^{-1} and ~720 cm^{-1} , respectively. The peak at 638 cm^{-1} is attributed to octahedral Al-O stretches from corundum. The small, sharp

peak at 668 cm^{-1} (unlabelled) was determined to be caused by an impurity in the KBr used to suspend the samples.

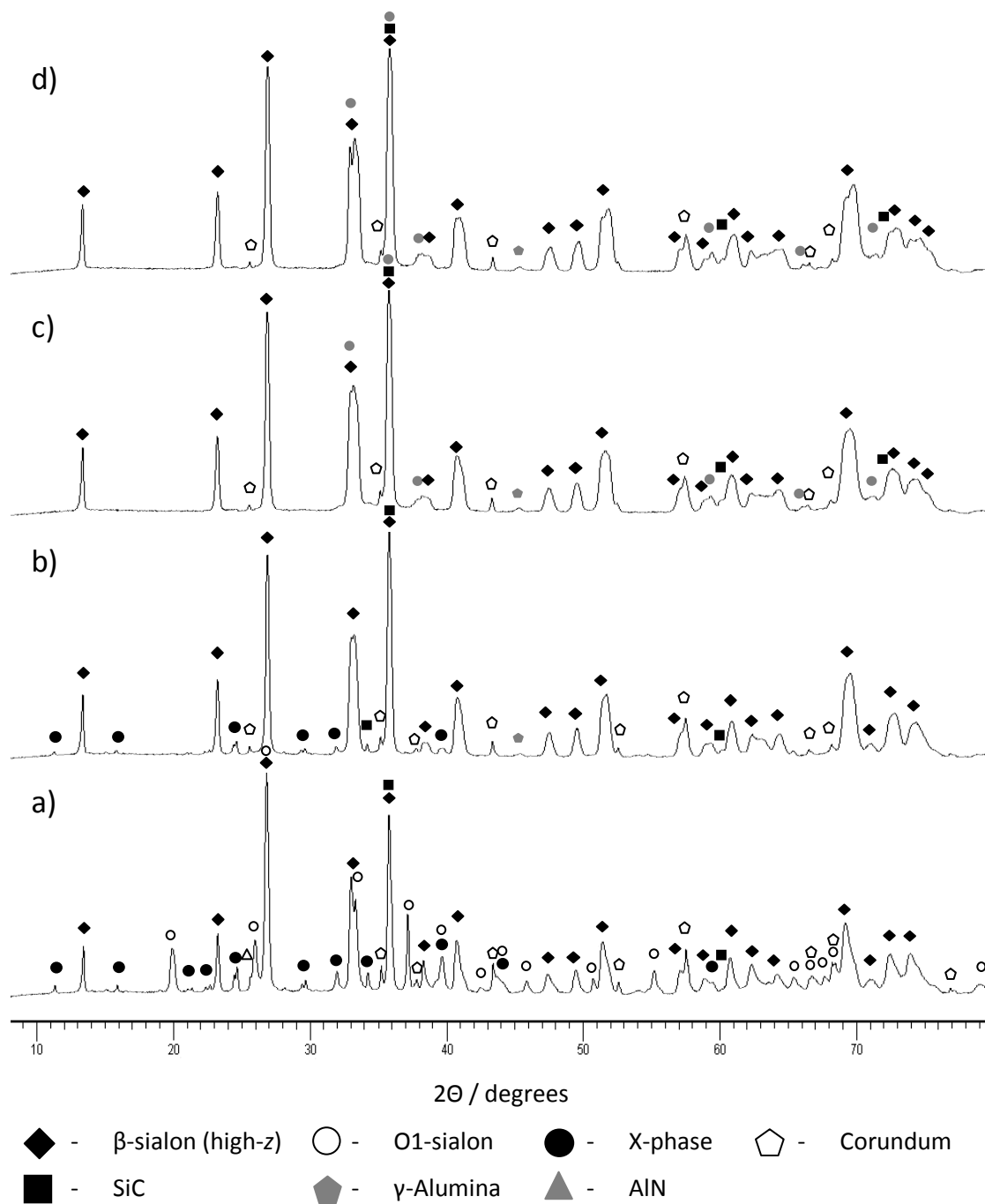


Figure 4.5. XRD patterns of samples fired in nitrogen at $1400\text{ }^{\circ}\text{C}$ for 10 hr: a) K1.0-CB, b) K1.1-CB, c) K1.2-CB and d) K1.3-CB.

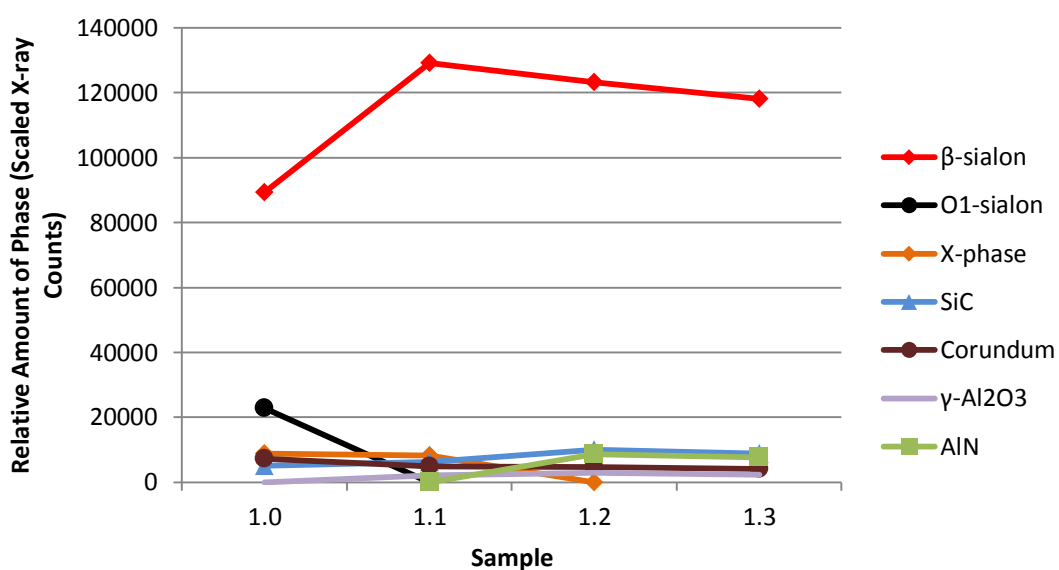


Figure 4.6: Semi-quantitative representation of the phases detected by XRD in potassium-carbon black composites with varying carbon content fired in nitrogen at 1400 °C for 10 hr.

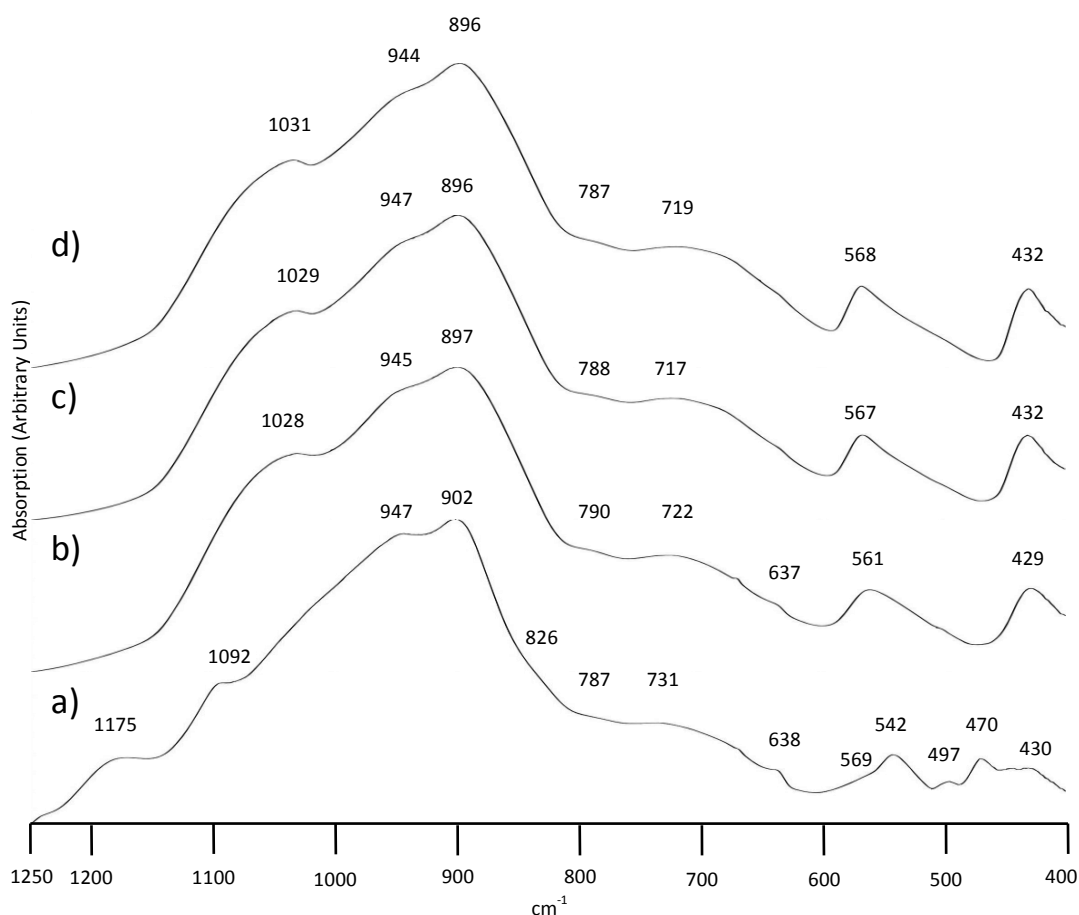


Figure 4.7: IR spectra of samples fired at 1400 °C for 10 hr in flowing nitrogen: a) K1.0-CB, b) K1.1-CB, c) K1.2-CB and d) K1.3-CB

The spectrum of K1.0-CB (Figure 4.7a) showed a number of bands below 600 cm^{-1} , with the peak at 542 cm^{-1} assigned as the ν_3 Si-N vibrational mode which overlaps the Si-O mode from X-phase (569 cm^{-1}).¹⁰⁴ The assignments of peaks at 497, 470 and 430 cm^{-1} is difficult due to a lack of definitive data concerning variations in X-phase and silicon oxynitrides in this region but comparison to the reference spectra suggests that the peak at 497 cm^{-1} is associated with O1-sialon and while the peak at 470 cm^{-1} may be a result of X-phase.¹⁰⁴ Based on the wavenumber of the ν_3 band, the ν_2 band is predicted to occur at $<400\text{ cm}^{-1}$ indicating that the peak at 430 cm^{-1} is from Si-O rocking modes. In samples with greater quantities of carbon, the ν_3 Si-N vibrational mode occurs between 560 and 568 cm^{-1} while the ν_2 band occurs at $\sim 430\text{ cm}^{-1}$.

Based on the values of the ν_3 and, where possible, the ν_2 bands, z-values were estimated using the data from Wild *et al.*⁹¹ and the derived formulas (Equations (30) and (31)). The z-values of the K1.0 – 1.3-CB samples were estimated, in order, as 1.96, 1.14, 0.93 and 0.90. These values indicate a progressive decline in z-value with increasing carbon content, likely due to increased SiO loss. This is consistent with studies carried out by Van Dijen *et al.*⁵⁴ and Cho and Charles.⁴⁸

To explore the reaction sequence of carbon-black composites, a series of K1.3-CB samples were fired in nitrogen at 1200, 1300 °C and at 1400 °C for times between 0 – 10 hr. A sample was also fired in flowing argon at 1400 °C for 10 hr. Although K1.2-CB is arguably a more suitable candidate for these experiments from the XRD results, due to a less formation of AlN, K1.3-CB was chosen due to the misidentification of AlN for SiC at the time. In studies by Narciso *et al.*,⁵⁶ the quantity of carbon is seen not to alter the reaction sequence to form β -sialon, causing only excess formation of corundum and SiC by-products and only otherwise affecting the rate of reaction and the amount of subsequent over-reaction of material to form 15R-sialon and AlN.

4.2.3 Reaction Sequence of Potassium-Carbon Black Composites

The reaction sequence of carbon black-composites was investigated by firing a series of K1.3-CB samples at elevated temperatures. The pre-synthesis behaviour was investigated by firings between 1200 °C, 1300 °C and 1400 °C without isothermal holds while the CRN

reaction mechanism was explored by firings of varying durations between 1 – 10 hr at 1400 °C. The fired samples were analysed by weight loss, XRD, IR, NMR and SEM with complimentary EDS.

4.2.3.1 Observations and Weight Loss

Samples were weighed before and after firing and their weight loss determined as a function of the original mass as according to Equation (27) in Section 2.1.3. As can be seen in Figure 4.8, weight loss between samples is gradual and almost linear in nature until about 4 hr, where after the decrease is only gradual. Like graphite composites, the initial weight loss of K1.3-CB is low at about 13%. However, in comparison, no dramatic weight loss between 1300 and 1400 °C was observed.

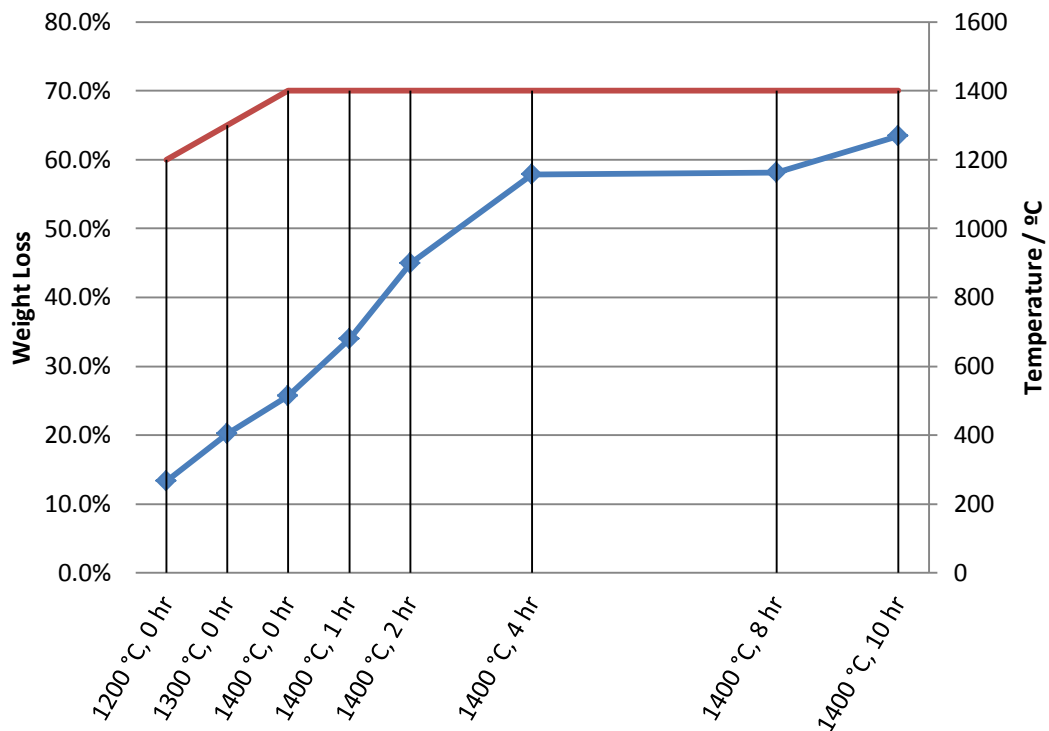


Figure 4.8: Weight loss of K1.3-CB samples fired at progressively higher temperatures for varying lengths of time. The red line indicates the temperature.

4.2.3.2 X-Ray Diffraction Studies

Figure 4.9 shows the pre-synthesis development of K1.3-CB samples. It can be seen that upon firing to 1200°C, the XRD pattern is mostly amorphous and contains reflections

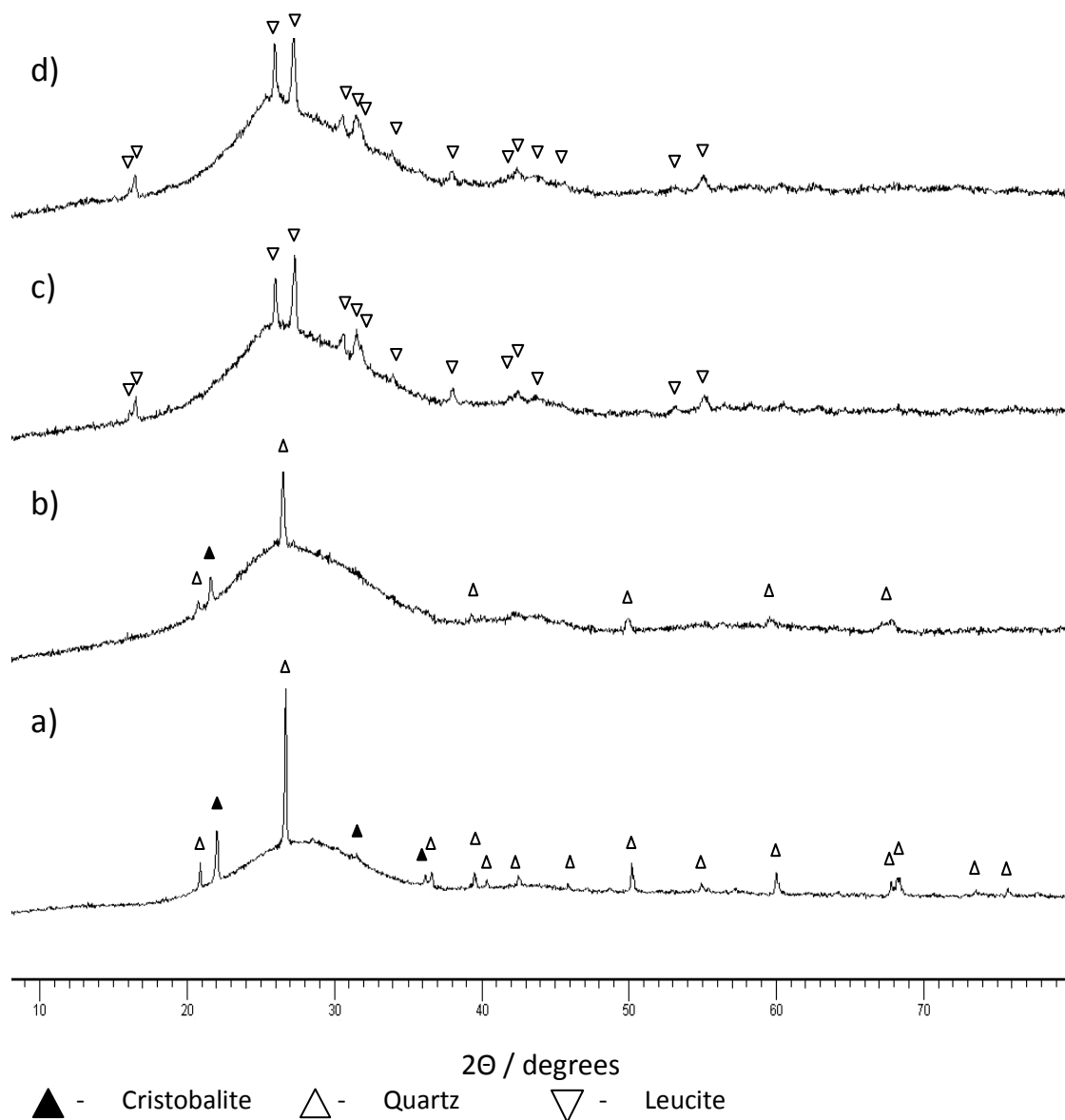


Figure 4.9: XRD patterns of K1.3-CB: a) Unfired and b) 1200 °C, c) 1300 °C and d) 1400 °C, all without isothermal holds.

from quartz and cristobalite, indicating that the geopolymer matrix has not incorporated these siliceous phases or crystallised. Further heating to 1300 °C shows the consumption and integration of the silica species into the matrix and the crystallisation of some of the geopolymer into leucite. It can be seen from the low intensity of the leucite reflections that a significant portion of the geopolymer matrix has not crystallised and this remains the case with further heating to 1400 °C.

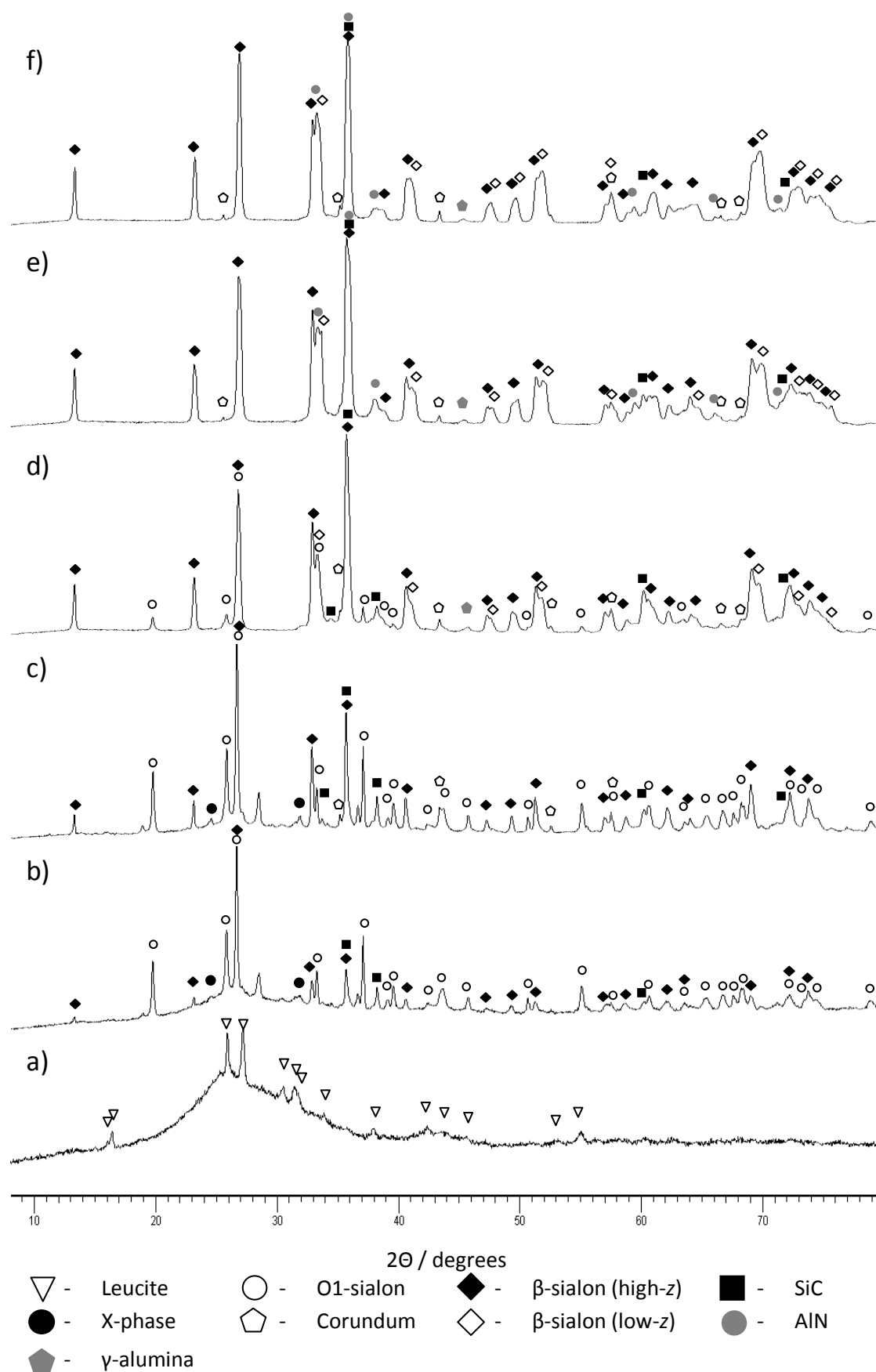


Figure 4.10: XRD patterns of K1.3-CB samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr, and f) 10 hr.

Treatment at the synthesis temperature of 1400 °C for 1 hr, shown in Figure 4.10b, saw the formation of O1-sialon, with a small quantity of β -sialon, trace amounts of SiC and X-phase with the retention of the an amorphous phase. An unidentified phase with peaks at 18.9, 27.1, 28.5, 31.5 and 36.6° was also observed. Cell dimensions calculated from the results of Rietveld modelling of the pattern showed the β -sialon phase to have a z-value of 3.2.

Using the data published by Bowden *et al.*,¹ the O1-sialon phase was also modelled. The resulting O1-sialon cell dimensions are shown in Table 4.1 and are compared to the literature results. These results show greatly expanded unit cell dimensions which suggest that the O1-sialon phase either contains a significant amount of aluminium with an x-value much greater than 0.2 or that a stuffed derivative phase has formed. At present, unlike β -sialon and O-sialon, there is insufficient information regarding O1-sialon to allow estimated of its aluminium content from cell dimensions but as it shares the orthorhombic structure of O-sialon comparisons between the two polymorphs can be made. In studies by Lindqvist *et al.*¹³ the formation of a $x = 0.4$ phase resulted in a 0.61% increase in unit cell volume when compared to a $x = 0$ phase. Comparison of the formed O1-sialon to the literature results indicates a 2.1% increase in unit cell volume above an already $x = 0.2$ sample. Assuming that the solubility limit of O1-sialon is similar to O-sialon, at ~ 0.4 , this strongly suggests that a potassium stuffed derivative has been formed.

Table 4.1. Comparative unit cell parameters of O1-sialons

Source	a / Å	b / Å	c / Å	Volume / Å ³	x-value
Bowden <i>et al.</i> ¹	8.8488(13)	5.3752(6)	4.8355(5)	230.00	0.2
O1-sialon from this study	8.979	5.388	4.853	234.82	-

Figure 4.11 shows the semi-quantitative analysis of firings, where it can be seen that after 2 hr of firing the quantity of the β -sialon, O1-sialon, SiC and corundum increased with the decline of X-phase and the amorphous phases. By 4 hr the sample was mostly reacted with β -sialon being the dominant phase and coincided with an increase in SiC. The appearance of γ -alumina is observed with a decrease in corundum while both X-phase and the amorphous phase disappeared altogether. The quantity of O1-sialon phase also reduced

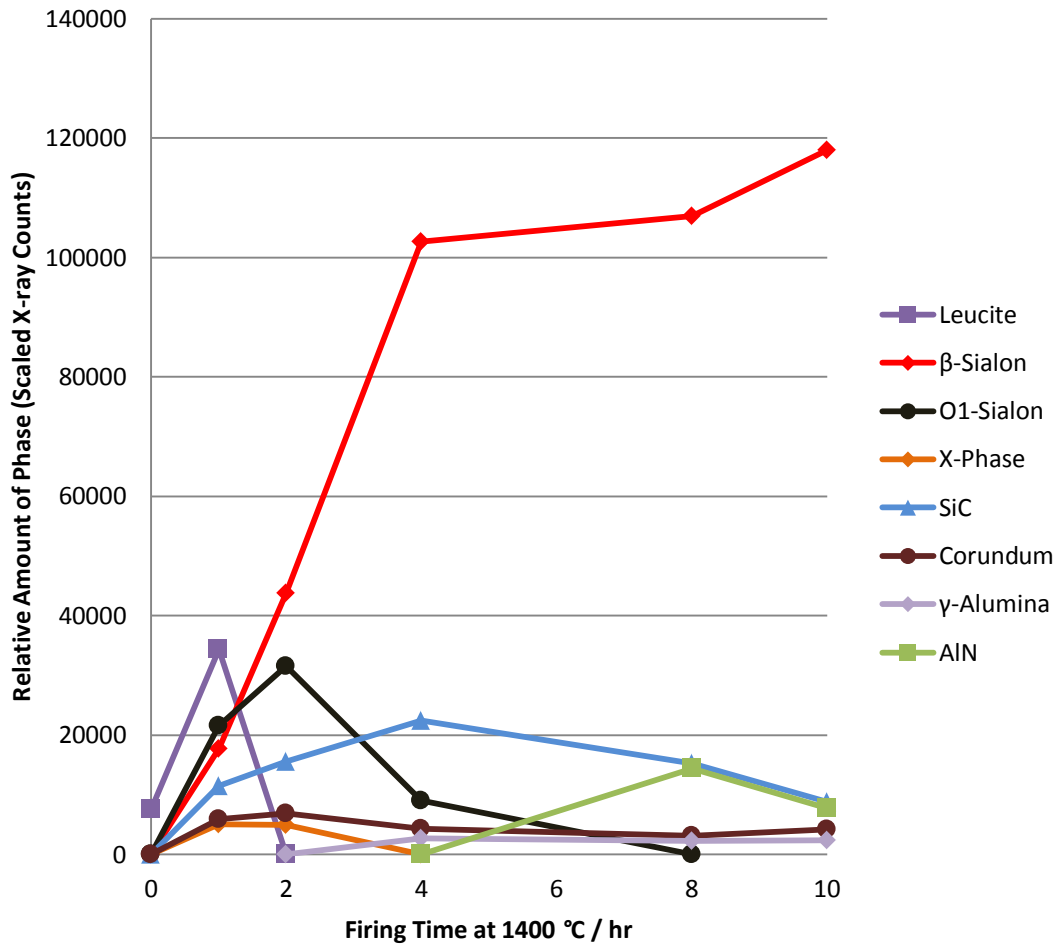


Figure 4.11: Semi-quantitative representation of the phases detected by XRD in K1.3-CB samples fired in nitrogen at 1400 °C for various durations.

considerably but its cell dimensions remained stable. The peaks at $\sim 33^\circ$ (Figure 4.10d) show that at least two distinct phases of β -sialon are present. These phases were modelled and give z -values of 2.9 and 1.4 indicating that a diphasic β -sialon material had formed.

After 8 hr the material was mostly β -sialon with small quantities SiC and corundum and γ -alumina. The presence of AlN was also observed, suggesting that the reaction had either gone past completion and some over-reaction had occurred or that some of the alumina present converted as per Equation (17). In this case, it can be determined that the formation of AlN occurs via the former mechanism due to the increase of low z -value β -sialon, which has formed at the expense of the high z -value phase. Modelling of these indicated new z -values of 3.0 and 0.4 for the two β -sialon phases.

The sample fired for 10 hr was very similar to the sample fired for 8 hr but contained no SiC, less AlN and more low z -value β -sialon. The amount of γ -alumina remained stable

with a small increase in the quantity of corundum. The z -values of the two β -sialon phases were 3.1 and 0.9. Overall, XRD analysis shows the good development of β -sialon with complete reaction estimated to occur between 4 and 8 hr of firing for K1.3-CB.

4.2.3.3 Infrared Spectroscopy

Like the graphite-composites, carbon-black composites have infrared spectra typical of geopolymers, with a major absorption band between $1200 - 850 \text{ cm}^{-1}$ comprised of a heterogeneous mixture of Si-O-T asymmetric environments, T-OH stretches, Si-O-T symmetric stretches at around 700 cm^{-1} and a Si-O-T bending band at 450 cm^{-1} . Unlike the graphite-composites, the carbon-composites were not seen to fully crystallise into leucite and this is reflected in the infrared spectra. During the pre-synthesis stage (Figure 4.12), the

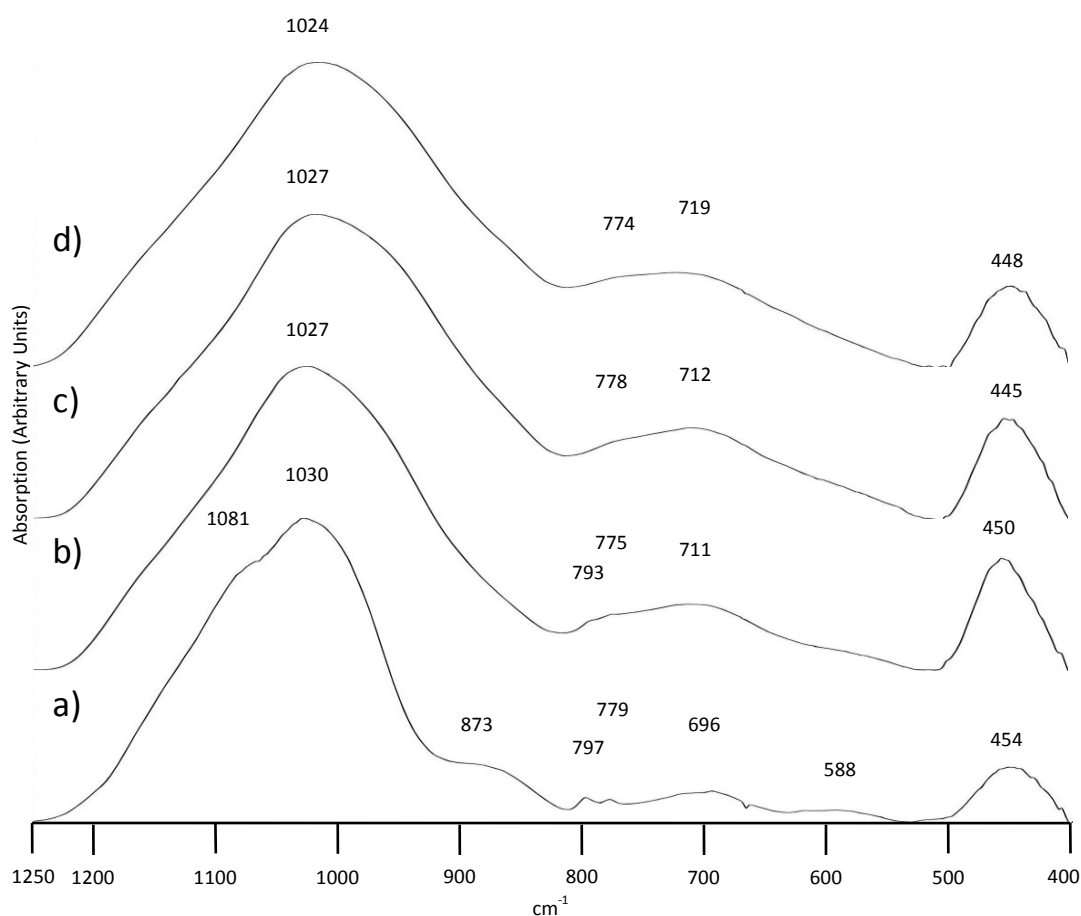


Figure 4.12: IR spectra of K1.3-CB samples: a) Unfired sample b) 1200°C , 0 hr, c) 1300°C , 0 hr and d) 1400°C , 0hr.

sample fired to 1200 °C shows broadening of the major band, the apex of which shifts to slightly lower wavenumbers, signalling dehydroxylation and the inclusion of more cross-linked aluminium into the geopolymer network. By 1300 °C, all remaining unreacted halloysite has also been incorporated into the network, however, even by the end of the pre-synthesis stage at 1400 °C, no ring vibrations which would distinguish the presence of well crystallised leucite were present.

A dramatic change in the infrared spectrum is observed upon entering the synthesis stage (Figure 4.13). After heating at 1400 °C for 1 hr, the formation of multiple new bands is

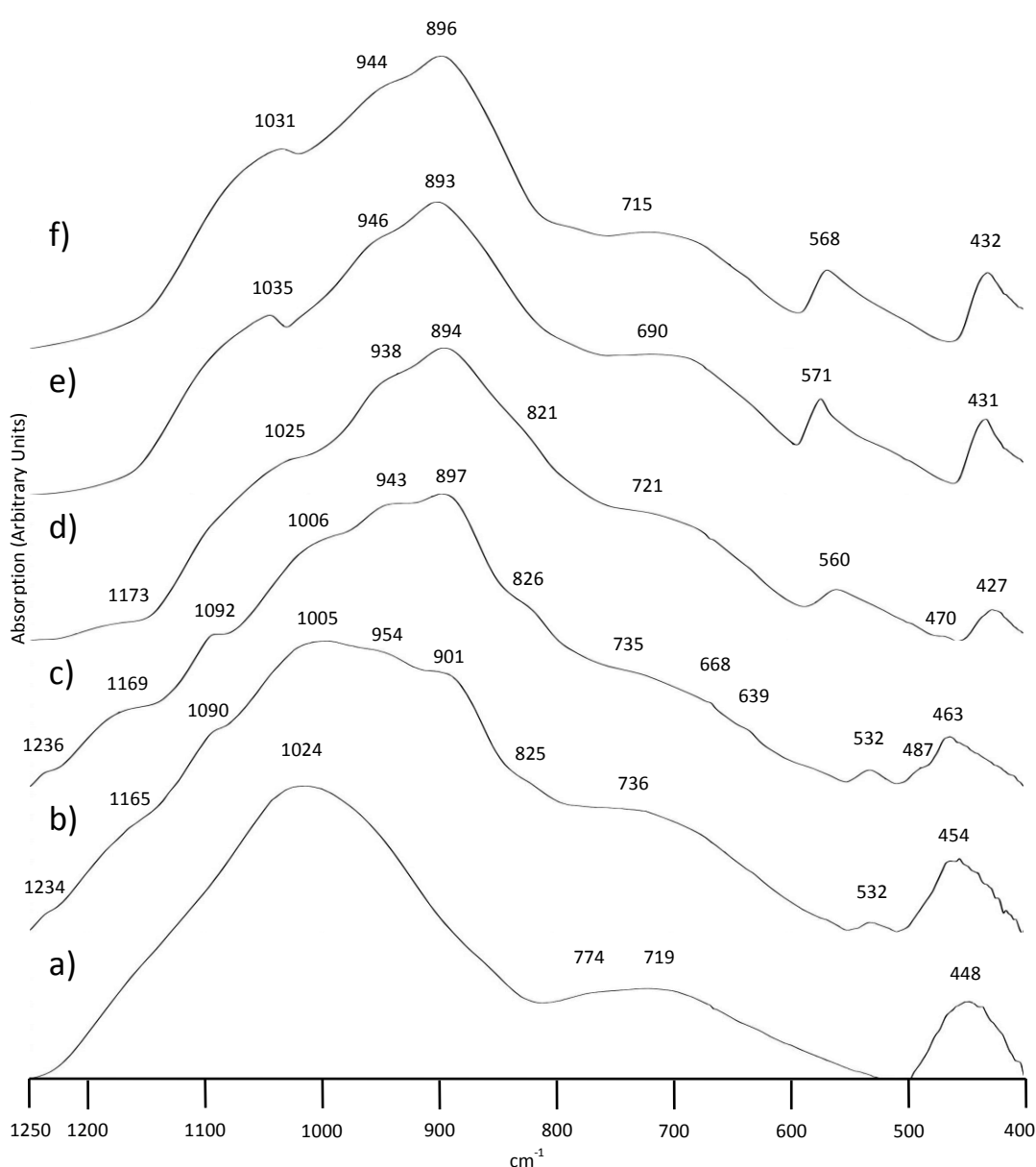


Figure 4.13: IR spectra of K1.3-CB samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr, f) 10 hr.

seen, including bands at 1165 cm^{-1} (silica), 1092 cm^{-1} (O1-sialon, Si-O), 954 cm^{-1} (ν_5 , Si-N) and 901 cm^{-1} (ν_4 , Si-N). The three broad bands observed for the mainly amorphous aluminosilicate mixture all shift with the major band observed at a wavenumber of 1005 cm^{-1} , the broadening of the T-O bending region and shift to higher wavenumbers observed for the Si-O-T rocking mode. The shoulder at 825 cm^{-1} is attributed to the presence of SiC in the sample. A ν_3 Si-N peak is also observed at 532 cm^{-1} .

Two hours at $1400\text{ }^\circ\text{C}$ sees the growth of all new peaks and the decline of all peaks associated with amorphous aluminosilicate phase. A new peak is also noted at 487 cm^{-1} and is associated with O-sialon. After 4 hr, the presence of O1-sialon was not detected by XRD whereas a silica band was observed at 1173 cm^{-1} . The emergence of the peak at 1025 cm^{-1} is assigned as the ν_6 vibrational mode.

Further heating to 8 and 10 hr resulted in spectra typical of β -sialons containing all ν_6 – ν_2 vibrational modes as well as a broad band from the Al-O and Al-N stretches ($800 - 600\text{ cm}^{-1}$) with the disappearance of the silica peak. Estimation of the z-values of the of the final three materials fired for 4, 8 and 10 hr gives values of 1.21, 0.89 and 0.93. While these values are not in agreement with the XRD results, they confirm the trend suggesting a greater loss either of SiO during firing or more pronounced over-reaction subsequent to reaction completion in the sample fired for 8 hr.

4.2.3.4 *Solid State Nuclear Magnetic Resonance*

As was the case with graphite-composites, the reaction of carbon-black composites was monitored by ^{27}Al and ^{29}Si solid state MAS NMR. Figure 4.14 shows the resulting ^{27}Al and ^{29}Si spectra from firings in the pre-synthesis region. The sample treated to $1200\text{ }^\circ\text{C}$ shows two peaks; a sharp, main peak at 55.2 ppm indicating AlO_4 environments and a second small, broad peak situated at ~ 13 ppm suggesting a small amount of octahedral aluminium, most likely from the unreacted clay seen in the IR spectra. The main AlO_4 resonance remains stable in samples fired to higher temperatures of $1300\text{ }^\circ\text{C}$ and $1400\text{ }^\circ\text{C}$ with the AlO_6 resonance decreasing to a small shoulder which has all but disappeared in the sample heated to $1400\text{ }^\circ\text{C}$.

During the synthesis stage (Figure 4.15) the AlO_6 resonance is observed to reappear at 16.0 ppm, due to the formation of corundum in samples. After 2 hr a marked decrease

and broadening of the AlO_4 resonance is observed with the simultaneous growth of the AlO_6 resonance (14.4 ppm) and the appearance of an AlN_4 resonance at 112.7 ppm. As no AlN is observed in the matching XRD pattern, this peak is attributed to the β -sialon phase. β -sialon has been observed to have AlN_4 resonances in studies examined the CRN reaction sequence of zeolites.⁶³ Other candidate sources for this resonance include the sialon-polytypes (e.g. 15R, 21R, etc.) and AlON , none of which are observed in the corresponding XRD patterns however. After 4 hr at 1400 °C, the major resonance has shifted to 66.4 ppm indicating the formation of a predominately β -sialon phase. A shouldering peak at 88.7 ppm indicates AlN_2O_2 environments which, coupled with the peak at 112.7 ppm, suggests a high z-value product. The peak at 13.6 ppm is the result of the presence of corundum/ γ -alumina while the downfield broad band which shoulders this resonance is thought to arise from multiple spinning side bands. In the sample fired for 8 hr, the strong, sharp AlN_4 resonance at

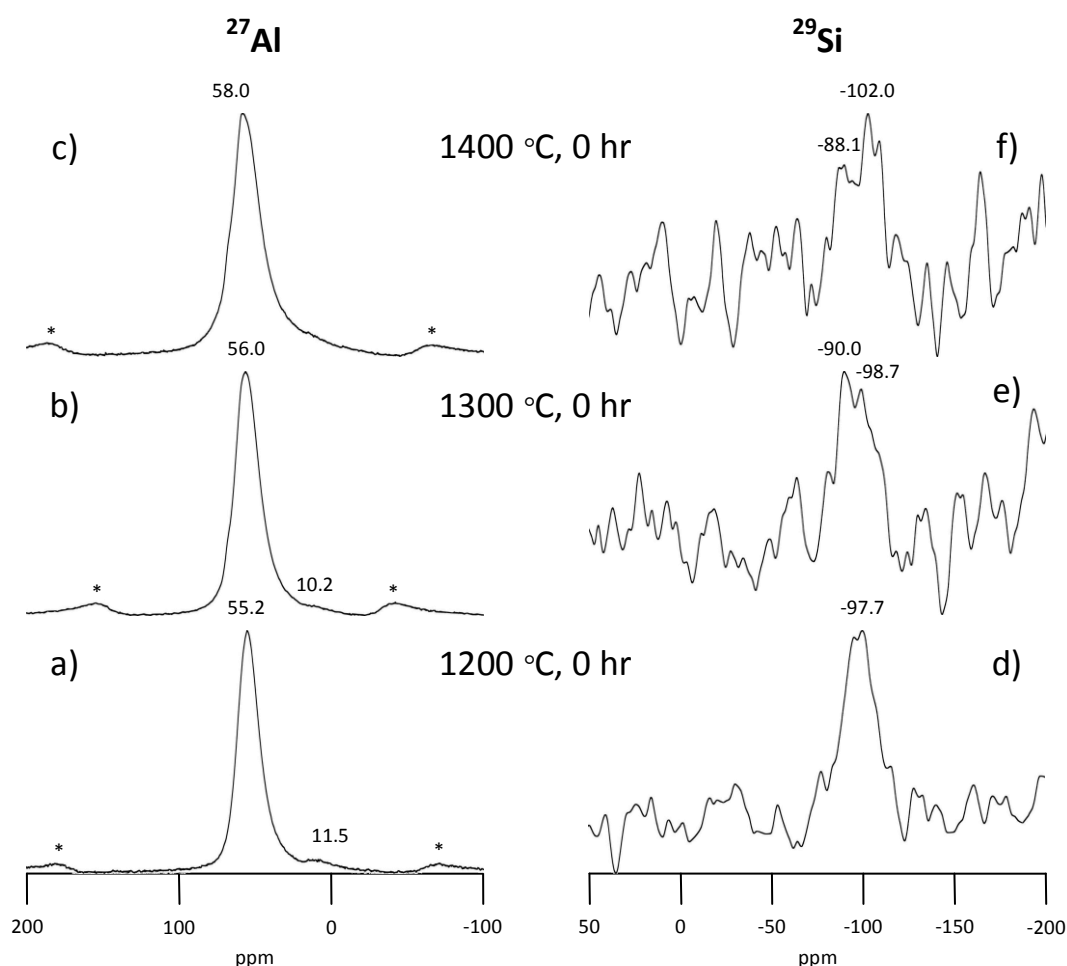


Figure 4.14: ^{27}Al and ^{29}Si NMR spectra of K1.3-CB samples fired at varying temperatures without isothermal holds. *Denotes spinning side band.

115.1 ppm indicates the formation of crystalline AlN. The broad resonance at 66.4 ppm stems from the β -sialon AlO_4 groups while the peak at 13.6 ppm is from the contingent AlO_6 environments of corundum/ γ -alumina. The peak at ~ 24 ppm is a spinning side band of the AlN_4 resonance. The final sample, fired at 1400 °C for 10 hr, is similar to the 8 hr sample in that it has the same 3 peaks although they differ in their intensities. Although the quantity of a particular environment is determined as a function of the integral of its resonance, in similarly ordered environments with sharp peaks this can be equated with height. Therefore, in comparison to the AlO_4 sialon resonance, the height of the AlN_4 peak is observed to decrease, whereas the AlO_6 peak increases. These results are concordant with the XRD and IR analyses which suggest a product of different composition to the 8 hr sample.

Despite using very long run-times when acquiring the ^{29}Si MAS-NMR experiments, it can be seen that similar to the graphite-composites, relatively ill-defined spectra were obtained. Nevertheless, the sample fired to 1200 °C shows one broad resonance at -97.7 ppm, indicative of aluminosiliceous SiO_4 environments. After firing to 1300 °C, this SiO_4 resonance remains the only feature but shows two separate peaks, identified at -90.0 ppm and -98.7 ppm. These peaks diverged further to ~ -88 ppm and -102 ppm after treatment to 1400 °C.

During the synthesis stage, the SiO_4 resonance (Figure 4.15h) narrows into one main peak at -88.3 ppm which has shoulders at -83.2 and -98.1 ppm. A peak at -59.2 ppm indicates the presence of a SiN_3O resonance which is attributed to the O1-sialon seen in the corresponding XRD pattern. A number of ambiguous peaks are also observed at -117 ppm, -45 ppm and broad band centred at ~ -7 ppm are possibly from siliceous SiO_4 (SiO_2), SiN_4 and SiC resonances, respectively. The spectrum obtained from the sample treated at 1400 °C for 2 hr shows a strong SiC resonance at -19.3 ppm, distinct SiN_4 and SiN_3O resonances at -48 ppm and -64.1 ppm respectively and a residual SiO_4 peak at -98.1 ppm. A large swarm of peaks below -105 ppm might contain some SiO_4 resonances from SiO_2 species but could just as equally be the result of spinning side bands. After 4 hr, three resonances could be identified; a SiC peak at -16.6 ppm, a sharp SiN_4 peak at -48.2 and a Si_3NO peak at -63 ppm. Unlike XRD and IR, the z-value of a β -sialon phase cannot be inferred from the location of resonances, although some line broadening of the peak is observed with higher z-values.

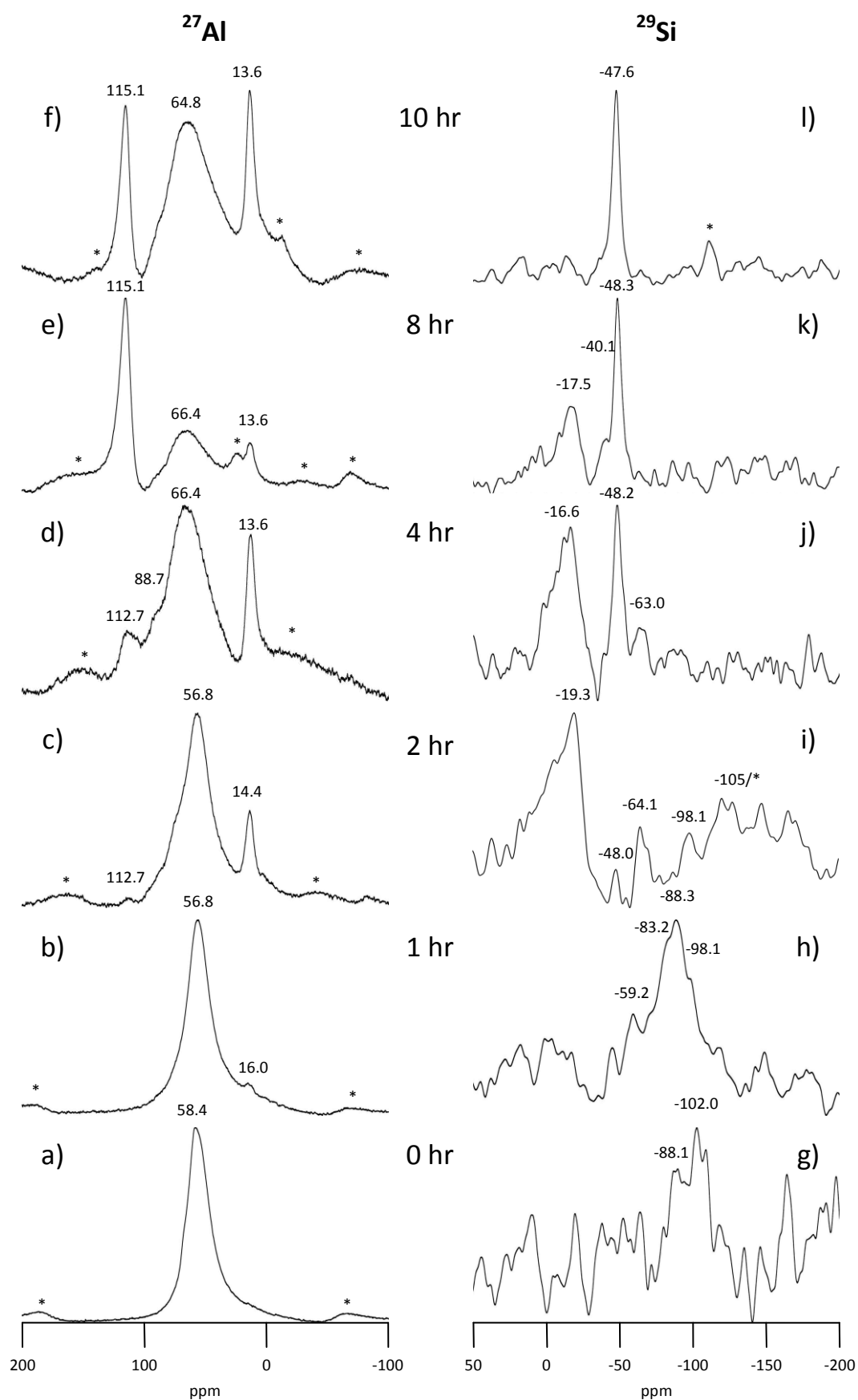


Figure 4.15: ^{27}Al and ^{29}Si NMR spectra of K1.3-CB samples fired in nitrogen at 1400 °C for varying durations. *Denotes spinning side band.

The spectrum of the sample fired for 8 hr has a SiC resonance at -17.5 ppm and a sharp, tall SiN₄ peak at -48.5 ppm with a small shoulder at -40.1 ppm, possibly indicating the presence of a polytypoid phase like 15R or 21R, neither of which are observed in the corresponding XRD pattern. Interestingly, the pattern fired for 10 hr lacks both the SiC and polytypoid SiN₄ peaks with only a peak for the β -sialon phase at -47.6 ppm. The peak at -110.5 ppm is most likely a spinning side band of the SiN₄ resonance.

4.2.3.5 *Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy*

Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) analyses were carried out on carbon black-composites that were fired at the synthesis temperature of 1400 °C for varying durations (0 – 10 hr).

It can be seen from EDS compositional analysis (Figure 4.16) that there is a progressive loss of potassium from samples when fired at 1400 °C for prolonged time with its disappearance from samples observed after 4 hr. A similar effect is observed for oxygen which initially drops at a rate almost equal to potassium but steadies after 4 hr before rising for the 10 hr sample. Nitrogen is positively detected after 2 hr and grows steadily with increasing firing duration. After an initial rise in the amount of silicon, its abundance is observed to drop in all samples relatively to the amount of aluminium present. These results are similar to the graphite-composites except occur across a smaller time frame indicating a faster reaction rate, especially in regards to the volatilisation of potassium from samples.

Figure 4.17a shows the backscatter image of the K1.3-CB sample fired at 1400 °C for 0 hr, where it can be seen that upon firing to synthesis temperature, the sample retains its homogeneous and well-mixed nature. Magnified scanning electron images (Figure 4.17b and Figure 4.17c) also show that samples retain their porous, nodular morphology, albeit with the development of some sintered flat surfaces. Further magnification (Figure 4.17d) reveals these surfaces to be of similar roughness to the internal surface of the corresponding K1.0-G sample. This suggests that the samples have undergone less sintering and rearrangement than the graphite-composites upon exposure to the same treatment temperature and time. Also, in contrast to the graphite-composites was the lack of rounded agglomerates with very few being observed.

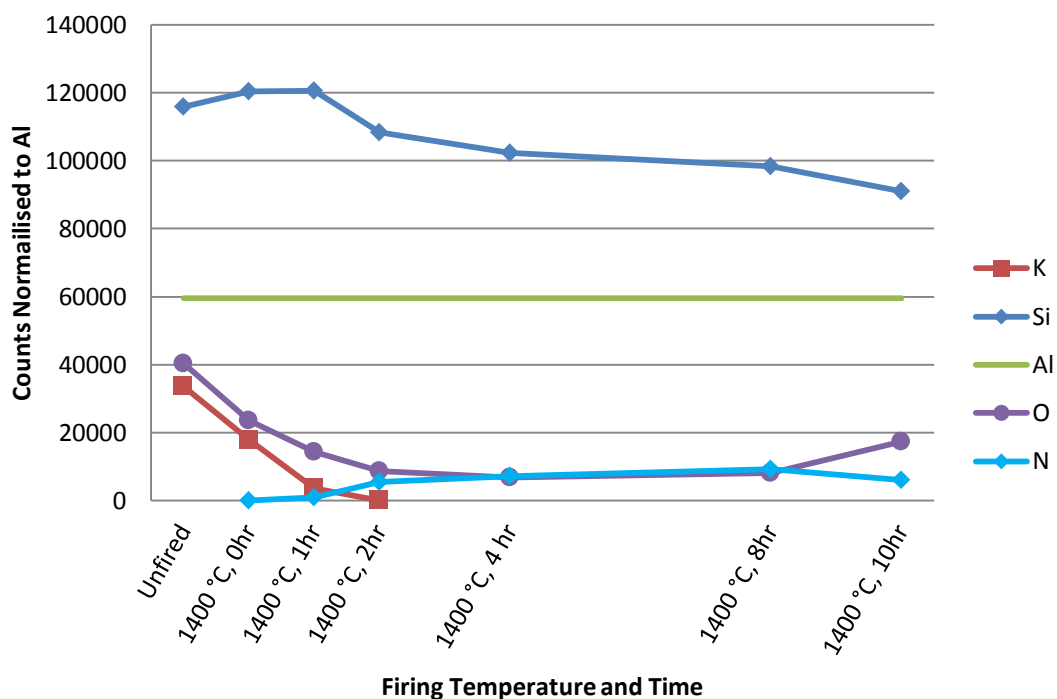


Figure 4.16: Normalised elemental counts of K1.3-CB samples fired at 1400 °C between 0 – 10 hr compared to the unfired precursor.

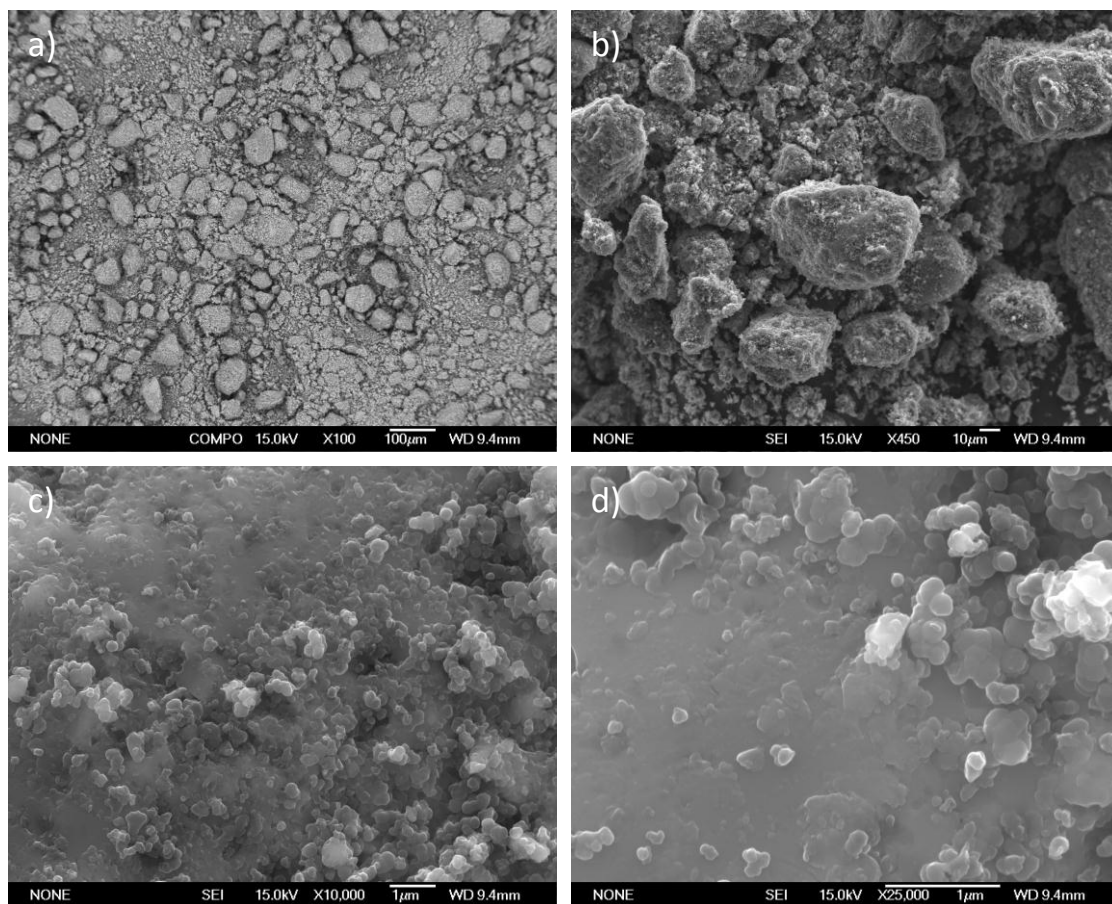


Figure 4.17: a) Backscattered image and selected SEI images of the K1.3-CB sample fired at 1400 °C for 0 hr at various magnifications showing b) particulates, c) retained spherical morphology and d) rough surface texture.

In samples exposed to 1400 °C for increasing time (Figure 4.18), the morphologies observed in samples varied greatly (Figure 4.18). A general tendency for samples to develop increasingly porous and textured surfaces with increasing time was noted but regions with well sintered surfaces were also seen (Figure 4.19). Samples, for the most part, retained their small, spherical morphology even in well-reacted samples fired for 8 and 10 hr.

The development of fibrous whiskers was also noted in samples fired for 2 hr or more (Figure 4.19c-f). These fibres were, in general, smaller, less numerous and less well-formed than the fibres observed in the corresponding graphite-composites. Seeing that few whiskers were observed in samples fired less than 2 hr, during which the potassium is volatilised, it seems unlikely that the presence of potassium plays a significant role in whisker formation.

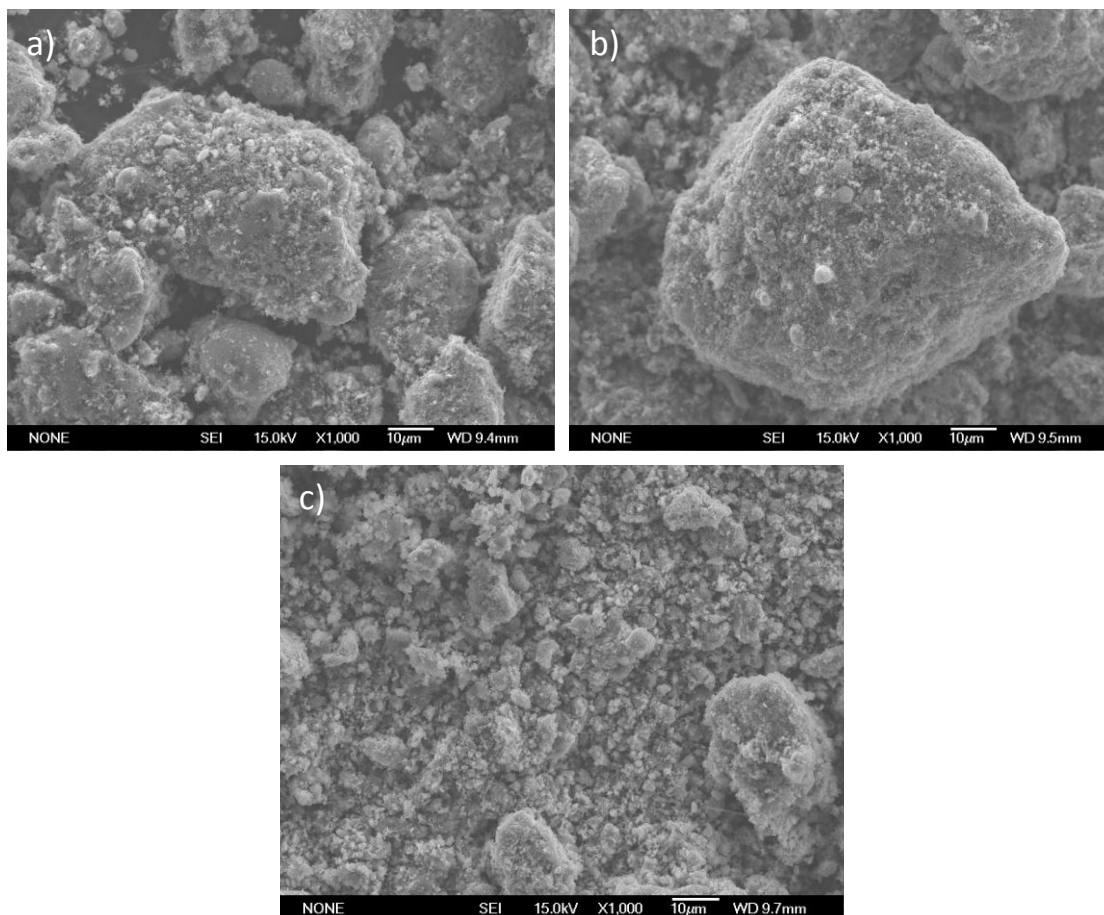


Figure 4.18: Selected SEI images of K1.3-CB samples fired at 1400 °C for a) 0 hr, b) 2 hr and c) 8 hr. Magnification is 1000x.

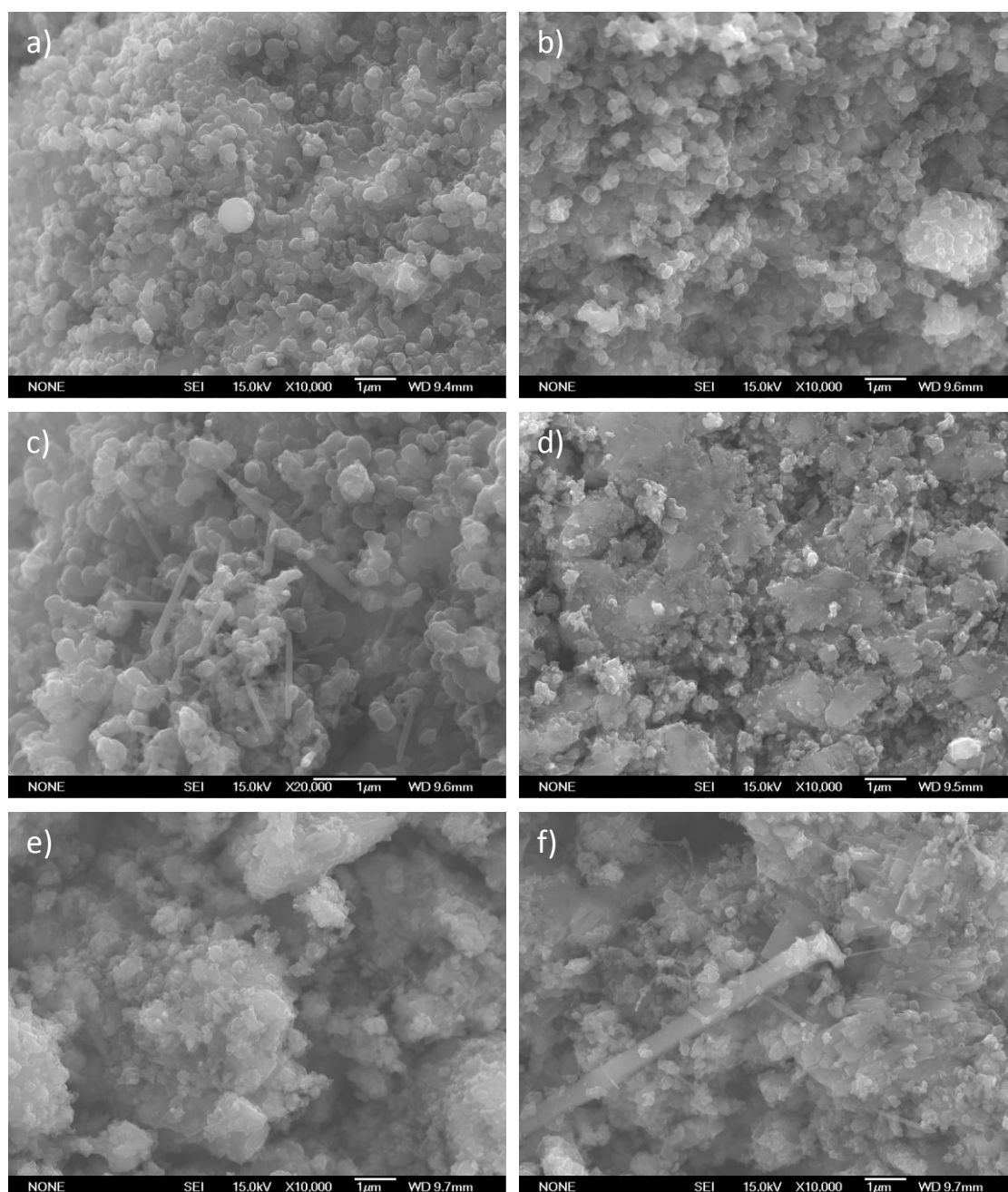


Figure 4.19: Selected SEI images of K1.3-CB samples fired at 1400 °C for a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr and f) 10 h showing varied surface morphologies. Magnification is 10000 or 20000x.

4.2.3.6 Firing under Argon

In order to determine whether any differences existed between the carbothermal reduction of the geopolymers prepared with carbon black rather than graphite, a K1.3-CB sample was fired at 1400 °C for 10 hr under in a flowing argon atmosphere. Figure 4.20 shows the resulting XRD pattern of the firing. It can be seen that the sample is comprised mainly of corundum, SiC and contains a trace amount of γ -alumina. The silicon carbide

formed is mostly 3C-SiC or β -SiC, which is its cubic form. However, the broad nature of the reflections between 33° and 39° and the peak at 33.7° (indicated by the red arrow) suggest that some polytypoid silicon carbide is also present, particularly in the 6H or α -SiC form. Bifurcation of the corundum peaks at higher angles is due to $K\alpha_2$ reflections being observed due to the small peak width, suggesting a large crystal size. As was the case with graphite-composites, no potassium bearing phase was observed suggesting its volatilisation by carbothermal reduction. In contrast, mullite was not detected as a constituent phase indicating either it did not form or was decomposed during firing.

As a significant quantity of corundum is observed in the fired product, it is thought that under these conditions the alumina in sample is more relatively stable when compared to silica as the geopolymer reacts and potassium is lost. It also suggests alumina does not go on to form reduced species, such as AlOC, AlO_2 , Al etc., under these conditions. This is concordant with the literature on Al_2O_3/SiC_x composites produced by carbothermal reduction of aluminosilicates.¹¹³⁻¹¹⁵

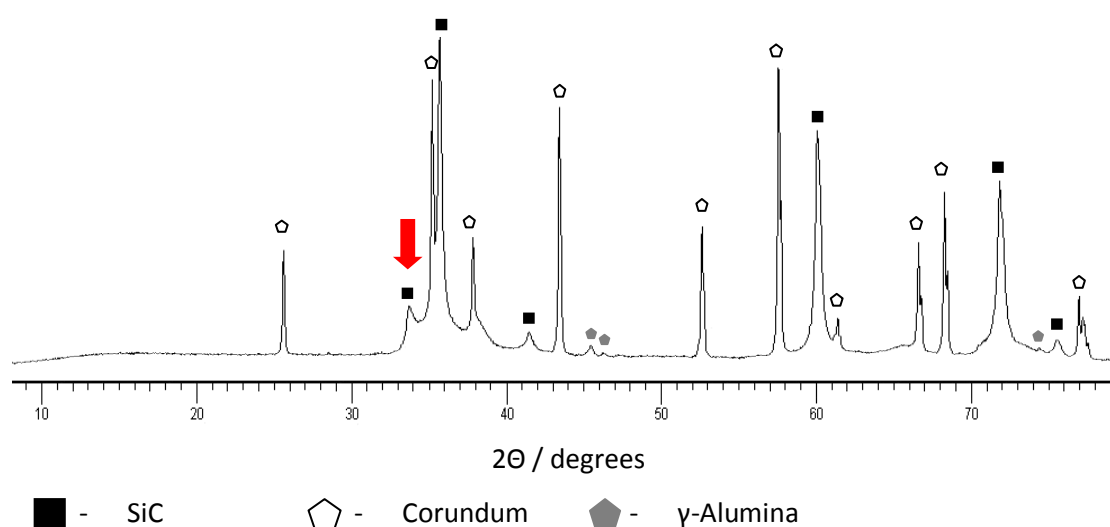


Figure 4.20: XRD pattern of K1.3-CB fired at 1400°C for 10 hr in flowing argon. The red arrow indicates a reflection caused by polytypoid SiC.

The infrared spectrum of the argon fired sample (Figure 4.21) shows a broad Si-C stretching band with a peak at 819 cm^{-1} with a shoulder at 916 cm^{-1} and four Al-O peaks from corundum at 637 , 583 , 491 and 444 cm^{-1} . A small, asymmetric Si-O-Si stretch at

1083 cm^{-1} indicates the presence of amorphous silica in the sample and its low wavenumber suggests that it may be a solid solution, possibly containing some aluminium.

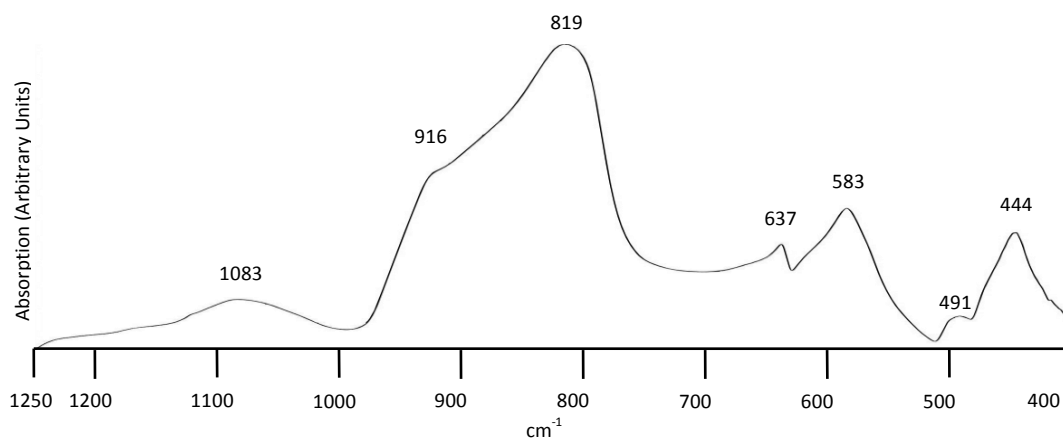


Figure 4.21: IR spectrum of K1.3-CB fired at 1400 °C for 10 hr in flowing argon.

4.3 Discussion

4.3.1 Mechanism of Sialon Formation from Potassium-Carbon Black

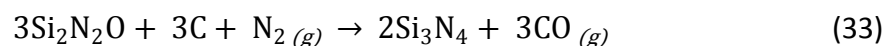
Composites

When fired to elevated temperatures, potassium derived geopolymer carbon black-composites were observed to retain their amorphous nature and did not readily crystallise into leucite. During the pre-synthesis-firing, K1.3-CB did not incorporate unreacted siliceous species of quartz and cristobalite or unreacted halloysite until 1300 °C. The emerging leucite phase crystallised with this incorporation but only in a limited way, even in the sample fired to 1400 °C. These results indicate that the integration of fine carbon black into the geopolymer matrix results in significant kinetic hindrance to the system, suppressing transformative processes of diffusion and atomic rearrangement (incorporation and crystallisation). This kinetic hindrance caused samples to remain in a largely amorphous state when the synthesis temperature of 1400 °C was reached, having implications for the reaction mechanism.

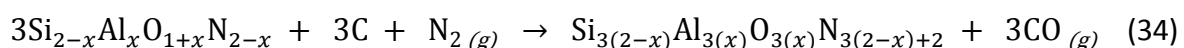
During firing at the synthesis temperature, the K1.3-CB sample reacted rapidly with the immediate loss of leucite and formation of several nitrogenous phases after only 1 hr. The minimal quantities of X-phase observed suggest that mullite had been formed during firing but that the dissociation of the geopolymer into mullite and SiO₂, presumably after potassium volatilisation, was suppressed. Also, as it was not observed, mullite either decomposes or undergoes carbothermal reduction and nitridation to form X-phase rapidly.

The formation of significant quantities of the silicon oxynitride type phase of O1-sialon suggests that rather than being a by-product in the reaction mixture and forming from nascent SiO (Equation (9)), this silicon oxynitride based phase is instead an intermediate in the reaction sequence. Furthermore, if O1-sialon was derived from SiO vapour then it would be reasonable to expect it to have formed woolly whiskers, as observed by Li *et al.*⁵¹ However, few whiskers were observed in samples fired at 1400 °C for 1 or 2 hr, which is when the O1-sialon phase was most prevalent. As silica was observed in the IR spectra it is possible that O1-sialon occurs as a result of eutectic formation in the sample during firing. This is in line with suggestions by Narciso *et al.*⁵⁶ that eutectic formation by CaO favours O-sialon formation and also similar to the observation by Ekström *et al.*⁵⁸ regarding K₂O in clays. Unit cell measurements showing an expanded unit cell volume indicate that the O1-sialon formed is a stuffed derivative which explains why O1-sialon and not O-sialon is formed. If this can be confirmed then this would be the first observation of a potassium stabilised sialon and with an ionic size of 152 pm would make it the largest ion substituted into a sialon phase.

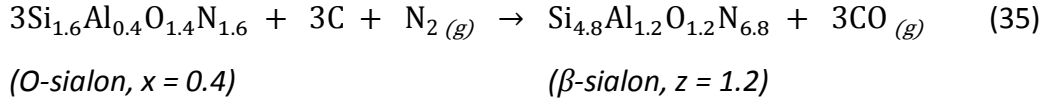
If silicon oxynitride or its aluminium containing derivatives of O- and O1-sialon are reaction intermediates then there must be a reaction pathway for them to transform into silicon nitride/ β -sialon. A theoretical reaction is therefore proposed below using Si₂N₂O as a starting point.



This equation can be modified to include the presence of aluminium to give the general formula shown below, where the z-value of the resulting β -silicon nitride phase is 3x:



Given that the solubility limit of aluminium in O-sialon is ~ 0.4 , this would mean a maximum z-value of 1.2 in the resulting phase which explains the appearance of the low z-value phase that becomes apparent by XRD after 4 hr. It would also explain the distributed z-values of β -sialons formed via CRN of amorphous zeolites with O-sialon as a preliminary phase seen in other studies.⁶³



It can therefore be assumed that the formation of high z-value sialons in the mixture is a result of a separate, simultaneous reaction pathway. As little X-phase and no mullite are observed, this pathway likely occurs from the direct carbothermal reduction and nitridation of the amorphous phase, similar to the processes suggested by Mazzoni and Aglietti⁶⁰ (shown in Equations (12) – (14)) and Yamakawa *et al.*⁶⁴ In these schemes, nitrogenous phases are a product of the CRN of either glassy (vitreous) or amorphous phases.

SiC is also seen to act as an intermediate by Mazzoni but not by Yamakawa, likely due to the latter's use of NH_3 gas as a reducing agent. It is therefore thought that the SiC seen in these experiments is similar in nature to the system examined by Mazzoni and acts as an intermediate. It can be seen from the results of the argon firing that the formation of SiC and aluminium oxide species (corundum and γ -alumina) is due to the carbothermal reduction of the geopolymer phase. Taking into account the presence of SiO_2 , this process can be summarised by the following equation using a 1.0 ratio of carbon as an example:



As this reaction was not studied in detail (i.e. under argon with varying reaction conditions of temperature and time) and has essentially gone to completion, it cannot be determined whether dissociation to form mullite occurred. It is thought that formation of SiC may occur from the carbothermal reduction of the geopolymer or, more probably, from the incomplete carbothermal reduction of the amorphous silica observed by IR.

Differences between samples fired for 8 hr and for 10 hr were noted by XRD, IR and NMR analysis. The 10 hr sample had a higher estimated z-value and contained less AlN and

no SiC when compared to the 8 hr sample. This result is anomalous as it is expected that the 10 hr sample should be more over-reacted, contain more AlN and have a lower z-value. This result cannot be explained simply by the inclusion of SiC into the 10 hr sample as SiC incorporation is typically a result of further reduction processes which would result in the formation of polytypoid phases and eventually AlN. One possible explanation is the differences in the firing conditions of samples. The 10 hr sample was fired at the same time as the K1.0-CB sample and the overall quantity of powder fired was much greater (2.09 g) than the 8 hr sample (1.65 g). This difference in powder quantity may have caused greater competition for the N₂ gas in the 10 hr sample slowing nitridation and affecting the resulting phase composition. This result suggests that the phase composition of resulting materials may be altered and optimised by factors not investigated in these studies.

4.3.2 Comparison to Potassium-Graphite Composites

Although the carbon content of the graphite- and carbon black-composites differed, the overall results of the investigation of carbon black-composites reveal behaviour in stark contrast to that of graphite composites. While differences between unfired samples were minor, during firing to the pre-synthesis stage between 1200 – 1400 °C, carbon-black precursors formed a mostly amorphous phase with only a small quantity of leucite whereas graphite-composites formed well-crystalline leucite. This is likely a result of kinetic hindrance caused by the carbon black which also impeded the dissociation of the geopolymer into mullite and SiO₂.

This retention of amorphousity resulted in β -sialon forming by carbothermal reduction and nitridation of a mainly amorphous phase and via intermediates of O1-sialon and SiC, in contrast to the conventional mechanism observed for potassium-graphite composites. However, similar to the potassium-graphite composite, a sample fired under argon revealed that SiC and alumina phases result from strictly CR and CRV processes. Also, carbon black samples were estimated to be fully reacted between 4 and 8 hr compared to graphite samples which were only partially reacted after 24 hr. It is therefore clear that the type of carbon, its size and differences in its intimate dispersion throughout the geopolymer

matrix results in significant changes to the reactivity of the geopolymer phase and alters the mechanism via which β -sialon is formed.

4.4 Summary

In this chapter, the CRN synthesis of β -sialon from potassium derived geopolymer-carbon black composites was investigated by exploring the effect of varying the carbon content of composites and by varying the firing atmosphere, temperature and time with the results compared to the graphite-composites presented in the preceding chapter.

Samples with varying carbon contents (1.0 – 1.3x stoichiometric quantity) were investigated by the firing of samples at 1400 °C for 10 hr in flowing nitrogen. The reaction products in the resulting materials differed but β -sialon was the dominate phase in all cases with the 1.0 and 1.1x mixtures containing some X-phase and O1-sialon whereas 1.2 and 1.3x mixtures contained small amounts of AlN, indicating that the some over-reaction had occurred.

To explore the reaction mechanism, the 1.3x mixture was chosen for further experimentation by the same method used for graphite-composites, namely by firing samples at 1200 °C, 1300 °C and 1400 °C without isothermal holds and at 1400 °C for between 1 – 10 hr in flowing nitrogen. A sample was also fired for 10 hr at 1400 °C under argon. From these firings, it was determined that the inclusion of carbon black into samples caused significant differences in the reaction mechanism due to considerable kinetic hindrance resulting in impeded crystallisation of the geopolymer matrix and subsequent dissociation. With the geopolymer phase retained in a mostly amorphous state, the reaction mechanism was observed to follow a non-typical pathway with the formation of β -sialon occurring via O1-sialon and SiC intermediates. This is in contrast to the conventional mechanism seen with the graphite composites. The argon firing indicated that the formation of SiC and by-product alumina phases were the result of carbothermal reduction of the geopolymer coinciding with the volatilisation of potassium. An equation to describe the formation of β -sialon from silicon oxynitride phases was proposed based on the observed results. Furthermore, the O1-sialon observed had an expanded unit cell volume and is suggested to be a potassium stuffed derivative phase resulting from the formation of eutectics in the amorphous system.

The reaction to form β -sialon was completed between 4 and 8 hr, in stark contrast to graphite samples which remained incompletely reacted after 24 hr. The anomalous result

seen in the sample fired for 10 hr suggests that the formation of β -sialon and by-products can be controlled and optimised by varying the gas flow and sample quantity.

5 Sodium Geopolymer-Carbon Black Composites

5.1 Introduction

In studies investigating the role of alkali on aluminosiliceous systems undergoing CRN, the effect of alkalis is often discussed indiscriminately and as such any differences between potassium and sodium have not been thoroughly explored. Due to their ability to be prepared with different activating alkalis, geopolymers represent an ideal system whereby these distinctions may be investigated and any differences can be studied in isolation and conclusions on the effects of alkali can be drawn.

To test this, a series of sodium carbon black-composites were prepared in the same way as potassium derived composites, namely by the activation of milled carbon-clay mixtures with a sodium silicate solution to prepare composites of similar compositions as potassium derived samples discussed in the preceding chapter. The effect of sodium on the synthesis of β -sialon by CRN of geopolymers was explored by reacting samples under a similar regime of firings as potassium samples seen in the previous two chapters. Samples were analysed using a range of analytical techniques including XRD, IR spectroscopy and SEM with complimentary EDS. As the ^{29}Si NMR results of the potassium-graphite and potassium-carbon black composites were of low quality and due to reasons of expedience and expense, solid state NMR experiments were not carried out on sodium samples.

5.2 Results

5.2.1 Synthesis of Sodium Geopolymer-Carbon Black Composites

Sodium geopolymer-carbon black composites and a non-carbon containing control sample were prepared from the same carbon clay mixtures described in the preceding chapter and an aged sodium silicate solution. The control sample was readily mixed into a viscous paste whereas carbon containing samples were too dry and could not be prepared without the use of excess water. As such, the $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio of the sodium composites is

12.00, slightly greater than the potassium composites $\text{H}_2\text{O}/\text{K}_2\text{O}$ ratio of 10.00. Entrained air bubbles could not be removed from the sodium composites by vibration due to their high viscosity. Samples were set and hardened by treatment at 40 °C for 24 hr before being pulverised in a concussion mortar and ground by hand. The resulting powders were passed through a #150 mesh sieve with openings of $\sim 105\ \mu\text{m}$.

In all, five sample mixtures were prepared for study; a control sample lacking carbon black and four composites with varying carbon black contents of 1.0, 1.1, 1.2 and 1.3 times the stoichiometric quantity of carbon as required by Equation (24). The non-carbon containing control sample was designated Na0 while the carbon black composites were designated Na1.0-G, Na1.1-G, Na1.2-G and Na1.3-G with increasing carbon content.

X-ray diffraction patterns (Figure 5.1) show behaviour consistent with potassium carbon black composites with the presence of unreacted silica species of quartz and cristobalite. Also similarly, the major amorphous hump broadened with the inclusion of the amorphous carbon black into the system (Figure 5.1b).

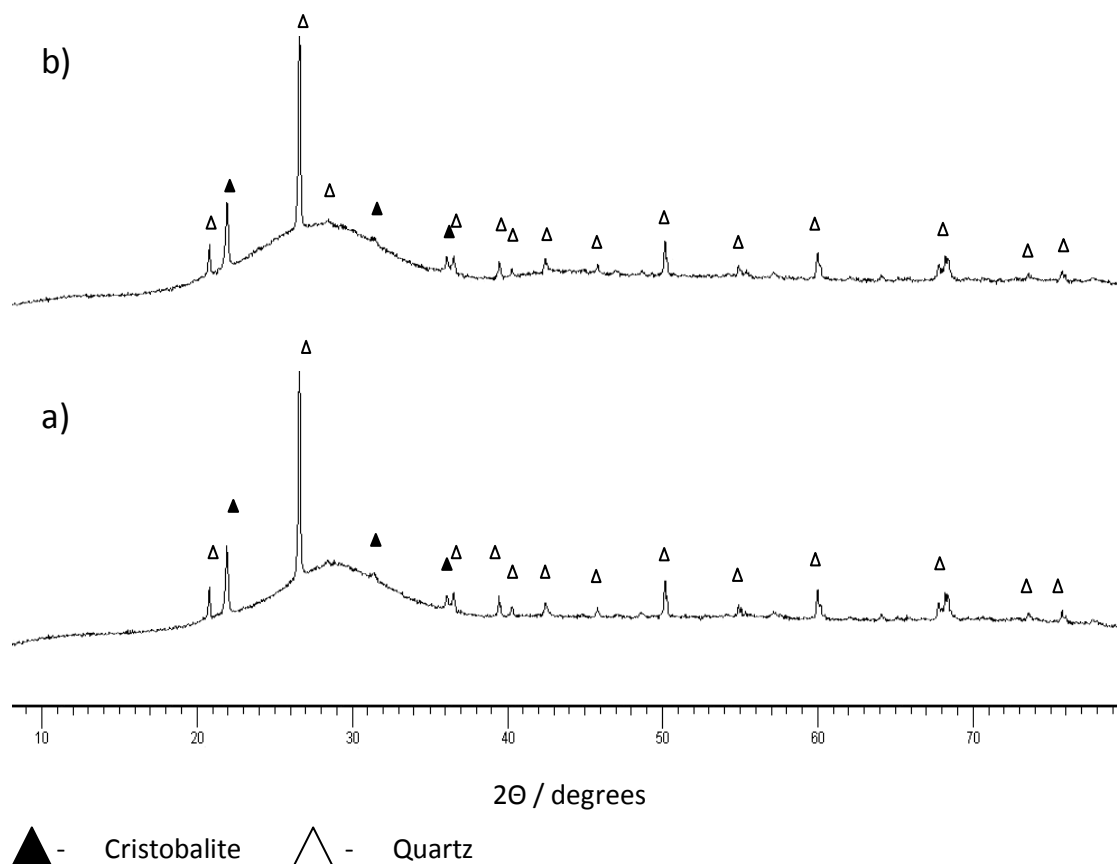


Figure 5.1: XRD patterns of a) Na0, the control sample and b) the Na1.1-CB sodium-carbon black composite.

Like its potassium analogue, the IR spectrum of the sodium geopolymer control (Figure 5.2a) contained 5 broad bands: a major Si-O-T asymmetric stretching band at with a peak at 1010 cm^{-1} and shoulder at $\sim 1080\text{ cm}^{-1}$ indicating a heterogeneous mixture of $\text{SiQ}_n(\text{mAl})$ environments, a T-OH stretch shoulder at 879 cm^{-1} , a broad band for symmetric Si-O-T stretches at 696 cm^{-1} , a small Si-O-T bending band at 591 cm^{-1} and finally, a Si-O-T rocking band at 448 cm^{-1} . The 10 cm^{-1} shift to lower wavenumbers in the major band (1010 cm^{-1}) compared to potassium samples is caused by sodium being the activating alkali in the geopolymer.

The addition of carbon black into the sodium geopolymer caused no significant changes in the resulting IR spectra (Figure 5.2b), the small Si-O asymmetric stretching band at 1200 cm^{-1} being the only difference. The two small, sharp peaks at 799 and 777 cm^{-1} in both spectra indicates the presence of unreacted dehydroxylated halloysite in samples.

A backscatter images obtained by SEM at low magnification (Figure 5.3a) shows homogeneous coloured particles with individual carbon particles unobserved. The smooth grey surface visible beneath particles is the carbon tape attaching and earthing the particles to the SEM stub. A higher magnification SEI image (Figure 5.3b) shows the same atypical, small, spherical morphology observed in potassium carbon black-composites reinforcing the view that the geopolymer matrix nucleates on the carbon black particles during

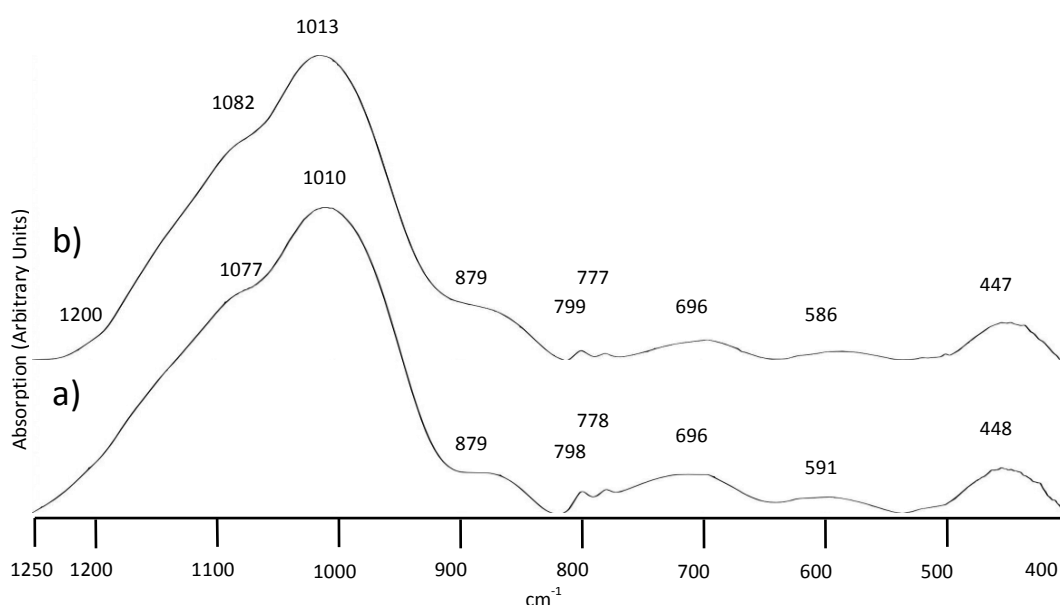


Figure 5.2: IR spectra of a) the unfired NaO control sample and b) Na1.1-CB sodium-carbon black composite.

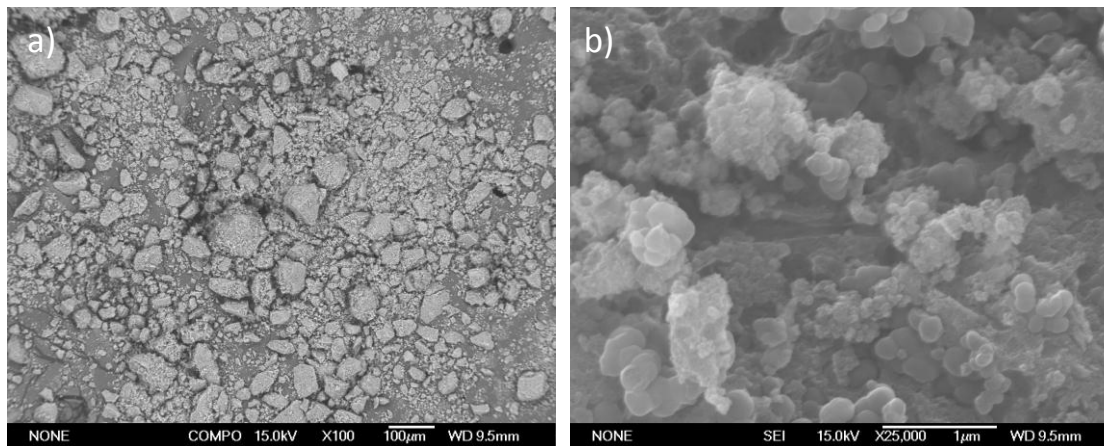


Figure 5.3: a) Backscatter image of unfired Na1.1-CB sample (100x) and b) a close up SEI image showing its small, spherical, nodular morphology (25000x).

geopolymerisation. EDS elemental analysis of the samples (Table 5.1) shows the composition of the sample to be close to the expected values for the geopolymer composite, albeit with a lower than expected sodium content.

Table 5.1: EDS elemental analysis of unfired Na1.1-CB at 100x magnification

Sample	Atom %				Si/Al Ratio	Na/Al Ratio
	Na	Si	Al	O		
Na1.1-CB	11.23	28.00	13.85	46.92	2.02	0.81

In comparison to the backscattered images, EDS maps (Figure 5.4) taken of the internal surface of a fractured particle at 1000x show the carbon black to be inhomogeneously distributed throughout the composite. The carbon rich regions are not

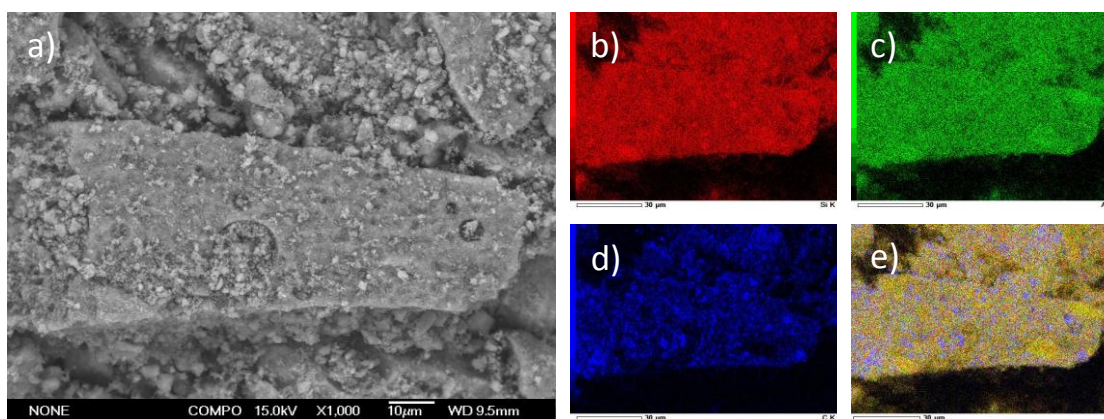


Figure 5.4: a) SEI image of ground, unfired Na1.1-CB with b) silicon, c) aluminium and d) carbon EDS maps and e) their overlay.

associated with either the Si or Al rich areas suggesting little preference for either unreacted clay or improperly mixed silicate solution but regions rich in both elements are particularly devoid of carbon.

This may be a result of insufficient mixing during synthesis due to the higher viscosity of sodium based samples. Poor milling of the carbon-clay mixture would result in similar behaviour but this is to be unlikely as this behaviour was not observed in potassium-carbon black composites, which were prepared from the same carbon-clay mixtures. In all, sodium carbon black-composites are very similar to their potassium analogues with the exception being harder to mix, potentially resulting in less homogeneous dispersion of the carbon black through the geopolymer matrix.

5.2.2 Firing of Samples with Varying Carbon Black Content

In the same way as potassium-carbon black- and -graphite composites, sodium-carbon black composites were prepared in several compositions, each with a different carbon content based on the stoichiometric ratio determined by Equation (24). Samples were then reacted by firing at 1400 °C for 10 hr in flowing nitrogen and compared to a control sample fired to at 1200 °C for 1 hr in an open air furnace.

The firing of carbon-containing samples resulted in well sintered but not completely melted grey powder compacts. Small quantities of whiskers were observed on boats at the down-stream of the firing tube outside of the hot-zone. The formation of glassy rings at the edges of the hot-zone was also noted. The quantity of observed whiskers appeared to be lower than fired potassium samples, suggesting that the liberation of less SiO during firing of sodium samples than what occurs with either potassium graphite- or potassium-carbon black composites. Upon firing, the control sample was observed to melt to form a glassy material, which could be predicted by the phase diagram (Appendix B).

XRD analysis of the fired samples indicated that the control sample fired to 1200 °C for 1 hr in open air is mostly amorphous but contains a trace amount of nepheline. The composites fired at 1400 °C for 10 hr (Figure 5.5) on the other hand, were comprised of mainly nitrogenous phases of β -sialon, O-sialon and X-phase with small quantities of SiC and γ -alumina. The samples with carbon content with greater than 1.0x also contained 15R-sialon indicating the over-reaction of these samples. A small quantity of AlN is also

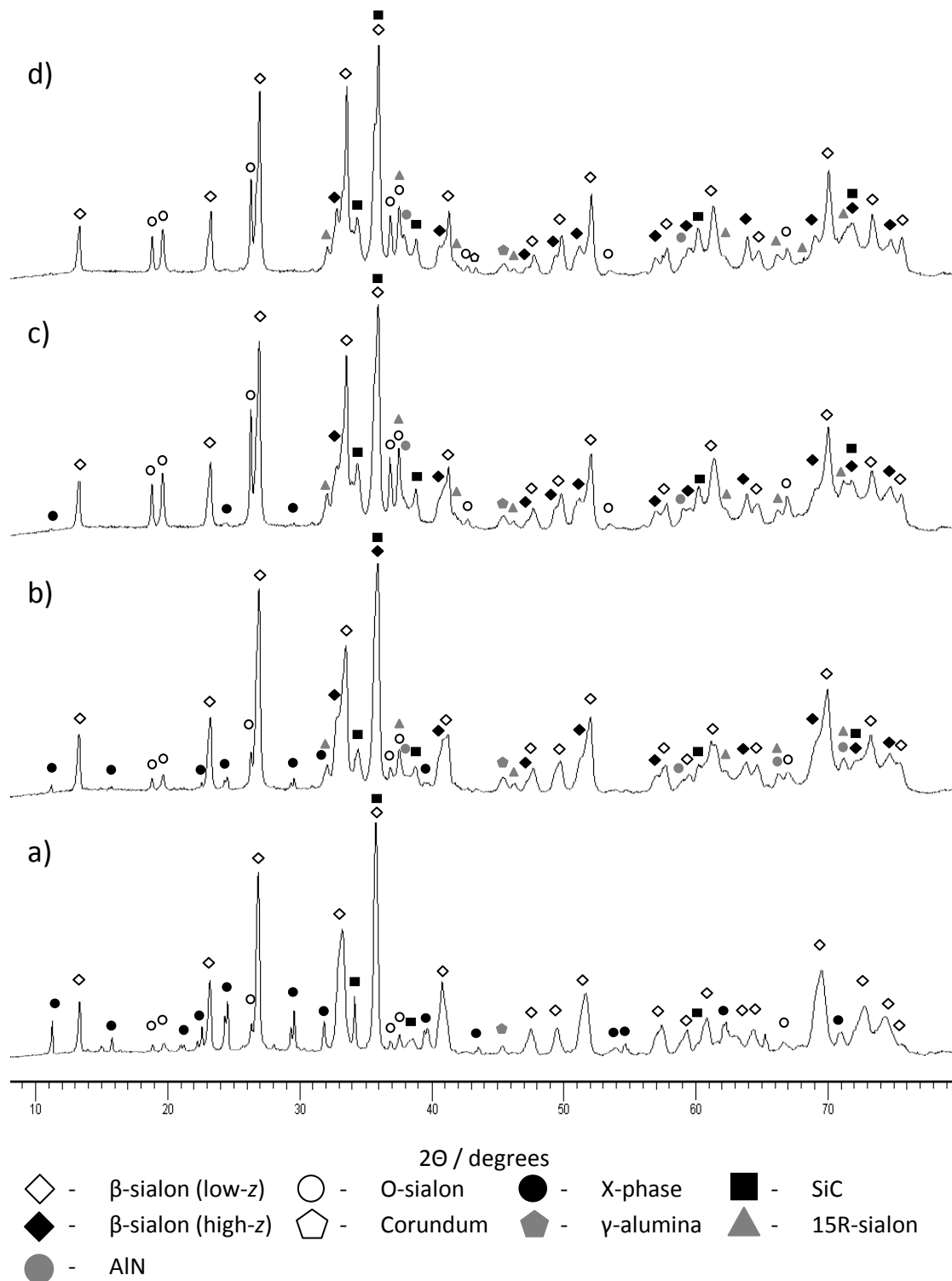


Figure 5.5: XRD patterns of samples fired in nitrogen at 1400 °C for 10 hr: a) Na1.0-CB, b) Na1.1-CB, c) Na1.2-CB and d) Na1.3-CB.

thought to be present in the X-ray patterns, specifically in samples Na1.1-CB, Na1.2-CB and Na1.3-CB, but its presence is difficult to positively identify due to the overlapping 15R-sialon reflections. The presence of both intermediary and over-reacted phases is likely a result of

the inhomogeneous distribution of carbon throughout the geopolymer matrix as observed in the unfired samples under SEM analysis.

Figure 4.6 shows the semi-quantitative data from samples where it can be seen that increasing carbon content is generally associated with decreasing β -sialon and X-phase content but an increase in O-sialon, SiC and 15R-sialon and AlN contents. The γ -alumina content is relatively constant throughout all samples, although sample Na1.3-CB also contains a small amount of corundum.

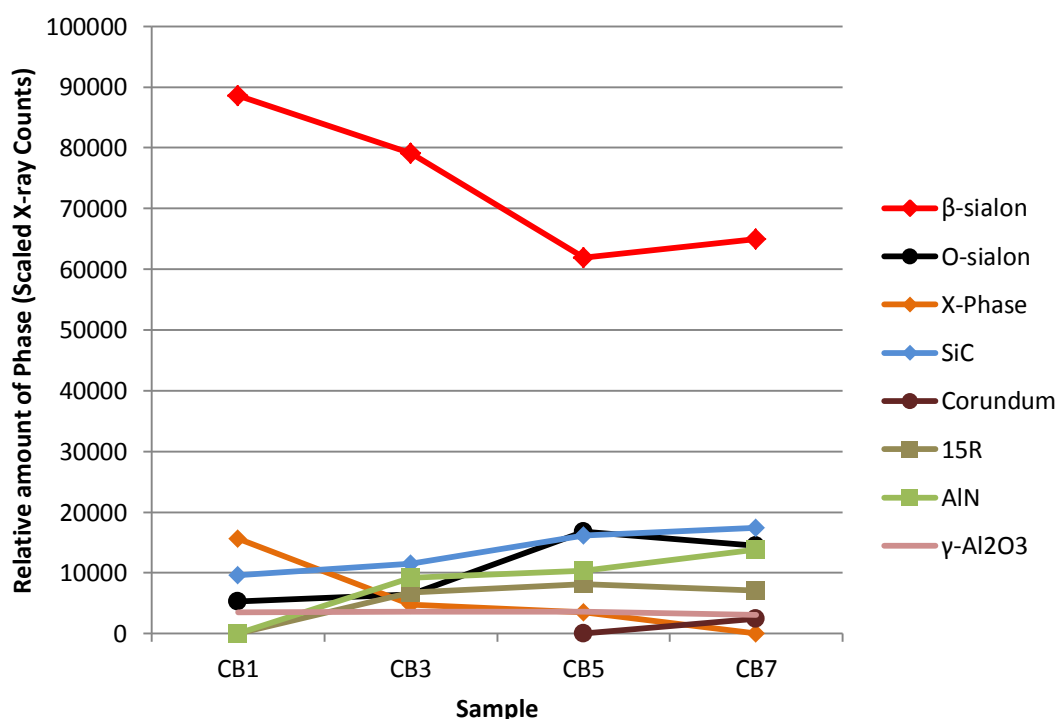


Figure 5.6: Semi-quantitative representation of the phases detected by XRD in sodium-carbon black composites with varying carbon content fired in nitrogen at 1400 °C for 10 hr.

Examination of the β -sialon reflections at $\sim 33^\circ$ indicates that the distribution of z -values within samples changes with increasing carbon content. Sample Na1.0-CB has a broad but singular peak whereas the other samples have two diverging peaks indicating a more diphasic nature with low z -value phases being dominant. The results of modelling these phases are shown in Table 5.2 and show that the two β -sialon phases become more divergent with increasing carbon content.

Table 5.2: Calculated z-values of the diphasic β -sialon produced by firing at 1400 °C for 10 hr.

Sample	Low z-value phase	High z-value phase
Na1.0-CB	1.23	2.34
Na1.1-CB	0.65	2.47
Na1.2-CB	0.45	2.58
Na1.3-CB	0.30	2.71

Between 1250 – 600 cm^{-1} , the IR spectra (Figure 5.7) of all carbon containing samples consist mainly of the $\nu_6 - \nu_4$ Si-N vibrational modes with small asymmetric Si-O stretches from amorphous silica ($\sim 1170 \text{ cm}^{-1}$) and broad overlapping Al-O and Al-N bands (800 – 600 cm^{-1}). Below 600 cm^{-1} , the two large peaks are the Si-N ν_3 and ν_2 vibrational modes with two peaks at 535 and 490 cm^{-1} associated with the O-sialon detected in the XRD patterns of Na1.1-CB, Na1.2-CB and Na1.3-CB. Interestingly the peaks of the Na1.0-CB spectrum are less

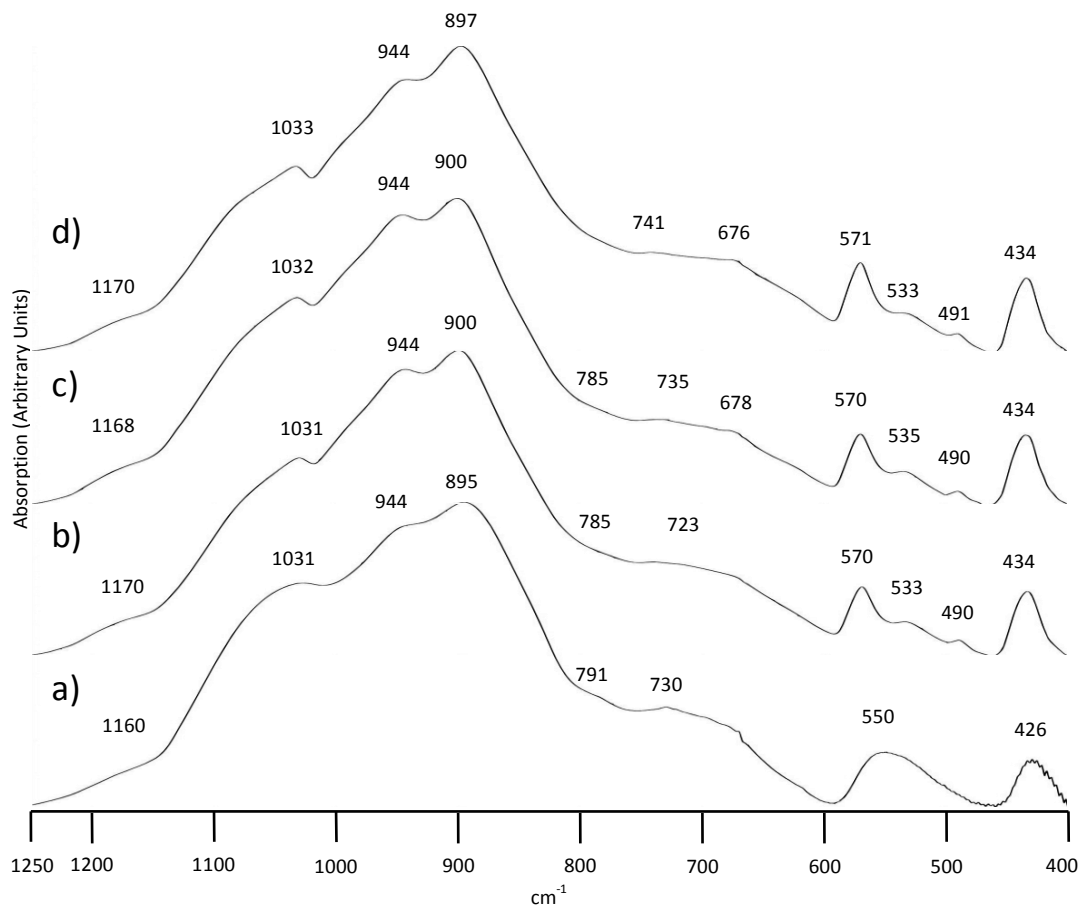


Figure 5.7: IR spectra of samples fired in nitrogen at 1400 °C for 10 hr: a) Na1.0-CB, b) Na1.1-CB, c) Na1.2-CB and d) Na1.3-CB.

well-defined than the other samples, possibly a result of the appreciable quantity of X-phase present or distribution of z -values causing broadening due to overlapping Si-N bands. Due to the over-lapping bands from the O-sialon and X-phase in all samples, the estimation of z -values from the wavenumbers of ν_3 and ν_2 modes is not appropriate.

To investigate the reaction mechanism of sodium geopolymer carbon black composites, the sample Na1.1-CB was chosen for further experimentation. Although this sample did not have the highest yield of β -sialon as determined by semi-quantitative measurements, it was decided that this sample best represented the compromise between under- and over-reaction in samples.

5.2.3 Reaction Sequence of Sodium-Carbon Black Composites

To investigate the reaction mechanism of sodium carbon-black composites, a series of Na1.1-CB powders were fired using the same regime as potassium-carbon black composites. The reaction mechanism and evolution of samples was determined by monitoring the weight loss of sample and analysis by XRD, IR spectroscopy and SEM with complementary EDS.

5.2.3.1 Observations and Weight Loss

During firing, all samples were observed to sinter and densify to form solid powder compacts regardless of firing temperature or time, likely due to viscous sintering. The degree of sintering was observed to be greater than samples from the analogous potassium-carbon black series. This difference in behaviour is expected as the composition of the sodium geopolymer matrix is less thermally stable than the potassium geopolymer composition. However, despite all firing temperatures being close to or exceeding the predicted melting temperature, samples were not observed to melt, suggesting that the inclusion of carbon causes considerable kinetic hindrance in sodium samples as well. Whiskers were observed on the boat and the firing tube after firing but not in a large abundance.

Figure 5.8 shows the weight lost from samples plotted against time for all firings. The Na1.1-CB sample fired to 1200 °C had an overall 27.6% reduction in mass, over double the

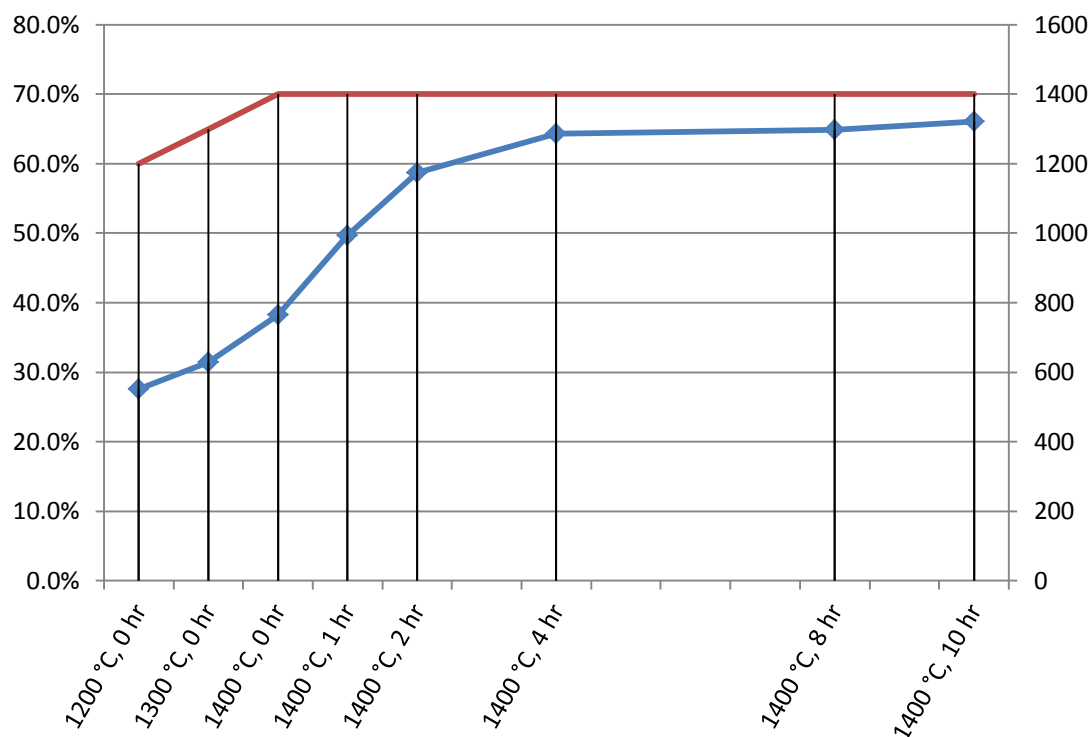


Figure 5.8: Weight loss of Na1.1-CB samples fired at progressively higher temperatures for varying durations. The red line indicates the temperature.

amount lost for the corresponding potassium sample, possibly indicating an earlier onset to the CRV process in sodium samples compared to potassium composites. The rate of weight loss during the rest of the pre-synthesis stage remains steady with a weight loss of almost 40% by 1400 °C. The rate increases slightly during at the beginning of the synthesis stage but decreases as samples are fired further, reaching a total weight loss of 66.1%, similar to potassium samples.

5.2.3.2 X-Ray Diffraction Studies

Figure 5.9 shows the XRD patterns of the unfired sample and pre-synthesis fired samples. Upon firing to 1200 °C, the unreacted silica phases are incorporated into the geopolymer and the sample remains amorphous with the observed humps being consistent with the pattern acquired from the carbon black with peaks centred at 25.5° and 44°. While still broadly amorphous, the humps present in the pattern of the sample fired to 1300 °C are no longer consistent with the carbon black. This suggests that the geopolymer matrix is undergoing some structural rearrangement, possibly from changes in composition due to

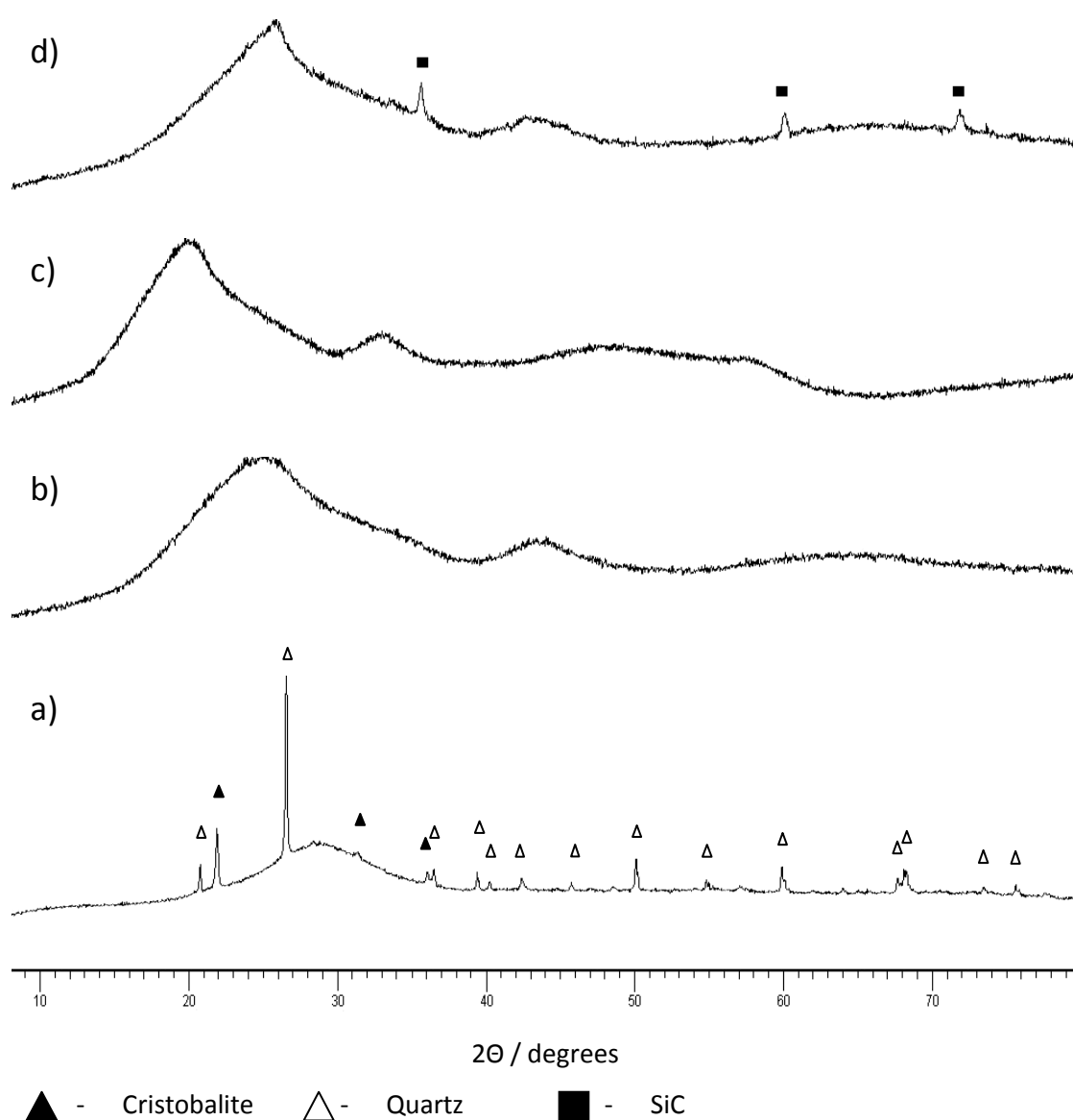


Figure 5.9: XRD patterns of Na_{1.1}-CB: a) Unfired, b) 1200 °C, 0 hr, c) 1300 °C, 0 hr and d) 1400 °C, 0 hr.

CRV or perhaps from the formation of glassy phases. By 1400 °C, the pattern (Figure 5.9d) is again broadly amorphous with humps more consistent with those of the carbon black. The presence of SiC was detected, indicating that either the onset of carbothermal reduction processes begins earlier or that they are more rapid than in the corresponding potassium carbon black-composites.

Figure 5.10 shows the reaction mechanism during the synthesis region with samples being held at 1400 °C for varying durations whereas Figure 5.11 shows the semi-quantitative

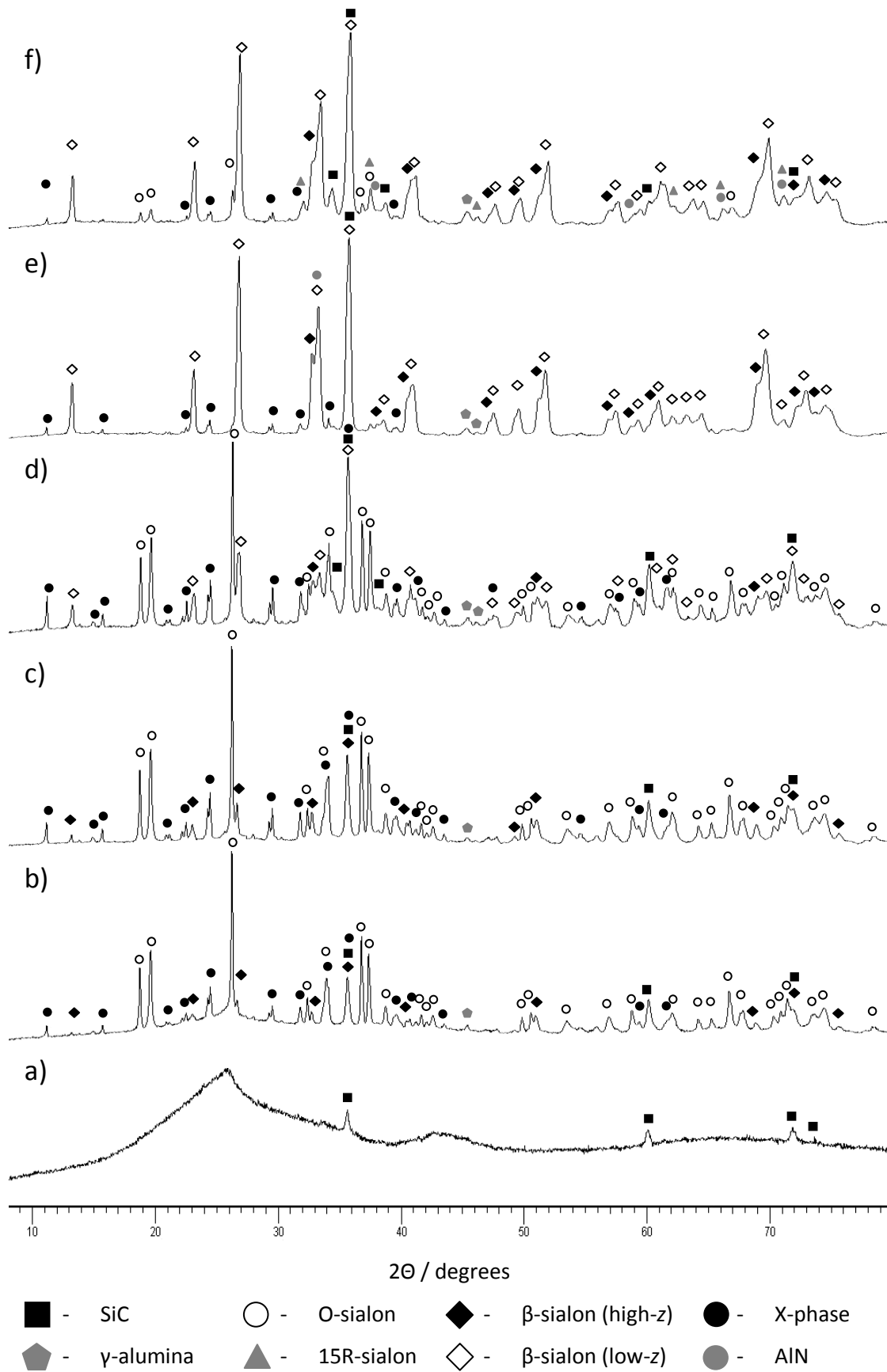


Figure 5.10: XRD patterns of Na_{1.1}-CB samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr and f) 10 hr.

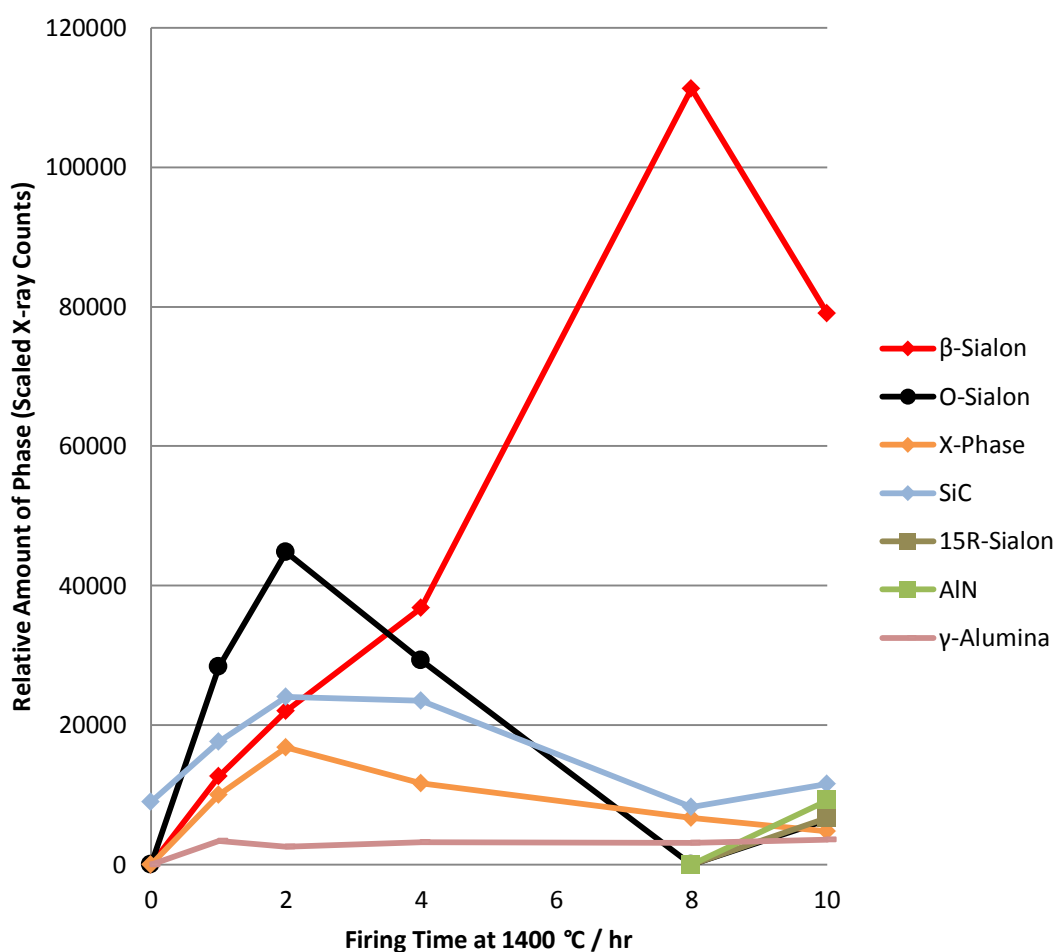


Figure 5.11: Semi-quantitative representation of the phases detected by XRD in Na1.1-CB samples fired in nitrogen at 1400 °C for various times

analysis of samples. After only 1 hr at 1400 °C, the sample undergoes significant change with the formation of nitrogenous phases including O-sialon, X-phase with an increase in SiC content and a trace of γ -alumina being present. A small quantity of high z-value β -sialon ($z = 3.4$) is also observed but O-sialon is the dominant phase at this point. A quantity of amorphous phase is also apparent.

After 2 hr of reaction, the growth of the nitrogenous phases and SiC is seen with a reduction in the amorphous content and γ -alumina. A slight decrease in the estimated z-value of the β -sialon phase was apparent with modelling indicating a value of $z = 3.0$. The amorphous content had all but disappeared with a decrease in the O-sialon and X-phase content after 4 hr whereas the quantity of β -sialon had increased with the notable emergence of a low z-value phase ($z = 1.31$), similar to potassium samples. After 8 hr, the sample is almost completely β -sialon with only a small quantity of X-phase and SiC being

otherwise detected. The complete disappearance of O-sialon from the sample is complemented with a large increase in the quantity of low z -value β -sialon ($z = 1.2$).

The sample fired for 10 hr is predominantly β -sialon but also contains O-sialon, X-phase, SiC and also over-reacted phases of 15R-sialon and AlN. Similar to the corresponding K1.3-CB sample, it would appear that the rate of reaction in this sample was too altered due to the quantity of sample present during firing changing the availability of nitrogen to samples during firing.

Rietveld modelling of unit cell dimensions of the O-sialon phases detected are shown in Table 5.3. These values indicate fairly consistent unit cell volumes between 240.85 – 242.75 Å³ with a axis lengths between 8.995 – 9.010 Å. When compared to the values provided by Lindqvist *et al.*,¹³ these results suggest an O-sialon with $x > 0.4$ and therefore above the accepted solubility limit of aluminium in the structure. This may indicate the inclusion of sodium into the O-sialon structure to form a stuffed derivative phase. The unit cell measurements of these O-sialons are not in agreement with the values provided by Zhu *et al.*¹⁶ for the Na-O-Sialon phase however. This difference may be the result of the variations in the amount of sodium substituted into the structure, with more sodium content and greater unit cell volume expected in the phase produced by Zhu due to their use of hot-pressing in that study. When compared to the $x = 0.4$ O-sialon phase produced by Lindqvist *et al.*¹³ the increases in unit cell volume for these phases were between 1.0 – 1.8%. This is in line with the O1-sialon phase discussed in the preceding chapter. The phase produced by Zhu has a unit cell volume expanded by 7.0%.

Table 5.3: Unit cell parameters of O-sialons from fired sodium composites compared to literature values

Source	a / Å	b / Å	c / Å	Volume / Å ³	x-value
Lindqvist <i>et al.</i>¹³	8.9254(5)	5.4974(3)	4.8593(3)	238.45(2)	0.4
1400 °C, 1hr	9.010	5.521	4.880	242.8	-
1400 °C, 2hr	8.986	5.509	4.874	241.3	-
1400 °C, 4hr	8.995	5.503	4.875	241.3	-
1400 °C, 10hr	8.995	5.488	4.879	240.8	-
Zhu <i>et al.</i>¹⁶	9.15	5.65	4.94	255.3	-

5.2.3.3 Infrared Spectroscopy

Figure 5.12 shows the results of the samples fired under pre-synthesis conditions compared to the unfired sodium control (Figure 5.12a). Firing to 1200 °C caused a marked change to the major band with the disappearance of the shoulder at 1082 cm^{-1} and the appearance of a large shoulder at 935 cm^{-1} . These changes are attributed to homogenisation of the Si-O-T environments and inclusion of sodium into the structure of the amorphous network causing a shift to lower wavenumbers. The band from the Si-O-T bending modes narrows and also shifts slightly to lower wavenumbers with the significant growth of the Si-O-T rocking mode (462 cm^{-1}). The small, sharp peak at 668 cm^{-1} (unlabelled) was determined to be caused by an impurity in the KBr used to suspend the samples.

Firing to greater temperatures caused the major band to shift back to higher wavenumbers, possibly as a result of the loss of sodium from samples due to CRV. A

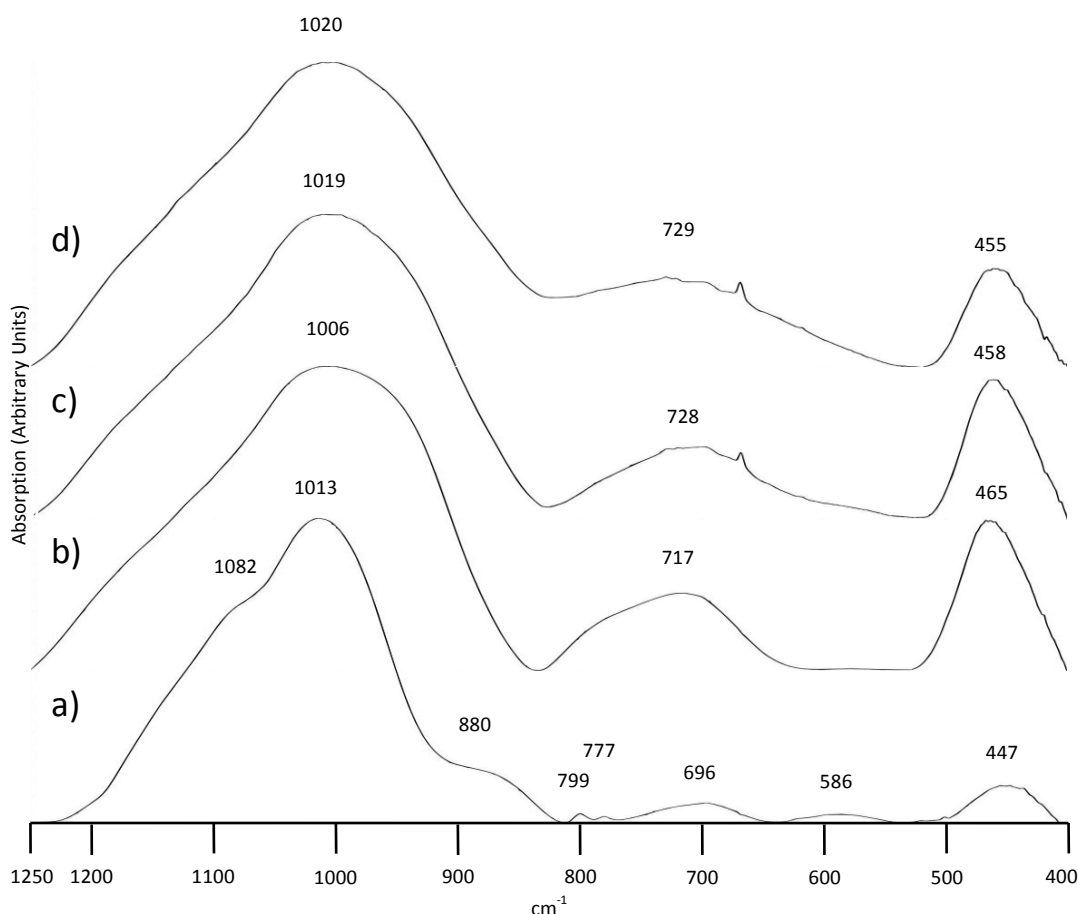


Figure 5.12: IR spectra of Na1.1-CB samples: a) Unfired sample, b), 1200 °C, 0 hr, c) 1300 °C, 0 hr and d) 1400 °C, 0hr.

corresponding shift to higher and lower wavenumbers was observed for the Si-O-T bending and rocking bands, respectively. These bands remain stable in the sample fired to 1400 °C.

Spectra of the samples treated at 1400 °C for between 0 – 10 hr are shown in Figure 5.13. After treatment for 1 hr, a number of new bands developed, including $\nu_6 - \nu_2$ Si-N vibrational modes at 1057, 946, 886, 531 and 439 cm^{-1} , respectively, and absorption bands associated with O-sialon at 992 and 487 cm^{-1} . The peak at 439 cm^{-1} is relatively intense due to overlapping with the Si-O-T rocking band from the unreacted phase. A broad Si-O-T bending band centred at 731 cm^{-1} spans the middle region of the spectrum with a SiC

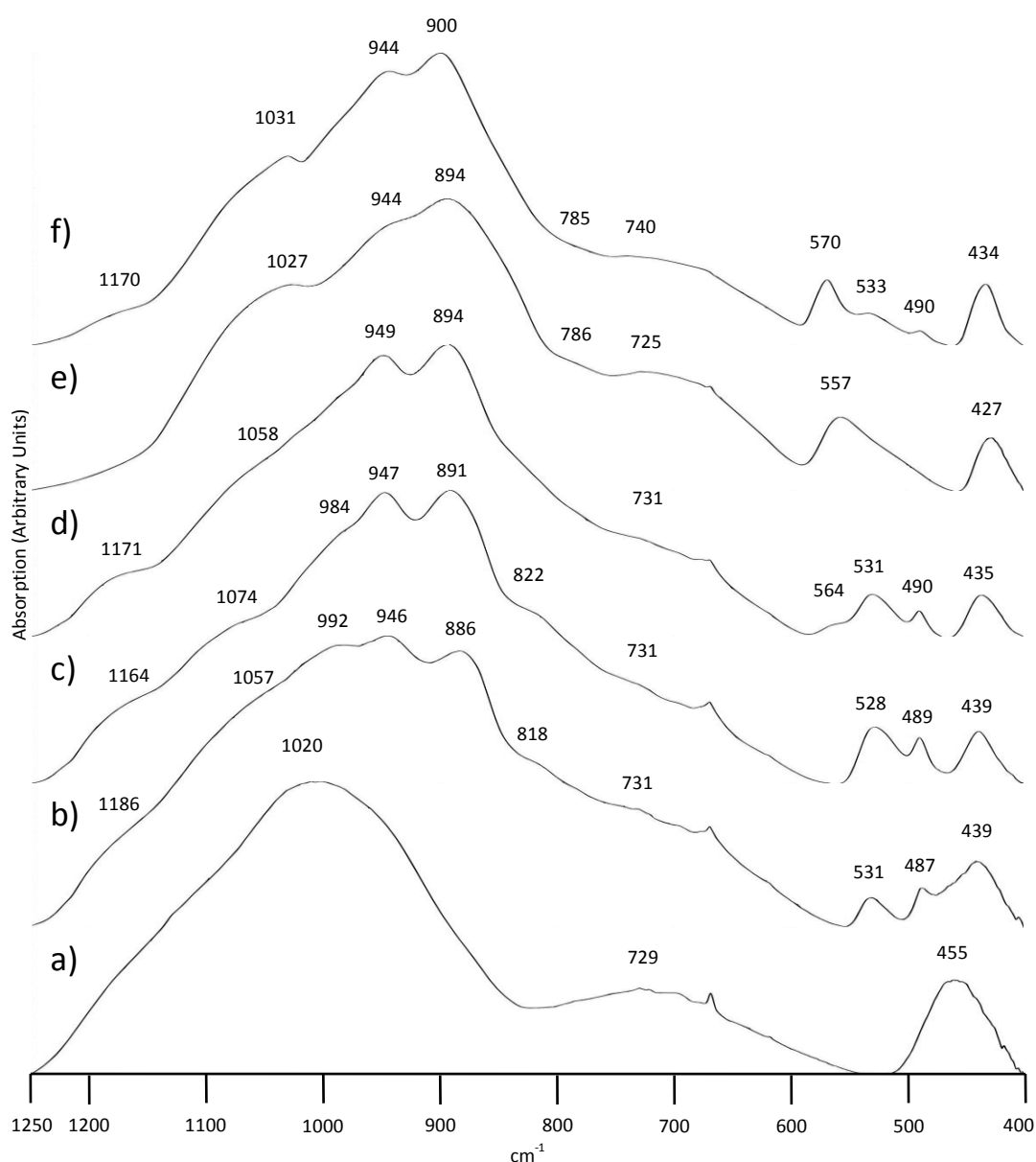


Figure 5.13: IR spectra of Na1.1-CB samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr and f) 10 hr.

shoulder apparent at 818 cm^{-1} . A Si-O shoulder at 1186 cm^{-1} possibly indicates the presence of some amorphous silica in the sample.

Further firing to 2 hr results in the growth of the ν_5 , ν_4 and ν_3 modes at 947, 894 and 528 cm^{-1} due to the increase in β -sialon and X-phase in materials. Despite its increase when analysed semi-quantitatively in the XRD patterns, a relative decline in the O-sialon peaks at 984 and 489 cm^{-1} is seen with a parallel decline in the intensity of the Si-O-T rocking band at 439 cm^{-1} . After 4 hr at 1400°C , the spectrum is predominately β -sialon with only a slight shoulder at 1058 cm^{-1} and a small peak at 490 cm^{-1} indicating the presence of O-sialon. The emerging peak at 564 cm^{-1} is attributed to the low z-value β -sialon phase seen in the XRD patterns. The continued presence of the Si-O band from amorphous silica is noted at 1171 cm^{-1} along with an emerging tetrahedral Al-N peak at 786 cm^{-1} .

The spectrum of the 8 hr sample is typical of a β -sialon material with a distribution of z-values due to the broad ν_3 and ν_2 Si-N modes. The estimated combined z-value of this sample is 1.3, marginally greater than the value determined by XRD analysis. Estimation of the z-values of the other samples is not appropriate due to the overlapping absorption bands from O-sialon and X-phase.

The reappearance of peaks associated with O-sialon with the tetrahedral Al-N peak indicates a different phase assemblage in the sample fired for 10 hr. This is consistent with the data from the XRD analysis.

5.2.3.4 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

The samples fired to the synthesis temperature of 1400°C for varying duration were examined by SEM and secondary electron and backscattered images of the bulk of samples and features of interest were acquired. EDS compositional analysis was carried out at a magnification of 100x to determine the bulk composition of the samples.

Figure 5.14 shows the results of the EDS experiments normalised to the aluminium content with increasing firing time compared to the unfired sample. It can be seen that, similar to potassium, sodium is mostly volatilised from the system after 2 hr with only a trace amount remaining at 4 hr and its complete disappearance after 8 hr. A simultaneous decline in oxygen content is observed and nitrogen is detected after 2 hr of firing. Also, like potassium, a slight initial rise in the silicon content is observed before its decline at 8 hr. The

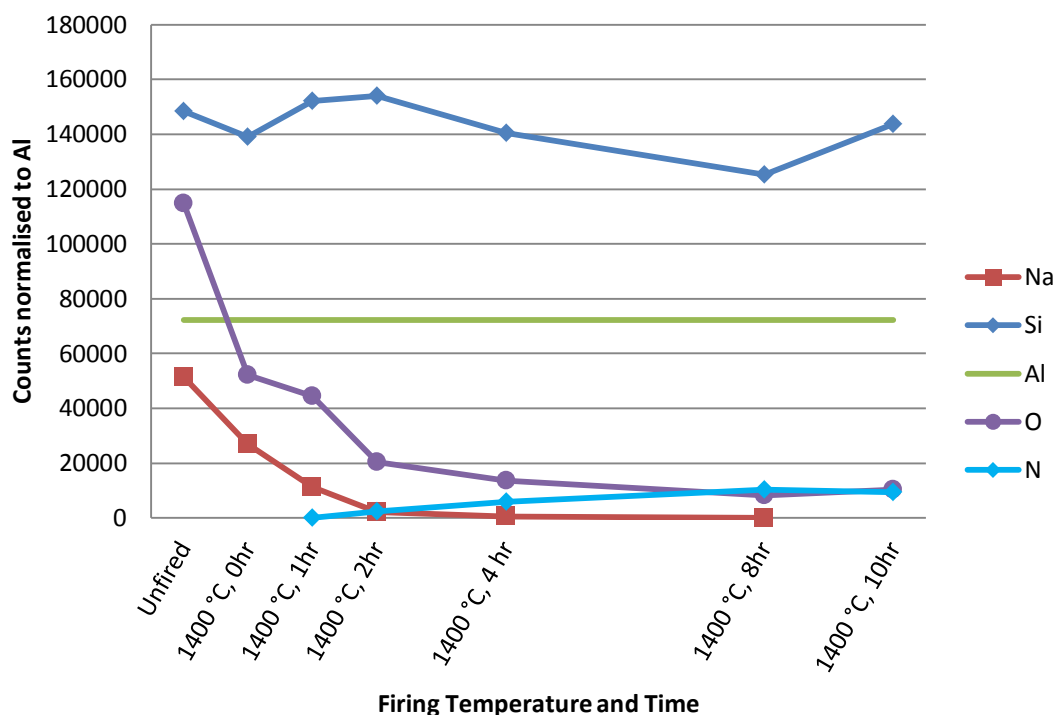


Figure 5.14: Normalised elemental counts of Na_{1.1}-CB samples fired at 1400 °C between 0 – 10 hr compared to the unfired sample.

composition of the sample fired for 10 hr contains a greater silicon content but similar oxygen and nitrogen content to the 8 hr samples suggesting that loss of Si via SiO formation from this sample is significantly reduced due to the different firing conditions (i.e. the previously mentioned difference in sample quantity). Some potassium was also detected in samples, particularly those fired for shorter durations. This contamination was likely due to vaporised potassium which had diffused into the firing tube only to be released during later firings.

Examination of the secondary electron and backscattered images revealed different behaviour from fired potassium samples. Figure 5.15 shows a selection of images taken of the sample fired 1400 °C without an isothermal hold with the backscattered image at 100x (Figure 5.15a) revealing the presence of large, spherical features of a different composition amongst the darker bulk. The bulk of the sample is made up of well sintered, porous grains with the same spherical, nodular morphology as the corresponding potassium sample.

Further examination of the large spherical, compositionally different features (Figure 5.16) revealed them to be melted particles indicating the presence of glassy phases with smooth, non-porous external and internal surfaces.

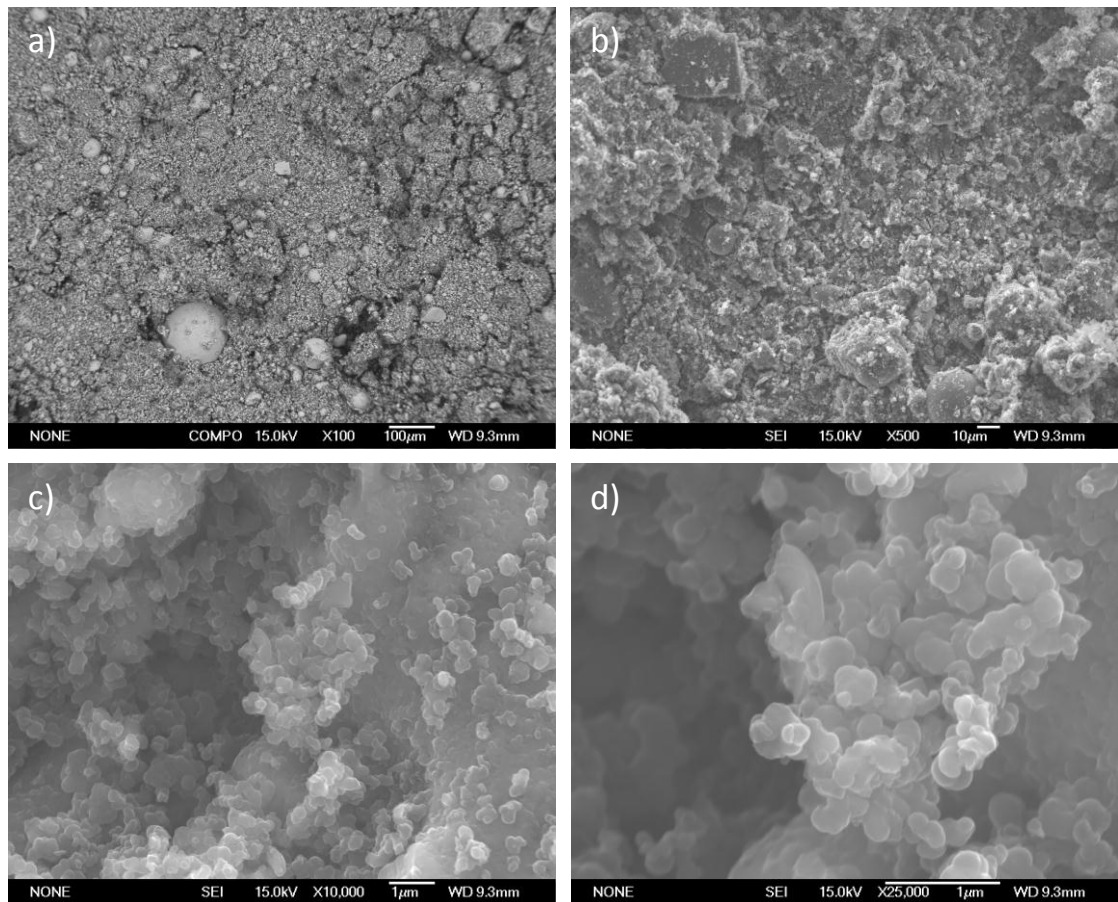


Figure 5.15: a) Backscattered image and selected SEI images of the Na1.1-CB sample fired at 1400 °C for 0 hr at various magnifications showing b) particulates, c) and d) retained spherical, nodular morphology.

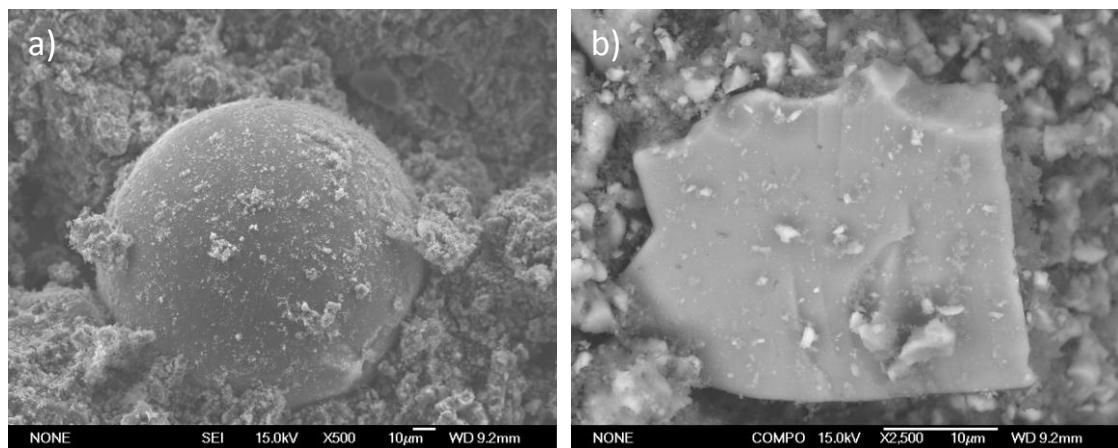


Figure 5.16: Selected SEI and backscatter images of Na1.1-CB samples fired at 1400 °C for 0 hr. a) Melted spherical particle and b) the internal surface of a fractured glassy particle.

Although samples were coated with carbon, EDS analysis (Table 5.4) indicated that these melted, glassy particles were relatively carbon deficient compared to the bulk. These results suggest that the glassy particles from due to the inhomogeneous distribution of

carbon in the unfired precursor and are consistent with the proposition that carbon stabilises the geopolymer matrix from melting due to kinetic hindrance.

Table 5.4: Averaged spot EDS elemental analyses of selected particles compared to the bulk

Particle	Atom %				
	Na	Si	Al	O	C
Bulk	2.04	12.32	5.74	4.06	75.85
Spherical	3.53	22.44	8.27	24.89	40.87
Fractured	3.72	32.59	17.29	23.90	22.49

When recalculated to exclude the carbon content (Table 5.5), it can be seen that the glassy phases are oxygen rich but sodium poor, having lost at least 30% of their sodium content due to CRV processes. Comparison of the Si/Al and Na/Al ratios suggests that even taking into account the loss of sodium, the sample melted incongruently, indicating that a range of glassy compositions will form as a result of the inhomogeneous distribution of carbon throughout the sample.

Table 5.5: Averaged spot EDS elemental analyses of selected particles compared to the bulk

Particle	Atom %				Si/Al Ratio	Na/Al Ratio
	Na	Si	Al	O		
Bulk	8.45	51.00	23.76	16.79	2.15	0.36
Spherical	5.97	37.95	13.98	42.09	2.71	0.43
Fractured	4.80	42.05	22.31	30.84	1.88	0.22

Figure 5.17 shows a selection of SEI images of samples fired for progressively longer durations at 1400 °C. These images, taken at 10000x magnification, illustrate a gradual loss of the small, spherical nodular morphology with the subsequent conversion in sintered particles with a rough, jagged texture. Glassy particles were observed in samples fired for shorter durations but their presence was noted to progressively decrease with their presence undetected under backscattering conditions in the samples fired for 8 and 10 hr. This disappearance of glassy particles coincides with the loss of sodium from samples.

Fibres were noted in the sample fired for 1 hr, but like potassium samples, the abundance of fibres was very low and with only small aspect ratios. The observation of

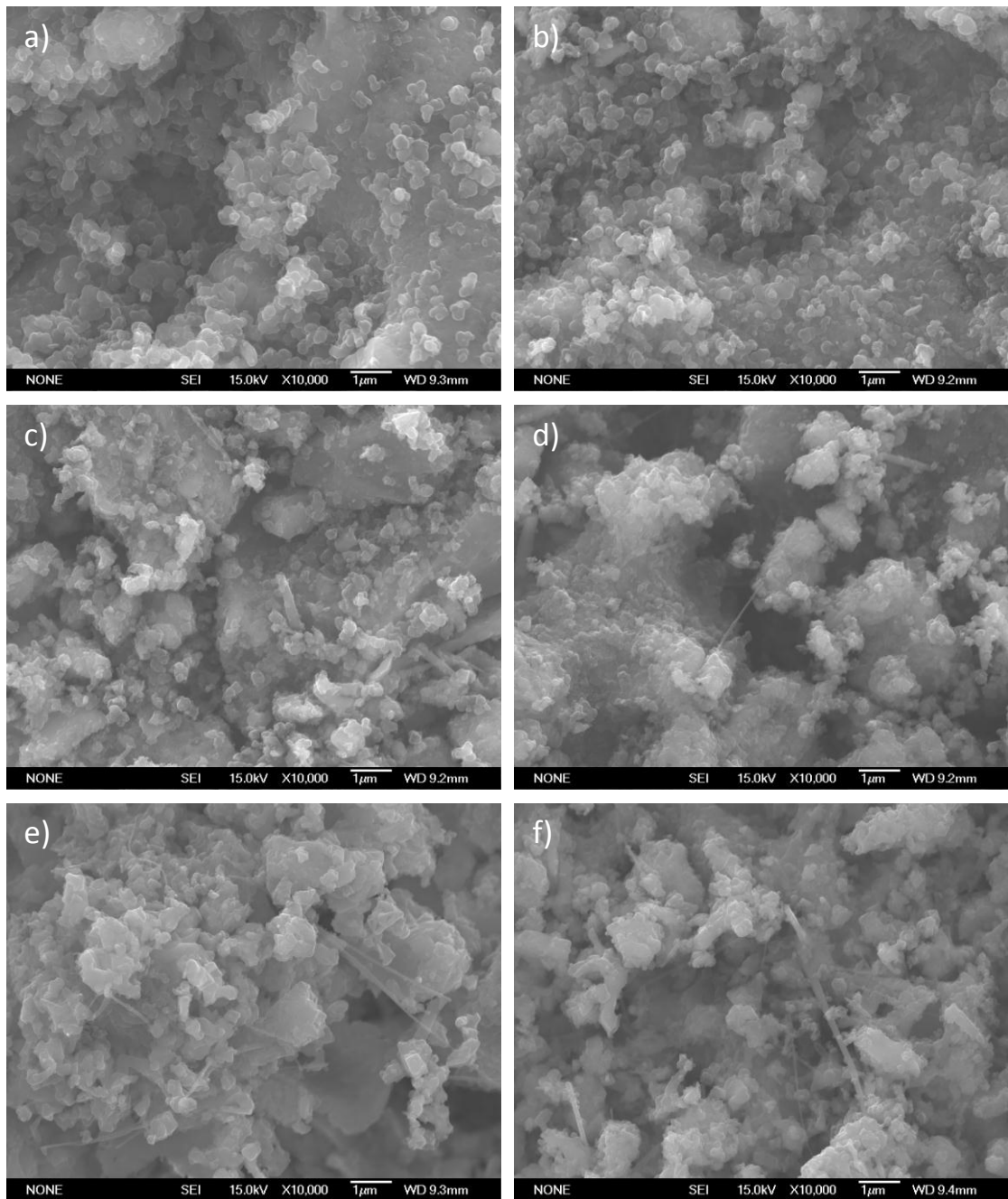


Figure 5.17: Selected SEI images of Na_{1.1}-CB samples fired at 1400 °C for a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr and f) 10 h showing varied surface morphologies. Magnification is 10000x.

longer fibres did not occur until late in the firing sequence after the majority of sodium had been lost suggesting that like the potassium-carbon black system, sodium does not play a significant role in the formation of sialon fibres during CRN.

5.2.3.5 Firing under Argon

To establish whether sodium composites undergo CRV processes similar to potassium composites, a Na1.1-CB sample was fired in flowing argon at 1400 °C for 10 hr. From the resulting XRD pattern (Figure 5.18), it can be seen that similar the K1.3-CB sample, the sodium composites forms corundum and both α - and β -SiC. Unlike the potassium sample however, is the observation of κ -alumina in a small quantity. Like γ -alumina, κ -alumina is a metastable aluminium oxide phase but with an orthorhombic structure instead of a face-centred arrangement. No sodium bearing phase was observed indicating that, like potassium composites, it too volatilises in the presence of carbon at high temperatures.

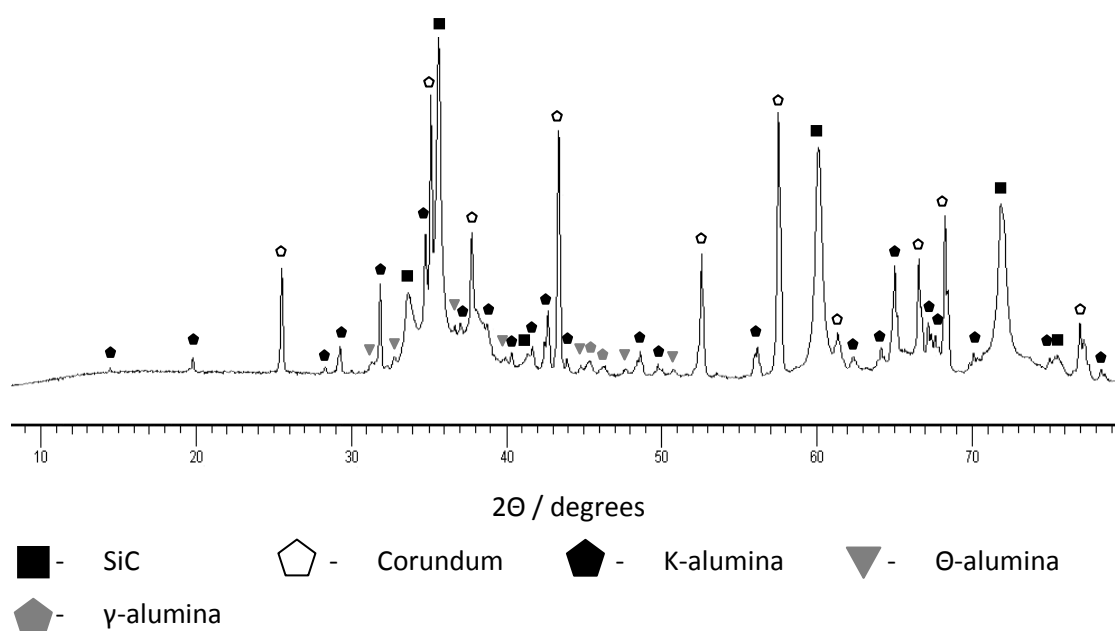


Figure 5.18: XRD pattern of Na1.1-CB fired at 1400 °C for 10 hr in flowing argon.

When analysed by infrared spectroscopy, the resulting spectrum (Figure 5.19) shows a large absorption band from Si-C stretches at 827 cm^{-1} with a shoulder at 894 cm^{-1} , similar to the potassium sample. However, in contrast, the octahedral Al-O stretches at 636 and 587 cm^{-1} from corundum are not prominent and are instead mixed in with a large series of overlapping bands from the other alumina phases causing a multitude of indistinct peaks below 800 cm^{-1} . The Si-O stretching band from silica present in the argon fired potassium-carbon black sample was also not observed, suggesting that carbothermal reduction to form

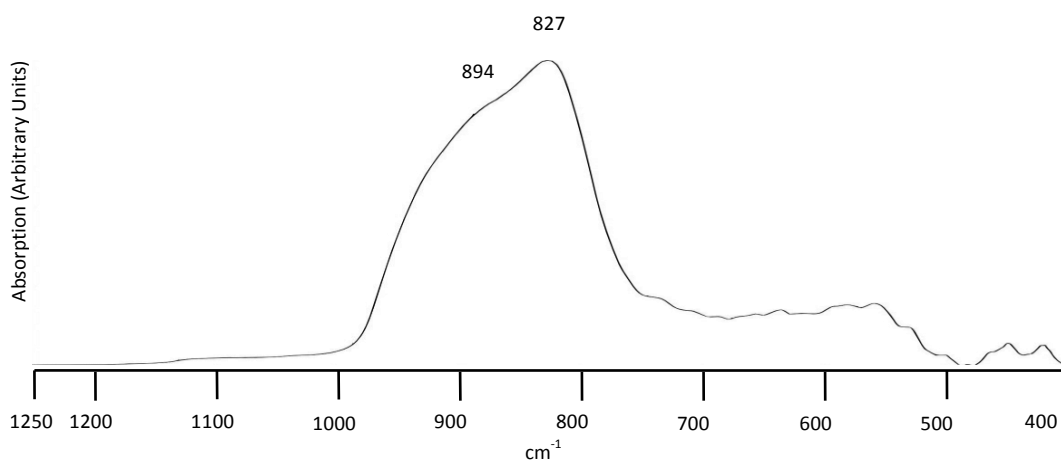


Figure 5.19: IR spectrum of Na1.1-CB fired at 1400 °C for 10 hr in flowing argon.

SiC occurs more rapidly in sodium samples, especially considering the fact that the sample contained considerably less carbon than the argon fired potassium composite.

5.3 Discussion

5.3.1 Mechanism of Sialon Formation from Sodium Carbon Black-Composites

When prepared with carbon black, sodium geopolymers formed inhomogeneous composites which when fired to elevated temperatures were observed to incorporate the unreacted silica phases and undergo transitions to form an amorphous phase. The presence of the carbon black provided sufficient kinetic hindrance to impede complete melting of the system, even at 1400 °C, with the formation of localised melts observed in carbon deficient regions resulting in well sintered powder compacts.

The carbothermal reduction and volatilisation (CRV) process was begun earlier in the sodium system with onset determined from weight loss measurements to occur at temperatures below those examined, likely due to the lower thermal stability of the sodium

geopolymer composition. This resulted in the comparatively early formation of SiC in the sample fired to 1400 °C with an isothermal hold.

Beyond this point the rapid formation of nitrogenous phases of O-sialon, β -sialon and X-phase was observed with further firing at 1400 °C initially causing the rapid growth of the O-sialon phase. The subsequent decline of this O-sialon led to the appearance of a second low z-value β -sialon phase suggesting that O-sialon converted to β -sialon via the same carbothermal reaction mechanism proposed in the preceding chapter (Equation (34)). After 8 hr of firing, the sample was mostly diphasic β -sialon product with a small quantity of X-phase and trace amounts of SiC, which probably remain unreacted due to the inhomogeneity of the original composite.

The formation of the diphasic β -sialon may be explained by the inhomogeneous precursor and the possibility of incongruent melting similar to the dissociation seen in aluminosilicates to form mullite and SiO₂. Both of these factors would lead to the formation of a range of compositions in the precursor including silica- and alumina-rich regions. The silica-rich regions have a lower predicted melting temperature from the phase diagrams and would likely form eutectics, promoting the formation the O-sialon phase in a similar manner as suggested for calcium catalysed systems.⁵⁶

Alumina-rich regions on the other hand, are predicted to be more thermal stable and would either remain amorphous or crystallise. The former of these two possibilities is suggested as more likely as the formation of crystalline phases such as nepheline or carnegieite during firing was not observed. Unless the formation and conversion of mullite is particularly rapid, it can be assumed that the formation of X-phase and high z-value β -sialon occurs directly from CRN of these alumina-rich phases.

The formation of SiC in samples could occur by the carbothermal reduction of the silica-rich or alumina-rich phases, the difference being that aluminium oxide phases like corundum, γ - or κ -alumina would form as a by-product of the reaction of the alumina-rich phases.

These processes can all take place simultaneously and would be controlled by the availability of carbon which would determine the extent of sodium volatilisation and subsequent formation of SiC or nitrogenous phases. Thus, a complex mixture of resulting phases is expected in such a system with the final phase assemblage mainly determined by homogeneity and carbon content. These results are consistent with the conclusions drawn

by Mazzoni and Aglietti⁶⁰ but add detail to the overall mechanism with the distinction of two possible routes; an amorphous pathway resulting in high or neutral z-values, and a eutectic based pathway causing the formation of low z-value β -sialon.

5.3.2 Comparison to Potassium-Carbon Black Composites

The unfired sodium composites were analogous to the potassium-carbon black composites in almost all respects. Their compositional ratios, IR spectra, XRD patterns and morphology are very similar with the only major difference being the inhomogeneous distribution of carbon through the sodium composites.

Although also kinetically hindered by the carbon black, sodium composites were observed to be less thermally stable, undergoing increased sintering with the eventual formation of melted regions in the sample. The onset of alkali volatilisation was determined to begin at lower temperatures but occurred over a longer duration, possibly due to the lower carbon content or the formation of non-porous, glassy phases in samples.

In contrast to potassium-carbon black composites, the major reaction pathway to synthesise β -sialon was via O-sialon intermediates forming low z-value β -sialon rather than the amorphous pathway which formed high z-value β -sialon. The formation of this low z-value phase supports the explanation proposed for the formation β -sialon from O1-sialon in the potassium samples and that eutectic formation promotes the formation of silicon oxynitride-type phases. This suggests that both types of samples reacted in similar ways but that the differences in high z-value to low z-value β -sialon are a result of the different thermal stabilities of the individual systems and the distribution of carbon throughout the samples.

Like potassium composites, the presence of fibres was not noted until late in the firing sequence after the majority of sodium had been volatilised. This suggests that neither alkali plays an extensive role in the formation of sialon fibres in samples.

5.4 Summary

In this chapter, the effect of having sodium as the activating alkali was investigated by reacting a series of sodium-carbon black composites, analogous to the potassium-carbon black composites, under the same firing conditions. The results were compared to a control sample fired at 1200 °C in open air for 1 hr and also to the corresponding potassium-carbon black series.

Prepared composites with varying carbon content (1.0 – 1.3x stoichiometric quantity) were analogous to the potassium samples except for their inhomogeneous composition and carbon distribution. These composites were fired at 1400 °C for 10hr resulting in multiphasic materials of predominately β -sialon. The other phases present included a mixture of intermediates of O-sialon, X-phase and SiC, with samples with higher carbon contents containing over-reacted phases of 15R-sialon and AlN. The control sample melted with the formation of an amorphous glass with a trace quantity of nepheline.

The pre-synthesis behaviour and β -sialon synthesis reaction was explored by a series of firings involving the 1.1x sample which was considered to be the best compromise between under and over-reaction. Below 1400 °C, the sample reacted to form a well sintered, amorphous composite which contained SiC and had significant mass loss indicating the early onset of CRV processes. The inclusion of carbon black caused significant kinetic hindrance impeding the out-right melting of the material.

After 1 hr of treatment at 1400 °C, samples formed nitrogenous phases of O-sialon, X-phase and a high z-value β -sialon. Further firing resulted in the formation of significant quantities of O-sialon, suggested to form from silica-rich eutectics in the inhomogeneous samples. This O-sialon had expanded unit cell dimensions, possibly indicating the formation of a Na-O-sialon stuffed derivative which underwent further carbothermal reaction to form a low z-value β -sialon. These results indicate that similar to potassium samples, β -sialon is synthesised via multiple pathways in a series of complex reactions potentially involving a range of incongruent phases. The reaction was complete by 8 hr with the presence of SiC and X-phase detected, possible due to the initial inhomogeneity and lack of available carbon.

As was the case with the corresponding potassium carbon black composite, the phase assemblage of the sample fired for 10 hr was different to the expected result. This again suggests that the quantity of available nitrogen may play a role in determining the resulting phase assemblage of materials.

6 Ammonium Geopolymer-Carbon Black Composites

6.1 Introduction

In the preceding chapters, alkali activated geopolymer systems were used to explore the effect of either potassium or sodium on the synthesis of β -sialon from alkali-activated geopolymers. To adequately characterise the effects of these alkalis, an alkali-free geopolymer is required for comparison. The preparation of an alkali-free geopolymer can be achieved using ion-exchange. This technique, commonly carried out on zeolites, can be used to replace the charge balancing cation within geopolymers with another suitable cation such as ammonium, which will thermally decompose upon firing.

Utilising these ion-exchanged geopolymer composites, the CRN development of aluminosilicates was determined utilising the same methods as in preceding chapters.

6.2 Results

6.2.1 Synthesis of Ammonium Geopolymer-Carbon Black Composites

Ammonium-exchanged geopolymer carbon black-composites (henceforth called ammonium-composites) were prepared by treating sodium-composite powders (Na0 and Na1.0-CB – Na1.3-CB) in ammonium chloride solutions several times before washing with water and isopropanol. During these washing treatments, samples were observed to lose small amounts of carbon black. After drying at 60 °C the resulting powder cake was lightly ground and the powders were passed through a #150 mesh sieve with opening of ~105 μ m to remove larger agglomerates.

It should be noted that although presently unexplored, based on the behaviour of comparable zeolite systems,⁸⁸ there is no reason to expect potassium-derived geopolymers not to exhibit similar behaviour and be reasonable candidates for ion-exchange. Sodium geopolymers were used in preference to potassium geopolymers simply due to their prevalence as precursors in the literature.^{69,75,77,80}

In all, five samples were prepared for study; a control sample lacking carbon black and four composites. As ammonium is lost with subsequent dehydroxylation, the resulting samples will be oxygen deficient compared to the sodium samples they were prepared from. As such, the stoichiometric quantity of carbon required will be lower and consequently the amount of carbon present in the resulting ammonium-composites will be greater than the stoichiometrically required amount. Consideration of Equations (25) and (26) shows that the amount of excess carbon is small and that samples can be appropriately relabelled as A0 for the control and A1.1-CB, A1.2-CB, A1.3-CB and A1.4-CB for the ammonium-carbon black composites, in order of increasing carbon.

To determine whether ion-exchange had occurred, samples were analysed via the same methods as O'Connor *et al.*,⁶⁹ namely, using IR spectroscopy and EDS. IR spectra of the NaO precursor with its ammonium-exchanged product, A0 and the A1.1.-CB sample were collected between 4000 – 400 cm^{-1} and are shown in Figure 6.1. The exchanged samples contained new peaks from the N-H asymmetric stretch at 3190 cm^{-1} and an asymmetric H-N-H bending band at 1420 cm^{-1} , confirming the presence of NH_4^+ in the geopolymer structure. The peak seen in all samples at $\sim 1445 \text{ cm}^{-1}$ stemmed from atmospheric

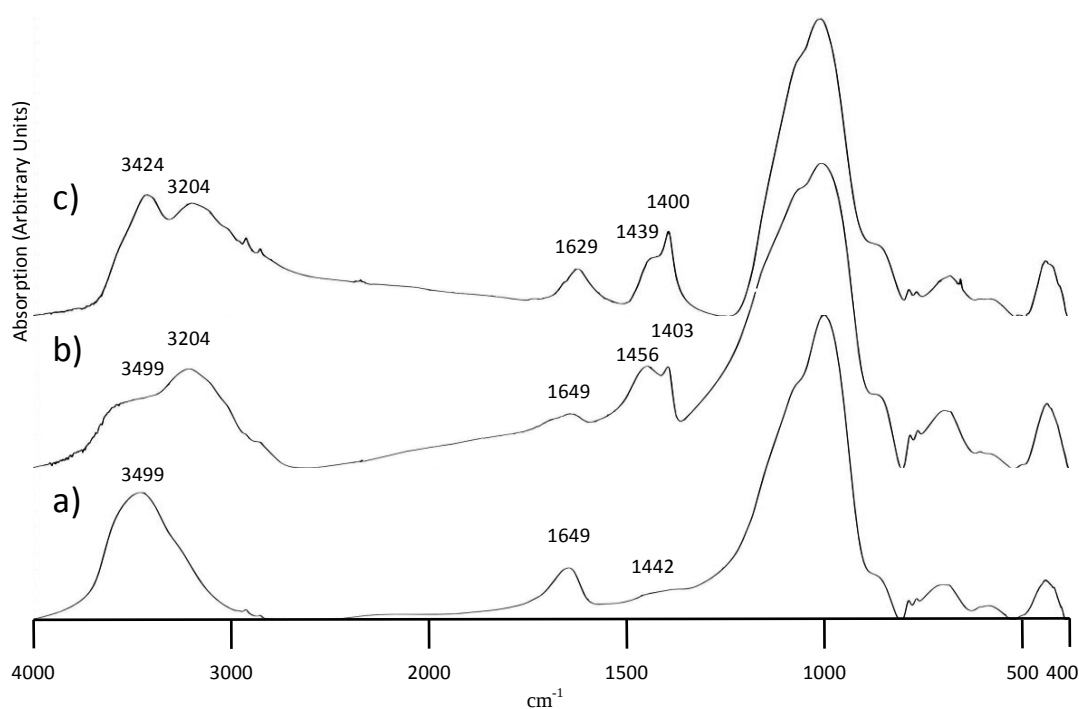


Figure 6.1: IR spectra of a) the unfired NaO precursor, b) the unfired, NH_4^+ -exchanged A0 control sample and c) an unfired composite sample, A1.1-CB.

carbonation of the sample while the band at $3500 - 3400 \text{ cm}^{-1}$ and peak at $1660 - 1620 \text{ cm}^{-1}$ occur from the presence of entrained water.⁶⁹ The small peaks at 2923 and 2853 cm^{-1} (unlabelled) were caused by an impurity in the KBr used. Characterisation of the bands associated with the geopolymer between $1250 - 400 \text{ cm}^{-1}$ are discussed in further detail below.

To determine the efficiency of the ion-exchange process, EDS spectra of Na0, A0 (carbon coated) and A1.1-CB (platinum coated) samples were obtained at 100x magnification. Figure 6.2a and Figure 6.2b show the disappearance of the sodium peak at 1.04 keV between the Na0 sample and the A0 sample indicating complete exchange of the ions. Similarly, the A1.1-CB sample (Figure 6.2c) contained no sodium, suggesting that the carbon black present in the sample did not affect the ion-exchange process. Table 6.1 gives the compositional values as determined by EDS and shows that the Si/Al ratio is slightly altered by the ion-exchange process, likely caused by overwashing of the sample.⁸⁸ Quantitative analysis of the nitrogen content was not assessed, due to the known issue of NH_4^+ decomposition under an electron beam.⁶⁹

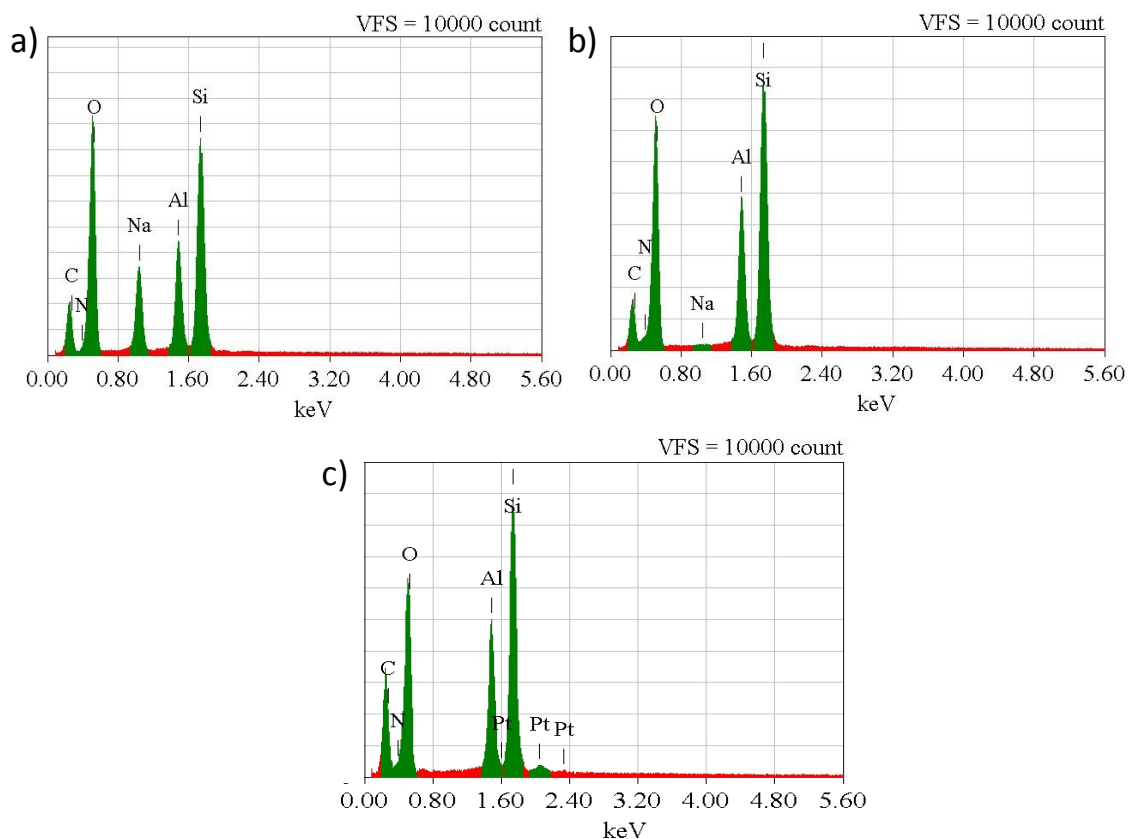


Figure 6.2. EDS spectra of a) the sodium geopolymer control (Na0), b) the ammonium control (A0) and c) the ammonium-carbon black composite A1.1-CB.

Table 6.1: EDS elemental analysis of unfired Na0, A0 and A1.1 samples at 100x magnification

Sample	Atom %				Si/Al Ratio
	Na	Si	Al	O	
Na0	10.61	24.90	12.71	51.78	1.95
A0	-	31.54	17.05	51.41	1.85
A1.1-CB	-	35.37	18.77	45.56	1.88

Figure 6.3 shows the XRD patterns of the A0 and A1.1-CB powder where it can be seen that the ion-exchange process did not affect the structure of the samples in any significant way. The XRD patterns of these samples are indistinguishable from their sodium precursors (Figure 5.1). The slight broadening of the amorphous hump at 26° between the control and the composite is attributed to the inclusion of carbon black in the geopolymer matrix.

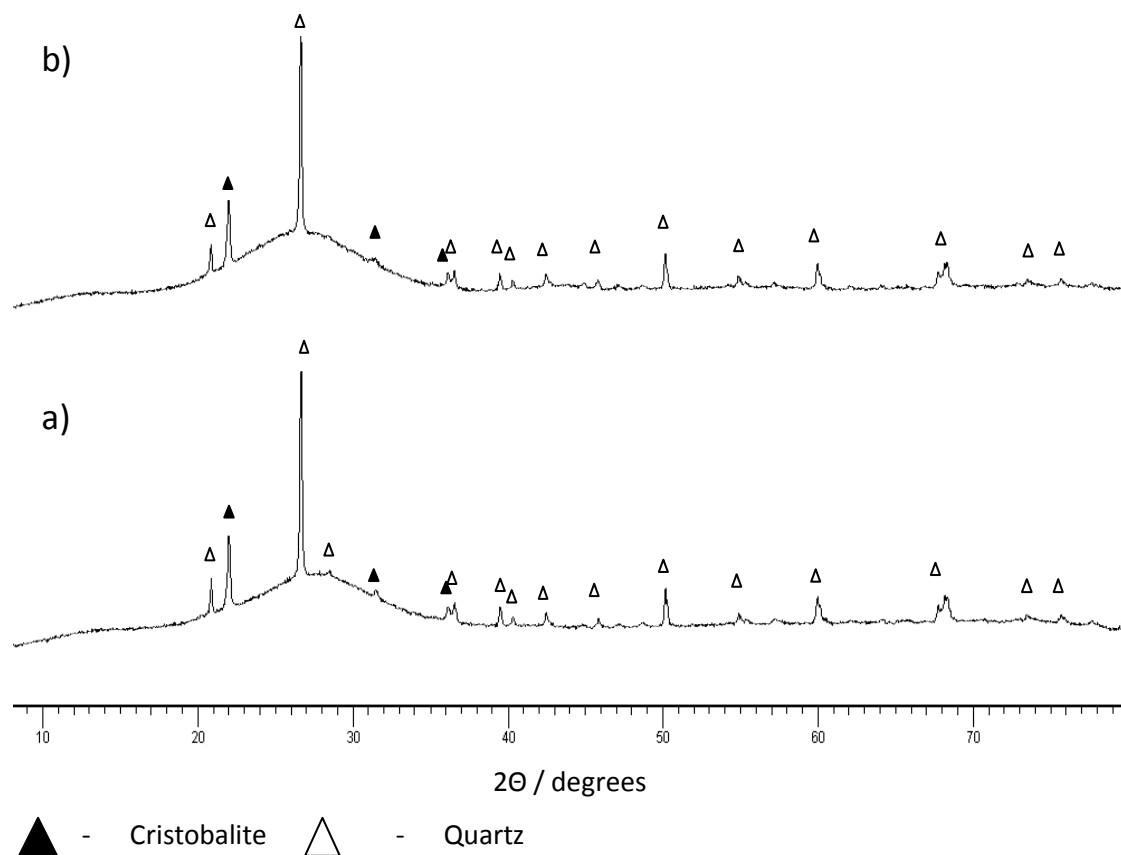


Figure 6.3: XRD patterns of a) ammonium exchanged geopolymer control (A0) and b) an ammonium carbon black-composite (A1.1-CB).

The corresponding IR spectra of the control sample and A1.1-CB are shown in Figure 6.4. Both samples have spectra typical of geopolymers with the major Si-O-T asymmetric stretching band and shoulder present at 1020 cm^{-1} and $\sim 1078\text{ cm}^{-1}$, respectively. Peaks from unreacted d-halloysite are observed at 798 and 779 cm^{-1} , with the symmetric Si-O-T stretching band at 696 cm^{-1} , the Si-O-T rocking band at 585 cm^{-1} and the Si-O-T bending band at 446 cm^{-1} . While the A1.1-CB sample is indistinguishable from the sodium samples, the control sample differs slightly with a broader Si-O-T asymmetric band suggesting greater silica rich domains. The shift in the T-OH stretch may be a result of either an increased quantity of hydroxyl groups or indicate differences in the bonding of NH_4^+ ions to the structure of the geopolymer matrix, possibly from hydrogen bonding.

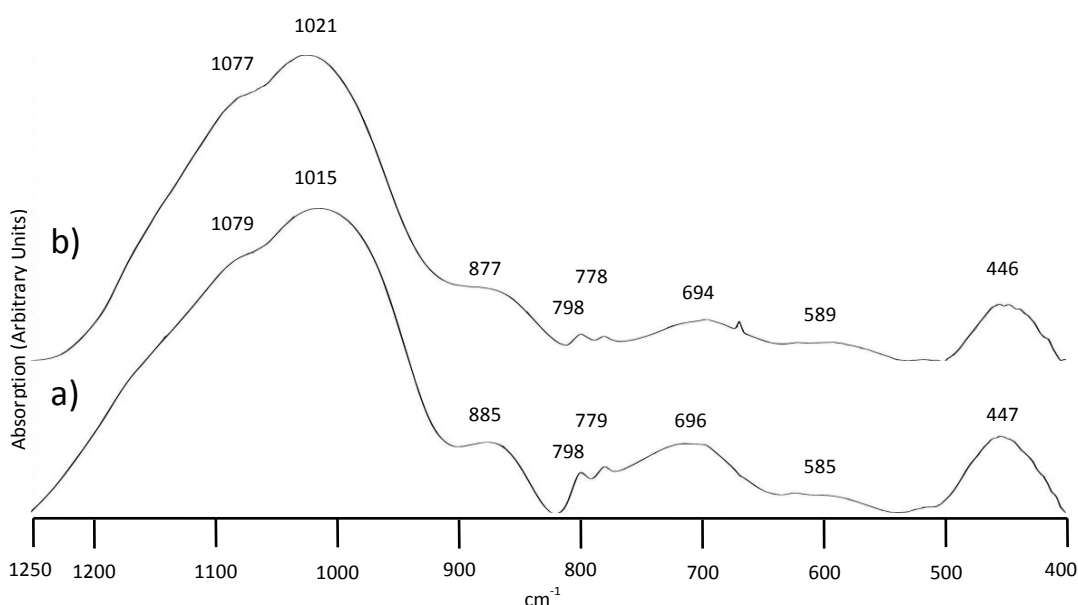


Figure 6.4: IR spectra of a) the A0 control sample and b) an unfired A1.1-CB sample.

A backscattered image of A1.1-CB is shown in Figure 6.5a. Like the potassium- and sodium-carbon black composites, the sample appears relatively homogeneous with no obvious carbon particles as seen in the potassium-graphite composites. Further magnification (Figure 6.5b) indicates that the samples also share the same surface morphology as the alkali-carbon black composites with the small, spherical, nodular features intact after ion-exchange.

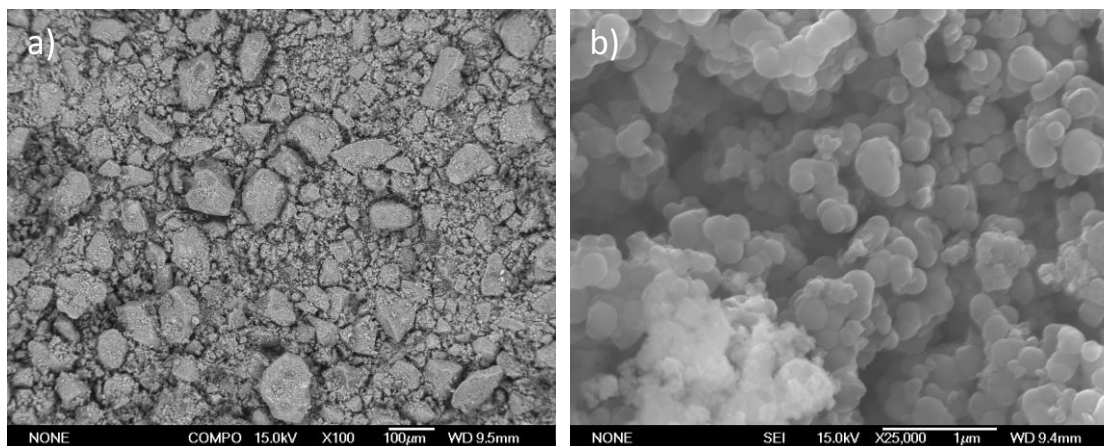


Figure 6.5: a) Backscatter image of unfired A1.1-CB sample (100x) and b) a close up SEI image showing its small, spherical, nodular morphology (25000x).

EDS maps of the surface of a selected particle (Figure 6.6), indicate that the similar to its sodium-composite precursor, the distribution of carbon throughout the ammonium-composite is inhomogeneous with carbon rich and carbon poor regions being apparent. This inhomogeneous carbon distribution is likely a result of the inhomogeneity observed in the sodium-composite but may have been exacerbated in by the loss of carbon during the ion-exchange process.

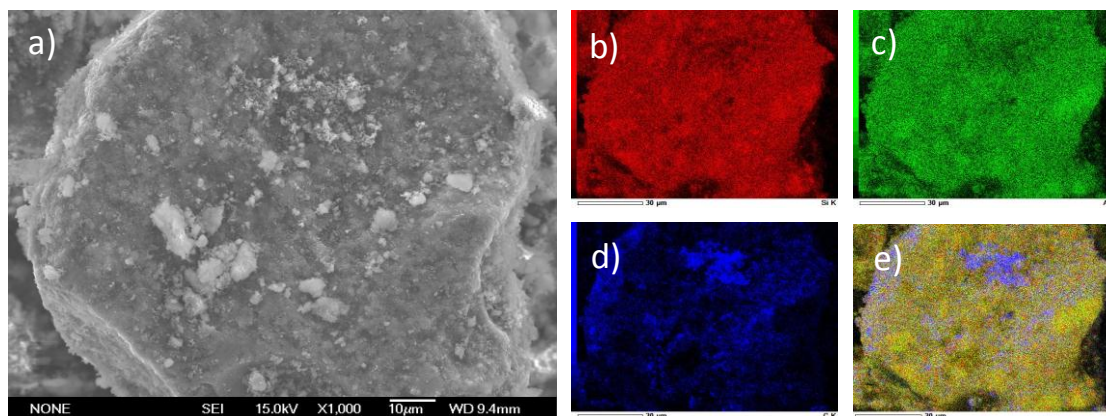


Figure 6.6: a) SEI image of unfired A1.1-CB with b) silicon, c) aluminium and d) carbon EDS maps with e) their overlay.

6.2.2 Firing of Samples with Varying Carbon Black Content

Subsequent to preparation, the four prepared ammonium-composites were fired at 1400 °C for 10 hr. A control sample was also fired but only to 1200 °C for 10 hr in an open air

furnace for comparison. Like the alkali-carbon black composites, the lowest and highest carbon content samples (A1.1-CB and A1.4-CB) were fired together as were the two composites samples of moderate carbon content (A1.2-CB and A1.3-CB). To avoid contamination by alkali during reaction, firings were carried out in a new, previously unused, firing tube.

After firing, composites were noted to be of a grey colour and were relatively unsintered compared to both potassium and sodium samples. The presence of a large quantity of whiskers, in the form of blue coloured foam, was recovered from the downstream end of the furnace outside of the furnace hot-zone. A small quantity of whiskers was also present on the firing boats. These materials were consistent with the AlN/SiC/SiO_x by-products described by Ekström *et al.*⁵⁸ Attempts at XRD analysis of the material after grinding in isopropanol, indicated a mostly amorphous material which contained trace quantities of SiC. Unlike firings containing alkali, no glassy rings were observed post-firing. The control sample was observed to form a mixture of mullite and cristobalite with a small amount of amorphous material.

The resulting XRD patterns are shown in Figure 6.7. All samples contained mainly diphasic β -sialon with significant quantities of SiC and AlN also present. A consistent small quantity of γ -alumina was also observed in samples with a small amount of corundum also present in the A1.1-CB sample.

Semi-quantitative analysis (Figure 6.8) indicates that with increasing carbon content comes a reduction in β -sialon, particularly the low-value phase. Interestingly, the quantity of AlN, indicative of over-reaction of samples, declines with increasing carbon content, with complimentary growth of SiC. This may indicate the loss of Al from samples, possibly in the form of an aluminium containing vapour.

The IR spectra (Figure 6.9) corresponded well with the XRD data. The five Si-N vibrational modes ($\nu_6 - \nu_2$) are present in all composites at ~ 1034 , ~ 940 , ~ 893 , ~ 571 and ~ 433 cm⁻¹, respectively, indicating mostly β -sialon samples. Peaks for Si-C (~ 815 cm⁻¹) and tetrahedral Al-O (~ 741 cm⁻¹) and Al-N (686 cm⁻¹) stretches are also detected. With increasing carbon content, a decline in the ν_3 and ν_2 Si-N stretching mode vibrational modes is observed with the growth of the Si-C stretching bands. The ν_4 Si-N appears more intense than is typical due to the overlapping Si-C shoulder at about 896 cm⁻¹). The estimated

z-value calculated for all samples was ~ 0.8 but the broad shoulder at lower wavenumbers indicates a distribution of z-values.

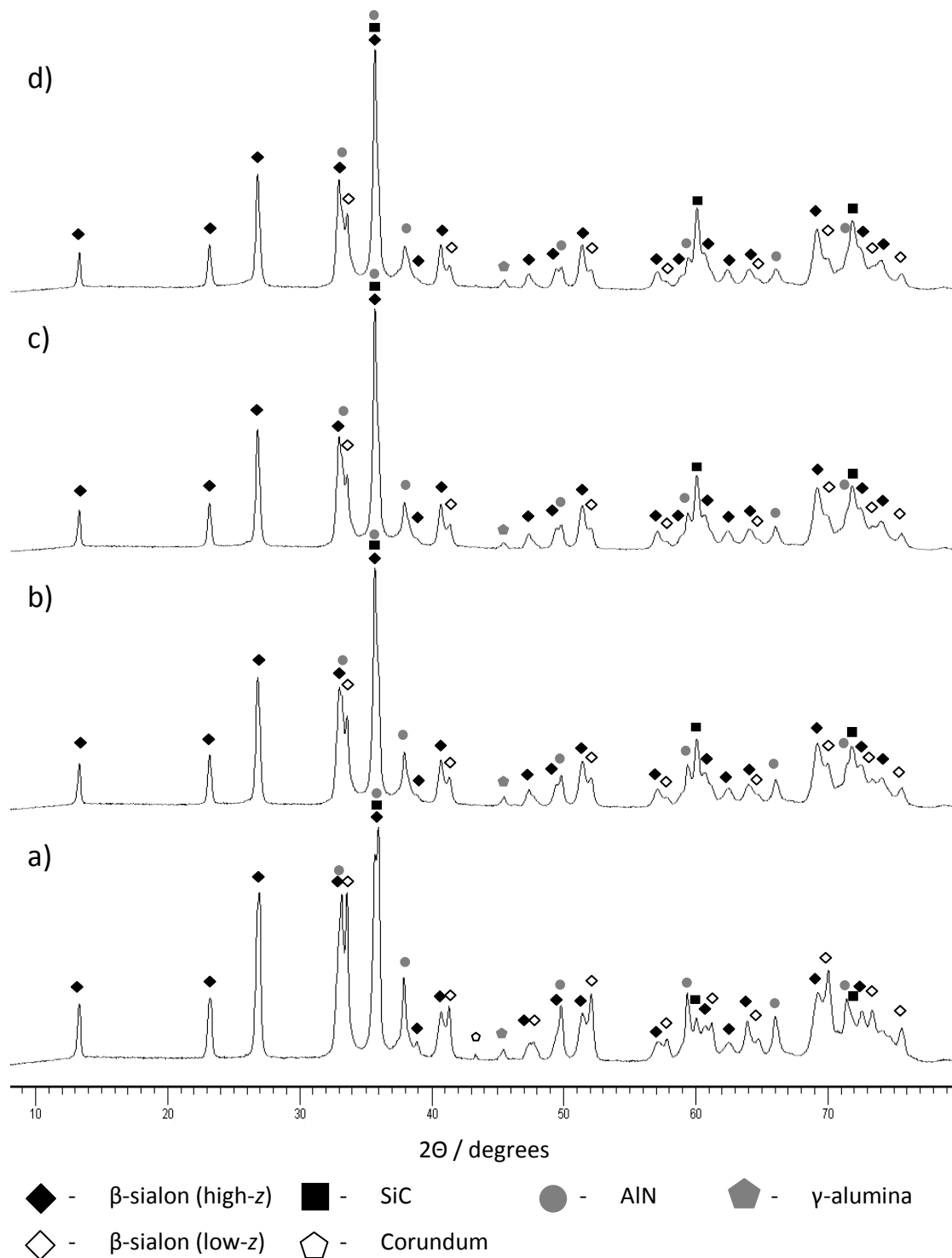


Figure 6.7: XRD results of samples fired in nitrogen at 1400 °C for 10 hr: a) A1.1-CB, b) A1.2-CB, c) A1.3-CB and d) A1.4-CB.

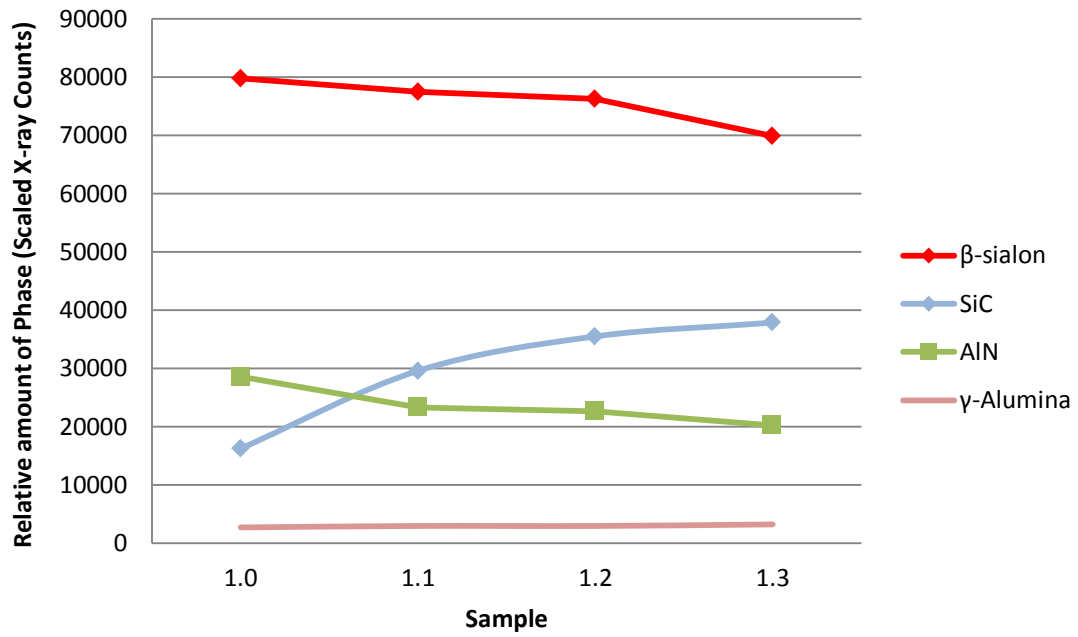


Figure 6.8: Semi-quantitative representation of the phases detected by XRD in ammonium-carbon black composite samples fired in nitrogen at 1400 °C for 10 hr.

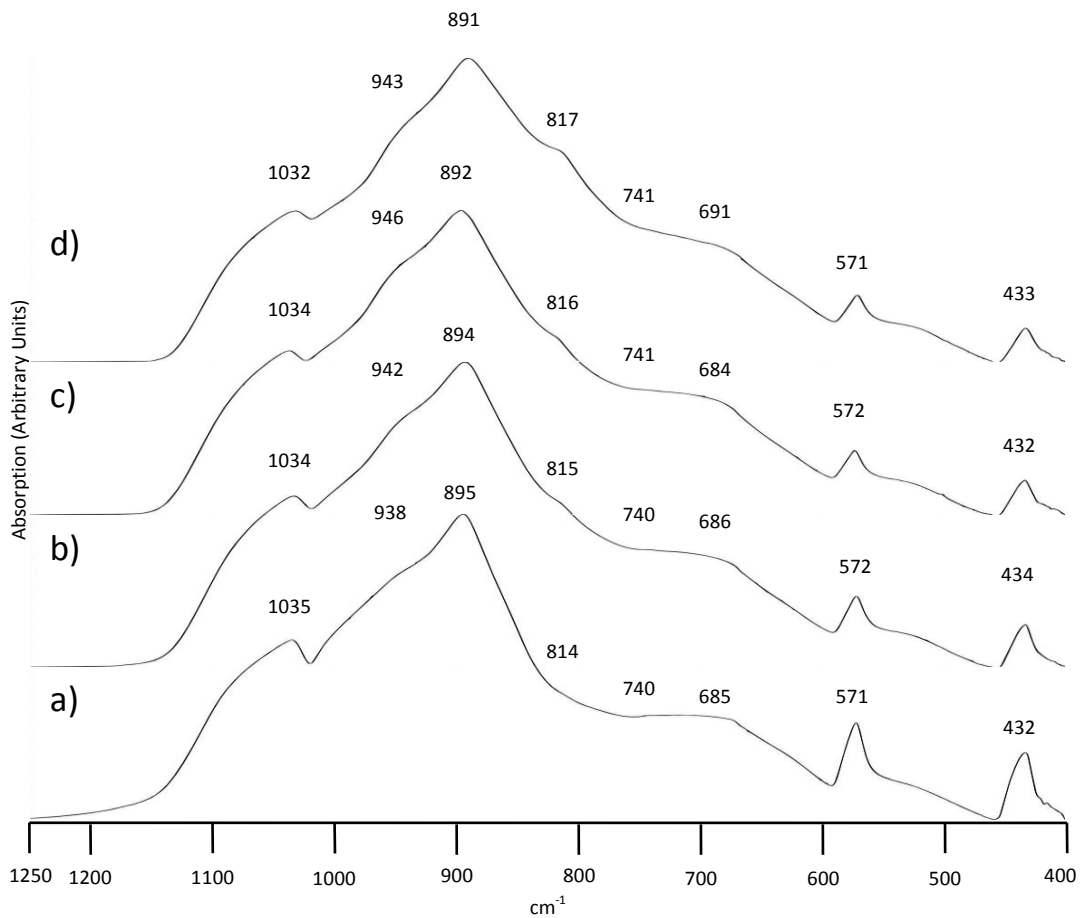


Figure 6.9: IR spectra of samples fired in nitrogen at 1400 °C for 10 hr: a) A1.1-CB, b) A1.2-CB, c) A1.3-CB and d) A1.4-CB.

To investigate the reaction sequence of ammonium-carbon black composites and their reaction mechanism, A1.1-CB was chosen as the best candidate for further experimentation due to having the highest β -sialon yield.

6.2.3 Reaction Sequence of Ammonium-Composites

To explore the reaction sequence of ammonium-composites, A1.1-CB samples were reacted in a series of firings with varying temperatures and times. The pre-synthesis behaviour was investigated by firings at 1200 °C, 1300 °C and 1400 °C, each for without an isothermal hold whereas its CRN behaviour was determined by a series of firing at 1400 °C for between 0 – 10 hr in duration. The resulting samples were characterised using XRD, IR spectroscopy and SEM with complimentary EDS analysis. As the ^{29}Si NMR results of the potassium-graphite and potassium-carbon black composites were of low quality and due to reasons of expedience and expense, solid state NMR experiments were not carried out on ammonium samples.

6.2.3.1 Observations and Weight Loss

The weight loss percentage of samples was determined by weighing samples before and after firing and evaluating these values using Equation (27). Figure 6.10 show the resulting weight loss percentages plotted against their firing temperature and time. Samples fired in the pre-synthesis region showed steadily increasing weight losses between 18.6% and 22.7%, stemming from a combination of dehydration, ammonium decomposition and dehydroxylation. The steady increase may also be caused the early onset of low levels of carbothermal reduction processes.

Rapid weight loss occurred once the samples reached synthesis temperature with the weight loss doubling to 45.0% after 1 hr at 1400 °C. The weight loss then progressively declined in a logarithmic fashion approaching a limit after 8 hr at 60.8% with the 10 hr sample having lost slightly less mass. This, like the potassium- and sodium- carbon black composites, indicates a difference in the extent of reaction, possibly due to the differing quantities and overall carbon content of the samples during firing. The total initial mass of samples in the 10 hr firing was 2.012 g compared to 1.017 g for the 8 hr firing.

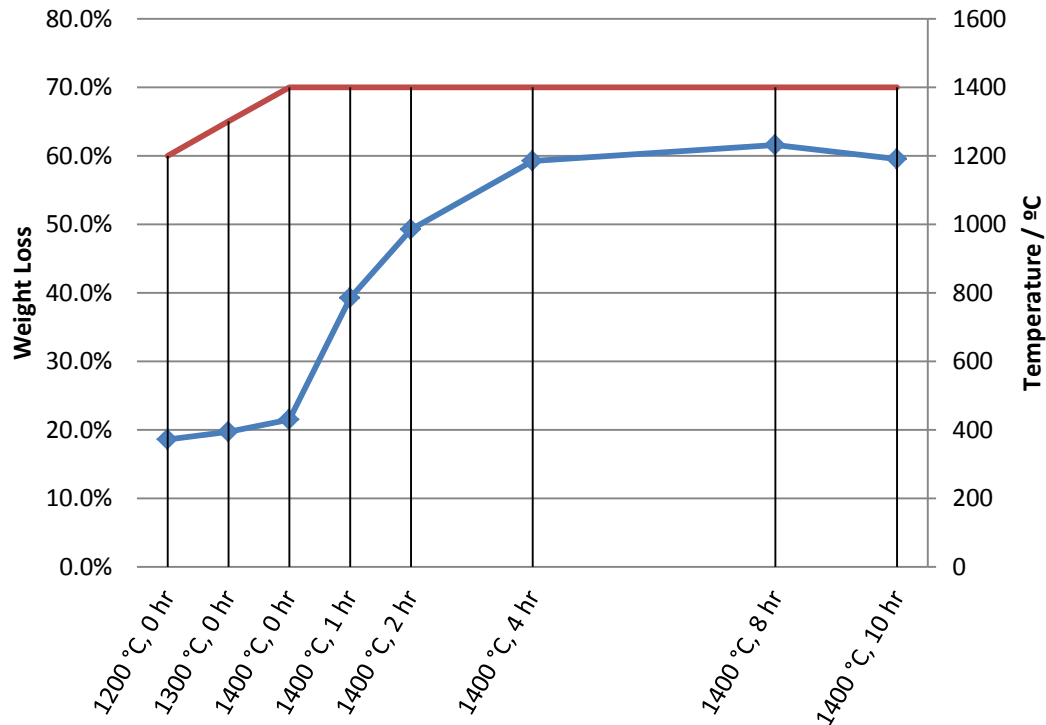


Figure 6.10. Weight loss of A1.1-CB samples fired at progressively higher temperatures for varying durations. The red line indicates the temperature.

6.2.3.2 X-Ray Diffraction Studies

The pre-synthesis development of samples is shown in Figure 6.11 and shows that upon heating to 1200 °C, the ammonium-composite began to dissociate to form mullite and silica; the latter evidence by the slight growth of the cristobalite peak at 22°. The unreacted quartz has not been incorporated into the amorphous phase which is observed to have undergone some small structural rearrangement reflected in a shift of its hump from 26° to ~23°. Firing to 1300 °C sees the growth of the mullite and cristobalite with the slight decline of the shifted amorphous hump. After firing to 1400 °C, the quartz previously present has been incorporated into the material with the significant growth of the cristobalite phase. Further analysis of the cristobalite reflections revealed a slight increase to the unit cell dimensions indicative of a cristobalite solid solution, likely containing a small quantity of aluminium. The formation of a small quantity of SiC is also seen.

The XRD patterns of the firings at 1400 °C of increasing duration are shown in Figure 6.12 while their semi-quantitative analysis is shown in Figure 6.13. These diagrams indicate that after 1 hr of firing, mullite and SiC grow at the expense of cristobalite and the

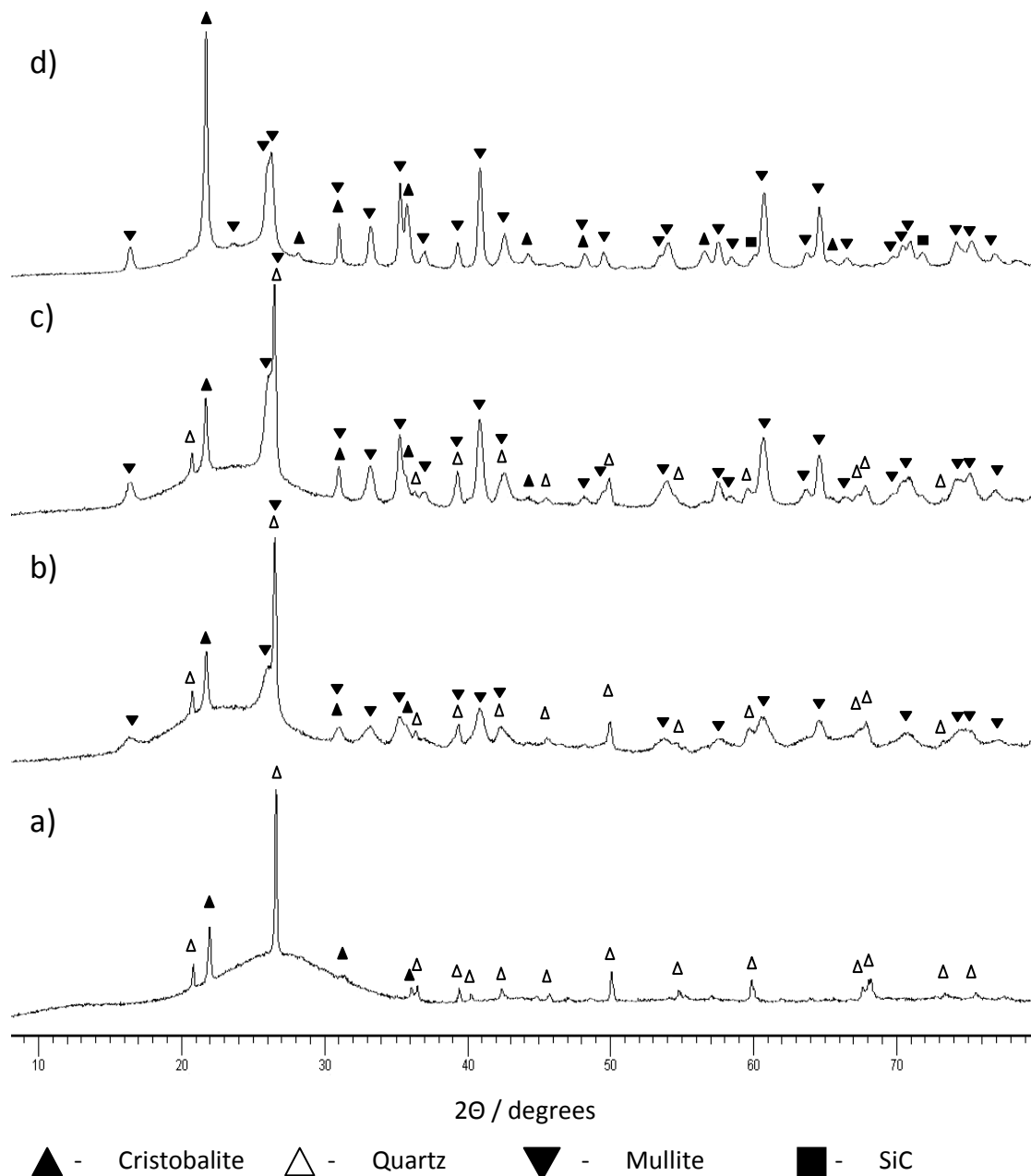


Figure 6.11: XRD patterns of A1.1-CB: a) Unfired, b) 1200 °C, 0 hr, c) 1300 °C, 0 hr and d) 1400 °C, 0 hr.

amorphous phase. The nitrogenous phase of O1-sialon is also observed to form. Further firing for 2 hr sees the formation of X-phase with the decline of mullite and the development of β -sialon. The quantity of SiC increases with the decline of cristobalite while the quantity of O1-sialon remains relatively steady.

Modelling of the O1-sialon phase gives lattice parameters of $a = 8.846 \text{ \AA}$, $b = 5.370 \text{ \AA}$ and $c = 4.837 \text{ \AA}$ with an overall cell volume of $229.7 \text{ \AA}^3$. These values correlate well with the

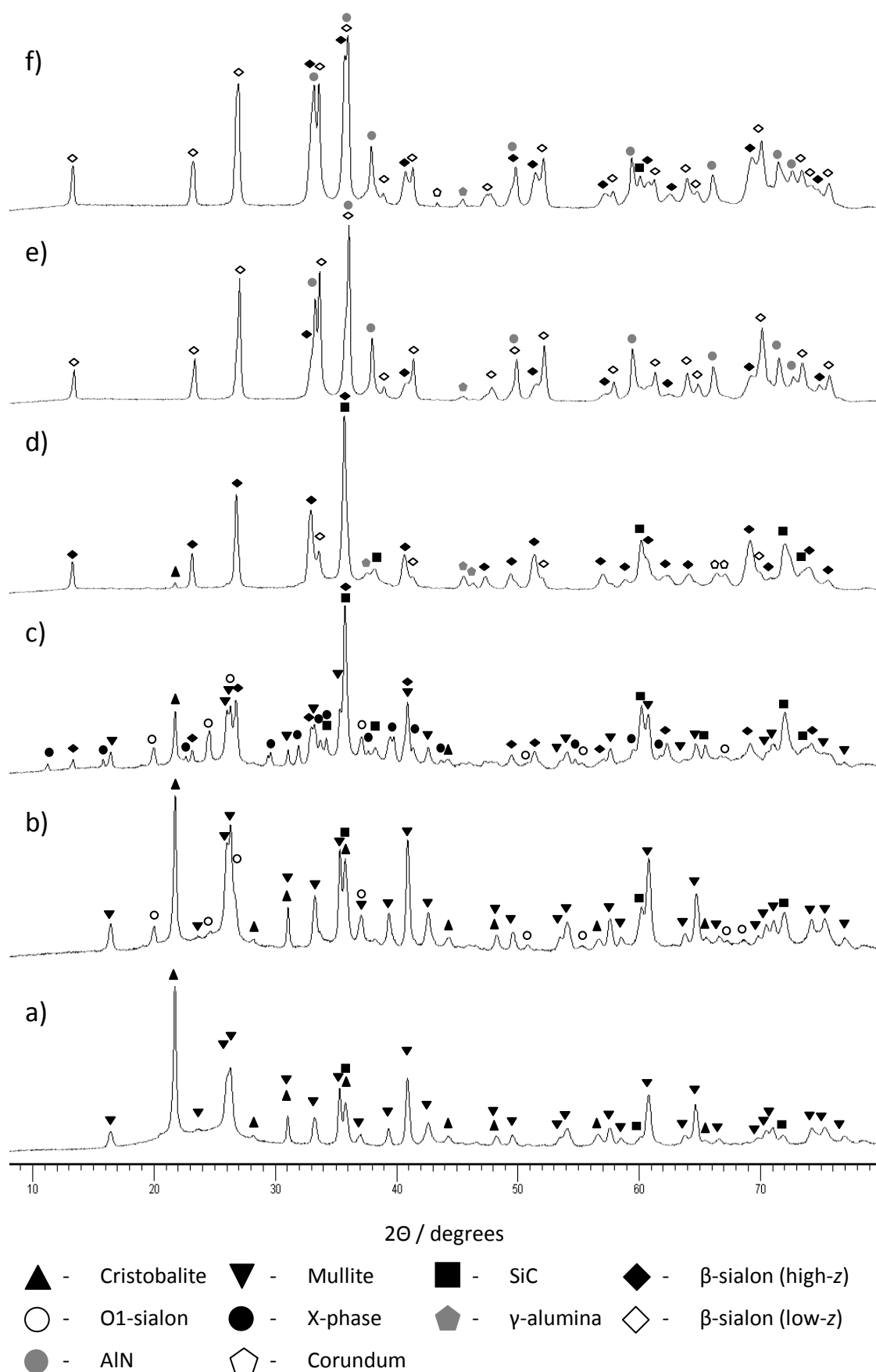


Figure 6.12: X-ray diffraction patterns of A1.1-CB samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr and f) 10 hr.

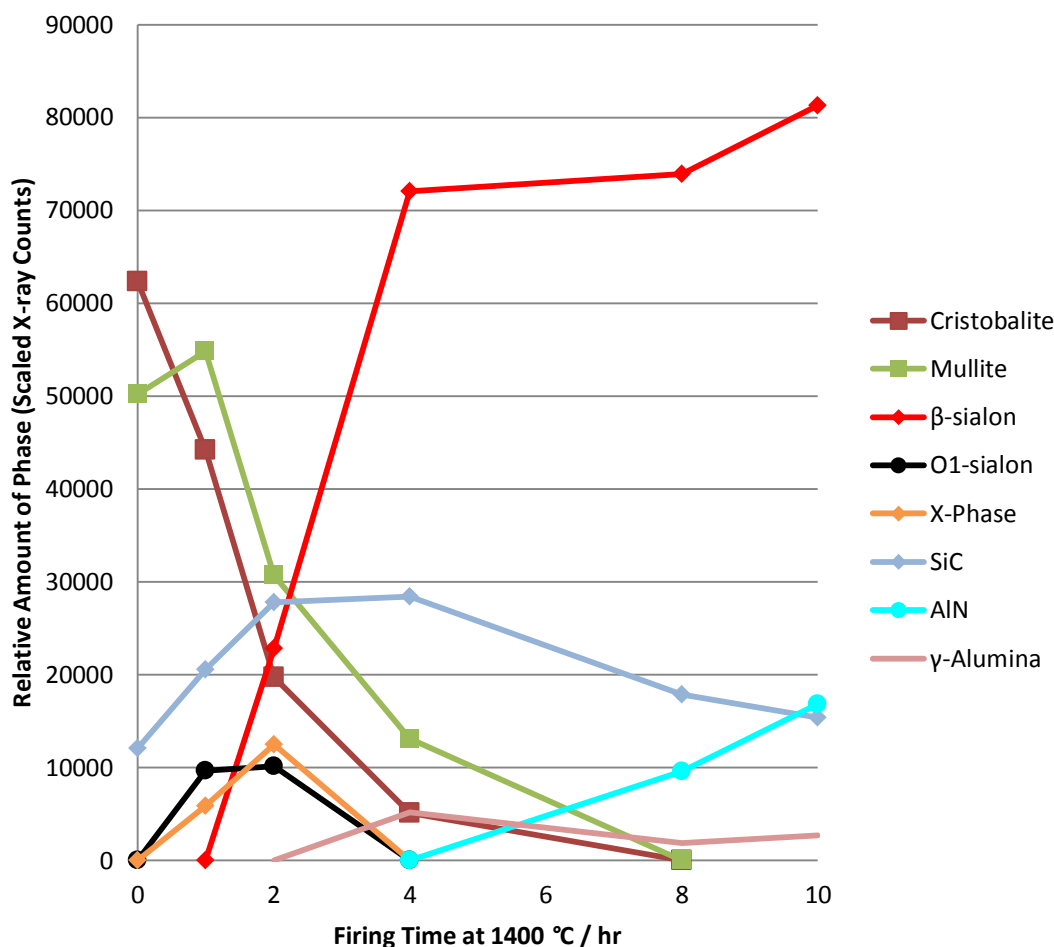


Figure 6.13: Semi-quantitative representation of the phases detected by XRD in A1.1-CB samples fired in nitrogen at 1400 °C for varying durations.

values taken from Bowden *et al.* which are shown in Table 4.1. The overlapping peaks between 32 - 35° stem from a number of phases including β-sialon, mullite, O1-sialon, X-phase and possibly β-SiC but modelling indicated that the β-sialon formed is monophasic and of a high z -value ($z = 2.8$). Attempts at modelling a low z -value phase resulted in impossible lattice parameters suggesting that the peak at 33.7° can be attributed to X-phase.

After 4 hr of firing, the resulting sample consisted of diphasic β-sialon and SiC with a small quantity of γ-alumina. The z -values of the β-sialon phase were determined to be 0.6 and 2.7 suggesting that the formation of β-sialon occurred through at least two separate pathways.

Further firing to 8 hr sees the formation of AlN, with further growth of β-sialon and the loss of SiC. The resulting β-sialon material has lost the majority of its high z -value phase

with the significant growth of the low z-value phase. The modelled z-values of these phases were 2.4 and 0.1 indicating a large loss of aluminium from the β -sialon phases. This indicates that the increase in low z-value β -sialon which occurs during the later stages of firing, does not form via the conversion of a silicon oxynitride type phase but through an over-reduction mechanism similar to the one described by Equation (11) in which AlN forms instead of 15R-sialon.

The sample fired for 10 hr had a significantly different phase assemblage in comparison to the 8 hr sample and contained more AlN but less SiC, with trace amounts of corundum and γ -alumina also being detected. The β -sialon present had almost equal quantities of high and low z-value phases with modelled z-values of 2.4 and 0.4. These results indicate that the quantity of materials present during firing has significantly influenced the resulting phase assemblage, likely due to increase competition for N_2 .

6.2.3.3 *Infrared Spectroscopy*

The IR spectra of the pre-synthesis firings are shown in Figure 6.14. It can be seen that upon firing to 1200 °C (Figure 6.14b) that unlike the major Si-O-T absorption band of alkali containing samples, which remained broad and either did not shift (potassium) or only shifted slightly (sodium), the ammonium-composite band narrows considerably and shifts by almost 75 cm^{-1} to higher wavenumbers. This indicates a more homogeneous range of Si-O-T environments and bond angles, a result of the alkali no longer being present as a network modifier where they distort the aluminosilicate structure. The loss of the broad shoulder of the T-OH stretches present in the unfired composites at 877 cm^{-1} indicates that dehydroxylation has occurred. Other bands observed include a Si-O stretching shoulder at 1163 cm^{-1} , Si-O-T rocking mode at $\sim 470\text{ cm}^{-1}$ and two lattice vibrations at 797 and 779 cm^{-1} from unreacted dehydroxylated halloysite. The Si-O-T bending band is obscured by the developing mullite absorptions but has also shifted from 695 cm^{-1} to higher wavenumbers at 735 cm^{-1} . The broad bands at 892 and 574 cm^{-1} are attributed to the emerging tetrahedral and octahedral Al-O stretches of mullite, respectively, while the small peak at 827 cm^{-1} stems from the tetrahedral Al-O bends of mullite.¹⁰⁵

Increased temperature caused the further emergence of peaks associated with mullite with the new peak apparent at $\sim 960\text{ cm}^{-1}$ attributed to Si-O stretches.¹⁰⁵ By 1400 °C,

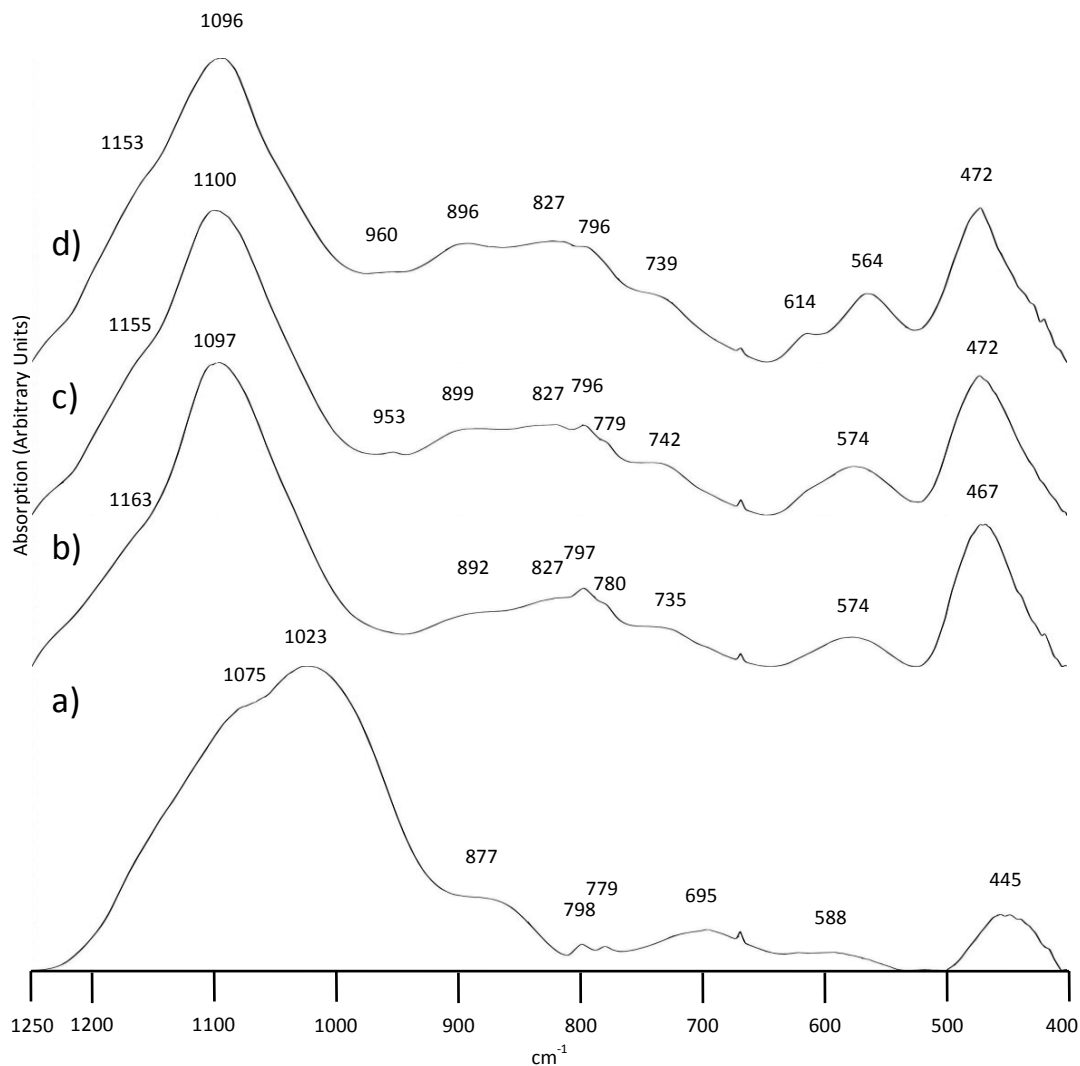


Figure 6.14: IR spectra of A1.1-CB samples: a) Unfired sample b) 1200 °C, 0 hr, c) 1300 °C, 0 hr and d) 1400 °C, 0hr.

the majority of halloysite had been incorporated in the material with the disappearance of the peaks at 797 and 779 cm^{-1} . The peak at 574 cm^{-1} splits into two peaks at 614 and 564 cm^{-1} , both from octahedral Al-O stretches. The small, sharp peak at 668 cm^{-1} (unlabelled) was determined to be caused by an impurity in the KBr used to suspend the samples.

Continued firing at 1400 °C for 1 hr (Figure 6.15b) sees the formation of Si-N and Si-C bonds with the emergence of a shoulder at 956 cm^{-1} (ν_5), peak at 902 cm^{-1} (ν_4) and shoulder at 828 cm^{-1} (SiC). These new peaks overlap and obscure the mullite peaks in the 1000 – 800 cm^{-1} region but the presence of mullite can be observed from the dual peaks at 614 and ~562 cm^{-1} and shoulder at 756 cm^{-1} . The amorphous phase can no longer be individually

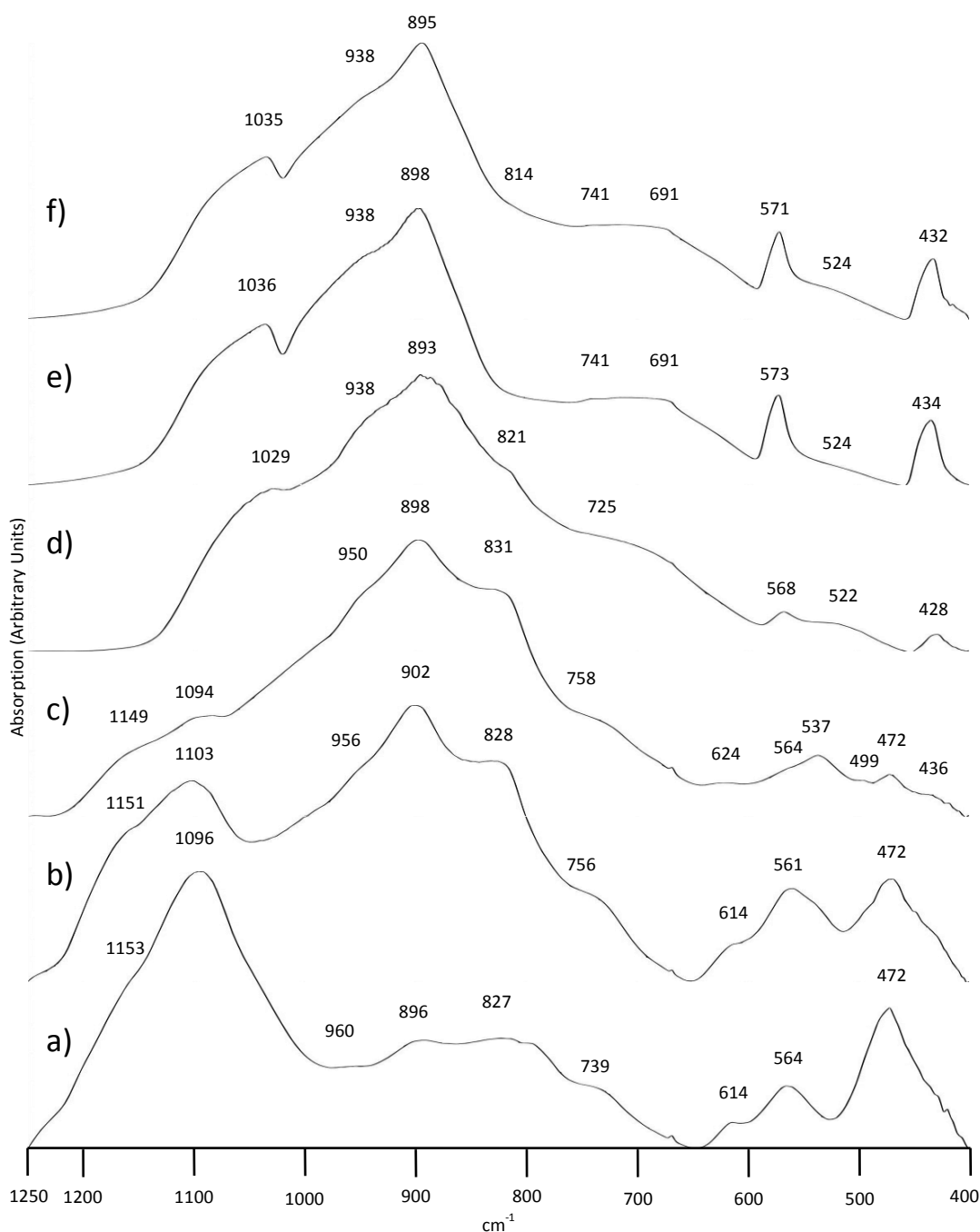


Figure 6.15: IR of A1.1-CB samples fired at 1400 °C for: a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr and f) 10 hr.

distinguished as its Si-O-T asymmetric stretches overlap with those of mullite and its Si-O-T rocking band overlaps with the absorbance from the siliceous phase; the continued presence of siliceous phases was observed by the Si-O stretching band at 1153 cm^{-1} .

After 2 hr of firing (Figure 6.15c), a reduction in the Si-O and Si-O-T stretching and bending bands is seen with little change in the intensity of to the ν_5 , ν_4 and Si-C bands. A

pronounced reduction in the mullite octahedral Al-O bands and Si-O-T bending band allows the distinction of the ν_3 and ν_2 Si-N absorptions at 537 cm^{-1} and 436 cm^{-1} . The peak at 499 cm^{-1} is attributed to the silicon oxynitride type O1-sialon phase.

The spectrum of the sample fired for 4hr (Figure 6.15d) shows the development of the ν_6 Si-N band at 1029 cm^{-1} , indicating a material comprised mostly of β -sialon with a small amount SiC (821 cm^{-1}). The low intensity and breadth of the ν_3 and ν_2 peaks indicates that the β -sialon has a wide distribution of z-values.

Samples fired for 8 and 10 hr (Figure 6.15e and f) are similar to the 4 hr sample but have more pronounced ν_6 , ν_3 and ν_2 peaks indicating a greater proportion of low z-value phase with the shoulder at 524 cm^{-1} originating from the small quantity of high z-value phase. The increased breadth of the band between $800 - 600\text{ cm}^{-1}$ is the result of the presence of AlN in samples which has an Al-N stretching band at 691 cm^{-1} . The spectrum of the 10 hr sample also has a small SiC peak at 814 cm^{-1} .

6.2.3.4 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

SEM and EDS were carried out on A1.1-CB samples fired in the synthesis region of $1400\text{ }^\circ\text{C}$ between 0 – 10 hr. Figure 6.16 shows the quantitative results of EDS spectra taken of the sample bulk at 100x magnification normalised to the Al count. Upon reaching the synthesis temperature of $1400\text{ }^\circ\text{C}$, the sample had already lost over 25% of its initial oxygen content. While most of this can be attributed to the dehydration and dehydroxylation processes, the simultaneous loss of Si content suggests that some carbothermal reduction had occurred, causing the loss of SiO vapour. The loss of oxygen continued approximately logarithmically with increasing duration, stabilising after 8 hr of firing. Although initially low, the loss of silicon increased between 1 and 2 hr before levelling at 4 hr. Both the 8 hr and 10 hr sample contained more Si than the 2 and 4 hr samples. Although some differences are expected in the 10 hr sample, due to having an odd phase assemblage observed by XRD, the 8 hr sample is anomalous. Like the 10 hr sample, this difference may be due to the quantity of material being fired affecting the nitridation rate allowing the formation of excess SiC which is retained in the system. Alternately, it may indicate the loss of aluminium from samples, previously assumed to be zero, to occur in appreciable quantities. Nitrogen is

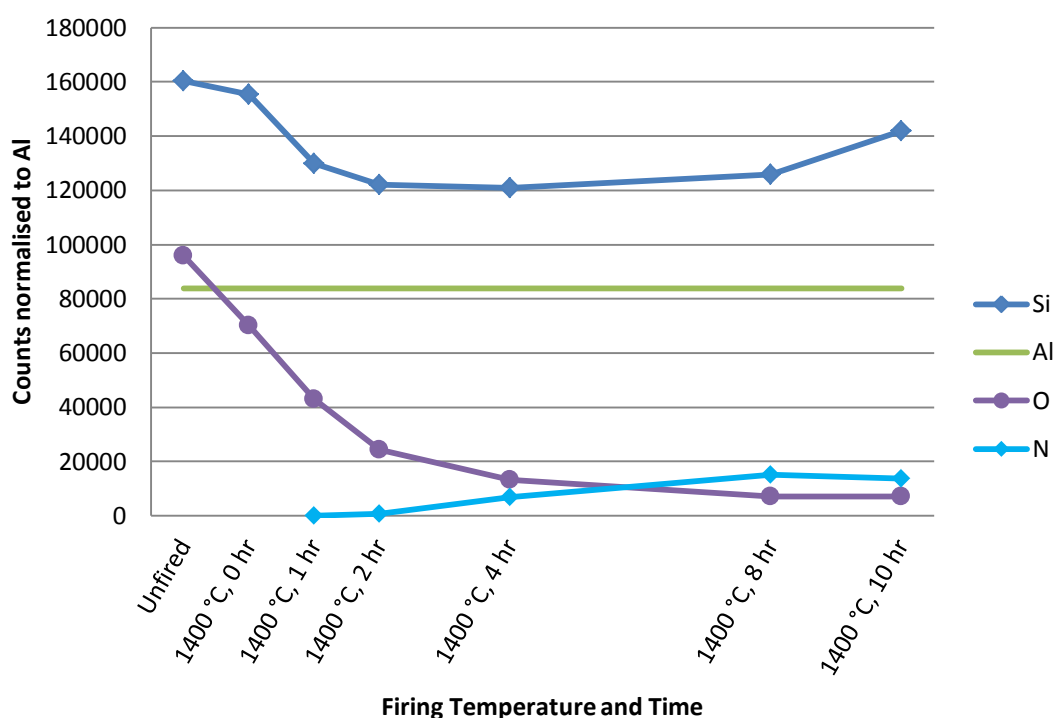


Figure 6.16: Normalised elemental counts of A1.1-CB samples fired at 1400 °C between 0 – 10 hr compared to the unfired sample.

observed in samples after 2 hr of firing and increases at a steady rate to the 8 hr sample but with a slight decrease in nitrogen content detected in the 10 hr sample.

Evaluation of 0 hr sample under backscattering and secondary electron conditions showed behaviour more consistent with the potassium-graphite and potassium-carbon black systems than the sodium-system that the samples were derived from. Figure 6.17 shows selected images of the sample fired for 0 hr. In a backscattered image at 100x, the sample appears homogeneous in colour with the darker grey area attributed to the carbon tape earthing the sample to the SEM stub. Magnified images (Figure 6.17b and c) show that the sample retains the spherical, nodular morphology seen in the unfired sample (Figure 6.5b) and also develops sintered areas (bottom left corner, Figure 6.17b).

EDS maps (Figure 6.18) of the sample of reveal that, like the unfired sample, the particles are not homogeneous and the spherical nodules are associated with carbon whereas the sintered areas are devoid of carbon and are a mixture of silicon and aluminium. Some silicon rich areas are also present.

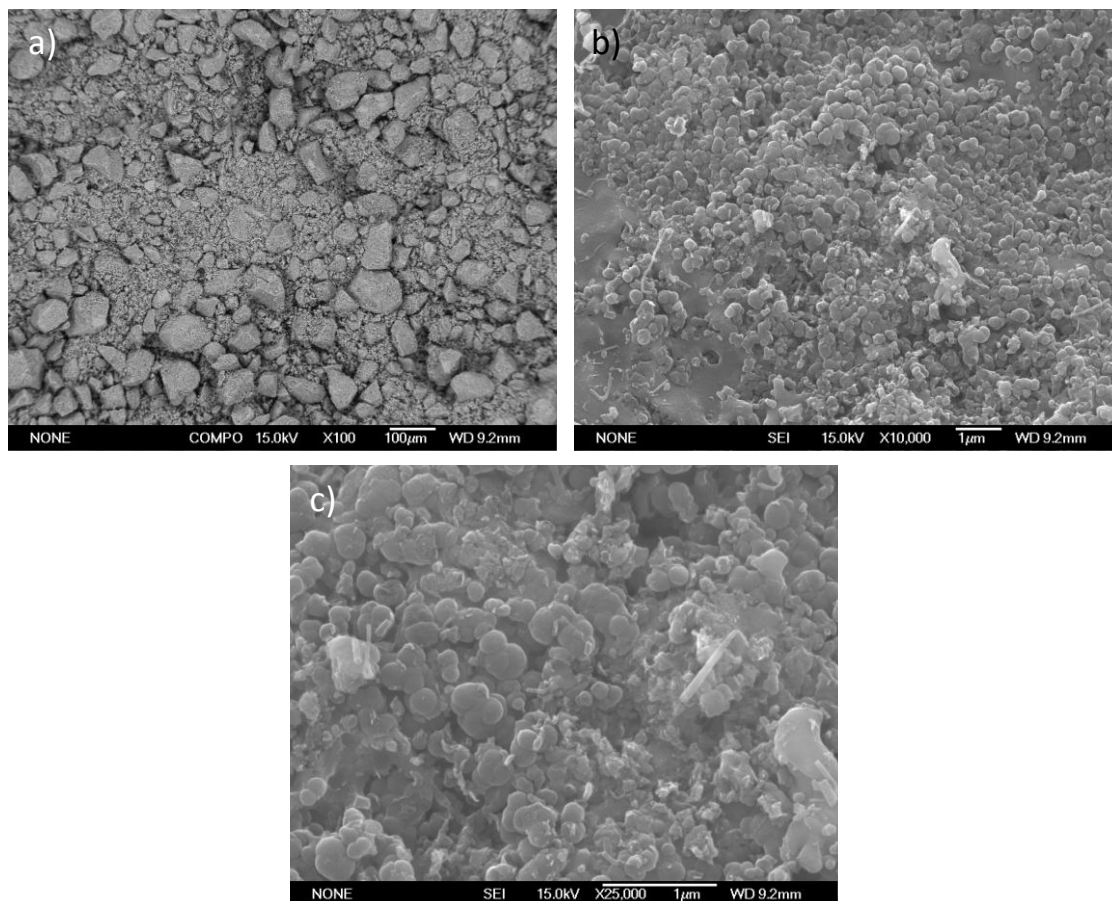


Figure 6.17: Backscattered image and SEI images of the A1.1-CB sample fired at 1400 °C for 0 hr at various magnifications. a) View of the bulk showing particulates, with b) and c) showing the retained spherical, nodular morphology and rough surface texture.

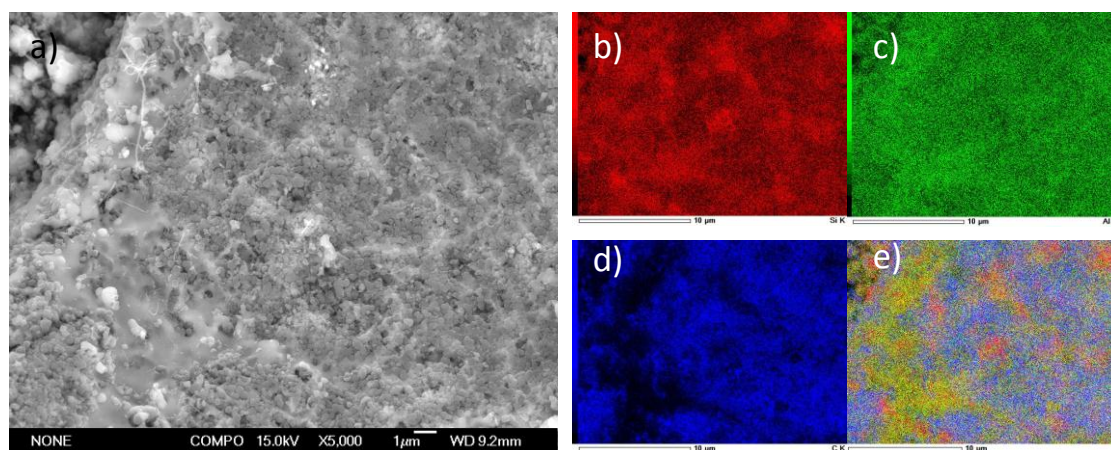


Figure 6.18: a) Backscattered image of A1.1-CB fired at 1400 °C for 0 hr with b) silicon, c) aluminium and d) carbon EDS maps and e) their overlay.

The evolution of sample morphology is illustrated in Figure 6.19 which shows a selection of SEI images at 10,000x magnification with increasing firing duration. This

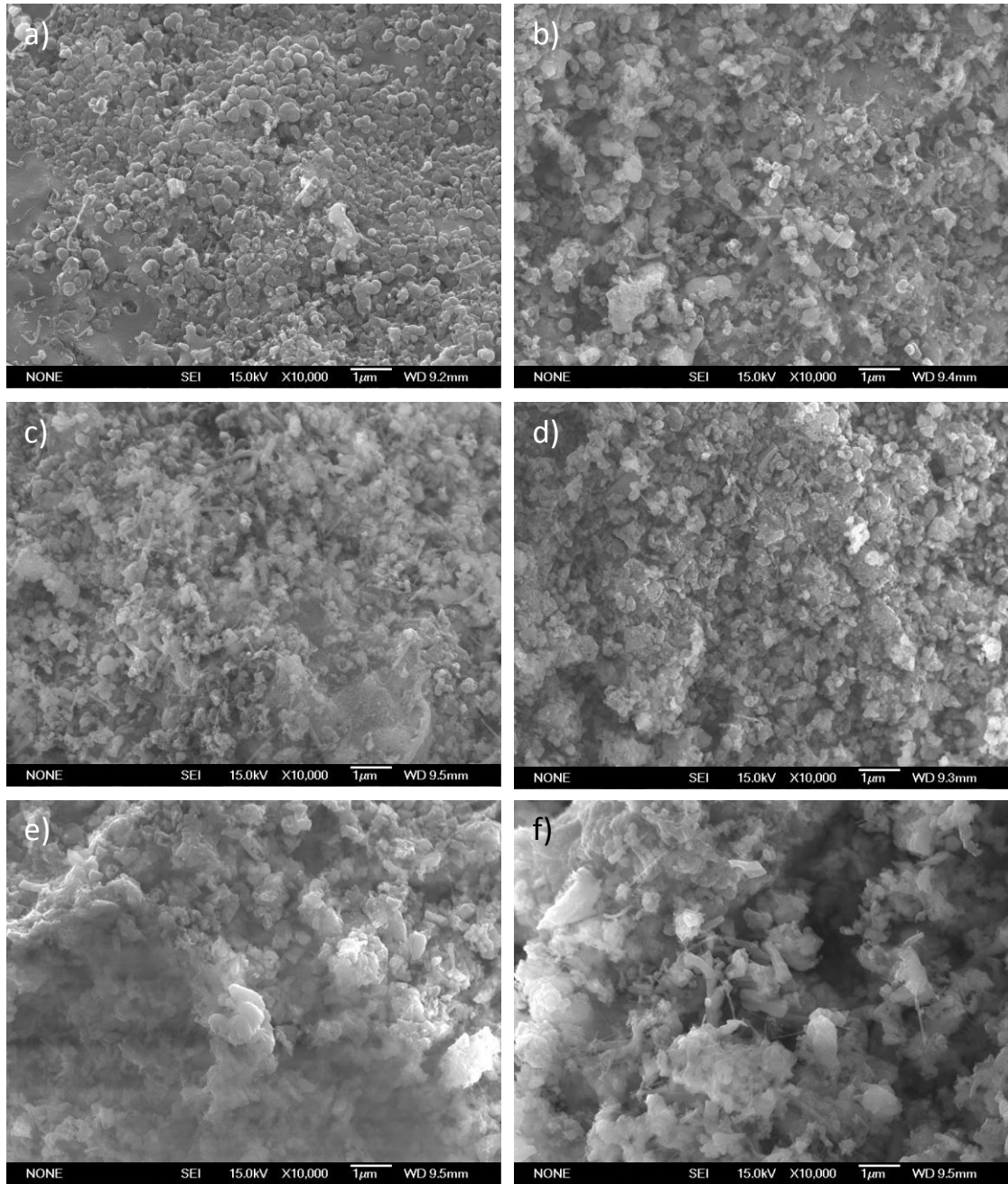


Figure 6.19: Selected SEI images of A1.1-CB samples fired at 1400 °C for a) 0 hr, b) 1 hr, c) 2 hr, d) 4 hr, e) 8 hr and f) 10 h showing varied surface morphologies. Magnification is 10,000x.

progression shows that, similar to the alkali-carbon black systems, the samples reacted to lose their nodular morphology and form a rough, jagged surface texture.

Fibres were present in all samples and can be seen particularly in Figure 6.19f. In general, the abundance of fibres was observed to decrease with increasing firing time, possibly by incorporation into the bulk phase. Figure 6.20a and b shows some fibres in the sample fired at 1400 °C for 0 hr. These fibres indicate that, like the potassium-graphite

samples and in contrast to potassium- and sodium carbon-black samples, the formation of fibres occurs early in the firing process, suggesting the early formation of SiO vapour.

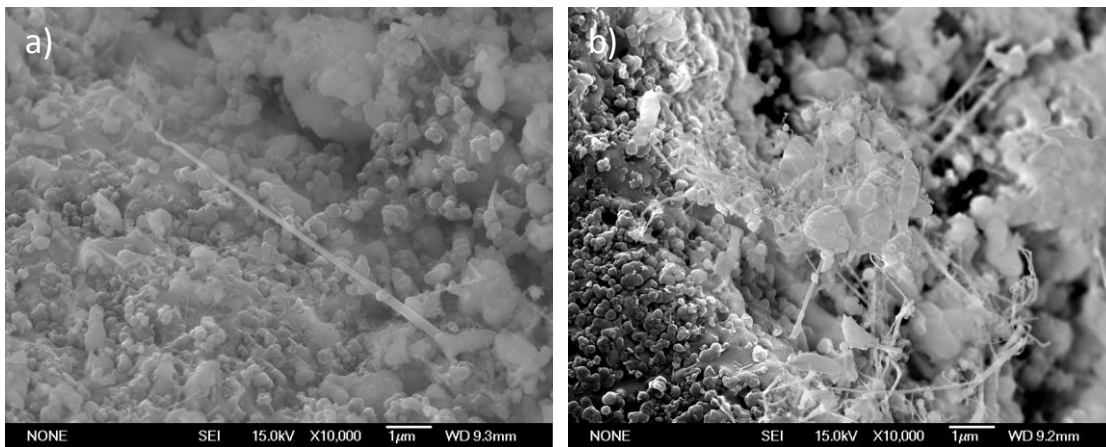


Figure 6.20: Selected SEI images of A1.1-CB samples fired at 1400 °C for 0 hr showing a) long straight fibres and b) a nest of woolly and straight fibres.

6.2.3.5 Firing under Argon

To investigate the behaviour of ammonium-composites under non-nitrating conditions, a A1.1-CB sample was fired at 1400 °C for 10 hr in flowing argon. The XRD pattern (Figure 6.21) shows behaviour consistent with other geopolymer-carbon black

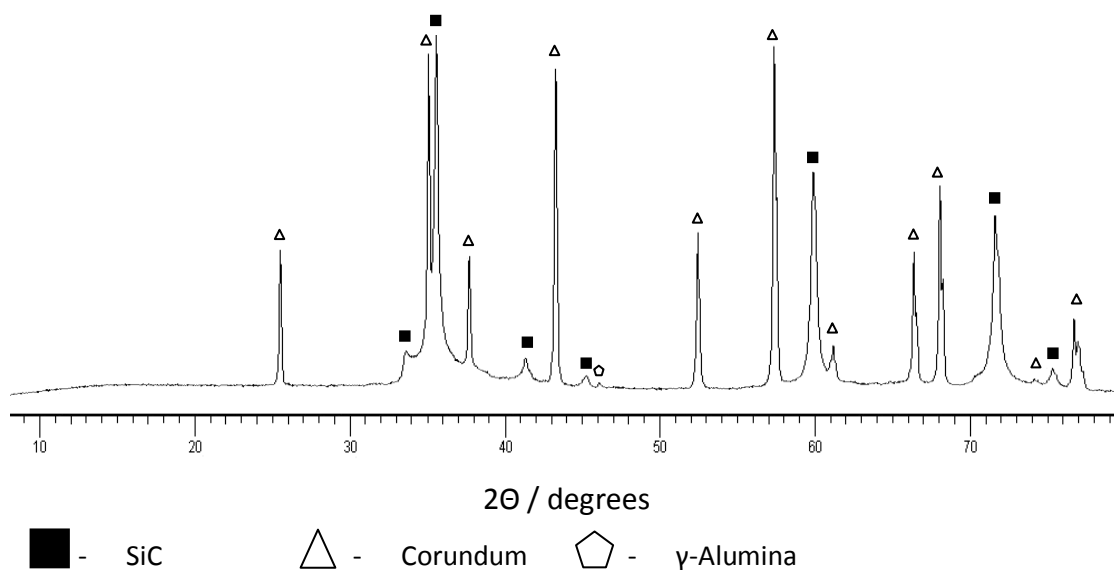


Figure 6.21: XRD pattern of A1.1-CB fired at 1400 °C for 10 hr in flowing argon.

samples in that the sample was carbothermally reduced to form SiC (both the α - and β -polytypes) and aluminium oxides, in this case predominately corundum with a trace of γ -alumina.

The IR spectrum, shown in Figure 6.22, agree with the XRD results, showing a broad peak (819 cm^{-1}) and shoulder (896 cm^{-1}) indicative of Si-C and peaks at 638, 587, 486 and 443 cm^{-1} from octahedral Al-O stretches and bends. The flat region from $\sim 750 - \sim 650\text{ cm}^{-1}$ is a result of broad overlapping Si-C and octahedral Al-O stretches. No Si-O peak near 1200 cm^{-1} is observed, indicating that if silica does form, than it is rapidly consumed to produce SiC. The reactions to form these phases are described in Equations (15) and (16).

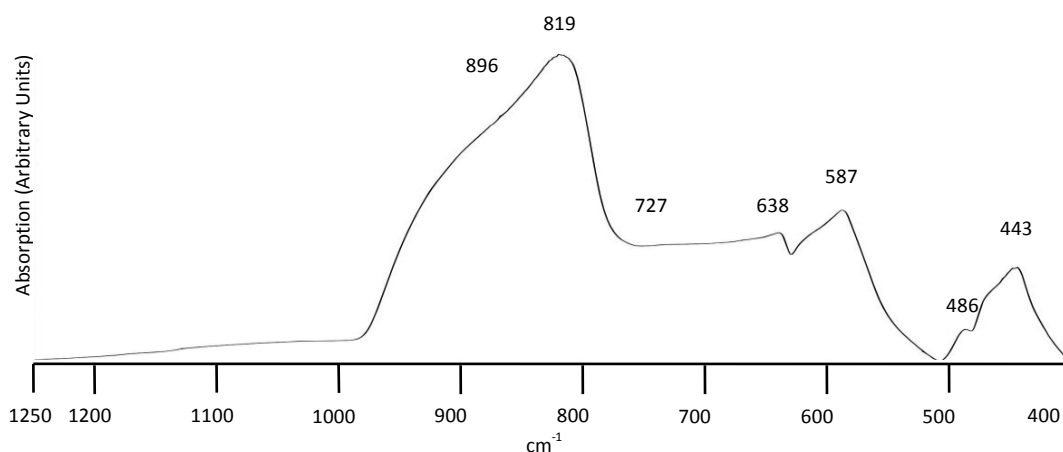


Figure 6.22: IR spectrum of A1.1-CB fired at $1400\text{ }^{\circ}\text{C}$ for 10 hr in flowing argon.

6.3 Discussion

6.3.1 Preparation of Ammonium-Exchanged Geopolymer Composites

It can be seen from the results that ammonium-geopolymer composites were readily fabricated from sodium precursor powders, with complete replacement of the charge balancing cation observed when analysed via EDS. When examined by XRD and IR, the formed ammonium-composites also retained the geopolymeric structure of their precursors albeit with some loss of silicon, likely due to overwashing of the samples. Examination under the electron microscope indicated that the exchange process did not affect the microstructure of the powders which maintained their porous, amorphous morphology with

the small, carbon containing nodules remaining intact in the composite sample. Although a small amount of carbon was lost during preparation, these results indicate that the ion-exchange process does not significantly impact the carbon bound into the matrix geopolymer and *vice versa*.

6.3.2 Mechanism of Sialon Formation from Ammonium-Composites

Upon firing the ammonium-composites formed a mixture of amorphous and crystalline phases. The presence of mullite and cristobalite indicates that these materials dissociate like clays; although possibly not to the same extent with some amorphous material present even after firing at 1400 °C for 2 hr. This is possibly due to kinetic hindrance caused by the carbon black in a similar manner as the sodium- and potassium-carbon black composites.

Beyond the pre-synthesis firing region, samples were observed to form firstly SiC and the nitrogenous phases X-phase and O1-sialon. The X-phase most likely forms from the mullite present but is never seen in large abundance, suggesting its rapid transformation into a high z-value β -sialon phase. Due to its increased cell dimension, the cristobalite phase is thought to have formed a solid solution by the incorporation of aluminium into its structure. Due to its reasonably large abundance and the formation of silicon oxynitride phases in the ammonium-composites, it is speculated that the O1-sialon is formed via the CRN reaction of the aluminous cristobalite rather than by the SiO vapour route proposed by MacKenzie *et al.*⁴¹ However, as sialon fibres were formed and the loss of silicon during firing was significant both reaction pathways are possible. As the firing temperature is above its known transition temperature and there is no stabilising cation present, it is not clear why O1-sialon is formed rather than O-sialon.

The formation of low z-value β -sialon initially occurs in samples from the transformation of the O1-sialon via the pathway proposed in Chapter 2. As this O1-sialon is consumed after 4 hr of firing however, it is clear that the large increase of low z-value β -sialon at the expense of the high z-value β -sialon in longer firings is caused by the over-reaction of the system due to excess carbon. As the resulting AlN content is significant, the

quantity of excess carbon is therefore considerable, indicating that a more precise control of the initial carbon content is required for optimal β -sialon yield.

These results indicate that ammonium-carbon black composites react, for the most part, in the same way as clays and β -sialon forms as a result of a conventional mechanism. However, some amount of reaction through a second pathway also occurs, as observed by the formation of O1-sialon and low z

6.4 Summary

In this chapter, the preparation of ammonium-geopolymers and ammonium composites was examined. It was concluded that ammonium geopolymer-composites may readily be synthesised using ion-exchange techniques, resulting in completely exchanged samples. These samples retained both the aluminosilicate atomic structure and microstructural morphology of their sodium precursors.

Firing of samples with varying carbon contents established that all samples contained carbon in excess of the amount necessary for the optimum formation of β -sialon and the presence of AlN, a product of over-reaction, was observed. For this reason, the sample with the lowest carbon content (A1.1-CB) was chosen for the investigation of the reaction mechanism. Whereas a firing in argon revealed similar behaviour to alkali-containing samples, with the formation of SiC and aluminium oxide phases occurring due to carbothermal reduction, firings under nitrogen reveal that these samples react via a dual mechanism. Samples were observed to dissociate forming mullite and cristobalite which reacted via X-phase, SiC and O1-sialon intermediates to form diphasic β -sialon. This reaction was rapid, with the almost complete conversion of the precursor having occurred after 4 hr. Firings of longer duration indicate that the excess carbon caused the breakdown of the high z-value phase into a low z-value phase with the subsequent formation of AlN.

7 Summary Discussion

7.1 Introduction

In the preceding chapters, the carbothermal reduction and nitridation of four different geopolymer systems was studied and samples were found to form nitrogenous materials via a number of mechanisms. It was seen that each system reacts in a different manner and through the formation of different intermediary phases. As such, a final chapter discussing the similarities and differences between these systems is warranted.

7.2 The Effect of Carbon Type

Comparison of the differences between the potassium-graphite and potassium-carbon black composites provides an opportunity to examine the role that carbon plays in the reaction of these geopolymeric systems. The differences in carbon content notwithstanding, changing the type and size of carbon used typically only affects the rate of reaction but not the reaction mechanism.^{40,52,60}

However, in the case of potassium geopolymer composites stark differences in behaviour were observed. Potassium-graphite composites were determined to react via the conventional mechanism while potassium-carbon black composites reacted via a dual mechanism involving CRN of an amorphous phase and silicon oxynitride type phases. These differences are attributed mainly the kinetic hindrance caused by carbon black. This kinetic hindrance, which was also observed to affect sodium- and ammonium-composites, is thought to be a result of the differences in the inclusion of the carbon into the geopolymer matrix. This was illustrated by the formation of the atypical small, nodular morphology observed by SEM for all carbon black composites.

The effect of the kinetic hindrance is that it impedes the composites from undergoing transformation processes that occur at high temperatures, preventing the potassium-carbon black composite from fully crystallising into leucite and stabilising it as a mainly amorphous phase. This stops further transformation processes (i.e. the dissociation

of mullite and silica) from occurring and the causes the samples to react through a non-conventional pathway. This may be a feature unique of geopolymers due their difference microstructural make-up, but may also have implications for the reaction of other systems. It suggests that other systems might display different reaction behaviour should an element creating sufficient kinetic hindrance be introduced.

7.3 The Effect of Alkali

The ammonium-carbon black composites reacted in a more-or-less similar manner to the conventional mechanism understood for clay based systems. The composites first underwent dissociation and crystallisation into mullite and cristobalite (silica) before being carbothermally reduced and nitrified to form β -sialon. The crystallisation of samples was incomplete however, with a small quantity of amorphous phase observed even after 2 hrs of firing. This indicated that the amorphous phase formed had good thermal stability and also suggests that the carbon black caused some kinetic hindrance to the ammonium-composites. The formation of X-phase and O1-sialon and the subsequent formation of a diphasic β -sialon product indicates that the ammonium-composite converted through at least two distinct mechanisms with the possibility of a third mechanism similar to the one proposed by Yamakawa *et al.*⁶⁴ also noted. The coincident formation of more low z-value β -sialon with AlN late in the reaction sequence is attributed to the further carbothermal reduction of the high z-value in a manner similar to Equation (11) due to the presence of excess carbon. This, along with the strictly CR processes observed by the presence of γ -alumina, are the likely cause of the large quantities of fibrous materials recovered after firing. These results indicate a system with similar properties to that of clays and which may also share similarities with the zeolites systems.

Comparing the reaction of the ammonium-composites to the sodium-composites from which they were derived, stark differences in behaviour were observed. In contrast to the crystalline, thermally stable phases of the ammonium-composites, sodium composites reacted via the formation of amorphous materials and vitreous phases of varying stoichiometry. That the system did not catastrophically melt, as predicted by the phase diagram and as observed in the control sample without carbon, is attributed to the kinetic

hindrance caused by the carbon black encapsulated by the geopolymer matrix. This kinetic hindrance conferred thermal stability on the sodium composites and allowed them to react to form SiC, X-phase and O-sialon phases, which upon further reaction, resulted in the formation of a mostly diphasic β -sialon material. The observation of β -sialon of high z-value early in the reaction sequence suggests that the composite may also undergo transition through an amorphous mechanism, this time similar to that of the one proposed by Mazzoni and Aglietti.⁶⁰

Due to the inhomogeneity apparent in the unfired precursors, it is unclear whether the amorphous and vitreous phases of varying composition are caused by this inhomogeneity or by incongruent melting. Both situations are plausible but the observation of nepheline in the melted control sample fired at 1200 °C for 1 hr suggests that at least some incongruity exists. Regardless of the cause, the sample forms both silica-rich and alumina-rich phases in a manner reminiscent of the dissociation of the clay and ammonium-composites. The silica-rich phases are predicted to be much less thermally stable by the phase diagram and are likely form eutectics in the system. This is the likely cause of the formation of the large quantities of O-sialon observed in firings and is concordant with the suggestions of Narciso *et al.*⁵⁶ and Ekström *et al.*⁵⁸ Despite the noted differences to the result reported by Zhu *et al.*,¹⁶ this O-sialon is thought to be a stuffed derivative Na-O-sialon due to the unusually large calculated unit cell dimensions which further support the proposition that its formation occurs from eutectic phases. With the loss of the sodium and with further CRN, this silicon oxynitride type phase was seen to undergo reaction to form a low z-value β -sialon. The simultaneous reaction of X-phase and the amorphous phase with SiC to form a high z-value β -sialon phase results in the mostly diphasic β -sialon material observed. The mixture of intermediary phases (X-phase and SiC) alongside over-reacted phases (15R-sialon and AlN) is attributed to the inhomogeneous distribution of carbon in samples.

In contrast to the sodium-composites, potassium-carbon black composites formed a thermally stable amorphous phase with a small amount of crystalline leucite upon heating. However, similar to sodium-composites, the samples reacted to form a stuffed derivative O1-phase which upon further reaction produced a low z-value β -sialon phase. The presence of a high z-value phases is attributed mostly to the direct reaction of the amorphous phase due to the small quantities of X-phase detected during reaction. It is conceded however,

that this may simply indicate that conversion of X-phase to β -sialon occurs very rapidly. These dual mechanisms are again seen as responsible for the formation of a diphasic β -sialon material and suggest that there may be some undetected incongruent processes also occurring. It is speculated that positive identification of the unknown crystalline phase in the 1 and 2 hr XRD patterns may help resolve this. Similar to the ammonium-composites, the coinciding formation of AlN and more low z-value β -sialon later in the reaction sequence is attributed to over-reaction due to excess carbon. Strictly CR processes are observed by the presence of corundum in samples.

Ignoring the effect of CRV processes diminishing the quantity of alkali present over time, it is generally evident from the results of the firing of the kinetically hindered carbon black composites that the presence of alkali encourages the retention of the amorphous nature of the samples heated to 1400 °C. In a similar fashion to the way in which the ammonium composites and clays dissociate to form the silica- and alumina-rich phases of silica and mullite, these amorphous phases undergo similar phase separation through incongruent processes. This results in the formation of silica-rich phases likely to form eutectics thereby promoting the formation of stuffed derivative silicon oxynitride type phases stabilised by the inclusion of the alkali. These silicon oxynitrides type phases convert to low z-value β -sialon phases through further CRN reaction with carbon. A likely by-product will be the formation of SiC through CR processes.

This reaction pathway occurs simultaneously with the reaction of the alumina-rich phase to form high z-value β -sialon through the direct CRN of the amorphous phase or via the combined reaction of X-phase and SiC. The combination of these dual mechanisms results in a diphasic β -sialon product. These reactions are invariably complicated by inhomogeneity in the distribution of carbon and by variations in concentration of nitrogen relatively to the amount of sample resulting in the CRN processes competing with the strictly CR processes. It is reasonable to suspect that these factors will favour or inhibit specific reaction pathways and may lead to products of mixed phase assemblage, as in the case of the sodium composites. The results of the ammonium- and potassium-composites show that in order to achieve a solely β -sialon product, even a diphasic one, precise control of the amount of carbon is necessary to avoid over-reaction. Judgement of the required carbon content is noted to be difficult however, due to the variations mentioned above.

7.4 Fibre Formation

Throughout all experiments, the in-situ formation of nano- and micro-sized fibres was observed. EDS analysis and comparison to the literature suggest that these fibres are β -sialon which explains the low z -values calculated by XRD modelling and from IR analysis. These fibres were observed via SEM in good abundance in the fired potassium-graphite and ammonium composites but were difficult to find in the potassium- and sodium-carbon black samples, especially those fired for shorter durations.

As the majority of potassium and sodium was lost during the early stages of firing, this suggests that the volatilisation of alkali does not play a role in the formation of fibres during firing. Also, as droplets were not observed at the tips of fibres, it is unlikely that the fibres form via a vapour-liquid-solid (VLS) mechanism. This suggests that fibres form via the conventional vapour-solid (VS) mechanism understood for the formation of silicon nitride fibres, outlined in Equations (7) and (8).

This explains why the ammonium and potassium-graphite systems generate the most fibres. They produce silica which upon dissociation which carbothermally reduces to form SiO vapour which in turn produces β -sialon fibres. The formation of SiO vapour in the potassium- and sodium-carbon black samples is likely impeded by the formation of the aluminium containing, silica-rich eutectics which has been suggested to inhibit the formation of SiO during firing.⁴⁶

This has implications for the design of systems undergoing CRN as it suggests that systems which dissociate to form silica will not more SiO vapour whereas stable amorphous systems or systems involving eutectics will generate less. Whether this is a bane or blessing depends on the desired outcome out the system undergoing CRN.

7.5 Reaction Pathways for β -Sialon Formation

Examination of the literature reveals that at least three mechanisms have been proposed for the formation of β -sialon by carbothermal reduction and nitridation of aluminosiliceous materials. They include the conventional mechanism understood for clay based systems, originally proposed by Higgins and Hendry⁵⁰ and examined by many

others,^{41,42,48,116} the reaction of glassy phases as proposed by Mazzoni and Aglietti⁶⁰ and the mechanism suggested for the direct conversion of completely amorphous phases by Yamakawa *et al.*⁶⁴

Based on the suggestions that different pathways can occur depending on whether a system crystallises or remains amorphous and the observation of the formation of diphasic β -sialon through Si-rich and Al-rich phases and O-sialon and X-phase intermediates, a series of new reaction pathways are proposed. These pathways are shown in a schematic representation (Figure 7.1) which includes the conventional mechanism, the direct amorphous mechanism and the mechanism proposed by Mazzoni augmented by these results. It should be noted that the proposed pathways ignore any loss of silicon content to the formation of SiO and do not take into account the competing strictly carbothermal reduction processes on materials resulting in alumina and excess SiC (Equations (15) and (16)). They also are based on ideal conditions whereby sufficient carbon and nitrogen are present and no over-reaction of β -sialon occurs. Furthermore, with the concept of high and low z -values already established, a new term of “neutral z -value” is introduced. This neutral z -value phase is the result of pathways which allow in the Si/Al ratio of the original aluminosiliceous material to be retained in the final product.

It can be seen from the schematic that reaction through a particular set of pathways will depend on the extent to which the aluminosilicate crystallises or remains/becomes amorphous. In both cases the formation of a neutral z -value phase may result if direct CRN takes place. In general, aluminosilicate systems such as clays and zeolites prefer to dissociate to form mullite and SiO₂ at elevated temperature which is the likely reason why the conventional mechanism is been observed in most cases.

This raises the question as to why Yamakawa observed the direct CRN of a zeolite. This may be rationalised by the observation that in the geopolymer-carbon systems studied, the fine inclusion of carbon into the matrix resulted in considerable kinetic hindrance. In their studies, Yamakawa used a reactive NH₃-C₃H₈ gas mixture as a carbon source. This reactive gas pyrolyses to deposit intimately on the surface of the zeolite pores and could result in sufficient kinetic hindrance to stop the dissociation from occurring and leading to the formation of β -sialon by the direct pathway. Furthermore, this would explain why intermediate phases of X-phase and O-sialon were observed with the late introduction of the reactive gas into the firing chamber. Late introduction would not allow the reactive gas

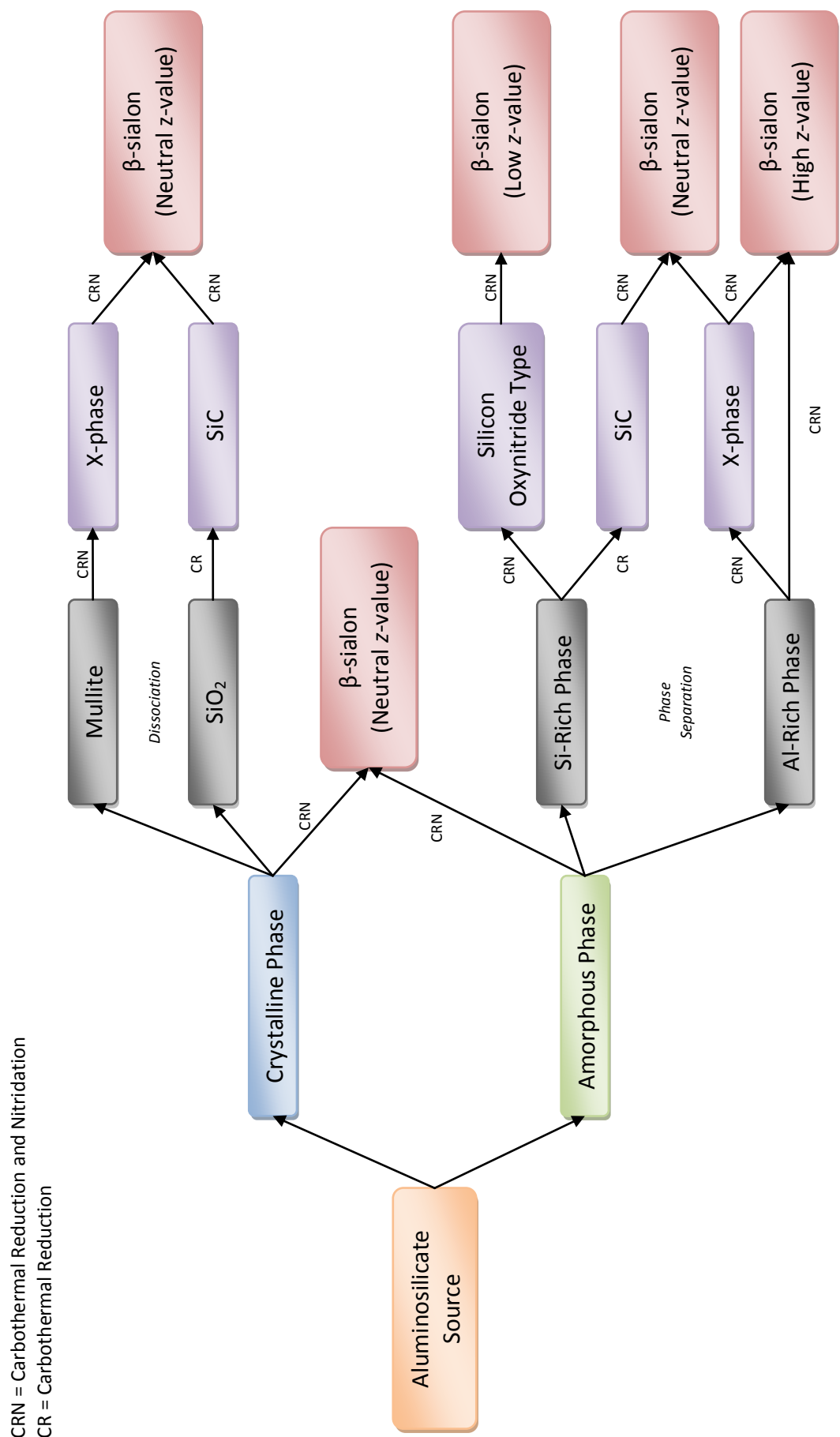


Figure 7.1: Schematic representation of proposed reaction pathways for the formation of β -sialon.

sufficient time to deposit on the zeolite leading to partial dissociation and the possibility of other reactions pathways occurring simultaneously. This is a similar situation to the ammonium-composites and suggests that they may have formed intermediates phases due to the inhomogeneity of the carbon throughout the geopolymer matrix.

In the case of potassium- and sodium-carbon black composites it was observed that the kinetic hindrance provided by the carbon black stabilised the formation of an amorphous phase. While some formation of β -sialon is suggested to have occurred by direct CRN, the presence of intermediates and the formation of low and high z-value β -sialon phases can be explained by phase separation caused by the formation of eutectics in the samples. This lead to the formation of silica-rich and alumina-rich phases which reacted to form a diphasic β -sialon material through either a silicon oxynitride type intermediate or CRN of X-phase or the alumina-rich phase. The lack of observation of a neutral z-value phase can be attributed to the phase separation which would cause the X-phase and SiC to form in different regions of the material. Therefore, similar to ammonium-composites, the observation of intermediates in the final products is likely a result of inhomogeneous carbon distribution in the geopolymer precursors.

If confirmed, these proposed extra pathways have significant implications for the fabrication of β -sialon materials and suggest that the preferential formation of materials of different z-values can be controlled by favouring particular reaction pathways. It is also suggested from observation of differing phase assemblage in reactions with excess quantities of material that the concentration of nitrogen gas will play a significant role in determining which reaction pathways are favoured or inhibited.

7.6 Summary

In summary, the effect of carbon type, alkali type, fibre formation and reaction mechanism were discussed and explored. It is apparent that geopolymer-carbon composites react to form β -sialon materials through a variety of reaction pathways dependent on the make-up of the original precursor.

It was found that the fine inclusion of carbon black caused appreciable kinetic hindrance to the composites resulting in the retention of the amorphous nature of the geopolymer prior to reaction. The presence of alkali in these carbon black samples caused the formation of eutectics in samples allowing the formation of silicon oxynitride type phases and X-phase intermediates and resulted in the formation of multiphasic materials with both high z-value and low z-value β -sialon phases apparent. As well as these pathways, the reaction via the conventional mechanism and through the direct conversion of the amorphous phase was also noted.

As a consequence of these observations a series of new reaction pathways were proposed in the context of results by others. A representative schematic for the carbothermal reduction and nitridation of aluminosiliceous materials was presented and commented on. Also, implications for the formation of β -sialon materials were discussed and limited suggestions about the particular pathways were made.

8 Conclusions and Future Prospects

8.1 Conclusions

The mechanism of carbothermal reduction and nitridation of geopolymers was studied by the reaction of potassium-graphite and potassium-, sodium- and ammonium-carbon black systems under a variety of reaction conditions and compared to fired non-carbon containing controls. To achieve this, series of samples with varying carbon content were first fired at 1400 °C in flowing nitrogen for 10 hrs to determine a suitable candidate composition for investigation of the reaction mechanism in a series of further firings. The pre-synthesis behaviour of these chosen samples was then investigated by firing samples at 1200 °C, 1300 °C and 1400 °C without an isothermal hold before a series of synthesis firings were carried out at 1400 °C using an isothermal hold between 1 – 24 hr in duration. For comparison, candidate samples were also fired in argon at 1400 °C for 10 hrs.

Each system was observed to react via a complex series of reaction pathways to form mostly β -sialon materials. Differences in the materials produced and the intermediates formed during firing were examined based on the type of cation present and also, in the case of potassium, the type of carbon used.

Ammonium-carbon black samples reacted to form β -sialon through dual pathways involving the conventional mechanism understood for clay based systems and a secondary silica-rich pathway involving the formation of O1-sialon which subsequently reacted to form a low z-value β -sialon phase. A third pathway was suspected to occur but could not be positively distinguished due to involving the conversion of an amorphous phase and the simultaneously occurring other reaction pathways. All samples were observed to have excess carbon and formed AlN and a low z-value β -sialon phase upon over-reaction.

Sodium-carbon black samples were observed to react through non-conventional dual pathways involving the formation of the silica-rich eutectics and an alumina-rich amorphous phase. The silica-rich pathway favoured the formation of SiC and a Na-O-sialon which subsequently reacted to form a low z-value β -sialon. The alumina-rich pathway, on the other hand, favoured the formation of X-phase resulting in a high z-value β -sialon phase. Together these produced a diphasic β -sialon product which also contained a number of

intermediates (X-phase, SiC) and over-reacted phases (15R-sialon and AlN) due to the inhomogeneous distribution of carbon in the starting sodium-carbon black composite.

Potassium-carbon black samples reacted to form β -sialon through up to three distinct pathways. Pathways similar to those seen in the sodium samples were observed with a silica-rich phase promoting the formation of an O1-sialon phase, thought to be a potassium stuffed derivative, which underwent further carbothermal reduction and nitridation to form a low z-value β -sialon. The amorphous alumina-rich phase coincidentally formed was observed to react to form a high z-value phase through direct carbothermal reduction and nitridation and also by the reaction of some X-phase. Excess carbon present caused the subsequent formation of AlN at the expense of the high z-value phase.

A potassium-graphite system comparable to the potassium-carbon black system above was observed to crystallise to form leucite and formed β -sialon only slowly and through the conventional mechanism understood for clays. This indicated that considerable kinetic hindrance affected the transformation processes available to the carbon-black systems with the effect of favouring the retention of the amorphous nature of the three systems described above resulting in atypical reaction pathways. The slow, conventional reaction of the potassium-graphite composites was accompanied by the formation of a large abundance of β -sialon fibres attributed to the in-situ formation of SiO vapour.

Overall it was determined that:

- The kinetic hindrance observed was determined to be a result of the fine incorporation of the carbon black into the geopolymer structure.
- The alkali promoted the formation of eutectics, resulting in the formation of silicon oxynitrides phases which underwent further carbothermal reduction and nitridation to form low z-value β -sialons, for which a general reaction mechanism was proposed (Equation (30)).
- The alkali was not observed to promote the formation of sialon whiskers.
- Different phase assemblages were observed as a result of variation in the quantity of material undergoing reaction, suggesting that the reaction pathway of the system may be controlled by the relative concentrations of material to nitrogen gas.

To explain these results, the reaction pathways were discussed in context of previously determined mechanisms proposed by others and a schematic representation for the formation of β -sialon presented. If confirmed, these new reaction pathways could have considerable implications for the design of reactive systems.

8.2 Future Prospects

Due to the exploratory nature of the work undertaken, a number of proposals made remained to be confirmed. Of particular significance is the proposed reaction mechanism through which O-sialon phases convert to β -sialon. This can be easily confirmed by simply reacting an equimolar mixture of O-sialon, preferably with significant aluminium content, and carbon under appropriate conditions.

Studies of the other silicon nitride phases suggested (K-O1-sialon and Na-O-sialon) is likely to be significantly more difficult as these systems will likely prove difficult to obtain in isolation. However, if it is confirmed that these phases do occur and that larger cations may be included into a sialon phase at reasonable temperatures then this may have considerable implications for the fabrication of sintering aids or even fluorescing materials which are always of keen interest to sialon ceramicists.

The exploration of kinetic hindrance to systems and stabilisation of amorphous aluminosilicates may be studied in a variety of ways and will be crucial to confirming the reaction mechanisms for β -sialon proposed. Reactive gas mixtures are particularly appealing as they can be used on any aluminosilicate but it is thought that considered experimental design will be necessary to allow sufficient distinction of effects due to the complex nature of reaction pathways available.

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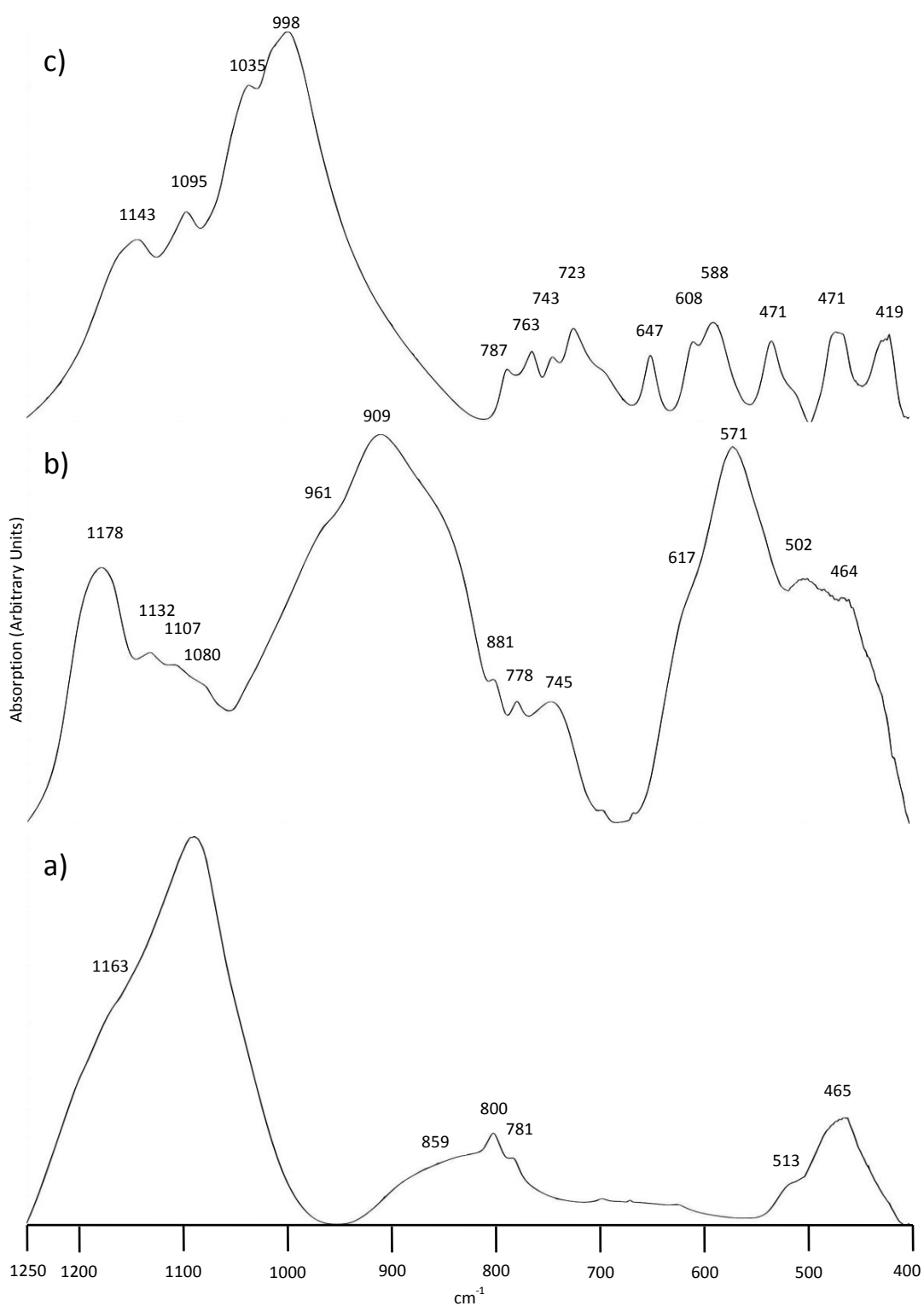
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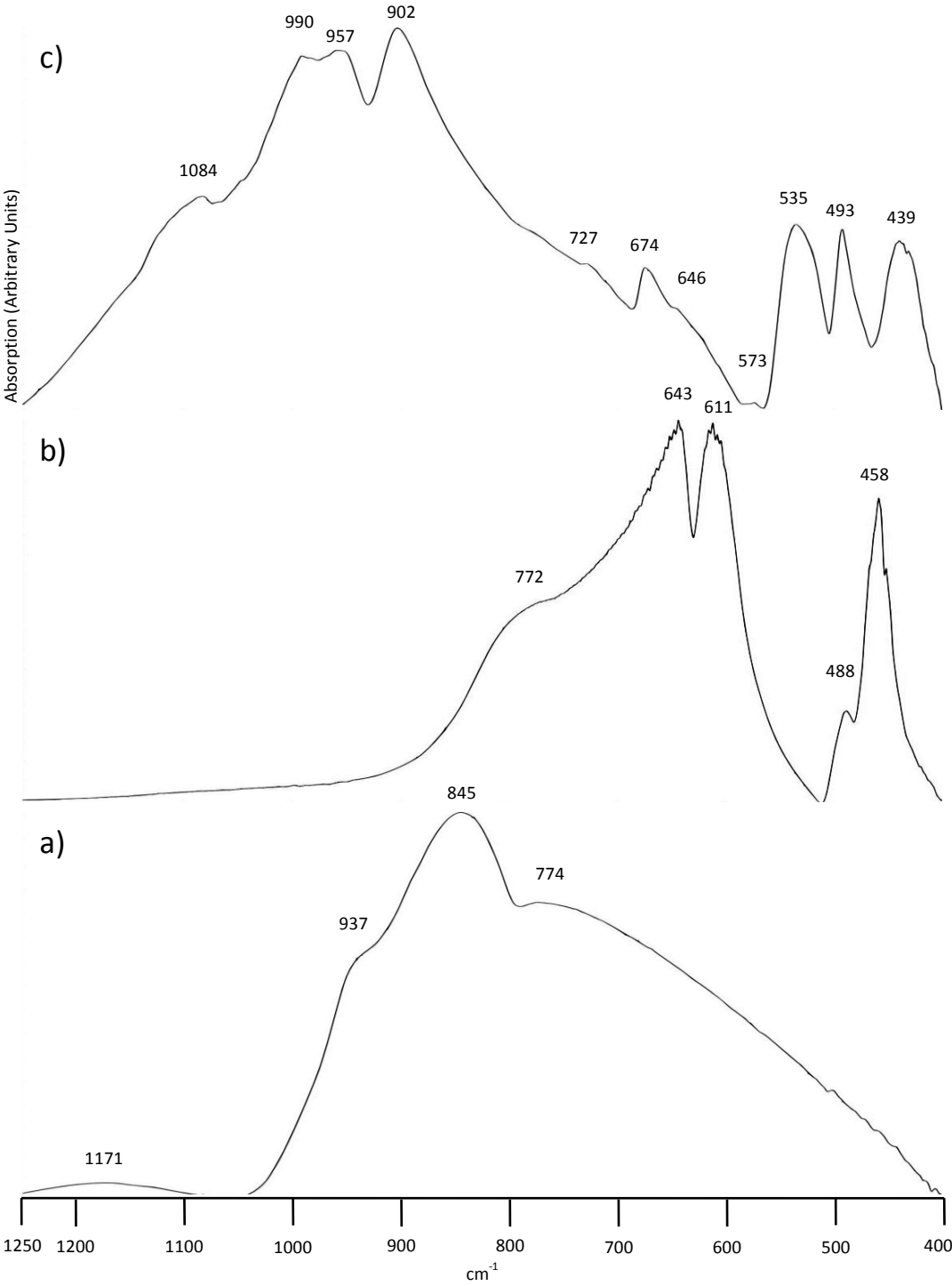
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Appendices

Appendix A: Infrared Spectroscopy Reference Spectra



IR spectra of reference materials: a) Dehydroxylated halloysite, b) Mullite (HF treated with SiO_2 impurities) and c) nepheline-syenite.



IR spectra of reference materials: a) SiC (α and β), b) Corundum (88% crystalline) and c) O-sialon ($x=0.2$).

Appendix B: Ternary Phase Diagrams

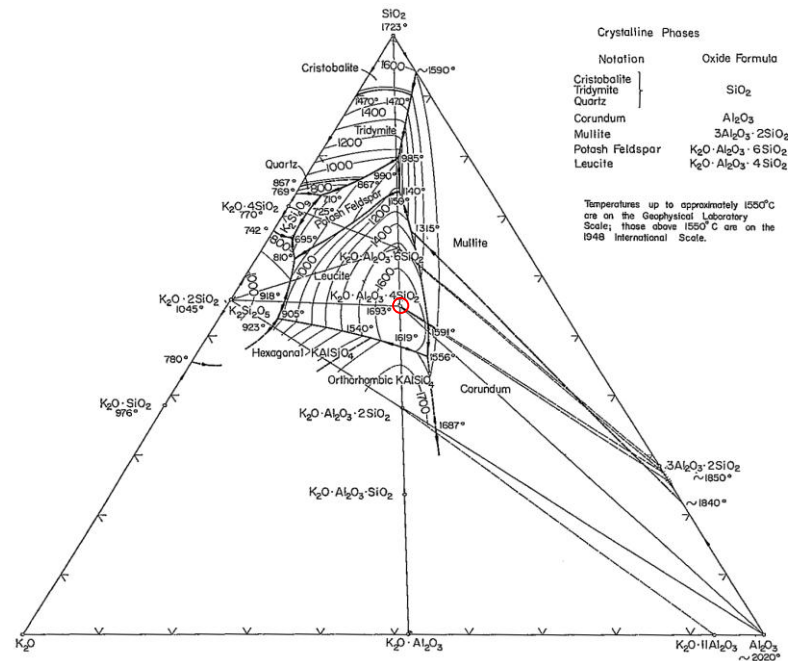


FIG. 407.—System $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 5, Published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

$\text{K}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ Ternary phase diagram showing composition of potassium geopolymer composites (red circle).

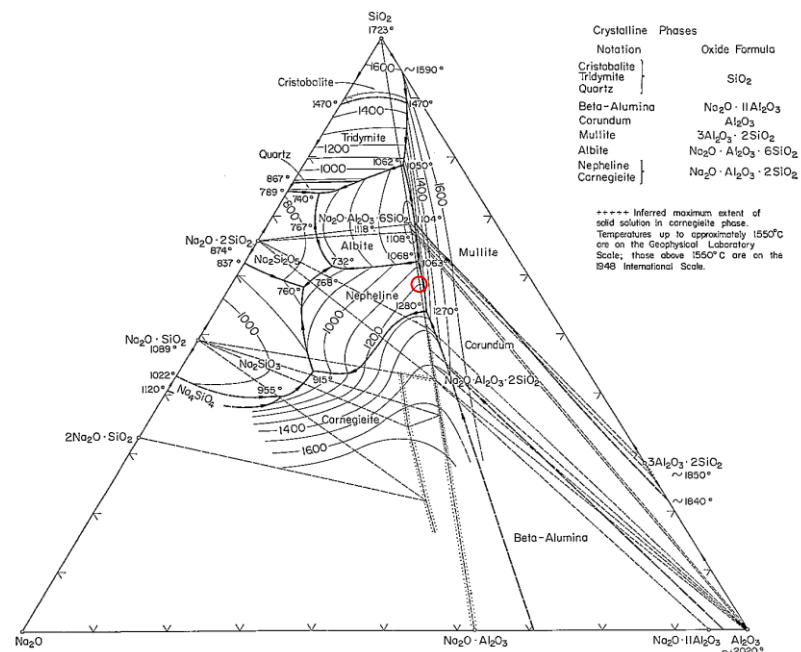


FIG. 501.—System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 4, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

$\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ Ternary phase diagram showing composition of sodium geopolymer composites (red circle).