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Crystal Chemical Adaptations of the Apatite Structure for the Incorporation of Simulated High Level Nuclear Waste (HLW)

*“Investigations of the crystal structure modifications for nuclear
waste immobilisation”*

**A thesis submitted for the degree of Doctorate of Philosophy
at the Nanyang Technological University for the School of
Materials Science and Engineering**

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Abstract

Singapore has achieved outstanding economic success since gaining independence, through the creation of industrial pillars in finance, shipping, semiconductors, petrochemicals, and more recently, biotechnology. These activities consume considerable raw materials and such progress is all the more remarkable in a city-state entirely dependent on importation of resources. The economy is also energy intensive, and to date, Singapore has relied primarily on oil-fired electrical power stations to meet its needs. However, in an uncertain world, diversification of energy supply is prudent, and for this reason Singapore is considering the nuclear power option. Clearly, the introduction of nuclear technology will require adaptation to the needs of a small island, and, of primary concern given the dense urbanization, will be the ultimate disposal of radioactive residues, particularly high level nuclear wastes (HLW) containing fission products (e.g. strontium-90) and transuranics (e.g. plutonium-239). This study was initiated to explore the scientific feasibility of immobilizing HLW in apatite-based phospho-silicate ceramics.

Ceramic nuclear wasteforms are generally polyphase, with different nuclides concentrating in specific compounds. This approach is flexible, but will be compromised if radiation damage ingrowth leads to differential swelling that reduces mechanical and chemical stability. Therefore, single phase wasteforms may prove superior. *It is the hypothesis of this thesis that the apatite crystal structure is sufficiently adaptable that all nuclides can be accommodated at specific crystal sites, and moreover, that such a ceramic can be fabricated as a closed system by uniaxial hot pressing to minimize losses of volatile species.* If the final product is single phase, and the distribution of nuclides homogeneous, the wasteform should swell uniformly and deliver superior long term durability.

The project is concerned with the fabrication of simplified apatite ceramics containing non-radioactive waste stimulants, the verification of crystallochemical incorporation, and the description of immobilization mechanisms. The experiments focus on simulated fission products (strontium, cesium and rare earths), transuranics (thorium), and processing contaminants (chromium, fluorine, chlorine). In this way, solid solution limits are established that provide guidance for tailoring precursor compositions to combine with nuclear waste streams and crystallize as apatite. In addition, a non-radioactive analogue of a United Kingdom defense program waste was stabilized at a 5.8 wt% loading in apatite fabricated by uniaxial hot pressing.

Although apatites are a diverse family, and their gross crystallographic features are readily confirmed by diffraction, inspection of published structures reveals many anomalies and inconsistencies. Therefore, a protocol for validating apatite structures containing simulated radionuclides was required. The majority of apatites are hexagonal ($P6_3/m$) and conform to the general stoichiometry $[A^I_4][A^{II}_6][(BO_4)_6][X_2]$. They are framework structures in which $A^I_4B_6O_{24}$ walls, composed of A^IO_6 metaprism columns corner-connected to the BO_4 tetrahedra, surrounding $A^{II}_6X_2$. As the relative size of the framework and tunnel contents vary, the metaprisms twist through an angle ϕ . Therefore, the determination of ϕ provides a direct, and highly sensitive, means to probe crystal chemistry.

To this end, three strontium apatite solid solution series - $[Ca_{10-x}Sr_x][(PO_4)_6][(OH)_2]$, $[Ca_{10-x}Sr_x][(PO_4)_6][F_2]$, $[Sr_{10}][(PO_4)_6][(F_{1-x}Cl_x)_2]$, $[Sr_{10}][(PO_4)_{6-x}(CrO_4)_x][F_2]$ - were synthesized and characterized using powder X-ray diffraction and powder neutron diffraction. In this way, characteristic trends in metaprism twist angle as function of A-site (Ca/Sr), B-site (P/Cr) and X-site (F/Cl) substitution were established. Because of A-site bifurcation, ϕ varies in a parabolic fashion with composition, while for the B- and X-sites the change is linear unless there is a transformation in symmetry, or change in composition due to volatilization; such concepts were employed throughout these studies.

Rare earth silicate britholite apatites $[Ca_{10-x}REE_x][(SiO_4)_x(PO_4)_{6-x}][O_2]$, $0 \leq x \leq 10$ from lanthanum (La) to lutetium (Lu) were found to invariably contain substantial A^I vacancies; the exception were cerium and praseodymium where Ce^{3+}/Ce^{4+} and Pr^{3+}/Pr^{4+} disproportionations may change the nature of this material. Moreover, while the large rare earth elements (REEs) were adequately modeled as $P6_3/m$ apatite, for the heavy REE ($> Er$) there is the suggestion that the symmetry may be lowered to monoclinic or triclinic. Thorium was used to mimic tetravalent actinide uptake in $[Ca_{10-x}Th_x][(PO_4)_{6-2x}(SiO_4)_{2x}][F_2]$ with the solid solution limited to $x \sim 1$. Uniaxial hot pressing was employed to synthesise cesium-bearing apatite and a wastefrom containing simulated weapons reprocessing waste. These initial studies confirm that this technique can fabricate near single phase and dense apatite ceramic wasteforms. Further optimization of the processing conditions is required.

It is concluded that the central hypothesis of this thesis, proposing that the apatite structural family possesses sufficient crystallochemical flexibility for exploitation as a ceramic wastefrom in HLW management, is credible.

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Chapter 1

Introduction

Will the nuclear option be adopted by Singapore? The potential benefits include diversification of energy supply, lowering green house gas emissions, supporting desalination and producing hydrogen fuel. While generation III nuclear reactors promise to be safe and efficient, the preferred strategy for treating radioactive residues remains unresolved. This study examines the crystallochemical viability of capturing radionuclides in apatite-based wasteforms prior to geological disposal.

1.1. Problem Statement

Secure and efficient energy delivery is essential for the development and advancement of society. As non-renewable reserves such as oil, coal and gas are depleted while urbanisation increases, the drive to explore and develop sustainable energy practices to maintain equitable living standards has gathered momentum. Nuclear power may serve as a bridging energy source until truly inexhaustible supplies from solar, wind and tidal technologies are refined and commercialized. Singapore is currently exploring the possibility of nuclear energy as a strategy for diversification beyond oil and gas as foreshadowed by Mr. S. Iswaran, Senior Minister of State for Trade and Industry in February 2010 who stated that studies should be undertaken to assess the feasibility of developing the nuclear option in the context of a small country.

Fission reactors have been operating for more than 60 years in many countries, the most significant being Russia, the United States of America, France, South Korea and the United Kingdom, with installations from 10 to 1400 MW [1]. Nuclear power plants can be incorporated in parallel green technology developments including desalination, hydrogen production and heating [2]. Moreover, the combined reserves of uranium and thorium are large, and when combined with reprocessing, assure an essentially infinite fuel supply. However, proliferation risks have delayed the wider adoption of nuclear technology [3], as has the absence of a consensus for the disposal of radioactive wastes [4]. These dual challenges are linked, as nuclear residues can be diverted towards terrorist activities (dirty bombs), or peaceful uses may be adapted for weapons programs.

Nuclear waste falls into four categories: (i) low level waste (LLW) or technologically enhanced naturally occurring radioactive material (TENORM); (ii) intermediate level waste (ILW) consisting of resins, chemical sludges and metal fuel cladding, and contaminated materials from reactor decommissioning; (iii) high level waste (HLW) rich in fission products; and (iv) transuranic waste (TRU) containing plutonium, neptunium, curium and americium [5]. Each waste class is managed distinctly, and generally, lower activity waste is voluminous, while highly radioactive waste is concentrated. This thesis is concerned with the investigation of apatite ceramics to

immobilize high level nuclear waste that contributes 95% of the radiogenic load, and transuranic radionuclides whose half lives are of geological timescales (e.g. Pu-239, $t_{1/2} = 24100$ years) [6]. A preferred approach for treating these wastes, that are unavoidable by-products of fission reactions, will be an integral part of Singapore accepting the nuclear option.

Essentially, the treatment of HLW and TRU always involves dispersion and stabilization within a non-radioactive matrix. In general, nuclear waste host matrices should:

- i) provide a *flexible structure* to accommodate all waste nucleotides homogeneously in solid form;
- ii) possess *chemical and radiologic durability* over hundreds of thousands of years in compatible geological settings; and
- iii) be *readily processed* so that immobilization is feasible and economical under high radiation conditions.

HLW solids are broadly classified as vitreous and crystalline [7], with the preferred option largely determined by waste composition. Vitrification generally employs borosilicate or phosphate glasses to encapsulate the waste; these wasteforms have been developed for almost 40 years in France [8]. However, during melting volatile nuclides may be lost, and glasses can devitrify with the crystalline fragments initiating stress corrosion cracking during radiation damage ingrowth [9]. Furthermore, glasses cannot stabilize all species (e.g. iodine) and the overall waste loading is low, leading to substantial bulking. High waste loadings (>10 wt %) intensify radiogenic heating that may remelt glass cores [10]. The adoption of refractory crystalline wasteforms offers the possibility of higher waste loadings [11], and includes a suite of metal oxides including those found in ordinary Portland cement (OPC), titanite (sphene), perovskite, hollandite, zirconolite, monazite, pyrochlore, zeolite and apatites [12-18].

Ceramics capture and retain waste in two ways - either radionuclides occupy specific atomic positions of the crystalline matrix [19], or waste sludges can be dried and encapsulated in non-radioactive titania or alumina [20]. Each approach presents its own challenges. The incorporation of radionuclides into crystalline phases requires relatively complex structures offering multiple substitutional schemes including cation and anion vacancies, interstitial defects, and atomic scale morphological modifications initiated by extensive nuclide substitution. In addition, ceramic immobilization involves tailoring the chemical composition of a precursor to ensure crystallization of the desired phases while maintaining a low processing temperature to minimize volatilization. Table 1.1 compares the primary characteristics of several better developed ceramic wasteforms from single phase to polyphase [7, 12, 14-18].

In 1978, Synroc (synthetic rock) pioneered by Professor Ted Ringwood and his colleagues from the Australian National University (ANU) and the Australian Nuclear Science and Technology Organization (ANSTO) provided a breakthrough in nuclear ceramic wasteform technology. By following geological precepts an assemblage consisting of four main titanate minerals – zirconolite, hollandite, perovskite and titanium oxide - was designed. These minerals have the capability to incorporate nearly all of the elements present in HLW as crystalline solid solutions. However, some nuclides were segregated along grain boundaries [8], where higher diffusion coefficients could compromise the overall leach resistance of the ceramic. Nonetheless, Synroc is clearly superior for TRU waste and will possibly be used to stabilize weapons grade plutonium [21].

Table 1.1: Ceramic wasteforms.

Mineral	Formula	Waste loading	Comments	Reference
Titaniite (sphene)	CaSiTiO_5	Ba, Sr, REE, actinides	superior to barosilicate glass	Ewing <i>et al</i> [12]
Perovskite	ABO_3	Sr, REE, Pu, Np	preference of light and intermediate REE (Ce-Gd) compared to zirconolite	Lutze <i>et al</i> [7]
Hollandite	$\text{A}_2\text{B}_4\text{C}_{10}\text{O}_{28}$	$\text{A} = \text{Cs}^+, \text{Sr}^{2+}, \text{Ba}^{2+}$, $\text{B, C} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Ga}^{3+}$, $\text{Cr}^{3+}, \text{Sc}^{3+}, \text{Mg}^{2+}$	excellent cesium immobilization when prepared in a strong reducing environment and presence of Ti^{3+} and Al^{3+} .	Lutze <i>et al</i> [7] Zandbergen <i>et al</i> [13]
Zirconolite	$\text{CaZrTi}_2\text{O}_7$	actinides	suitable to immobilize partitioned actinide-rich waste stream	Lutze <i>et al</i> [7] Zhang <i>et al</i> [14]
Morazite	CePO_4	REE, Sr^{2+} , Ba^{2+}	- hexagonal (La-Dy), monoclinic, tetragonal (Er-Y) - negative temp. coefficient of solubility, chemical durability increases with temp.	Ewing <i>et al</i> [12] Sales <i>et al</i> [15]
Pyrochlore	$\text{A}_2\text{B}_2\text{O}_6\text{Y}$	$\text{A} = \text{Ca, Na, actinides, REE}$, $\text{B} = \text{Ti, Zr, Sn}$, $\text{H, Y} = \text{O}^{2-}, \text{OH}^-, \text{F}^-$	transforms to fluorite structure prior to amorphisation	Wang <i>et al</i> [16]
Zeolite	$\text{CaAl}_2\text{Si}_4\text{O}_{12}$	Cs, Sr, Cd, Pb, Cr, Co^{2+}	ion exchange, waste ions are not chemically bonded, so poor leach resistance.	Rodriguez-Tejeda <i>et al</i> [17]
Apatite	$\text{A}_{10}(\text{BO}_4)_6\text{X}_2$	$\text{A} = \text{Sr}^{2+}, \text{Cs}^+, \text{REE, actinides}$, $\text{B} = \text{P}^{5+}, \text{Cr}^{5+}, \text{Si}^{4+}, \text{V}^{5+}, \text{As}^{5+}$, $\text{X} = \text{O}^{2-}, \text{OH}^-, \text{halides}$.	self annealing after amorphisation restores crystal structures	Boujdalet <i>et al</i> [18]

The uncontrolled partitioning of radioactive species to less durable interfaces or pores remains a potential limitation of polyphase ceramics [22]. Therefore, an idealized wasteform would be single phase to:

- i) *eliminate radionuclide partitioning* between phases which will experience differential swelling during damage ingrowth that promotes stress cracking;
- ii) *achieve uniform mechanical properties*, including coefficients of thermal expansion, which may be problematic if centreline temperatures of ceramic blocks reach several hundred degrees during early disposal;

- iii) allow *simpler corrosion modeling* by minimizing the number of solubility products considered, and permit greater assurance when extrapolating to long disposal times in different geological settings; and
- iv) favour the development of *less complex processing routes*.

Phosphates have long been recognised as potential ceramic matrices for nuclide immobilization [23]. For example, monazite (CePO_4) has a demonstrated capacity to accommodate nearly all of the radionuclides into a single phase [8], but the fixed P^{5+} valence limits the substitutions possible. The most common apatite minerals are also phosphates, but unlike monazite and its chemical analogues, contain several cation acceptor sites where complete replacement of P^{5+} by Si^{4+} , S^{6+} and certain transition metals (e.g. V^{5+}) is possible [24]. This structural flexibility greatly enhances the capacity of apatite to incorporate chemically complex waste streams. Synthetic apatite minerals have become prominent as possible immobilization matrices for nuclear waste owing to their chemical stability and radiation resistance [25]. Their potential is evident from studies of natural apatite from the fossil nuclear reactor at Oklo (Gabon) where these minerals withstood high doses of external and internal alpha and fission fragment irradiation while retaining radioactive elements quantitatively [26, 27]. Phosphate apatites also fulfil the stringent requirement that waste matrices should have low dissolution rates [28].

1.2. Objectives & Scope

The premise for these studies is that single phase apatite-type ceramic waste forms will be more easily processed and show greater resilience after geological emplacement than polyphase assemblages. The objectives of this research were to:

- (i) *establish a comprehensive understanding of the crystallochemical capabilities of apatite-based ceramics* to incorporate simulated ionic species representative of fission products, actinides and processing contaminants; and

- (ii) *design and fabricate a wasteform apatite* by hot uniaxial pressing to incorporate waste arising from the reprocessing of plutonium metal.

Of these, the first was fully realized, and in particular the diagnostic value of the ‘apatite metaprism twist angle’ developed to validate the crystal structures of apatite containing simulated waste. The second objective was partially demonstrated as it was not possible to fabricate a comprehensive suite of hot pressed apatite wasteforms in the time available.

The scope of this work consists of:

(I) Apatite fabrication

(I-i) *Apatites containing processing contaminants, chromium:* A common processing contaminant in high level waste (HLW) liquors derived from the corrosion of stainless steel vessels is chromium, which serves as a proxy for a range of transition metal ions that appear in nuclear waste. The powders of chromate-substituted phosphate apatite, $[\text{Sr}_{10}][(\text{PO}_4)_{1-x}(\text{CrO}_4)_x]_6[\text{F}_2]$ were synthesized by double decomposition and the precipitated apatite was calcined at 800-1000°C for 10 hours under nitrogen (purity: 99.99%, flow rate: 1L/min) with a ramp rate of 1°C/min to improve crystallinity.

(I-ii) *Apatites containing fission products, strontium:* Several radioactive isotopes of the alkali earth metals are found in HLW, the most significant of which is strontium-90. Non-radioactive analogues of strontium substituted calcium hydroxylapatite $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_2]$ and fluorapatite $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$ were precipitated via double decomposition. In addition, the strontium fluoro-chlorapatite $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$ was produced by wet and dry routes as fluorine and chlorine can be substantial components of certain HLW. Furthermore, deuterated analogues $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OD})_2]$ were prepared to better differentiate hydroxy and oxyapatite, as the latter may dominate in wasteform ceramics and modify radiation resistance.

(I-iii) *Apatites containing fission products, rare earths*: Stoichiometric mixtures of CaO , H_2SiO_3 and rare earth oxides (Pr_4O_7 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 , REE_2O_3 , REE=rare earth) were used in these syntheses. Although these apatites, commonly referred to as britholites in nuclear literature, have been widely studied, questions remain concerning the crystal site preference of the rare earth, nonstoichiometry and changes in symmetry. These compounds $[\text{Ca}_2\text{REE}_8][(\text{SiO}_4)_6][\text{O}_2]$ were prepared by manually grinding the reagents for homogenization, then cold pressing into pellets before sintering in air from 1200-1700 °C for 24 hours.

(I-iv) *Apatites containing transuranic products, thorium*: Th^{4+} is a suitable proxy for U^{4+} , Pu^{4+} and Np^{4+} and the $[(\text{Ca}_{10-x}\text{Th}_x)][(\text{PO}_4)_6\text{--}_{2x}(\text{SiO}_4)_{2x}][\text{F}_2]$, $0 \leq x \leq 3$) series was prepared by solid state reaction in air at 1400 °C for 6-24 hours. In these syntheses, yield was controlled primarily by reagent homogeneity, and while longer firing times were generally advantageous, excessive heat treatment lead to partial separation into a silica-rich glass. The effective solid solution limit was $x = 1$, but as Th^{4+} is larger than transuranic ions, this is likely a conservative estimate of actinide uptake.

(II) Characterization

(II-i) *Powder diffraction*: X-ray and time-of-flight neutron powder diffraction data were analysed by the Rietveld method to extract crystallochemical data (unit cell parameters and composition), conduct quantitative phase analysis and establish the partitioning of waste elements over the available crystallographic sites.

(II-ii) *Electron microscopy*: Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were employed for imaging at atomic to micron scales and for chemical analysis. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) screened for structural defects, however many apatites rapidly alter under high energy electron beam irradiation, and

this technique was used sparingly. SEM secondary (SEI) and back-scattered (BEI) electron imaging, and energy dispersive X-ray (EDX) spectroscopy of polished surfaces examined homogeneity.

(II-iii) *Spectroscopy*: Fourier transformed infrared spectroscopy (FTIR) was used to identify organic and inorganic components of the wasteforms. In particular, infrared absorption bands specific to common molecular components in apatites, especially the functional groups in the tunnel (e.g. OH^- , CO_3^{2-}) were identified. This technique was also used to confirm deuteration in $[\text{Ca}_{10}][(\text{PO}_4)_6][((\text{OH})_{1-x}(\text{OD})_x)_2]$.

(III) Demonstration of uniaxial hot pressing for waste immobilization

(III-i) Cs-137 is a relatively abundant and hazardous fission product. Chemically, cesium proved volatile and is not readily retained during sintering in air. Furthermore, the capacity of apatite to accommodate Cs^+ is poorly understood.

(III-ii) While this thesis is concerned with understanding the mechanisms of incorporating simplified, non radioactive waste in apatite wasteforms, real nuclear waste will contain many species. Therefore, a simulated waste from the United Kingdom weapons program was solidified by hot pressing to demonstrate the feasibility of capturing all the components in a single wasteform. This waste was chosen based on it encompassed representative wastes with different oxidation states and ionic radii to demonstrate the flexibility of apatite structure. In this way, a dense polycrystalline single phase apatite was fabricated. The influence of temperature, pressure, and waste concentration were examined.

1.3. Dissertation Overview

The thesis addresses the mechanisms and optimization of waste incorporation in phosphate and silicate based apatites and provides an in-principle demonstration of the fabrication by hot pressing of tailored apatites or britholites for the treatment of a chemically complex waste. *Chapter 1* roadmaps the motivation and significance of this project, and defines its objectives and scope.

Chapter 2 reviews apatite literature, especially with respect to synthesis and performance as nuclear waste matrices. The strengths and shortcomings of the characterization techniques employed in this study are discussed, including their complementarities.

Chapter 3 shows that the $A^I\text{O}_6$ metaprism twist angle of apatite can be used as a diagnostic tool to validate Rietveld refinements. Three strontium apatite solid-solutions – $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$, $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$ and $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$ - where the chemistry of the A^I/A^{II} , B and X sites were varied independently underpin this study. These compositions were chosen as Sr-90 is an important fission product, and chromium, fluorine and chlorine are often processing contaminants. In addition, the analysis also revisits published crystallographic data sets, which through an evaluation of ϕ , serve to emphasise the difficulty in obtaining reliable convergence during Rietveld refinement, and the sensitivity of apatite products to the effects of disequilibrium and stoichiometric changes during synthesis. This chapter provides a rationale, employed throughout the thesis, for monitoring metaprism twisting as a means of analysing wasteform crystallographic data and assessing its validity.

Chapter 4 confirmed the structural flexibility of apatite wasteforms through the synthesis of the $\text{Ca}_2\text{REE}_8(\text{SiO}_4)_6\text{O}_2$ compounds with REE radii ranging from 0.861 Å (Lu^{3+}) to 0.990 Å (Pr^{3+}). The site preference of rare earths in apatites as a function of size and the structural adjustments accompanying their incorporation serve to validate the use of silicate-rich varieties for fission product immobilization. Also, for the first time in apatite wasteforms, the appearance of calcium vacancies is documented. This study also considered the possibility of symmetry changes caused by small rare earth

element substitution. Trivalent REEs, also provide guidance for the incorporation of trivalent transuranics (Am^{3+} , Cm^{3+}).

Chapter 5 explores the saturation of apatite with thorium, as a stimulant for the abundant tetravalent actinides (U^{4+} , Pu^{4+} , Np^{4+}). The synthesis route established by Terra et al [29] was adopted, and the present study, supplements this published work with detailed crystallographic analysis of $[\text{Ca}_{10-x}\text{Th}_x][(\text{PO}_4)_{6-2x}(\text{SiO}_4)_{2x}][\text{F}_2]$, $0 \leq x \leq 3$. In addition, the dependence of the phase assemblage on precursor selection is examined.

Chapter 6 provides the first detailed assessment of proton incorporation in wasteform apatites, and the differentiation of hydroxy and oxy compounds. Deuteration enables neutron diffraction to examine these substitutions in $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2-2y}\text{O}_y]$. It was found by Fourier transform infrared spectroscopy that the surface of the calcium endmember is fully hydroxylated, while the calcium-strontium apatite surfaces are oxidized. However, in all cases the bulk is hydroxylated and exchangeable with OD.

Chapter 7 demonstrates the tailoring of an apatite precursor to incorporate a non-radioactive analogue of nuclear waste arising from weapons material reprocessing. Using uniaxial hot pressing in a pyrolytic graphite die, all radionuclide analogues were immobilized in a high density, single phase apatite. The optimal hot-pressing conditions are established. A reconnaissance study of cesium immobilisation in apatite proved inconclusive, and surprisingly lead to the crystallisation of CsPH_2 . This suggests that the charge balance mechanism employed ($\text{Ca}^{2+} + \text{OH}^- \rightarrow \text{Cs}^+ + \square$) was not operative, and it is proposed that the joint substitution $2\text{Ca}^{2+} \rightarrow \text{REE}^{3+} + \text{Cs}^+$ may prove effective.

Chapter 8 provides an overview of the work undertaken and the implications for developing apatite as a HLW solid. The hypothesis that chemically complex nuclear wastes can be incorporated in single phase apatite is discussed and avenues for future research considered. It is concluded that there is no crystallochemical reason preventing the fabrication of single phase apatite wasteforms suitable for geological disposal.

The objectives of this research were met by:

- (i) establishing a *comprehensive understanding of the crystallochemical capabilities of apatite* for accommodating simulated waste using neutron and X-ray diffraction techniques, and especially the use of the metaprisism twist angle to monitor apatite framework flexibility and validate waste incorporation; and
- (ii) demonstrating that *uniaxial hot-pressing is a viable method* for the solidification of HLW in an apatite waste form, and identifying the optimal conditions for fabrication.

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Chapter 2

Apatite Wasteforms: Crystal Chemistry, Performance and Characterization

Apatite is derived from the Greek etymon “apatite” meaning to deceive, as its range of colours and morphologies lead to misidentification with other minerals. The variable appearance of natural apatites is a manifestation of their substantial crystal chemical variability, and this property is exploited when designing high level nuclear wasteforms. The key to producing single phase apatites is to use crystallochemical tailoring to balance the proportions of additives and waste constituents to eliminate secondary compound formation.

Apatite Wasteforms: Crystal Chemistry, Performance and Characterization Chapter2

In this chapter, the current understanding of apatite crystallography, mineralogy and synthesis, especially as it pertains to nuclear waste management is reviewed. In particular, the key properties – radiation resistance and chemical durability – are considered.

2.1 Occurrence, Synthesis and Use of Apatites

“Apatite” is strictly a group name for minerals of ideal composition $(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F},\text{Cl})_2)$ that are of wide geological occurrence and persistence, as in Gabon where fission products have been retained quantitatively for 2000 million years [1], or biogenic origin, as in human bone and teeth [2]. According to the Gemological Institute of America, apatites appear in a range of colours and tints including white, yellow, blue, red, brown, grey and purple with significant deposits in Burma, Brazil, India, Kenya, Madagascar, Mexico, Norway, Sri Lanka, South Africa and the United States of America; however, only the yellow-green “asparagus” and blue-green varieties are used in jewellery [3]. Biological apatites deviate from ideal hydroxyapatite chemistry, through the incorporation of Mg^{2+} , Na^+ , K^+ , Cl^- and F^- , in addition to carbonate, which is a major substituent (5-8 wt%) [4, 5]. Generally, skeletal and dental apatites are calcium-deficient with poor crystallinity and crystallite sizes of $\leq 0.2\mu\text{m}$ [6].

Apatites are readily synthesized via: (i) *solid state reaction*, where oxides are mixed and annealed at high temperatures, and is appropriate in the absence of volatile metals [7-9]; (ii) *sol-gel methods*, that employ homogeneous precursors combined under stringent experimental conditions (e.g. pH, temperature) to provide superior control over purity [10-11]; (iii) *double decomposition*, that is a simple and flexible technique where water soluble chemicals are combined and pH adjusted to precipitate the desired phase [12-14]; and (iv) *hydrothermal reaction*, where pressure (0.001-0.1kbar) and moderate temperature (200-300°C) promote crystallization from super-saturated solutions, sometimes with a mineraliser added to control particle size and morphology [15-17].

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Besides nuclear and hazardous waste immobilization, apatites find use as heterogeneous catalysts for polymerization and selective gas reduction [18, 19], matrices for photoluminescent phosphates, silicates and phospho-silicates containing rare earth elements that display non-degenerate $^5D_0 \rightarrow ^7F_0$ transitions [20-22], separation media in liquid chromatography for the concentration of sugars, alkaloids, enzymes and proteins [23], solid oxide fuel cell (SOFC) electrolytes [24, 25], and as biocompatible dental and orthopaedic implants [26, 27].

2.2 Apatite Structural Prototype and Adaptation

The apatite structural family is conventionally represented by the formula $A_{10}(BO_4)_6X_2$ where A includes larger mono-, di- and trivalent cations, B represents metalloids and X are halides and anion radicals. Apatites most commonly adopt $P6_3/m$ hexagonal symmetry that includes A^I and A^{II} acceptor cation sites with bifurcation across the $4f$ and $6h$ Wyckoff positions; the complete crystallochemical formula is $[A^I]_4[A^{II}]_6[(BO_4)]_6X_2$. The A -sites show different anion coordination. A^IO_6 is metaprismatic and lies between octahedral and trigonal prismatic coordination, while A^{II} bonds with seven to nine anions. Cations partition over A^I and A^{II} according to size, electronic structure and other factors including the presence of co-dopants. The A^IO_6 form face-sharing columns that are connected to BO_4 tetrahedra to create large channels into which the $A^{II}X_2$ component is inserted. The channel framework is flexible and relaxes to better accommodate its contents. Formally, the A^I cation is in $(6+3)$ oxygen coordination - a tri-capped metaprism - but the descriptive crystallography is more simply rationalized by considering the shortest bonds only. It is not unusual for apatite to adopt lower symmetries with monoclinic [28] and triclinic [29] varieties being increasingly identified. White and Dong [30] who surveyed 74 chemically distinct apatites reported symmetry frequency as follows; $P6_3/m$ (57%), $P6_3$ (21%), $P-3$ (9%), $P-6$ (4.3%), $P2_1/m$ (4.3%) and $P2_1$ (4.3%); at the time of their review several $P-1$ triclinic varieties were not recognised [29].

Chemically complex apatites are possible, with charges balanced through homovalent or heterovalent replacements, and a great variety of substituents can be accommodated in this manner [31]. Therefore, the apatite family of minerals

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encompasses a rich and diverse solid state chemistry. Distortion from the underlying regular hexagonal net of anions can be used to track systematic crystallographic changes across solid solution series [31]. In particular, the metaprism twist angle ϕ derived from the [001] projection of oxygen triangles in AO_6 has proven a sensitive measure of departures in $P6_3/m$ symmetry or cation ordering [30, 32]. For all symmetries, ϕ can be used to investigate crystal chemical trends; hexagonal and trigonal types possess a single twist angle per metaprism, whilst in monoclinic apatites the AO_6 are distorted with three unique twist angles, where the average serves as a proxy for a single value [33]. Triclinic apatite twist angles are treated similarly. Table 2.1 summarized apatite structural family space groups and AO_6 metaprism twist angles [29, 34-39].

Figure 2.2: Polyhedral representation of hydroxyapatite with various metaprism twist angles (a) 0° , (b) 23.42° and (c) 60° (adapted from White & Dong, 2002).

Table 2.1: Examples of apatite structural family space groups and AO_6 metaprism twist angles.

Space group	Composition	ϕ ($^\circ$)	Reference
$P6_3/m$	$Ca_{10}(PO_4)_6F_2$	23.3	Sudarsanan <i>et al</i> [34]
$P6_3$	$Sr_{10}(CrO_4)_6Cl_2$	22.8	Mueller-Buschbaum <i>et al.</i> [35]
$P-3$	$Ba_4Nd_3Na_3(PO_4)_6F_2$	13.8	Mathew <i>et al.</i> [36]
$P-6$	$Ba_6La_2Na_2(PO_4)_6F_2$	14.5	Mathew <i>et al.</i> [36]
$P2_1/m$	$Ca_{10}(SiO_4)_3(SO_4)_3((OH)_{1.87}Cl_{0.26}F_{0.09})_2$	23.3	Sudarsanan [37]
$P2_1/b$	$Ca_{10}(PO_4)_6Cl_2$	14.9	Mackie <i>et al.</i> [38]
$P2_1$	$Na_{1.46}La_{8.55}(SiO_4)_6(F_{0.9}O_{0.11})$	24.6	Hughes <i>et al.</i> [39]
$P-1$	$Ca_{10}(AsO_4)_6F_2$	24.6	Baikie <i>et al.</i> [29]

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Baikie *et al.* [40] collated seven structural adaptations of apatites that lead to crystallochemical diversity. These include:

- i) Cation ordering when metaprism twist angles φ are less than $\sim 25^\circ$, that gives rise to $P6_3/m$, $P6_3$, $P-6$ or $P-3$ apatites;
- ii) Intra- and inter-tunnel anion ordering of the X -site leading to $P2_1/b$ varieties;
- iii) Framework topological tuning to accommodate small tunnel contents with $\varphi > \sim 25^\circ$ leading to $P2_1/m$, $P2_1$ or $P-1$ symmetry;
- iv) Partial or complete replacement of BO_4 tetrahedra by BO_5 and BO_3 polyhedra, accompanied by a lowering of symmetry from $P6_3/m$;
- v) Polymorphic transformations initiated by temperature or pressure that change relative ionic sizes, and hence, framework tuning;
- vi) Pseudopolymorphism where small compositional adjustments force breaches in critical limits of metaprism twist angle that are accommodated by a change in symmetry; and
- vii) Polysomatism that arises by rotational twinning of $A_5B_3O_{18}X_6$ modules in ordered and disordered sequences.

To summarise key chemical and structural features of mineralogical apatites, Pasero *et al.* [41] created a taxonomy consisting of five supergroups:

- i) *Apatite group*: hexagonal and pseudo-hexagonal with the generic formula $[A_2][A_3][(BO_4)_3][X]$ where A is homoatomic and B is P, As or V;
- ii) *Hedyphane group*: hexagonal and pseudo-hexagonal with the generic formula $[A_{5-x}A'_x](BO_4)_3X$ where A and A' are distinct and B is P, As or S;
- iii) *Belovite group*: hexagonal and trigonal phosphates with A^I site splitting into A^I and A^{Ib} ;
- iv) *Britholite group*: hexagonal and pseudo-hexagonal silicates, with partially ordered A^I and A^{II} cations; and
- v) *Ellestandite group*: hexagonal and pseudo-hexagonal sulfato-silicates with the ratio $(SiO_4)^{4-} : (SO_4)^{2-} = 1:1$.

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With respect to the general apatite composition, it is noted that in mineralogy the formula unit $A_5(BO_4)_3X$ (often expressed as $M_5(TO_4)_3X$) is commonly used, while in materials science the contents of the hexagonal unit cell $A_{10}(BO_4)_6X_2$ is preferred. According to Pasero *et al.* [41], the apatite and britholite groups are relevant to HLW immobilization.

2.2.1 Durability

Naturally occurring apatite is well known to confine actinides and fission products over geological timescales [1]. Apatites (fluoro, hydroxyl and chloro varieties) are resistant to degradation at elevated temperatures even when exposed to radiation (α , β , γ) [42], and this feature is key for ultimate geological disposal. The chemical durabilities of natural and synthetic apatites are similar [43].

Matrix durability can be compromised by “leaching”, which includes several processes where inorganic and/or organic pollutants or radionuclides are released from the solid phase to ground or surface waters, and can include dissolution, desorption, pH dependent complexation, redox reactions or microbiological activity. These mechanisms are universal, as any material exposed to water will undergo surface corrosion and sub-surface dissolution, the latter being porosity dependant. In almost every case, the leach rate will increase with temperature and prove more severe when the wasteform is newly prepared and radiogenically heated.

By understanding the mechanisms of leaching, measures can be taken during wasteform fabrication to minimize losses. Ceramic matrices commonly lose integrity in three ways: (i) rapid dissolution of surface material, (ii) diffusion-limited release through pores and along grain boundaries, and (iii) slow dissolution of materials from surfaces and pores, perhaps accompanied by re-precipitation. Rahman *et al.* [44] reported that leaching during surface wash-off and diffusion is rapid, dissolution is insignificant. The American National Standard Institute (ANSI) defined a leachability index, L , of a diffusing species [45], with $L = 6$ the accepted threshold for immobilization [46] and given by

$$L = \log (\beta/ D)$$

2-1

where β is a defined constant ($1.0 \text{ cm}^2/\text{s}$), and D is the diffusion coefficient (cm^2/s) of the species of interest, assumed to be independent of time during the course of leaching. Table 2.2 listed the diffusivities of waste species in apatite matrices [47, 48].

Leaching can be reduced by lowering diffusion coefficients, however in real materials, porosity aids diffusion through the matrix and can accelerate dissolution of the ceramic [49]. Therefore, it is important to consolidate wasteforms through appropriate processing.

Table 2.2: Diffusivities of waste species in apatite matrices [47, 48].

Simulated waste	Diffusivity in apatite (m^2s^{-1})	Temperature range
Strontium (Sr^{2+}), Manganese	$5.4 \times 10^{-7} \exp(-288 \text{ kJ mol}^{-1}/\text{RT})$	
Lanthanum (La^{3+})	$2.6 \times 10^{-7} \exp(-324 \pm 9 \text{ kJ mol}^{-1}/\text{RT})$	800-1250°C
Neodymium (Nd^{3+})	$2.4 \times 10^{-7} \exp(-348 \pm 13 \text{ kJ mol}^{-1}/\text{RT})$	800-1250°C
Samarium (Sm^{3+})	$6.3 \times 10^{-7} \exp(-298 \pm 17 \text{ kJ mol}^{-1}/\text{RT})$	750-1100°C
Dysprosium (Dy^{3+})	$9.7 \times 10^{-7} \exp(-340 \pm 11 \text{ kJ mol}^{-1}/\text{RT})$	800-1250°C
Ytterbium (Yb^{3+})	$1.3 \times 10^{-8} \exp(-292 \pm 23 \text{ kJ mol}^{-1}/\text{RT})$	800-1250°C
Uranium (U^{4+})	$1.3 \times 10^{-6} \exp(-394 \text{ kJ mol}^{-1}/\text{RT})$	1000-1300°C

Leaching tests are divided into static and dynamic extractions. In the former protocols, a single, specified volume of leachant is used without replacement of leaching fluid. Contrarily, in dynamic protocols, there is a regular renewal of the leachant. In the static tests, a steady-state condition is assumed at the conclusion of the experiment, whilst dynamic tests focus on the kinetics of contaminant mobilization and generates information as a function of time [50].

Each leach test protocol has its strengths and limitations, and selection of an appropriate test is essential to obtain validate stabilization after disposal. Summary of static and dynamic leaching tests are described in Table 2.3 and 2.4 respectively [51-61].

Table 2.3: Summary of static leaching tests.

Type of test	Description	Properties measured	Example(s)
Agitated test	<ul style="list-style-type: none"> waste and leachant co-mingled and agitated particle size reduction to increase surface area, hence reduce time to reach steady state 	chemical	<ul style="list-style-type: none"> TCLP [51, 52]
Non-agitated test	<ul style="list-style-type: none"> co-mingled and not agitate assum: physical integrity of matrix affect leaching 	physical, rate-limiting	<ul style="list-style-type: none"> Strategic Leach test High Temp. Static Leach test [53, 54]
Sequential chemical extraction test	<ul style="list-style-type: none"> a series of agitated extraction test, increasing chemical aggressiveness of leachant, will increase amount of extracted contaminants 	chemical	<ul style="list-style-type: none"> ASTM sequential batch extraction of wastes with acidic Extraction [55, 56]
Concentration build-up test	<ul style="list-style-type: none"> repetitive contact between waste and same leachant at very low liquid to solid ratio fluid flowing through matrix, with concentration of extracted waste build up 	Pore water composition of waste	<ul style="list-style-type: none"> Wisconsin's Standard Leach Test, Procedure C

Table 2.4: Summary of dynamic leaching tests.

Type of test	Description	Properties measured	Example(s)
Serial batch test	<ul style="list-style-type: none"> granular samples mixed with lechant and agitated, successive batch of fresh lechant temporal release of leachable constituents 	kinetic information on contaminant dissolution	<ul style="list-style-type: none"> Multiple Extraction Procedure (SW-846 Method 1320) [57]
Flow-around test	<ul style="list-style-type: none"> a sample of waste in leaching vessel and flow of fresh leachant around driving force to maintain leaching usually for monolithic samples 		<ul style="list-style-type: none"> ISO Leach test 6961 ANSI/ANS 16-1 [58, 59]
Flow-through test	<ul style="list-style-type: none"> open container packed with porous solid through which leachant is passed 		<ul style="list-style-type: none"> ASTM D4874-95 column test [58, 60]
Soxlet test	<ul style="list-style-type: none"> continuously contact waste sample with fresh leachant without adding or removing leachant from apparatus 	maximum amount of a constituent leachable from waste sample	<ul style="list-style-type: none"> Soxlet Test (MCC-5s) [61]

2.2.2 Radiation Resistance

Radiation resistance is a fundamental requirement of a host phase for nuclear waste isolation. Of the three emissions (α , β , γ), it is the alpha-decay events from within the host structure that are of most concern as the passage of the α -particle (actually He^{2+}) causes ionization damage. Changes in physical properties due to amorphization lead to a significant decrease in density and characteristic adjustments of refractive index and birefringence, known in mineralogy as metamictization [62]. Alpha emission modifies crystal periodicity by:

- (i) high velocity alpha particles may cause ionisation of atoms along their path;
- (ii) low velocity alpha particles may collide with atomic nuclei;
- (iii) heat can be released for a short periods along the path of alpha particles, leading to thermal disorder; and
- (iv) during the accumulation of alpha particles, helium bubbles form within the structure to create voids and pores.

Mechanisms (ii) and (iii) are most important [63] as they contribute to radiation induced amorphization that can lead to an order of magnitude increase in dissolution rate; for instance in silicate apatites, the release rate of actinides is 16 times greater from the amorphous state [64]. In addition, fission fragments create damage cascades that can eventually overlap and destroy the periodic crystal structure.

Natural apatite is less affected by metamictization than zircon and sphene [65], owing to its ability to self-anneal to remove dislocations and recrystallize [66]. Shuster *et al.* have investigated the effect of radiation damage on both synthetic and natural apatites by natural and artificial radiation damage and discovered that synthetic apatites possess the radiation tolerance of mineral analogues [67, 68]. To study radiation effects, noble gas thermochronometry and ion beam-radiation experiments are employed to extrapolate to the low temperatures and long timescales that closely simulate geological settings [67-70]. Lian *et al.* [71] performed in-situ transmission electron microscopy (TEM) during heavy ion radiation (He^{2+}) of apatites to determine the critical amorphization dose, D_c for a given temperature where the ceramic will become wholly aperiodic, and the critical temperature, T_c , above which the material

anneals with crystallographic recovery. It was discovered that phosphate apatite amorphized at a lower dose than the equivalent silicate at low temperature, and at high temperatures (> 350 K) the phosphate apatite has a higher critical amorphization dose attributed to its lower activation energy for recovery [71]. In this respect, a mixed phospho-silicate apatite (a britholite type) may offer the best compromise to enhance radiation resistance.

2.3 Characterization Methodology

The validation of apatite wastefrom properties requires materials characterization from atomic to micron scales. Evidentially, a combination of techniques is essential and a range of methods were employed based upon discrete physical phenomena (e.g. diffraction, X-ray fluorescence, infrared absorption and so on) that in combination provide more complete analyses. It is not therefore, the purpose of this section to discuss the principles of these techniques, but to emphasize the different information gathered and how these results prove complementary.

2.3.1 Microstructure

2.3.1.1 Scanning Electron Microscopy (SEM)

Secondary electron images (SEI), backscattered electron images (BEI) and energy dispersive X-ray spectra (EDX) were collected with a scanning electron microscope operating at 10-15keV for imaging and 30keV for spectroscopy. For SEI samples, powders were deposited on double sided carbon tape attached to an aluminium sample holder, prior to gold sputter coating to improve conductivity under the electron beam for crystal morphology examination. Backscattered electron imaging requires wastefrom disks to be mirror polished to reduce topological artefacts. BEI and EDX analyses also demand the polished ceramics be carbon coated to permit compositionally different regions to be distinguished and elemental chemical analysis to be conducted respectively.

2.3.2 Crystal Structure Refinement

The methodology for crystal structure refinement will be considered in detail for each of the experiments described in later chapters. Here, an overview the general approach is given.

2.3.2.1 Powder X-ray Diffraction (PXRD)

When an X-ray wave-front encounters an obstruction that behaves as a diffraction grating, coherent scattering will result. In the case of powdered crystalline specimens, these interactions produce an interference known as the X-ray diffraction pattern. In these studies, crystal structure parameters were extracted from powder X-ray diffraction (XRD) patterns collected using a Shimadzu LabX XRD600 with $\text{CuK}\alpha$ radiation step-scanned over the 2θ range $10\text{--}140^\circ$ at intervals of 0.02° . X-ray diffraction is the only method available for several rare earth and actinide bearing apatites, as neutron diffraction will lead to activation (Chapters 4 and 5). Quantitative phase analysis and unit cell parameters were extracted by Rietveld analysis with TOPAS V3.0 (Bruker AXS) [72]. The refinement is a whole pattern algorithm where the position and intensities of the peaks from the calculated diffraction profile are fitted to the experimental data set. The differences between calculated and experimental intensities are minimized through least squares adjustment of instrumental and crystallographic parameters to arrive at a structure refinement. However, X-ray diffraction cannot readily detect low atomic number (light) elements such as O and H due to their small X-ray scattering factors which are proportional to the number of electrons in the atom. This limitation is especially significant for the study of anions in apatite tunnels, and, as considered in Chapter 3, can lead to incorrect structural models.

2.3.2.2 Powder Neutron Diffraction (PND)

Neutron diffraction can provide accurate positional information on low atomic number elements in apatites, including site occupancies and anisotropic thermal parameters. Armed with such knowledge, metaprisim twist angle systematics can be better monitored (as compared to X-ray diffraction), especially when the tunnels contain light anions such OH^- , O^{2-} and halides (especially F^-), as the scattering lengths

for these species are quite distinct. The collection of powder neutron diffraction patterns was conducted at ISIS in the Science and Technology Facilities Council, Rutherford Appleton Laboratory, United Kingdom using time-of-flight (TOF) methods with both high resolution and high intensity instruments (Chapters 4 and 6)

2.3.3 Infrared Spectroscopy

Fourier transformed infrared spectroscopy (FTIR) is an analytical technique that can identify organic, and some inorganic, species by measuring infrared absorption. The absorption bands are specific to molecular components and structures. In this study, the infrared (IR) spectra were measured in the region 400-4000 cm^{-1} using a Perkin Elmer FTIR Spectrum GX with a resolution of 4.0 cm^{-1} using translucent pellets prepared by mixing apatite powder with potassium bromide. The number of scan cycles for each sample was set at 40. Of special concern, was the incorporation of carbonate and hydroxyl in apatites.

2.4 Integrated Synthesis, Characterization and Testing

In this work, numerous techniques were employed to synthesize a range of apatites containing simulated radionuclides to establish solid solution limits and allow crystallographic refinements. Compounds synthesized included nominal $A_{10}(\text{BO}_4)_6\text{X}_2$ compositions where substituents can be divided into fission products with $A = \text{Sr}^{2+}$, Cs^+ , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+} , Lu^{3+} (Chapter 4), transuranic elements for $A = \text{Th}^{4+}$ (Chapter 5), and processing contaminants for $B = \text{Cr}^{5+}$ (Chapter 3). Often charge balance was achieved by mixing Si^{4+} and P^{5+} on the B site. Substitution on $X = \text{F}^-$, O^{2-} , OH^- , Cl^- were used to study the effect of tunnel species on metaprisim twist angles and role of oxyapatites in nuclide incorporation (Chapter 6). In solid state syntheses, oxides and carbonates were used as starting materials to yield highly crystalline products to simplify crystallographic studies. Soft chemical routes involved the use of nitrates and phosphates to produce finely divided crystalline precursors, suitable for compaction by hot pressing. Correlations between crystal structure and chemical analysis were established (Chapter 3) through constrained and unconstrained refinement of X-ray and neutron powder diffraction patterns. These data were supplemented by microanalysis (SEI, BEI, EDS) and

spectroscopy (FTIR), and monitoring trend in the A^1O_6 metaprism twist angle with composition.

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Chapter 3

Strontium-Bearing Apatites – Validating Waste Uptake by Metaprism Twist Angle Systematics

The validation of waste loading and the distribution of radionuclides over the available acceptor sites of apatite HLW ceramics are required to optimize composition, tailoring and fabrication. Here, the metaprism twist angle (ϕ) is demonstrated to be a useful tool to monitor waste uptake and partitioning in several simulated wasteform strontium apatites containing chromium, fluorine and chlorine as representative processing contaminants.

3.1 Introduction to Metaprism Twist Angle Systematics

Systematisation of the crystal chemistry of $A^I_4A^{II}_6(BO_4)_6X_2$ apatites is essential to tailor functionality for specific technologies, and devising a classification scheme requires access to reliable crystal structures. While single crystal determinations are preferable, Rietveld refinement is used extensively because model structures are easily constructed and many apatites are readily synthesised as powders. However, the least-squares procedure can lead to false minima due to the propagation of errors during matrix inversion [1]. Nonetheless, the accuracy and numerical stability of Rietveld analysis can be enhanced either by applying soft constraints to the BO_4 tetrahedra [2] or controlling atomic trajectories through introducing geometrical parameterisations [3], and these approaches are particularly valuable for locating oxygen within the relatively fixed $D8_8$ cation sub-lattice of apatite [4].

While these techniques can be applied to new refinements, it would be useful to possess a quantitative means to assess the existing body of reported apatite structures in a manner that goes beyond a conventional analysis of bond lengths and angles. In Chapter 2 it was shown that apatites can be considered as one-dimensional channel structures in which a framework, composed of face-sharing A^IO_6 metaprism columns are corner-connected to BO_4 tetrahedra that host the $A^{II}_6X_2$ component (Figure 3.1). The tunnel diameter adjusts according to the size (of A^{II} and X) and stoichiometry (X) of its contents by counter-rotation of the opposing triangular faces of the metaprism through a $[001]$ projected angle (ϕ) and the extent of metaprism twisting varies inversely with tunnel cross section. For $P6_3/m$ structures $5^\circ \leq \phi \leq 25^\circ$, and when apatites contain the same A -component, but different B and X constituents, there is a linear relationship between ϕ and the average crystal radii [5]. Metaprism twisting is established through the O(1) and O(2) positions, that together with O(3), form the semi-rigid framework BO_4 tetrahedron whose location is determined through bonding to the A^{II} tunnel cation. Because ϕ arises from the interplay between several atoms, this single parameter proves exquisitely sensitive to crystallochemical variations. Ideally, metaprism twisting follows three trends:

- i. As the A^I/A^{II} radius ratio decreases, then the tunnel expands and ϕ becomes smaller;

- ii. If A^I/A^II is fixed, as the ionic radii of B increases, the tunnel contracts and ϕ increases; and
- iii. As X increases, the tunnel dilates and ϕ decreases.

Across a solid solution series deviations from trend usually reflect departures from nominal stoichiometry, polymorphism (*2H*, *2T*, *2M*, *2A* for di-modular stacking) or poor structure refinement.

Strontium-90 is no hazardous fission product due to type of radiation and dose with short half-life ($t_{1/2} = 28.8$ years) and chemical similarity to calcium that allows its accumulation in bone. The affinity of strontium for apatite can also be exploited for immobilization. Strontium apatite (SrAp) has been extensively studied. Its similarity with hydroxyapatite (CaHA) results in high biocompatibility, and thus SrAp has found wide application as a bioceramic [6], catalyst [7] and chemical sensor [8]. In the field of biomaterials, Sr ions are exploited as a Ca marker, and employed for the treatment of osteoporosis, where strontium administration to bone reduces resorption and stimulates growth [9]. Collin [10] was the first to synthesize the complete Ca/Sr solid-solution by co-precipitation. Since then, solid state [11], solid-gas [12] and sol-gel [13] reactions have been demonstrated. Despite numerous studies of the fabrication and physiochemical properties of Sr-substituted CaHA [14], there have been no detailed crystallochemical studies, where changes in the tunnel size are rationalised to composition, cation-ordering, and the twisting of the framework metaprism.

Because the apatite structure is inherently adaptable, its capacity to immobilize complex waste streams is considerable, but the validation of nuclide partitioning is challenging. Nonetheless, changes in the unit cell metric and modification of symmetry will ultimately be controlled by the need to satisfy local bonding and the ‘merging’ of ions in discrete Wyckoff sites. In this chapter, it is shown that for simplified wastefoms containing non-radioactive Sr, the metaprism twist angle can be used to track the distribution of species over the tunnel and framework sites. Specifically, the accurate determination of ϕ in $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_2]$ -*2H* pseudomorphs after selective substitutions at the three available acceptor sites (*A*, *B* and *X*) are described for $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$, $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$ and $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_2]$.

$x\text{Cl}_x$]. Also revisited are several published crystallographic data sets, which through an evaluation of φ , serve to emphasise the generality of twist angle systematics, and the diagnostic potential for assessing the reliability of Rietveld refinements, and detecting disequilibrium and non-stoichiometry.

Figure 3.1: Polyhedral representation of $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$ emphasizing the metaprism twist angle (this work).

3.2 Synthesis

The starting materials used in this study were calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ -Alrich, 99%), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$ -Acros, 99%), ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$ -Aldrich, 99%), ammonium chromate ($(\text{NH}_4)_2\text{CrO}_4$ -Fluka, +99%), ammonium fluoride (NH_4F -Acros, 98%), ammonium chloride (NH_4Cl -Merck, 99.8%), strontium fluoride (SrF_2 -Strem, 99%) and strontium chloride (SrCl_2 -Riedel, 99%).

3.2.1 Strontium - calcium fluorapatite, $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$

The synthesis is a modified version of the route developed by Collin [5] and required two stock solutions. In Solution I, calcium nitrate and strontium nitrate were dissolved in 100ml of deionised water at 85°C while maintaining a cation concentration of 0.2M. Ammonia was added to raise the pH above 10. In Solution II, ammonium hydrogen phosphate 1.6007g (0.2M) and ammonium fluoride 0.3024g (0.13M) were dissolved in 60ml of deionised water and the pH adjusted with ammonia to be > 10 . Solution II was added drop-wise to Solution I with heating and stirring to obtain a

total volume of approximately 200ml. The precipitate and solution were maintained at 85°C with stirring for 3 hours and filtered while warm. The solid was dried overnight at 100°C then calcined at 700°C for 6 hours under flowing nitrogen.

3.2.2 Strontium chromate-phosphate fluorapatite, $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$

Strontium nitrate (4.2326g) was dissolved at 85°C in 100ml (0.2M) of deionised water. Ammonium fluoride 0.3024g (0.13M) was introduced to 60ml of room temperature deionised water, together with stoichiometric amounts of ammonium hydrogen phosphate and ammonium chromate. The pH of both solutions was adjusted to 10 with ammonia. The fluoride containing solution was slowly added to the strontium solution with heating and magnetic stirring. The precipitate and solution were mixed at 85°C for 3 hours then left to age for 24 hours at room temperature. Subsequently, the precipitate was dried overnight (100°C) followed by calcination (800-1000°C/10 hours) under flowing nitrogen with a heating ramp of 1°C/min.

3.2.3 Strontium fluoro-chlorapatite, $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$

For these compounds, two syntheses were investigated: a ‘precipitation’ route readily yielded chlorapatite and fluorapatite end-members, while solid state ‘crystallisation’ provided superior control of the fluorine and chlorine content. In the precipitation method, strontium nitrate (4.2326g) was dissolved in deionised water (100ml/85°C). A second solution containing 1.6007g of ammonium hydrogen phosphate was dissolved in 60ml of deionised water at room temperature, together with stoichiometric amounts of ammonium fluoride and ammonium chloride that maintained the total halide concentration at 0.13M. The pH of both solutions was adjusted to 10 with ammonia. The halide solution was dropped into the strontium solution at 85°C, with stirring continued for 3 hours before ageing (24 hours at room temperature). The precipitate was dried overnight (100°C) and calcined (600°C/6 hours) under nitrogen. Alternatively, the crystallisation route used tri-strontium phosphate ($\text{Sr}_3(\text{PO}_4)_2$) prepared by combining strontium nitrate (0.36M) in deionised water with 0.10M ammonium hydrogen phosphate. The mixture was stirred for 3 hours at room temperature, filtered, and dried at 100°C overnight. The filter cake was heated at 900°C for 2 hours in nitrogen to produce $\text{Sr}_3(\text{PO}_4)_2$, which was then mixed

with stoichiometric quantities of strontium fluoride and strontium chloride powder before calcination at 500°C to obtain fluoro-chlorapatite.

3.3 Materials Characterization

Powder X-ray diffraction (PXRD) patterns were collected using a Shimadzu LabX XRD-6000 with $\text{CuK}\alpha$ radiation step-scanned from 10-140° 2 θ at intervals of 0.02°, with a total collection time of approximately 12 hours. The intensity of the strongest peak ranged from 5000-18000 counts and the whole patterns were analysed by Rietveld refinement using *TOPAS V3* (Bruker AXS, 2005) that employs the fundamental parameters approach [15]. Refinement parameters included the zero point error, a 4 coefficients Chebyshev polynomial background fitting, and ‘crystallite size’ to simulate microstructure-controlled line broadening. To maintain reasonable B-O bond lengths within the BO_4 units a ‘Parabola N ’ penalty function was employed with expected bond lengths selected in accordance with standard ionic radii [16].

Powder neutron diffraction (PND) patterns were collected at the ISIS Rutherford Appleton Laboratory on Polaris, a medium resolution high intensity diffractometer [17] and the high-resolution powder (HRPD) diffractometers. Due to limited accessibility, Polaris was used for $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$ and HRPD for $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$ and $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$. Approximately 1~2 cm³ of each apatite powder was loaded into 8 mm diameter vanadium cans. Data sets from two banks of detectors were combined for the refinement; the first from the backscattering detector bank (average 2 $\theta \approx 145^\circ$) and the second from the 90° detector bank. Rietveld refinements were performed with *GSAS* [17].

The quality of the Rietveld refinements was checked by calculating the metaprism twist angle using the method of White & Dong [5]. For the X-ray diffraction data collected from $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$ a tetrahedral constraint lying between P-O ($\approx 1.54\text{\AA}$) and Cr-O ($\approx 1.64\text{\AA}$) was used but this approach was not always effective and twist angles were sometimes far too small to be reasonable. As expected, neutron diffraction refinements were more robust for determining oxygen positions and bond-length constraints were unnecessary.

Figure 3.2: Rietveld profile of PND for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. Data were collected on Polaris and refined (GSAS) observed counts are shown as crosses, the calculated pattern by a solid black line, background in green, and the difference in blue.

3.4 Results and Discussion

3.4.1 Strontium - calcium fluorapatite, $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$

Powder X-ray diffraction confirmed the synthesis of the entire solid-solution series. Rietveld refinements used the model structures of Nikčević *et al.* [18] and Swafford & Holt [19] with appropriate chemical substitutions. For all samples PXRD and PND converged to comparable lattice parameters; atomic positions and selected bond lengths (Tables 3.1 and 3.2) lie within expected ranges, and vary appropriately with the Ca/Sr substitution. The lattice parameters are in good agreement with previous work [5, 9, 20], and c/a lies in the range 0.732 to 0.745 as found by Pujari & Patel [21]. However, the Sr/(Ca+Sr) ratios were invariantly larger than nominal, consistent with Collin [5]. The Ca-deficiency becomes more pronounced as Sr/(Ca + Sr) becomes larger, suggesting the solvent for pH adjustment leads to preferential strontium precipitation. The cell edges dilate linearly (Figure 3.3a) as strontium is

introduced because Sr^{2+} (1.18Å) is larger than Ca^{2+} (1.00Å), confirming the solid-solution is homogeneous.

Table 3.1: Lattice parameters and crystallographic data from neutron diffraction for $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$

Composition x	0	2.56	5.00	7.56	10.00
Space Group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	9.7133(1)	9.6301(2)	9.5622(2)	9.4589(1)	9.3672(1)
c (Å)	7.2843(1)	7.1819(3)	7.0792(2)	6.9754(1)	6.8844(1)
V (Å ³)	595.19(1)	576.81(2)	562.00(2)	540.47(1)	523.14(1)
φ (°)	23.82	22.67	22.39	22.57	23.57
P-O bond length (Å)	1.53	1.53	1.53	1.53	1.53
R_{wp} (%)	0.0153	0.0189	0.0173	0.0177	0.0144
R (%)	0.0317	0.0382	0.0333	0.0355	0.0267
$\text{Sr}(1)$, $4f$ (1/3, 2/3, z)					
z	-0.0002(2)	0.0006(3)	0.0004(2)	0.0001(2)	0.0007(2)
Occ. Fac. (Sr)	1.00	0.77(2)	0.39(1)	0.19(2)	0
Uiso	0.0065(3)	0.0069(4)	0.0085(3)	0.0095(4)	0.0074(4)
$\text{Sr}(2)$, $6h$ (x , y , 1/4)					
x	0.0148(2)	0.0154(2)	0.0134(2)	0.0108(2)	0.0076(2)
y	0.2545(2)	0.2544(2)	0.2523(2)	0.2494(2)	0.2482(2)
Occ. Fac. (Sr)	1.00	1.00	0.57(1)	0.23(1)	0
Uiso	0.0064(3)	0.0082(2)	0.0098(3)	0.0100(3)	0.0082(3)
P , $6h$ (x , y , 1/4)					
x	0.3994(2)	0.4003(2)	0.4009(2)	0.3993(2)	0.3982(2)
y	0.3683(2)	0.3716(2)	0.3712(2)	0.3703(2)	0.3689(2)
Uiso	0.0044(2)	0.0054(3)	0.0084(3)	0.0076(2)	0.0050(2)
$\text{O}(1)$, $6h$ (x , y , 1/4)					
x	0.3305(2)	0.3331(2)	0.3339(2)	0.3312(2)	0.3266(1)
y	0.4808(2)	0.4837(2)	0.3712(2)	0.4855(2)	0.4839(1)
Uiso	0.0083(3)	0.0087(2)	0.0136 (4)	0.0121(3)	0.0085(2)
$\text{O}(2)$, $6h$ (x , y , 1/4)					
x	0.5821(2)	0.5849(2)	0.5858(2)	0.5872(2)	0.5873(2)
y	0.4632(2)	0.4625(2)	0.4616(2)	0.4641(2)	0.4663(2)
Uiso	0.0094(2)	0.0155(2)	0.0186(3)	0.0158(2)	0.0102(2)
$\text{O}(3)$, $12i$ (x , y , z)					
x	0.3447(2)	0.3440(2)	0.3448(2)	0.3436(2)	0.3421(2)
y	0.2615(2)	0.2623(2)	0.2627(2)	0.2609(2)	0.2580(2)
z	0.0795(3)	0.0781(2)	0.0756(2)	0.0731(2)	0.0711(2)
Uiso	0.0112(3)	0.0156(3)	0.0198(4)	0.0181(3)	0.0124(2)
$\text{F}(1)$, $2a$ (0, 0, 1/4)					
Occ. F	0.98(1)	1.00	1.00	0.83(1)	1.00
Uiso	0.0216(5)	0.0326(6)	0.0400(3)	0.0236(5)	0.0178(3)

Table 3.2: Bond length and angle from neutron diffraction for $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$.

Composition x	0	2.56	5	7.56	10
Bond length (Å)					
Sr(1)-O(1)	2.555(1)	2.512(2)	2.480(1)	2.437(1)	2.403(1)
Sr(1)-O(2)	2.572(1)	2.527(2)	2.492(1)	2.463(1)	2.451(1)
Sr(1)-O(3)	2.901(1)	2.884(2)	2.853(1)	2.824(1)	2.800(1)
BVS Sr(1)	2.16 (8)	2.13(9)	2.15(9)	2.17(9)	2.05(8)
Sr(2)-O(1)	2.738(1)	2.735(2)	2.744(2)	2.721(2)	2.685(1)
Sr(2)-O(2)	2.504(1)	2.492(2)	2.483(2)	2.439(2)	2.383(1)
Sr(2)-O(3)	2.527(1)	2.481(1)	2.444(1)	2.393(1)	2.356(1)
Sr(2)-F	2.403(1)	2.379(2)	2.351(1)	2.312 (2)	2.291(1)
BVS Sr(2)	2.10 (8)	2.00(8)	1.91(8)	1.97(9)	1.93(9)
P-O(1)	1.540(1)	1.511(2)	1.517(1)	1.519(2)	1.528(1)
P-O(2)	1.538(1)	1.540(3)	1.532(2)	1.539(2)	1.535(1)
P-O(3)	1.533(1)	1.535(1)	1.530(1)	1.525(1)	1.525(1)
BVS P	4.81(1)	4.88(4)	4.92(3)	4.93(3)	4.91(2)
Angle (°)					
O(1)-P-O(3)	110.3 (3)	110.8(1)	111.0(1)	111.1(1)	110.9(1)
O(1)-P-O(2)	110.8 (1)	110.8(1)	112.2(1)	111.6(1)	111.3(1)
O(3)-P-O(3)	109.5 (2)	108.2(1)	108.0(1)	108.0(1)	107.7(1)
O(3)-P-O(2)	106.0 (3)	108.1(1)	107.3(1)	107.4(1)	107.9(1)

Figure 3.3: Fitted lines of lattice parameters for (a) $[Sr_{10-x}Ca_x][(PO_4)_6][F_2]$, (b) $[Sr_{10}][(P_{1-x}Cr_xO_4)_6][F_2]$ and (c) $[Sr_{10}][(PO_4)_6][F_{2-x}Cl_x]$. Solid lines – fitted and dotted line – guided.

3.4.2 Strontium phosphate-chromate fluorapatite, $[Sr_{10}][(P_{1-x}Cr_xO_4)_6][F_2]$

Previously, $Sr_{10}(CrO_4)_6F_2$ has only been synthesised by solid state reaction [22, 23] and early attempts to prepare $[Sr_{10}][(PO_4)_{6-x}(CrO_4)_x][F_2]$ compounds were unsuccessful (Grisafe & Hummel [24]). There is, however, no obvious crystallochemical reason to limit miscibility in the $Sr_{10}(PO_4)_6F_2$ - $Sr_{10}(CrO_4)_6F_2$ system. Here, the double decomposition technique was successful in producing near single phase apatite, with hexavalent chromium in the ammonium chromate reagent reduced to Cr^{5+} for isovalent substitution.

3-1

Maintaining a heating rate of $100^{\circ}\text{C h}^{-1}$ was crucial to minimise volatilisation of fluorine and promote chromate reduction [23]. The mixed cation chromate-phosphate apatites were similarly sensitive to annealing temperature.

Whilst the double decomposition technique proved superior, apatite often coexisted with secondary ($< 10\text{wt}\%$) quantities of SrCrF_4 and/or SrF_2 . Nevertheless, the PXRD and PND patterns were readily analysed and the lattice parameters, atomic positions and selected bond lengths of apatite derived from the latter are collected in Tables 3.3 and 3.4. As anticipated, the lattice metric dilated as Cr^{5+} ($0.35\text{\AA}$) replaced P^{5+} ($0.17\text{\AA}$) through an increase in $B\text{-O}$ bond distance in agreement with Vegard's law (Figure 3.3b).

3.4.3 Strontium fluoro-chlorapatite, $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$

As already noted, the precipitation technique poorly controlled the F/Cl content in this series, while the solid state method provided better regulation of the fluorine-chlorine ratio (Table 3.5). Crystallochemical observations of selected samples synthesised from both techniques are presented.

Fluorine and chlorine are susceptible to volatilisation, and halogen loss invariably occurred as evidenced by the significant departures from linearity of the lattice metric (against expected composition) due to the exchange of halogen species with oxygen, or less likely given the processing temperature, hydroxyl groups. The refinement of tunnel site occupancies also supports this interpretation.

Table 3.3: Lattice parameters and crystallographic data from neutron diffraction for $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$.

Composition x	0	1/3	2/3	1
Space Group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	9.7133(1)	9.7403(2)	9.8267(2)	9.9745(3)
c (Å)	7.2843(1)	7.2979(3)	7.3472(1)	7.4281(2)
V (Å ³)	595.19(1)	599.61(3)	614.92(2)	640.02(4)
ϕ (°)	23.82	24.21	24.50	25.21
B -O bond length (Å)	1.53	1.55	1.61	1.66
R_p (%)	0.0153	0.1734	0.0124	0.0134
R_b (%)	0.0317	0.0975	0.0151	0.0141
Sr(1), $4f$ (1/3, 2/3, z)				
z	-0.0002(2)	-0.0022(3)	0.002(3)	0.007(3)
Uiso	0.0065(3)	0.0324(2)	0.0328(3)	0.0493(2)
Sr(2), $6h$ (x , y , 1/4)				
x	0.0148(2)	0.0172(2)	0.013(1)	0.251(1)
y	0.2545(2)	0.2551(3)	0.252(1)	0.014(1)
Uiso	0.0064(3)	0.0231(2)	0.0333(2)	0.0594(2)
P, $6h$ (x , y , 1/4)				
x	0.3994(2)	0.3962(2)	0.388(1)	0.370(1)
y	0.3683(2)	0.3696(2)	0.319(1)	0.395(1)
Occ. Fac. (P)	1.00	0.6667(2)	0.3333(2)	0
Uiso	0.0044(2)	0.025(3)	0.0173(2)	0.0173(2)
O(1), $6h$ (x , y , 1/4)				
x	0.3305(2)	0.3296(2)	0.356(1)	0.483(1)
y	0.4808(2)	0.4815(2)	0.482(2)	0.314(2)
Uiso	0.0083(3)	0.0257(4)	0.0353(3)	0.0314(3)
O(2), $6h$ (x , y , 1/4)				
x	0.5821(2)	0.5837(2)	0.587(2)	0.480(2)
y	0.4632(2)	0.4677(3)	0.466(1)	0.598(1)
Uiso	0.0094(2)	0.0376(3)	0.0451(4)	0.0281(3)
O(3), $12i$ (x , y , z)				
x	0.3447(2)	0.3438(2)	0.587(2)	0.253(1)
y	0.2615(2)	0.2605(2)	0.466(1)	0.343(1)
z	0.0795(3)	0.0802(3)	0.072(1)	0.061(1)
Uiso	0.0112(3)	0.0304(3)	0.0419(2)	0.0246(3)
F(1), $2a$ (0, 0, 1/4), $4e$ (0,0, z)				
Z	0.2500	0.2500	0.2101(4)	0.2500
Occ. F	0.98(1)	1.00	0.4821(2)	1.00
Uiso	0.0216(5)	0.025(4)	0.0376(3)	0.0366(4)

Table 3.4: Bond length and angle from neutron diffraction for $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$.

Composition x	0	1/3	2/3	1
Bond length (Å)				
Sr(1)-O(1)	2.547 (3)	2.556 (5)	2.556 (6)	2.614 (9)
Sr(1)-O(2)	2.588(2)	2.547 (4)	2.622 (5)	2.635 (7)
Sr(1)-O(3)	2.937 (5)	2.905 (8)	2.978 (8)	3.022 (13)
BVS Sr(1)	2.11(9)	2.22(9)	2.04(8)	1.78(8)
Sr(2)-O(1)	2.728 (6)	2.741 (12)	2.709 (12)	2.738 (18)
Sr(2)-O(2)	2.487 (4)	2.536 (7)	2.469 (7)	2.505 (11)
Sr(2)-O(3)	2.519 (3)	2.495 (5)	2.519 (5)	2.556 (8)
Sr(2)-F	2.399 (2)	2.414 (2)	2.421 (3)	2.471 (4)
BVS Sr(2)	2.15(8)	2.08(8)	2.19(8)	1.98(7)
Cr-O(1)	1.552 (3)	1.594 (6)	1.628 (7)	1.639 (9)
Cr-O(2)	1.550 (5)	1.601 (8)	1.627 (9)	1.666 (14)
Cr-O(3)	1.556 (3)	1.612 (5)	1.626 (6)	1.674 (8)
BVS Cr	4.59(1)	4.68(3)	5.16(1)	5.49(6)
Angle (°)				
O(1)-P-O(3)	110.3 (3)	110.9 (3)	110.3 (5)	111.4 (6)
O(1)-P-O(2)	110.8 (1)	113.7 (5)	111.4 (4)	112.5 (7)
O(3)-P-O(3)	109.5 (2)	108.4 (4)	110.0 (4)	110.1 (5)
O(3)-P-O(2)	106.0 (3)	106.4 (9)	103.7 (4)	100.8 (6)

The position and concentration of F^- , Cl^- and O^{2-} were best established by PND. Extensive Fourier difference mapping via Fullprof was used to identify Cl at $2b$ (0, 0, 0), fluorine at $2a$ (0, 0, $\frac{1}{4}$) (Figure 3.4) and an additional scattering centre at $4e$ (0, 0, z) for O^{2-} . Using this methodology, the “end-member” chloro-apatite $\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$ was found to contain both Cl^- and O^{2-} (Table 3.5), with the charge balance achieved as

A typical difference Fourier map is shown in Figure 3.4 and depicts a cross section of the apatite channel of $\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$. It was generated when Cl and its site occupancy was refined at (0, 0, 0) and reveals a region of deficit contours indicating unaccounted nuclear density centered at (0, 0, z) ($z \approx 0.2$).

Table 3.5: Lattice parameters and crystallographic data from neutron diffraction for $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$.

Composition x	0	0.5	2
Space Group	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	9.7133(1)	9.8452(2)	9.8124(2)
c (Å)	7.2843(1)	7.1902(2)	7.2500(2)
V (Å ³)	595.19(1)	603.57(3)	604.53(3)
φ (°)	23.82	23.01	22.02
P-O bond length (Å)	1.53	1.53	1.53
R_{wp} (%)	0.0153	0.0134	0.0494
R (%)	0.0317	0.0141	0.0490
Sr(1), $4f$ (1/3, 2/3, z)			
z	-0.0002(2)	-0.0025(3)	-0.0006(3)
Uiso	0.0065(3)	0.0117(2)	0.0334(5)
Sr(2), $6h$ (x , y , 1/4)			
x	0.0148(2)	-0.0280(2)	0.0150(2)
y	0.2545(2)	0.1949(2)	0.2590(2)
Uiso	0.0064(3)	0.0036(3)	0.0278(3)
P $6h$ (x , y , 1/4)			
x	0.3994(2)	0.4920(2)	0.4016(3)
y	0.3683(2)	0.4163(2)	0.3731(2)
Uiso	0.0044(3)	0.0083(3)	0.0270(4)
O(1), $6h$ (x , y , 1/4)			
x	0.3305(2)	0.4004(2)	0.3360(2)
y	0.4808(2)	0.4225(2)	0.4815(2)
Uiso	0.0083(3)	0.0524(4)	0.0317(6)
O(2), $6h$ (x , y , 1/4)			
x	0.5821(2)	0.6071(2)	0.5833(2)
y	0.4632(2)	0.4796(3)	0.4640(2)
Uiso	0.0094(2)	0.0029(2)	0.0373(4)
O(3), $12i$ (x , y , z)			
x	0.3447(2)	0.3351(3)	0.3502(2)
y	0.2615(2)	0.2311(2)	0.2647(2)
z	0.0795(3)	0.0557(2)	0.0783(2)
Uiso	0.0112(3)	0.0644(2)	0.0451(4)
O(4), $4e$ (0, 0, z)			
z	-	-	0.179(1)
Occ. Fac. O	-	-	0.227(8)
Uiso	-	-	0.017(4)
F(1), $2a$ (0, 0, 1/4); Cl (1), $2b$ (0, 0, 1/2)			
Occ. Fac. (F)	0.98(1)	0.75(2)	0
Occ. Fac. (Cl)	0	0.25(2)	0.2535(5)
Uiso	0.0216(5)	0.0311(3)	0.002(3)

Table 3.6: Bond lengths and angles from neutron diffraction for $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$.

Composition x	0	1	2
Bond length (Å)			
Sr(1)-O(1)	2.547 (3)	2.606 (7)	2.561 (5)
Sr(1)-O(2)	2.588(2)	2.628 (6)	2.570 (4)
Sr(1)-O(3)	2.937 (5)	2.494 (11)	2.887 (8)
BVS Sr(1)	2.11(9)	2.64(5)	2.16(8)
Sr(2)-O(1)	2.728 (6)	2.723 (16)	2.809 (12)
Sr(2)-O(2)	2.487 (4)	2.410 (9)	2.470 (6)
Sr(2)-O(3)	2.519 (3)	2.462 (7)	2.502 (5)
Sr(2)-F	2.399	2.451	3.067
BVS Sr(2)	2.16(8)	2.52(11)	2.01(9)
P-O(1)	1.552 (3)	1.545 (8)	1.549 (7)
P-O(2)	1.550 (5)	1.536 (13)	1.572 (9)
P-O(3)	1.556 (3)	1.561 (7)	1.544 (5)
BVS P	4.59(1)	4.62(4)	4.61(4)
Angle (°)			
O(1)-P-O(3)	110.3 (3)	110.2 (6)	109.1 (4)
O(1)-P-O(2)	110.8 (1)	112.5 (5)	111.7 (2)
O(3)-P-O(3)	109.5 (2)	109.4 (6)	109.9 (4)
O(3)-P-O(2)	106.0 (3)	105.9 (4)	107.6 (3)

Figure 3.4: [100] difference-Fourier map at $x=0$ from refinement of $\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$ in the space group $P6_3/m$ showing positions of chlorine are at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$.

3.5 Twist Angle (ϕ) Systematics in Strontium Apatites

3.5.1 A-site Correlations in $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$

In this work, the metaprism twist angles in $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$ show parabolic behaviour as x increases due to the non-statistical distribution of alkali earths across

the $4f$ and $6h$ sites. At lower concentration, Sr^{2+} initially occupies the larger $6h$ sites, causing the tunnel to expand and ϕ to become more acute (Figure 3.5a). However, once the $6h$ site is fully tenanted by strontium, ϕ increases as Sr^{2+} partitions to the $4f$ site. Over the entire solid solution, relative tunnel size is inversely proportional to metaprism twist angle as readily confirmed by considering the ratio of the average ionic size of the A^{I} and A^{II} site contents (Figure 3.5b). For the end-members, the relative sizes of the framework and tunnel are similar and the metaprism twisting is comparable as evidenced by comparing ϕ for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ($\phi = 23.2_1^\circ$) and $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$ (22.8_3°); $\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2$ yields similar ϕ (22.2_0°) because the A -sites are homoatomic (Table 3.7). Separately, Michie *et al.* [25] showed with quantum mechanical simulations for $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$ that internal energy calculations conform to a similar parabolic distribution. This behaviour is general for isovalent A -site substitutions in apatites, as for example, in $[\text{Ba}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][\text{F}_2]$ [26] (Table 3.7, Figure 3.5c). Whenever there is a size difference between A species of the same valence, the larger ion will preferentially enter the $6h$ tunnel position rather than the $4f$ framework site leading to a parabolic ϕ trend. This simple rule will not be applicable if there are mixtures of higher valence cations (e.g. rare earth³⁺) or monovalent species (e.g. Na^+); the former prefer $6h$ to better distribute higher charge, while the reverse is true for large monovalent cations. Ionic charge always takes precedence over size.

Figure 3.5: Fitted lines for (a) Crystallochemical trends for $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$, with triangles and crosses representing the metaprism twist angles from X-ray and neutron diffraction respectively, and (b) $4f/6h$ relative site size. (c) The metaprism twist angle against atomic percentage of barium in $[\text{Ba}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][\text{F}_2]$ by Aissa *et al.* [26], illustrates the generality of parabolic ϕ behaviour for $A^{\text{I}}/A^{\text{II}}$ partitioning.

Table 3.7: Trends and anomalies in metaprisim twist angle variance for $[A_{10}][(\text{BO}_4)_6][X_2]$ apatites.

Substitution Type	Compound	ϕ (°)	Unit Cell Volume ($\text{\AA}^3$)	Twist angle systematics	Reference
A-Type	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	24.3 ₅	523.63	Sr^{2+} preferentially fills the tunnels, before entering the framework. The size of the framework with respect to the tunnel is minimised at intermediate Ca/Sr compositions with the channel dilating by reducing ϕ . For the end-members, the relative sizes of the framework and tunnel are similar and the metaprisim twists are comparable.	This Work
	$\text{Ca}_{6.66}\text{Sr}_{3.34}(\text{PO}_4)_6\text{F}_2$	22.9 ₅	545.37		
	$\text{Ca}_{4.02}\text{Sr}_{5.98}(\text{PO}_4)_6\text{F}_2$	21.6 ₆	559.16		
	$\text{Ca}_{1.66}\text{Sr}_{8.34}(\text{PO}_4)_6\text{F}_2$	21.4 ₆	573.33		
	$\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$	23.9 ₅	596.14		
	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	23.2 ₁	528.67	The twist angles for Ca^{2+} and Sr^{2+} hydroxy and fluoro apatites are similar as the X anion (F/OH^-) occupy nearly the same volumes. Ba^{2+} apatite yields similar ϕ as the relative size of framework are similar because the A-sites are homoatomic.	Sudarsanan & Young [20]
	$\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$	22.8 ₃	597.49		
	$\text{Ba}_{10}(\text{PO}_4)_6(\text{OH})_2$	22.2 ₀	694.29		
	$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	17.8 ₆	544.50	The twist angles for chloro apatites are less than fluoro and hydroxyl analogues as Cl^- is a substantially larger X anion, with the tunnel opening by decreasing ϕ . While following the parabolic trend for differential Ca/Sr site partitioning, ϕ for $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ appears to be anomalously small compared to the $\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$ end-member. In fact, this reflects a change in symmetry from $P6_3/m$ to $P2_1/b$. In the original refinement of chlorapatite (Hendricks, 1932) the symmetry was taken as $P6_3/m$ which lead to $\phi = 19.1^\circ$.	Sudarsanan & Young [27]
	$\text{Ca}_{9.8}\text{Sr}_{0.2}(\text{PO}_4)_6\text{Cl}_2$	17.4 ₆	545.20		
	$\text{Ca}_{9.45}\text{Sr}_{0.55}(\text{PO}_4)_6\text{Cl}_2$	17.1 ₈	546.40		
	$\text{Ca}_5\text{Sr}_5(\text{PO}_4)_6\text{Cl}_2$	16.8 ₃	576.50		
	$\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$	21.1 ₀	606.60		
	$\text{Ca}_{9.95}\text{Sr}_{0.05}(\text{PO}_4)_6(\text{OH})_2$	22.2 ₈	532.29	The twist angles for $\text{Ca}_9\text{Sr}_1(\text{PO}_4)_6(\text{OH})_2$ and $\text{Ca}_5\text{Sr}_5(\text{PO}_4)_6(\text{OH})_2$ grow larger as the compounds become increasingly strontian when the opposite behaviour is expected due the favoured introduction of Sr to the tunnel. In this case, oxidation of the X anion ($2\text{OH}^- \rightarrow \text{O}^{2-} + \square$) creates tunnel vacancies with a corresponding reduction in diameter and increase in ϕ .	Bigi <i>et al.</i> (2007) [9]
	$\text{Ca}_9\text{Sr}_1(\text{PO}_4)_6(\text{OH})_2$	22.5 ₂	533.89		
	$\text{Ca}_5\text{Sr}_5(\text{PO}_4)_6(\text{OH})_2$	22.4 ₆	570.43		
	$\text{Ca}_8\text{Pb}_2(\text{PO}_4)_6(\text{OH})_2$	16.1 ₃	542.41	Pb^{2+} is driven towards tunnel positions as it is larger than Ca^{2+} , and in addition, requires space to accommodate stereochemically active lone pair electrons. Parabolic ϕ trend is as expected.	Bigi <i>et al.</i> [28]
	$\text{Ca}_{5.5}\text{Pb}_{4.5}(\text{PO}_4)_6(\text{OH})_2$	13.7 ₀	565.90		
	$\text{Ca}_2\text{Pb}_8(\text{PO}_4)_6(\text{OH})_2$	18.1 ₃	604.98		
	$\text{Na}_2\text{Pb}_8(\text{VO}_4)_6\square_2$	26.1 ₇	643.84	In lacunar apatites, tunnels are devoid of X anions ($X = \square$). As the tunnel is vacated it must constrict and this is achieved by increasing ϕ . These compounds show the largest ϕ of all $[A_{10}][(\text{BO}_4)_6][X_2]$ apatites.	Azrour <i>et al.</i> [29] Koumiri <i>et al.</i> [30]
	$\text{K}_2\text{Pb}_8(\text{VO}_4)_6\square_2$	29.0 ₃	659.41		
	$\text{Na}_2\text{Pb}_8(\text{PO}_4)_6\square_2$	24.0 ₂	588.88		
	$\text{Ca}_5\text{Pb}_5(\text{VO}_4)_6\text{F}_2$	14.4 (equilibrated)	616.70	Apatite A-site ordering and/or compositions can change with annealing. For the non-equilibrated $\text{Ca}_5\text{Pb}_5(\text{VO}_4)_6\text{F}_2$ annealed for 1 day the nominal composition is correct but the Ca/Pb are distributed statistically over the A sites, the average A cation size over the framework and tunnel are the same, and $\phi = 22^\circ$ is similar to other homoatomic A-site apatites e.g. $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$. After long annealing (1 week) Ca/Pb order is established, the framework is small relative to the tunnel ϕ is small to dilate the channel. In this case, there is some loss of fluorine ($2\text{F}^- \rightarrow \text{O}^{2-} + \square$) which would tend to increase ϕ , but this is less significant than Ca/Pb ordering.	Dong & White [31]
	$\text{Ca}_5\text{Pb}_5(\text{VO}_4)_6\text{F}_2$	22.0 (non-equilibrated)	624.04		

B-Type	Ba ₁₀ (PO ₄) ₆ F ₂	22.2 ₃	691.38	Whenever the is a size difference between <i>A</i> species of the same valence the larger ion will preferentially enter the <i>6h</i> tunnel position rather than the <i>4f</i> framework site leading to a parabolic ϕ trend. This simple rule will not be applicable if there are higher valence cations (e.g RE ³⁺) or monovalent species (e.g. Na ⁺) ; the former prefer <i>6h</i> to better distribute higher charge while the reverse is true for large monovalent cations. Charge considerations will always take precedence over size.	Aissa <i>et al.</i> [24]
	Ba _{9.01} Sr _{0.99} (PO ₄) ₆ F ₂	21.8 ₁	680.32		
	Ba _{6.92} Sr _{3.08} (PO ₄) ₆ F ₂	19.1 ₆	665.06		
	Ba _{5.05} Sr _{4.95} (PO ₄) ₆ F ₂	18.7 ₆	639.39		
	Ba _{2.92} Sr _{7.08} (PO ₄) ₆ F ₂	20.0 ₃	619.35		
	Ba _{1.03} Sr _{8.97} (PO ₄) ₆ F ₂	22.3 ₃	604.79		
	Sr ₁₀ (PO ₄) ₆ F ₂	23.9 ₃	596.35		
	Sr ₁₀ (PO ₄) ₆ F ₂	23.9 ₅	596.14	In <i>P6₃/m</i> apatites the <i>B</i> -site is unique. The BO ₄ tetrahedron contributes to the framework, and for <i>B</i> -site substitution, ϕ will vary linearly and become more obtuse as the average ionic size of the <i>B</i> ions increases.	This work
	Sr ₁₀ (P _{1.5} Cr _{0.5} O ₄) ₆ F ₂	24.2 ₁	599.61		
	Sr ₁₀ (CrO ₄) ₆ F ₂	25.2 ₁	642.28		
	Ca ₁₀ (PO ₄) ₆ (OH) ₂	23.4 ₈	529.81	For Ca ₁₀ (P _{1-x} As _x O ₄) ₆ (OH) ₂ apatites the twist angle increases as larger As ⁵⁺ displaces P ³⁺ as expected. However, at the highest As concentrations ϕ reverses trend. This is an indicator that the structure is undergoing additional modification. It is believed the arsenous compounds are triclinic and may be isostructural with Ca ₁₀ (AsO ₄) ₆ F ₂	Lee <i>et al.</i> [32]
	Ca ₁₀ (P _{0.89} As _{0.11} O ₄) ₆ (OH) ₂	24.5 ₅	535.89		
	Ca ₁₀ (P _{0.76} As _{0.24} O ₄) ₆ (OH) ₂	25.3 ₉	541.59		
	Ca ₁₀ (P _{0.57} As _{0.43} O ₄) ₆ (OH) ₂	25.4 ₇	549.42		
	Ca ₁₀ (P _{0.34} As _{0.66} O ₄) ₆ (OH) ₂	25.9 ₆	558.73		
	Ca ₁₀ (P _{0.20} As _{0.80} O ₄) ₆ (OH) ₂	25.5 ₃	565.37		
	Ca ₁₀ (AsO ₄) ₆ (OH) ₂	23.4 ₆	571.05		
	Ca ₁₀ (PO ₄) ₆ F ₂	23.0 ₆	524.63	The Ca ₁₀ (V _{1-x} P _x O ₄) ₆ F ₂ apatites behave in a similar fashion to Ca ₁₀ (P _{1-x} As _x O ₄) ₆ (OH) ₂ and again show a reversal in ϕ when the framework is large relative to the tunnel. For many apatites the maximum twist angle that is compatible with <i>P6₃/m</i> symmetry appears to be in the range of ~24-25°. Observations to date suggest that to satisfy bond valence requirements the BO ₄ tetrahedron will twist and thereby reduce the symmetry to <i>P2₁/m</i> or <i>P-1</i> . This leads to 3 unique ϕ for each A ^I O ₆ metaprism (Baikie <i>et al.</i> , [40]).	Mercier <i>et al.</i> [2]
	Ca ₁₀ (V _{0.10} P _{0.90} O ₄) ₆ F ₂	22.0 ₉	524.92		
	Ca ₁₀ (V _{0.20} P _{0.80} O ₄) ₆ F ₂	23.0 ₆	533.02		
	Ca ₁₀ (V _{0.30} P _{0.70} O ₄) ₆ F ₂	23.1 ₄	538.04		
	Ca ₁₀ (V _{0.40} P _{0.60} O ₄) ₆ F ₂	23.5 ₄	543.35		
	Ca ₁₀ (V _{0.50} P _{0.50} O ₄) ₆ F ₂	23.2 ₅	550.48		
	Ca ₁₀ (V _{0.60} P _{0.40} O ₄) ₆ F ₂	23.6 ₆	553.65		
	Ca ₁₀ (V _{0.70} P _{0.30} O ₄) ₆ F ₂	24.0 ₈	556.74		
	Ca ₁₀ (V _{0.80} P _{0.20} O ₄) ₆ F ₂	24.6 ₀	562.80		
	Ca ₁₀ (V _{0.90} P _{0.10} O ₄) ₆ F ₂	23.9 ₃	568.36		
	Pb ₁₀ (PO ₄) ₆ Cl ₂	18.4 ₆	634.85	Locating oxygen in apatite structures by X-ray diffraction is challenging. In this series, X-ray scattering is dominated by lead. Therefore the expected trend of an increase in ϕ as larger As ⁵⁺ displaces P ³⁺ was not observed. Rather, the twist angles are random. This apatite system may also suffer from oxidation (2Cl ⁻ → O ²⁻ + □) that would increase metaprism twisting. In addition, the possibility of chemical heterogeneity cannot be ruled out as the materials were treated at low temperatures. Changes in symmetry may also play a role as both hexagonal and monoclinic varieties natural Pb ₁₀ (PO ₄) ₆ Cl ₂ single crystals have been reported (Dai <i>et al.</i> [53]). The refinement approach of Mercier <i>et al.</i> [2] to control oxygen trajectories may be useful.	Flis <i>et al.</i> [33]
	Pb ₁₀ (As _{0.10} P _{0.90} O ₄) ₆ Cl ₂	19.5 ₂	638.91		
	Pb ₁₀ (As _{0.20} P _{0.80} O ₄) ₆ Cl ₂	17.1 ₂	643.09		
	Pb ₁₀ (As _{0.30} P _{0.70} O ₄) ₆ Cl ₂	18.1 ₉	647.45		
	Pb ₁₀ (As _{0.40} P _{0.60} O ₄) ₆ Cl ₂	17.5 ₉	652.12		
	Pb ₁₀ (As _{0.50} P _{0.50} O ₄) ₆ Cl ₂	17.5 ₉	656.67		
	Pb ₁₀ (As _{0.60} P _{0.40} O ₄) ₆ Cl ₂	18.1 ₅	661.64		
	Pb ₁₀ (As _{0.70} P _{0.30} O ₄) ₆ Cl ₂	19.0 ₉	665.74		
	Pb ₁₀ (As _{0.80} P _{0.20} O ₄) ₆ Cl ₂	19.3 ₄	670.78		
	Pb ₁₀ (As _{0.90} P _{0.10} O ₄) ₆ Cl ₂	20.9 ₁	674.05		
	Pb ₁₀ (AsO ₄) ₆ Cl ₂	19.5 ₂	677.93		

X-Type	Sr ₁₀ (PO ₄) ₆ F ₂	23.9 ₅	596.14	For <i>P</i> 6 ₃ / <i>m</i> apatites there is a single <i>X</i> site. Small anions are located at 2 <i>a</i> (000) while larger ions are at 2 <i>b</i> (00½). For stoichiometric compounds there is linear change in ϕ . However it is often difficult to prevent halide losses, and/or partial inclusion of carbonate or hydroxlation. These changes in chemistry will be reflected in both unit cell parameters and ϕ . In the present work loss of chlorine was not entirely prevented.	This work
	Sr ₁₀ (PO ₄) ₆ FCl	21.5 ₂	603.57		
	Sr ₁₀ (PO ₄) ₆ O _{0.91} Cl _{0.1}	21.0 ₃	604.53		
	Ca ₁₀ (PO ₄) ₆ F ₂	23.1 ₇	523.73	For Ca ₁₀ (PO ₄) ₆ (F _{1-x} Cl _x) decreases as larger Cl ⁻ replaces F ⁻ . The doubled unit cell volume arises because there is order correlation of chlorine from tunnel-to-tunnel that is usually modeled as statistically occupancy of an (00 <i>z</i>) site in monoclinic <i>P</i> 2 ₁ / <i>b</i> . The refinement of Ca ₁₀ (PO ₄) ₆ Cl ₂ by O'Donnell <i>et al.</i> [34] and Hendricks (1932) should be considered.	O'Donnell <i>et al.</i> [34]
	Ca ₁₀ (PO ₄) ₆ FCl	22.2 ₇	532.42		
	Ca ₁₀ (PO ₄) ₆ Cl ₂	18.1 ₉	1088.05		

These prescriptions to predict A^I/A^{II} site partitioning assume bonding is predominantly ionic in nature. However, cadmium appears to behave in a different fashion. On the basis of size it would be expected in $[\text{Ca}_{10-x}\text{Cd}_x][(\text{PO}_4)_6][(\text{OH})_2]$ apatite that Cd^{2+} (IR = 0.95 Å) would displace Ca^{2+} (IR = 1.00 Å) in the smaller A^I framework site. In fact, several studies [7, 35, 36] suggest that Cd^{2+} preferentially occupies the tunnel. Most recently, Terra *et al.* [37] used a combination of computation and synchrotron powder diffraction to propose that the significantly greater covalent character of Cd-O bonds results in energetically favoured tenancy of the A^{II} site. The superior crystallographic refinements of Terra *et al.* [37] support this view via an analysis of twist angle systematics. As Cd^{2+} is smaller than Ca^{2+} the tunnel must contract as cadmium displaces calcium, leading to an increase in ϕ . In other words, the parabolic trend will be concave up, rather than concave down as in the case of $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$. Thus for $x = 0, 0.2, 1.23, 2.349$ in $[\text{Ca}_{10-x}\text{Cd}_x][(\text{PO}_4)_6][(\text{OH})_2]$ the twist angle progression is $23.2_0^\circ, 23.4_8^\circ, 23.6^\circ, 23.2^\circ$. It is also of note that $P6_3/m$ $[\text{Cd}_{10}][(\text{PO}_4)_6][(\text{OH})_2]$ [38] yields $\phi = 25.8^\circ$. This value appears anomalously high with a homoatomic A^I/A^{II} phosphate apatite expected to show ϕ in the range 22–25°. In this regard, it may be significant that in a subsequent paper Hata & Maruro [39] presented a revised supercell for the $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$, prepared in the presence of minor manganese, that was $P6_3$ ($a = 16.1990(3)\text{Å}$, $c = 6.6485(1)\text{Å}$) and contains two unique framework A^I sites each with two unique ϕ near to 25° (Table 3.8). An alternate description based on the recent investigation of Baikie *et al.* [40] may be as a triclinic $P-1$ apatite since $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$ shows PO_4 tetrahedral tilting reminiscent of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. Complete $[\text{Ca}_{10-x}\text{Cd}_x][(\text{PO}_4)_6][(\text{OH})_2]$ solid solutions have been prepared (Zhu *et al.* [41]) as verified through contraction of the unit cell volume; however, in the absence of detailed structure refinements it is not possible to examine twist angle variations.

Table 3.8: Metaprism twist angle of $[\text{Ca}_{10-x}\text{Cd}_x][(\text{PO}_4)_6][(\text{OH})_2]$ apatites from published works.

x Cd	a (Å)	c (Å)	ϕ (°)	Volume (Å ³)		
				Citation	Zhu <i>et al.</i> [41]	Reference
0	9.4322(5)	6.891(2)	23.2 ₀	530.93	530.41	Kim <i>et al.</i> [42]
0.2	9.4326	6.8833	23.4 ₈	530.38		Terra <i>et al.</i> [37]
1.23	9.4227	6.9658	23.6 ₁	535.61		Terra <i>et al.</i> [37]
2.349	9.41	6.8448	24.1 ₅	524.89		Terra <i>et al.</i> [37]
10	9.335(2)	6.664(3)	25.8 ₀	502.91	501.45	Hata <i>et al.</i> [38]
10	16.1992(3)	6.6485(1)	25.0 ₉ , 25.3 ₀	1510.88		Hata & Marumo [39]

Equally, when crystallographic studies yield discontinuities in ϕ over a solid solution series, or fail to conform to the parabolic trend, changes in composition or symmetry are suspected. For example, using Rietveld analysis Badraoui *et al.* [43] refined the structures of the fluoro-apatites $[\text{Sr}_{10-x}\text{Cd}_x][(\text{PO}_4)_6][\text{F}_2]$, but the metaprism twist angle (Figure 3.6a) showed irregularities, especially for $\text{Sr}_4\text{Cd}_6(\text{PO}_4)_6\text{F}_2$, where $\phi = 34.4^\circ$. This greatly exceeds the maximum twist angle (26.7°) so far observed in any stoichiometric hexagonal apatite for $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$ [44]. Similarly, over the limited compositional range reported in the hydroxyl-apatite series $[\text{Sr}_{10-x}\text{Cd}_x][(\text{PO}_4)_6][(\text{OH})_2]$ the twist angles reported [43] appear at odds with single crystal determinations of the endmembers [20, 39] (Figure 3.6b). As a further example, Bigi *et al.* [9] reported the twist angles for $\text{Ca}_9\text{Sr}_1(\text{PO}_4)_6(\text{OH})_2$ and $\text{Ca}_5\text{Sr}_5(\text{PO}_4)_6(\text{OH})_2$ grew larger with strontium content, when the opposite behaviour is expected due to the favoured introduction of Sr to the tunnel (Table 3.7). This contrarian observation can be explained if there is oxidation of the X anion ($2\text{OH}^- \rightarrow \text{O}^{2-} + \square$) that creates tunnel vacancies with a corresponding reduction in diameter and increase in ϕ .

Figure 3.6: Metaprism twist angles derived from Badraoui *et al.* [43] in (a) $[\text{Cd}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][\text{F}_2]$, and (b) $[\text{Cd}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_2]$. (c) Fitted line of $[\text{Ca}_{10-x}\text{Cd}_x][(\text{PO}_4)_6][(\text{OH})_2]$ twist angles calculated from Kim *et al.* [42], Terra *et al.* [37] and Hata *et al.* [38].

The twist angles for chlorapatites are less than fluoro- and hydroxyl- analogues as Cl^- is a substantially larger X anion, with the tunnel opening by decreasing ϕ (Table 3.7). Sudarsanan & Young [27] examined the $[(\text{Ca}_{1-x}\text{Sr}_x)_{10}][(\text{PO}_4)_6][\text{Cl}_2]$ series and determined structures with a parabolic ϕ trend for differential Ca/Sr site partitioning, but $\phi = 17.8^\circ$ for $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ is “anomalously” small compared to the $\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$ endmember. In this instance, this reflects crystallisation in $P2_1/b$ rather than $P6_3/m$ due to Cl displacements and inter-tunnel correlations. In the original

refinement of chlorapatite [45] the symmetry was forced to $P6_3/m$ which lead to $\phi = 19.1^\circ$, and somewhat closer to $\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2$ (21.1°).

Divalent lead (Pb^{2+}) being larger than Ca^{2+} is driven towards tunnel A^{II} positions, and in addition, requires space to accommodate stereochemically active lone pair electrons to produce the expected the parabolic ϕ trend (Table 3.7). In lacunar apatites, the tunnels are devoid of X anions ($X = \square$) which must constrict by increasing ϕ ; consequently these compounds show the largest ϕ of all $[\text{A}_{10}][(\text{BO}_4)_6][\text{X}_2]$ apatites (Table 3.7).

Apatite A -site ordering and/or composition can be modified by annealing [31]. For non-equilibrated $\text{Ca}_5\text{Pb}_5(\text{VO}_4)_6\text{F}_2$ annealed for 1 day the nominal composition is correct, but the Ca/Pb ions are distributed statistically over the A sites. As the average A cation size over the framework and tunnel are the same, $\phi \sim 22^\circ$ and similar to other homoatomic A -site apatites e.g. $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$. After long annealing (1 week) Ca/Pb order is established, the framework is small relative to the tunnel causing ϕ to decrease to 14.4° , which is counteracted to a small extent by some loss of fluorine ($2\text{F}^- \rightarrow \text{O}^{2-} + \square$) which would tend to increase ϕ .

3.5.2 B-site Correlations in $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$

In $P6_3/m$ apatites the B -site is unique. The BO_4 tetrahedron contributes to the framework and for B -site substitution ϕ will vary linearly and become more obtuse as the average ionic size of the B ions increases. The metaprism twist angles in $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$ increased linearly as P^{5+} is displaced by Cr^{5+} (Figure 3.7a), and the interpretation is straightforward with larger Cr^{5+} dilating the BO_4 tetrahedra as the B -O bond lengths increase from $1.54\text{\AA}$ for PO_4 to $1.69\text{\AA}$ for CrO_4 , and causing the tunnel to contract and ϕ to increase consistent with Baikie *et al.* [23]. The difference between X-ray and neutron diffraction data is possibly due to stoichiometrically anomalous domains that would be studied more completely using the latter technique as neutron penetrates into samples. Elsewhere, Lee *et al.* [32] found similar behaviour in the $[\text{Ca}_{10}][(\text{P}_{1-x}\text{As}_x\text{O}_4)_6][(\text{OH})_2]$ series with the twist angle increasing as As^{5+} replaces P^{5+} (see also Henderson *et al.* [46]). However, for the $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$ end-member ϕ decreased anomalously, perhaps due to a change of symmetry, although

this could not be confirmed in that study. It is noted that the fluoro-analogue $\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2$ is triclinic [23] and $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$ may be isostructural. In any event, ϕ systematics suggest the crystal chemistry of the arsenic end-member is distinct.

Figure 3.7: Metaprisim twist angle against (a) fitted line for atomic percentage chromium in $[\text{Sr}_{10}][(\text{P}_{1-x}\text{Cr}_x\text{O}_4)_6][\text{F}_2]$, the diamonds and squares are from X-ray diffraction and neutron diffraction respectively, (b) fitted line for arsenic in $[\text{Ca}_{10}][(\text{P}_{1-x}\text{As}_x\text{O}_4)_6][(\text{OH})_2]$ (Lee *et al.* [32]) and (c) $\text{Pb}_{10}(\text{P}_{1-x}\text{As}_x\text{O}_4)_6\text{Cl}_2$ (Flis *et al.* [33]) in diamonds and other works (Krivovichev & Burns [47]; Dai & Hughes [50]; Ito [51]; Calos & Kennard [52]; Dai *et al.* [53]) in squares.

The $[\text{Ca}_{10}][(\text{V}_{1-x}\text{P}_x\text{O}_4)_6][\text{F}_2]$ apatites behave in a similar fashion to $[\text{Ca}_{10}][(\text{P}_{1-x}\text{As}_x\text{O}_4)_6][(\text{OH})_2]$ and again show a reversal in ϕ when the framework is large relative to the tunnel. As already noted, for many apatites the maximum twist angle compatible with $P6_3/m$ symmetry is in the range of $\sim 24\text{--}25^\circ$. Observations to date suggest that beyond this limit, the BO_4 tetrahedron will twist to satisfy bond valence requirements and thereby reduce the symmetry to $P2_1/m$ or $P-1$. This leads to 3 unique ϕ for each AO_6 metaprism [40]. Alternatively, twisting may result in $P6_3$ supercells, but this possibility is yet to be examined.

The difficulty in locating oxygen accurately in apatites where the metal matrix is a strong X-ray scatterer is illustrated in the $[\text{Pb}_{10}][(\text{P}_{1-x}\text{As}_x\text{O}_4)_6][\text{Cl}_2]$ series [33] (Table 3.7). Here, the powder X-ray patterns will be dominated by lead resulting in relatively poor sensitivity to oxygen, and possibly errors in occupancy values of the tunnel X-site due to the stereographically active Pb^{2+} lone pair electrons directed towards the channel centre. It would be anticipated that as P^{5+} ($0.17 \text{ \AA}$) is displaced by larger As^{5+} ($0.335 \text{ \AA}$) that ϕ will increase provided the Pb_6Cl_2 tunnel contents are fixed. The absence of trend in ϕ over the series is indicative of poorer refinements, disequilibrium (the materials were produced by a low temperature route), or unexpected compositional variations. For example, where the twist angle appears large relative to single crystal structure determinations of the endmembers it might be suspected that some oxidation has accompanied chlorine volatilization, and in this respect it is noted that the oxy analogue $\text{Pb}_{10}(\text{PO}_4)_6\text{O}$ [47] has a relatively larger ϕ as the tunnel occupancy is half that of the Cl-apatite.

3.5.3 X-site Correlations in $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$

For $P6_3/m$ apatites there is a single X site. Small anions are located at $2a$ ($0, 0, \frac{1}{4}$) while larger ions are at $2b$ ($0, 0, 0$); anions of intermediate size statistically enter $4e$ ($00z$) positions. For stoichiometric compounds there is linear change in ϕ . However it is often difficult to prevent halide losses, or the partial inclusion of carbonate or hydroxyls. These changes in chemistry will be reflected in both unit cell parameters and ϕ . In the present work, loss of chlorine was not prevented (Table 3.5).

For $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$, ϕ decreases as larger Cl^- ($1.81\text{\AA}$) displaces F^- ($1.33\text{\AA}$) causing the tunnel to dilate and the twist angle to reduce, with a linear variation observed in the combined data for metaprisms twist angles of Sudarsanan *et al.* [20], Mackie & Young [48] and Sudarsanan & Young [27] (Table 3.7). The non-linearity observed in this study is in agreement with the structure refinement where the Cl/F deviated from that expected from the synthesized composition. This difference highlights the sensitive nature of the apatite twist angle and how departures from expected trends can indicate stoichiometric anomalies and/or nanodomain intergrowths. Similarly, for $[\text{Ca}_{10}][(\text{PO}_4)_6][(\text{F}_{1-x}\text{Cl}_x)_2]$ ϕ decreases as larger Cl^- replaces F^- (O'Donnell *et al.* [34]), but the unit cell volume doubles because of order correlation of chlorine from tunnel-to-tunnel that is usually modeled as statistical occupancy of an $(0\ 0\ z)$ site in monoclinic $P2_1/b$. More recent work suggests this order is incommensurate [49].

Figure 3.8: Variation of metaprisms twist angle against atomic percentage of chlorine (fitted lines) in (a) $[\text{Sr}_{10}][(\text{PO}_4)_6][\text{F}_{2-x}\text{Cl}_x]$, where the diamonds and squares are X-ray diffraction and neutron diffraction respectively and (b) $[\text{Ca}_{10}][(\text{PO}_4)_6][(\text{F}_{1-x}\text{Cl}_x)_2]$ by Sudarsanan *et al.* [20], Mackie & Young [48] and Sudarsanan & Young [27].

3.6 Conclusions

Metaprisms twist angles can be used as a diagnostic tool to validate apatite structures especially in solid solution series. In this work, the three possible sites for substitutions, namely cationic, metalloid and anionic were considered. The following was demonstrated:

- i) In A^I/A^{II} substitution by divalent ion pairs ϕ varies in a parabolic fashion due to differences in partitioning co-efficient, with the larger ion entering the $6h$ tunnel position before occupying the smaller $4f$ framework position. The exception is Cd^{2+} where bonding is more nearly covalent.
- ii) In B substitution the variation in ϕ is linear, providing there is no change of symmetry. However, for large ϕ the BO_4 tetrahedra may twist to achieve acceptable bond valence sums and $P2_1/m$ or $P-1$ polymorphs may result.
- iii) In X substitution deviations from ideal stoichiometry especially through oxidation and/or volatilization, can be detected, and provide an independent measure of site occupancy.
- iv) Where apatites equilibrate slowly during volatilisation or domain formation, ϕ will continue to be variable until kinetic or thermodynamic equilibrium is reached.

Thus, it has been demonstrated that the $A^I O_6$ metaprism twist angle provides the means to recognize inferior apatite structure refinements or unanticipated modifications of crystal chemistry. This methodology will be applied throughout the thesis as a tool for validating simulated wastefrom apatites and britholites. Moreover, as apatites are also under investigation for an increasing range of technologies, but the precise control of composition is often challenging, the routine calculation of ϕ can provide a rapid method to isolate problematic structural features.

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Chapter 4

Britholite Apatites for the Incorporation of Rare Earth Fission Products

Clockwise from top centre: oxides of praseodymium, cerium, lanthanum, neodymium, samarium and gadolinium.

The rare earth elements or lanthanides are a technologically significant group that find application in lasers, magnets, colourants and capacitors. The number of naturally occurring nuclides is usually quite limited, e.g. La^{139} (99.911% abundance) and La^{138} (0.081%), but nuclear fission creates a far wider range of short-lived isotopes requiring immobilization and isolation from the biosphere. Britholites are mineral apatites that contain rare earths in significant amounts and the incorporation of the fission products in synthetic analogues provides a means for long term stabilization.

4.1 Understanding Rare Earth Britholites

Rare earth phospho-silicate apatites are known in mineralogy as britholites [1] and can be represented as $[\text{Ca}_{1-x-y-z}\text{REE}^{2+}_x\text{REE}^{3+}_y\text{REE}^{4+}_z]_{10}[(\text{P}_{1-y-2z}\text{Si}_{y+2z}\text{O}_4)_6][(\text{OH})_2]$ compounds. In nature, these minerals are more complex chemically and found neither as pure silicates or phosphates, but form solid-solutions between a range of end-members [2]. In the Oklo fission reactor and similar geological features, britholites incorporate up to 970 ppm plutonium and uranium [3], that has prompted numerous investigations of lanthanide silicates, especially Nd^{3+} containing species, which crystallochemically mimics Pu^{3+} [4-8]. In general, rare earth elements (REE) or lanthanides (*Ln*) possess similar chemical and physical properties (ionic radii, oxidation states, coordination numbers) as actinides (ACT), and can be used as analogues of transuranic species that are too hazardous for study in conventional laboratories [9]. Synthetic britholite was reported by Terra *et al.* [10] to successfully retain 3.5-5.9 wt% of uranium ($[\text{Ca}_9\text{Nd}_{1-x}\text{U}_x][(\text{PO}_4)_{5-x}(\text{SiO}_4)_{1+x}][\text{F}_2]$) depending on the method of preparation, and synthetic thorium-bearing britholite ($[\text{Ca}_9\text{Nd}_{1-x}\text{Th}_x][(\text{PO}_4)_{5-x}(\text{SiO}_4)_{1+x}][\text{F}_2]$) contains up to 10 wt% thorium [11]. Apart from nuclear waste matrices, britholites are exploited as phosphors and laser materials [12] and electrolytes in solid oxide fuel cells [13], although in this literature they are simply identified as ‘apatites’.

Despite intensive study, there is ongoing debate concerning the partitioning of REEs over the A^{I} tunnel and A^{II} framework sites in britholite. As discussed in Chapter 3, the distribution of A-site substituents depends on size and other properties including polarizability, electronegativity and valence [14]. Several predictive models have been proposed. On the basis of bond valence sums, Hughes *et al.* [15] observed in $P6_3/m$ apatite that REEs will partition to both A cation sites (4*f* and 6*h*) with the larger La (1.032Å) $\rightarrow$ Pr (0.99Å) showing preference for 6*h* and mid-sized Pm (0.97Å) $\rightarrow$ Sm (0.958Å) more strongly partitioning to 4*f*. Elsewhere, it is reported that the synthesis method, and particularly the source of neodymium (NdF_3 or Nd_2O_3), will determine the site preference of this REE [16], implying the ease of equilibration is dependent upon the precursor. In contrast, molecular dynamic and density functional theory calculations suggest that Nd should reside on 6*h* [4, 17] as supported experimentally by Carpena *et al.* [18]. Urusov *et al.* [19] proposed that the partition

coefficients were largely determined by bond type, with the covalent bonds of more electronegative dopants favouring the $4f$ site. This is somewhat at odds with Terra *et al.* [20] who found covalently bonded Cd^{2+} is tenanted at the $6h$ position.

As most REE are trivalent, charge balance through coupled substitutions is essential, and frequently involves the A and B sites (Equation 4-1). If $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is taken as the prototype then

Less commonly, REEs are divalent (Eu^{2+}) and tetravalent (Ce^{4+} , Pr^{4+}) and incorporation conforms to (4-2) and (4-3).

Another charge balancing mechanism could include monovalent alkali ions, as in

The coupled substitution of $(\text{REE}^{3+}, \text{SiO}_4^{4-})$ for $(\text{Ca}^{2+}, \text{PO}_4^{3-})$ often leads to britholites that are isostructural with $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ which most commonly, but not exclusively, adopts $P6_3/m$ symmetry. However, several studies suggest that incorporation of REEs significantly smaller than Ca^{2+} is accompanied by a change in symmetry [21]. As written, equations 4-1 to 4-4 provide no information concerning $A^{\text{I}}/A^{\text{II}}$ cation partitioning. The present chapter seeks clarification of this question through the synthesis and characterization of an extensive range of rare earth britholites to establish the structural adaptations required to accommodate the trivalent lanthanide contraction. Such information is essential to tailor waste forms for the stabilization of mixed fission products of variable oxidation state, and also provides guidance for the treatment of transuranic nuclides (Chapter 5).

A key aspect of this study is the validation of simulated waste form britholite synthesis and crystal chemistry through consideration of the $A^{\text{I}}\text{O}_6$ metaprism twist

angle as developed in Chapter 3. Of particular concern, is the recognition of unexpected excursions in stoichiometry, particularly losses or oxidation of the tunnel X anion, as compositional control is not always straightforward. For example, in a study of $[\text{Ca}_{9.98}\text{Eu}_{0.02}][(\text{PO}_4)_6][\text{F}_{1-x-y}\text{Cl}_x\text{Br}_y]$ apatites the syntheses and Rietveld structure refinements were compromised by halide losses [42, 43, 45-47] (Figure 4.1) – the impossibly large twist angles arising from refinement to false minima are noted. When the reliable twist angles from single crystal determinations and neutron powder patterns are overlaid on this data [42, 43, 45-47], the departures from acceptable ϕ become more obvious. Because of these difficulties in treating powder X-ray diffraction patterns for structure refinement, neutron diffraction was used here to provide a baseline against which XRD structure refinements were compared. An extensive compilation of britholite-type apatite properties including $A^{\text{I}}/A^{\text{II}}$ rare earth partitioning, symmetry and metaprisim twist angle are presented in Table 4.1a, 4.1b and 4.1c.

Figure 4.1: The large twist angles calculated from Noetzold & Wulff [42, 43, 45-47] (diamond) show either unexpected compositional variation or Rietveld refinement to false minima (Table 4.1) Crosses and fitted line are derived from the higher quality data for $[\text{Ca}_{10}[(\text{PO}_4)_6][(\text{F}_{1-x}\text{Cl}_x)_2]$ (Sudarsanan *et al.* [53]; Mackie & Young [54]; Sudarsanan & Young [55] and $[\text{Ca}_{10}[(\text{PO}_4)_6][\text{Br}_2]$ (Elliott *et al.* [56]).

Table 4.1a: Crystallographic parameters of REE bearing alkali and alkali earth britholites. Twist angles generally vary as expected with composition, however some data sets are anomalous.

Composition	A ^I	A ^{II}	B	X	Symmetry	Volume (Å ³)	φ (°)	Remarks	Reference
[Na _{1.08} Eu _{8.18}](SiO ₄) ₆ (OH) _{1.62}	Eu, Na	Eu, Na	Si	O, H	<i>P</i> 6 ₃ / <i>m</i>	538.25	22.8 ₇	Na is consistently located in A ^I (4f) site, Other alkali metals (K, Rb, Cs) follow the similar trend. As S ²⁻ > O ²⁻ the twist angles are smaller.	[22]
[Na _{1.2} Eu _{3.96} Gd _{3.96}](SiO ₄) ₆ (OH) _{1.86}	Eu, Gd, Na	Eu, Gd	Si	O, H	<i>P</i> 6 ₃ / <i>m</i>	538.42	22.4 ₃		[22]
[Na _{1.5} Sm _{8.5}](SiO ₄) ₆ FO	Sm, Na	Sm, Na	Si	O, F	<i>P</i> 6 ₃ / <i>m</i>	540.35	24.4 ₆		[23]
[Na _{1.33} Ce _{8.67}](SiO ₄) ₆ O _{1.34} F _{0.68}	Na, Ce	Ce	Si	O, F	<i>P</i> 6 ₃ / <i>m</i>	569.79	24.3 ₈		[25]
[NaPr ₉](SiO ₄) ₆ S ₂	Na, Pr	Pr	Si	S	<i>P</i> 6 ₃ / <i>m</i>	574.86	18.0 ₆		[26]
[NaSm ₉](SiO ₄) ₆ S ₂	Na, Sm	Sm	Si	S	<i>P</i> 6 ₃ / <i>m</i>	557.27	16.0 ₈		[24]
[Ca ₉ Nd](PO ₄) ₅ (SiO ₄)F _{1.5} O _{0.25}	Ca, Nd	Ca, Nd	Si, P	O, F	<i>P</i> 6 ₃ / <i>m</i>	527.41	23.9 ₂	Ca enters both A ^I and A ^{II} positions but with a clear preference for A ^I regardless of tunnel content.	[27]
[Ca _{2.24} Ce _{6.76} Sr](SiO ₄) ₆ (OF) _{0.76}	Ce, Ca, Sr	Ce, Ca	Si	O, F	<i>P</i> 6 ₃ / <i>m</i>	569.64	22.3 ₄		[28]
[Ca _{3.5} La ₆](SiO ₄) ₆ F(H ₂ O)	La, Ca	La, Ca	Si	F	<i>P</i> 6 ₃	573.44	23.4 ₄		[29]
[Ca _{3.40} La _{6.60}](SiO ₄) ₆ O _{0.94} (OH) _{0.72}	La, Ca	La, Ca	Si	O, H	<i>P</i> 6 ₃ / <i>m</i>	573.84	20.7 ₂		[30]
[Ca _{3.10} La _{6.90}](SiO ₄) ₆ (CuO) _{0.62} O _{0.90} (OH) _{0.48}	La, Ca	La, Ca	Si	Cu, O, H	<i>P</i> 6 ₃ / <i>m</i>	577.65	19.2 ₀		[30]
[Ca _{2.60} La _{7.40}](SiO ₄) ₆ (CuO) _{0.32} O _{1.40} (OH) _{0.28}	La, Ca	La, Ca	Si	Cu, O, H	<i>P</i> 6 ₃ / <i>m</i>	579.96	20.5 ₈		[30]
[Sr _{2.80} La _{7.20}](SiO ₄) ₆ O _{1.20} (OH) _{0.80}	La, Sr	La, Sr	Si	O, H	<i>P</i> 6 ₃ / <i>m</i>	589.82	24.2 ₅	In the presence of REE (La), Sr is statistically likely to reside in A ^I , despite La ³⁺ (1.032Å) < Sr ²⁺ (1.18Å), to better distribute charge.	[30]
[SrLa ₉](Si _{5.5} Al _{0.5} O ₂₄)O _{2.25}	La, Sr	La	Si, Al	O	<i>P</i> 6 ₃ / <i>m</i>	590.40	21.7 ₂		[31]
[Sr _{2.80} La _{7.20}](SiO ₄) ₆ (CuO) _{0.44} O _{1.20} (OH) _{0.36}	La, Sr	La, Sr	Si	Cu, O, H	<i>P</i> 6 ₃ / <i>m</i>	597.26	23.8 ₄		[30]
[Sr _{3.40} La _{6.60}](SiO ₄) ₆ (CuO) _{0.74} O _{0.60} (OH) _{0.72}	La, Sr	La, Sr	Si	O, H	<i>P</i> 6 ₃ / <i>m</i>	597.62	23.1 ₂		[30]
[SrLa ₉](Si _{5.5} Al _{0.5} O ₂₄)O _{2.25}	La, Sr	La	Si, Al	O	<i>P</i> 6 ₃ / <i>m</i>	603.19	22.3 ₈		[31]
[Ba ₂ Sm ₈](SiO ₄) ₆ Se ₂	Sm, Ba	Sm	Si	Se	<i>P</i> 6 ₃ / <i>m</i>	577.87	11.3 ₂	Ba locates in A ^I while REE is found in A ^{II} . In [Ba ₄ Ce ₆](SiO ₄) ₆ F ₂ φ is unexpectedly small, due to Ce ³⁺ → Ce ⁴⁺ oxidation.	[32]
[Ba ₄ La ₆](SiO ₄) ₆ F ₂	La, Ba	La, Ba	Si	F	<i>P</i> 6 ₃ / <i>m</i>	608.76	22.7 ₉		[33]
[Ba ₄ Ce ₆](SiO ₄) ₆ F ₂	Ba	Ce	Si	F	<i>P</i> 6 ₃ / <i>m</i>	612.81	14.2 ₃		[34]
[Gd _{4.33} Ho _{4.33}](SiO ₄) ₆ (OH) ₂	Gd, Ho	Gd, Ho	Si	O, H	<i>P</i> 6 ₃ / <i>m</i>	503.46	20.5 ₃	Smaller REEs (e.g. Ho) and transition metals (e.g. Cr, Ti) partition into the A ^I framework.	[35]
[Sm ₈ Cr ₂](SiO ₄) ₆ N ₂	Sm, Cr	Sm	Si	O, N	<i>P</i> 6 ₃	535.01	21.2 ₉		[36]
[La ₉ Ti](SiO ₄) ₃ (SiNO ₃) ₃ O ₂	La, Ti	La	Si	O	<i>P</i> 6 ₃ / <i>m</i>	589.60	25.6 ₃		[37]

Table 4.1b: Crystallographic parameters of REE bearing alkali and alkali earths phosphate apatites.

Composition	A ^I	A ^{II}	B	X	Symmetry	Volume (Å ³)	φ(°)	Remarks	Reference
[Na ₂ Ca ₆ Sm ₂](PO ₄) ₆ F ₂	Na, Ca, Sm	Ca, Sm	P	F	<i>P</i> 6 ₃ / <i>m</i>	526.44	25.0 ₅	φ may be	[38]
[Na ₂ Ca ₆ Eu ₂](PO ₄) ₆ F ₂	Ca, Eu, Na	Ca, Eu	P	F	<i>P</i> 6 ₃ / <i>m</i>	525.78	27.2 ₁	anomalously	[39]
[Na _{0.1} Ca _{9.8} La _{0.1}](PO ₄) ₆ Cl ₂	Ca, Na, La	Ca, La	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	546.17	17.8 ₆	high due to	[40]
[Na _{0.18} Ca _{9.64} Nd _{0.18}](PO ₄) ₆ Cl ₂	Ca, Nd	Ca, Na, Nd	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	546.06	17.9 ₄	oxidation 2X ⁻ →	[40]
[Na _{0.17} Ca _{9.66} Sm _{0.17}](PO ₄) ₆ Cl ₂	Ca, Na, Sm	Ca, Sm	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	545.63	17.7 ₅	□ _x + O ²⁻ (See	[40]
[Na _{0.14} Ca _{9.72} Dy _{0.14}](PO ₄) ₆ Cl ₂	Ca, Na, Dy	Ca, Dy	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	545.44	17.6 ₃	Fig. 4.1)	[40]
[Ca _{8.256} Nd _{0.48}](PO ₄) ₆ F _{1.824}	Ca	Ca, Nd	P	F	<i>P</i> 6 ₃ / <i>m</i>	523.14	23.3 ₈	REE dominantly	[41]
[Ca _{8.184} Nd _{0.48}](PO ₄) ₆ F _{1.812}	Ca	Ca, Nd	P	F	<i>P</i> 6 ₃ / <i>m</i>	523.11	23.3 ₅	enters A ^{II} . As	[41]
[Ca _{9.98} Eu _{0.02}](PO ₄) ₆ Cl ₂	Ca	Ca, Eu	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	544.88	19.0 ₇	Chloro-apatites	[42]
[Ca _{4.90} Sr _{5.08} Eu _{0.02}](PO ₄) ₆ Cl ₂	Ca, Sr, Eu	Ca, Sr, Eu	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	577.26	17.3 ₉	show smaller φ.	[42]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Cl _{0.50} F _{1.50}	Sr, Eu	Sr, Eu	P	Cl, F	<i>P</i> 6 ₃ / <i>m</i>	597.33	26.5 ₂	REEs consistently	[43]
[Sr _{9.918} Nd _{0.054}](PO _{0.975} O ₄) ₆ F ₂	Sr	Sr, Nd	P	F	<i>P</i> 6 ₃ / <i>m</i>	595.20	23.1 ₉	reside in both sites,	[44]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ F ₂	Sr, Eu	Sr, Eu	P	F	<i>P</i> 6 ₃ / <i>m</i>	595.75	22.8 ₁	but mostly in A ^{II} . However, the twist	[43]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ F ₂	Sr	Sr, Eu	P	F	<i>P</i> 6 ₃ / <i>m</i>	595.75	22.8 ₁	angles are without	[45]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Br _{0.50} F _{1.50}	Sr	Sr, Eu	P	Br, F	<i>P</i> 6 ₃ / <i>m</i>	595.92	28.7 ₁	trend. This may be	[45]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ BrF	Sr	Sr, Eu	P	Br, F	<i>P</i> 6 ₃ / <i>m</i>	600.02	27.4 ₈	due to false minima,	[45]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ ClF	Sr, Eu	Sr, Eu	P	Cl, F	<i>P</i> 6 ₃ / <i>m</i>	602.33	22.0 ₆	halide losses or both.	[43]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Cl _{1.50} F _{0.50}	Sr, Eu	Sr, Eu	P	Cl, F	<i>P</i> 6 ₃ / <i>m</i>	607.11	19.0 ₂		[43]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Cl ₂	Sr, Eu	Sr, Eu	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	607.45	15.5 ₉		[46]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Cl ₂	Sr, Eu	Sr, Eu	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	607.51	17.4 ₅		[42]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Cl _{1.50} Br _{0.50}	Sr, Eu	Sr, Eu	P	Cl, Br	<i>P</i> 6 ₃ / <i>m</i>	609.45	20.7 ₇		[47]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ ClBr	Sr, Eu	Sr, Eu	P	Cl, Br	<i>P</i> 6 ₃ / <i>m</i>	611.40	18.3 ₉		[47]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Br _{1.50} F _{0.50}	Sr	Sr, Eu	P	Br, F	<i>P</i> 6 ₃ / <i>m</i>	612.62	20.8 ₁		[45]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Br ₂	Sr	Sr, Eu	P	Br	<i>P</i> 6 ₃ / <i>m</i>	619.53	24.4 ₉		[45]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Br ₂	Sr, Eu	Sr, Eu	P	Br	<i>P</i> 6 ₃ / <i>m</i>	619.53	24.4 ₉		[47]
[Sr _{9.98} Eu _{0.02}](PO ₄) ₆ Cl _{0.50} Br _{1.50}	Sr, Eu	Sr, Eu	P	Cl, Br	<i>P</i> 6 ₃ / <i>m</i>	622.89	21.7 ₉		[47]
[Sr _{5.08} Ba _{4.90} Eu _{0.02}](PO ₄) ₆ Cl ₂	Sr, Eu	Sr, Ba, Eu	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	645.12	21.6 ₅		[46]
[Ba ₆ La ₂ Na ₂](PO ₄) ₆ F ₂	La, Na, Ba	Ba, La, Na	P	F	<i>P</i> -6	636.67	10.3 ₇	REEs reside in	[48]
[Ba _{9.98} Eu _{0.02}](PO ₄) ₆ Cl ₂	Ba, Eu	Ba, Eu	P	Cl	<i>P</i> 6 ₃ / <i>m</i>	698.93	26.7 ₉	both sites.	[46]

Table 4.1c: Crystallographic parameters of REE bearing alkali and alkali earth silica-phosphate apatite.

Composition	A ^I	A ^{II}	B	X	Symmetry	Volume (Å ³)	φ(°)	Remarks	Reference
[Ca _{9.168} Na _{0.316} Dy _{0.516}](P _{5.75} Si _{0.24} O ₂₄)F ₂	Ca, Na, Dy	Ca, Dy	P, Si	F	<i>P6₃/m</i>	524.3	23.8 ₈	REEs reside in	[49]
[Ca _{9.04} Na _{0.346} Gd _{0.614}](P _{5.72} Si _{0.28} O ₂₄)F ₂	Ca, Na, Gd	Ca, Na, Gd	P, Si	F	<i>P6₃/m</i>	525.41	23.9 ₁	both sites. The	[49]
[Ca _{9.283} Ce _{0.617} Na _{0.10}](Si _{0.44} P _{5.56} O ₂₄)F ₂	Ca, Na, Ce	Ca, Ce	P, Si	F	<i>P6₃/m</i>	526.88	23.6 ₃	twist angles	[50]
[Ca ₉ Nd](PO ₄) ₅ (SiO ₄)F _{1.50} O _{0.25}	Ca, Nd	Ca, Nd	P, Si	F, O	<i>P6₃/m</i>	527.41	23.9 ₂	are of similar	[51]
[Ca _{8.662} Na _{0.514} Nd _{0.818}](P _{5.68} Si _{0.32} O ₂₄)F ₂	Ca, Na, Nd	Ca, Na, Nd	P, Si	F	<i>P6₃/m</i>	527.74	24.2 ₁	magnitude as	[49]
[Ca _{9.692} Na _{0.04} Sm _{0.271}](P _{0.963} Si _{0.037} O ₄) ₆ (OH) ₂	Ca, Na, Sm	Ca, Sm	P, Si	O, H	<i>P6₃/m</i>	528.98	23.6 ₃	the dopant	[52]
[Ca _{9.616} Na _{0.064} Nd _{0.317}](P _{0.952} Si _{0.048} O ₄) ₆ (OH) ₂	Ca, Na, Nd	Ca, Nd	P, Si	O, H	<i>P6₃/m</i>	529.12	23.7 ₀	level with	[52]
[Ca _{7.79} Ce _{1.26} Na _{0.95}](Si _{0.32} P _{5.68} O ₂₄)F ₂	Ca, Nd, Ce	Ca, Ce	P, Si	F	<i>P6₃/m</i>	529.54	24.7 ₇	respect to	[50]
[Ca _{8.994} Na _{0.356} La _{0.65}](P _{5.71} Si _{0.29} O ₂₄)F ₂	Ca, Na, La	Ca, La	P, Si	F	<i>P6₃/m</i>	530.00	23.5 ₄	Ca ₁₀ (PO ₄) ₆ (F,	[49]
[Ca _{9.674} Na _{0.045} La _{0.286}](P _{0.964} Si _{0.036} O ₄) ₆ (OH) ₂	Ca, Na, La	Ca, La	P, Si	O, H	<i>P6₃/m</i>	531.46	23.5 ₇	OH) ₂ is low and the ratio of framework to tunnel size is broadly similar.	[52]

4.2 Synthesis

Britholites are generally synthesized via solid state reaction, but preparative routes can vary from mechanochemical activation by grinding or ball milling [10, 57] to Pechini complexation methods [58]. For the $[\text{Ca}_{10-x}\text{La}_x][(\text{SiO}_4)_x(\text{PO}_4)_{6-x}][\text{O}]$ oxyapatites, Boyer *et al.* [59] found that high synthesis temperatures ($\geq 1400^\circ\text{C}$) were necessary to accelerate the reaction rate and obtain a pure phase, with the same procedure applicable to all REEs. To obtain high yields at lower temperature, soft chemical routes have been investigated including aqueous-based sol-gel [60], gel casting [61] and hydrothermal [62] approaches.

Here, a comprehensive suite of the silicate apatites $[\text{Ca}_2\text{REE}_8][(\text{SiO}_4)_6][\text{O}_2]$ incorporating lanthanides from praseodymium (Pr) to lutetium (Lu), but excluding promethium (Pm), were produced using a modified solid state reaction of Fahey *et al.* [7]. Rare earth oxides were mixed with fresh calcium oxide (formed by decomposing calcium carbonate at 900°C for 4 hours) and silicic acid in stoichiometric amounts and firing from 1400°C to 1700°C for 24 hours to produce oxyapatite powders. The nominal reactions are:

Because silicate apatites lose water below 1100°C the products will not be hydroxylated; the incorporation of OH ions in silicate apatite requires hydrothermal reaction or lower calcination temperature [2].

The sol-gel technique was found suitable to prepare Nd, Sm, Eu, Gd and Dy britholites. In this method, stoichiometric quantities of rare earth oxide powders were dissolved in 50 ml of stock nitric acid (HNO_3) diluted in a 1:9 ratio of acid to deionised water. Separately, calcium nitrate (2.125g) was dissolved in 50 ml of deionised water. The two solutions were mixed and stirred with tetraethylorthosilicate (TEOS) added drop-wise to form an emulsion, that dissipates with stirring and forms a coloured or clear solution depending on the rare earth

element used. Stirring was continued for a further 2 hours before the sol was oven-dried (1 day/100°C) to form a gel that was crystallized (700°C/12 hours/air) for subsequent structural analysis.

4.3 Materials Characterization

4.3.1 Powder X-ray Diffraction (PXRD)

The absolute phase proportions and cell metrics were derived from powder X-ray diffraction patterns collected using a Shimadzu LabX XRD600 with $\text{CuK}\alpha$ radiation step-scanned over the 2θ range 10–140° at intervals of 0.02°. Prior to scanning, the apatite powder was manually ground for 5 minutes in an agate mortar and pestle to improve homogeneity and minimize X-ray adsorption that would attenuate the diffracted intensities. The diffraction patterns were analyzed using the Rietveld method [63] as implemented in Topas V3.0 to extract apatite crystallographic data and quantitatively measure secondary phases, if present. The parameters refined were the zero error, a user-specified number of coefficients for Chebyshev polynomial fitting of the background, a pseudo-Voigt function to model the peak shapes, and the ‘crystallite size’ to account for microstructure-controlled line broadening. Only isotropic atomic displacement parameters were refined, with a common value ($1\text{\AA}^2$) assumed for all oxygen positions due to strong scattering of *REE*, and the *REE*/Ca taken as occupying the same crystallographic site. To maintain consistency across the series, all refinements were carried out in the conventional apatite space group $P6_3/m$, but potential deviations to lower symmetry were considered.

4.3.2 Time-of-flight Neutron Powder Diffraction

Powder neutron diffraction (PND) data was acquired at the Science and Technology Facilities Council, Rutherford Appleton Laboratory (United Kingdom) using the high resolution powder diffractometer (HRPD) with $\Delta d/d$ resolution of 4×10^{-4} at room temperature. The diffractometer was equipped with ZnS-scintillator detectors in the equatorial and vertical planes that may be decoupled from the Debye-Scherrer geometry. HRPD collects three sets of data in a single scan; 90°, low angle and backscattered neutron. A vanadium cylindrical sample container (8mm diameter) was used during the measurement. All neutron data (backscattering) were analyzed using

GSAS [64] with an instrumental resolution file provided by ISIS serving to model the Bragg reflection peak shapes.

Many of the lanthanide elements are strong neutron absorbers, and to avoid significant activation, only the least absorbing Pr, Nd, Tb Ho and Yb britholites were studied. Yb has high chemical similarity with Lu and half of neutron absorption than Lu; hence Yb is a good candidate to extract the possibly same information as Lu with less associated risk. Refinements were carried out in a similar manner to the powder XRD, but because neutrons are point scatterers and more sensitive to oxygen, it was possible to refine the atomic positions with anisotropic displacement parameters (ADPs). To maintain consistency between the XRD and PND refinements the *REE*/Ca cation distributions across the two *A* cation acceptor sites were fixed at those determined from the XRD refinements, where Ca is readily distinguished from REE due to the large difference in X-ray form factors. Table 4.2 listed the coherent and incoherent neutron scattering lengths and cross sections of the selected lanthanides and Lu.

Table 4.2: Coherent and incoherent neutron scattering lengths and cross sections for Ca, Pr, Nd, Tb, Ho, Yb and Lu.

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
Ca	---	4.7	---	2.78	0.05	2.83	0.43
Pr	100	4.58	-0.35	2.64	0.015	2.66	11.5
Nd	---	7.69	---	7.43	9.2	16.6	50.5(1.2)
Tb	100	7.38	-0.17	6.84	0.004	6.84	23.4
Ho	100	8.01	-1.7	8.06	0.36	8.42	64.7(1.2)
Yb	---	12.43	---	19.42	4	23.4	34.8
Lu	---	7.21	---	6.53	0.7	7.2	74

4.4 Results and Discussion

4.4.1 Crystal Chemistry – PXRD

PXRD confirmed the incorporation of all trivalent REE elements with ionic radii ranging from Pr^{3+} (0.99Å) to Lu^{3+} (0.861Å) (all ionic radii are from Shannon's work [65], for coordination number 6). Within the limits of detection (~1 wt%), the products were single phase for Nd through to Ho, while Pr apatite coexisted with low cristobalite (SiO_2) (< 6wt%). The smaller lanthanide britholites i.e. Er, Tm, Yb and Lu always appeared with $\text{RE}_2\text{Si}_2\text{O}_7$ (c.f. $\text{Yb}_2\text{Si}_2\text{O}_7$ keivyite in *C1/m*), which became more

abundant (7 to 42 wt%) as the lanthanide became smaller (see Table 4.3). Rietveld method was used for quantitative analysis. No obvious deviation from hexagonal symmetry was observed in any samples and Bragg reflections were consistent with $P6_3/m$ symmetry. However, as discussed below, subtle departures from the hexagonal metric are detected by the observation of unusual atomic displacement parameters and/or unexpected departures from predicted metaprisism twist angle trends.

Table 4.3: Refined lattice parameters, cation stoichiometries and refinement reliability parameters determined from powder X-ray diffraction.

Refined Cation Distributions	PXRD					
	<i>a</i>	<i>c</i>	Vol	<i>R_{wp}</i>	<i>R_{Bragg}</i>	GoF
[Pr ₂ Ca ₂] ^I [Pr ₆] ^{II}	9.5598(2)	7.0556(2)	558.42(3)	20.24	9.04	1.40
[Nd _{2.17} Ca _{1.43} □ _{0.40}] ^I [Nd _{5.43} Ca _{0.57}] ^{II}	9.5270(4)	7.0200(3)	551.80(5)	11.31	3.42	1.36
[Sm _{2.23} Ca _{1.28} □ _{0.49}] ^I [Sm _{5.28} Ca _{0.72}] ^{II}	9.4697(1)	6.9487(1)	539.64(1)	12.29	5.42	1.41
[Eu _{2.18} Ca _{1.38} □ _{0.44}] ^I [Eu _{5.38} Ca _{0.62}] ^{II}	9.4437(2)	6.9181(2)	534.32(2)	16.41	3.24	1.11
[Gd _{2.16} Ca _{1.56} □ _{0.28}] ^I [Gd _{5.56} Ca _{0.44}] ^{II}	9.4190(8)	6.8904(6)	529.40(1)	13.57	2.19	1.09
[Tb _{2.22} Ca _{1.46} □ _{0.32}] ^I [Tb _{5.46} Ca _{0.54}] ^{II}	9.3872(1)	6.8517(1)	522.87(2)	8.99	1.64	1.15
[Dy _{2.23} Ca _{1.15} □ _{0.62}] ^I [Dy _{5.15} Ca _{0.85}] ^{II}	9.3685(1)	6.8236(1)	518.66(1)	9.79	1.70	1.15
[Ho _{2.22} Ca _{1.58} □ _{0.20}] ^I [Ho _{5.58} Ca _{0.42}] ^{II}	9.3437(1)	6.7932(1)	513.62(2)	10.88	2.07	1.16
[Er _{2.35} Ca _{1.65}] ^I [Er _{5.65} Ca _{0.35}] ^{II*}	9.3227(5)	6.7633(4)	509.06(7)	13.06	5.12	1.46
[Tm _{2.27} Ca _{1.55} □ _{0.18}] ^I [Tm _{5.55} Ca _{0.45}] ^{II*}	9.3075(2)	6.7319(1)	505.05(3)	10.10	5.14	2.41
[Yb _{2.28} Ca _{1.55} □ _{0.17}] ^I [Yb _{5.55} Ca _{0.45}] ^{II*}	9.2944(1)	6.6990(1)	501.18(2)	12.32	2.03	1.15
[Lu _{2.35} Ca _{1.55} □ _{0.10}] ^I [Yb _{5.55} Ca _{0.45}] ^{II*}	9.2887(1)	6.6742(1)	498.70(1)	9.29	2.62	2.40

* The Er, Tm Yb and Lu apatite phases co-existed with REE₂Si₂O₇ with a weight % of 7.80%, 27.07%, 32.72% and 42.64% respectively.

Figure 4.2: Variation with REE size of (a) lattice parameter, a -axis and c -axis; and (b) unit cell volume. Diamonds (PXRD) and crosses (PND) are from the current work, while triangles are those of Ito, 1968.

Figure 4.2a shows that the unit cell parameters contract linearly in passing from light to heavy *REE* in accordance with the relative ionic radii, such that the c -axis changes somewhat more rapidly, possibly due to the site preference of rare earth elements for the $6h$ site. Plotting unit cell volume against ionic radii (Figure 4.2b) for each lanthanide shows a discontinuity for Er ($a = 9.3227\text{\AA}$, $c = 6.7633\text{\AA}$) that coincides

with the appearance of the secondary $\text{REE}_2\text{Si}_2\text{O}_7$, $\text{REE} > \text{Er}$ phase, and is possibly indicative of a change in britholite symmetry consistent with previous work [2].

In order to investigate the distribution of the REE ions across the two available cation acceptor sites Rietveld analyses were performed. Initially refinements were carried out assuming the A^{I} and A^{II} sites were fully occupied by both REE and Ca, however, this procedure always resulted in an overall Ca stoichiometry > 2 . This was initially puzzling because Ca was added stoichiometrically to arrive at ideal formulae of $\text{REE}_8\text{Ca}_2(\text{SiO}_4)_6\text{O}_2$. As none of the reagents were volatile, the “excess” Ca cannot be rationalised through mass balance with $\text{REE}_2\text{Si}_2\text{O}_7$. However, recent work on silicate and germanate electrolyte apatites such as $\text{REE}_{9.33}(\text{BO}_4)_6\text{O}_2$ ($\text{REE} = \text{La}$ and Nd ; $B = \text{Si}$ or Ge) has revealed vacancies at the $4f$ A^{I} site [66]. If REE , Ca and vacancies are coincident on the $4f$ site and the total occupancy of REE and Ca were constrained to equal 100% (without considering vacancies), then the apparent scattering could be rationalised (incorrectly) by increasing the amount of Ca. Therefore, the refinement strategy was modified to allow for framework vacancies and ensure the total Ca content agrees with the nominal synthetic composition. REE deficiencies have never been reported at the $6h$ site and so REE and Ca content refined at the A^{II} site is correct [67]. Therefore, refinements were initially carried out as described previously with both sites containing REE and Ca and their occupancy constrained to be fully tenanted to determine Ca content at the $6h$ site, and once established, the remaining Ca required for the ideal Ca stoichiometry of 2 per unit cell was placed at the $4f$ site. The Ca occupancies were then fixed at $6h$ and $4f$ and the REE occupancy in the framework refined to investigate $4f$ vacancy concentration. Using this procedure, all data converged to excellent fits and the refined crystal data are presented in Tables 4.4 (a, b), with selected bond lengths (Table 4.5) and refined stoichiometry (Table 4.3) also collated. Two typical refined profiles are shown in Figure 4.3.

It is clear that all britholites, with the exception of the Pr compound, contain minor Ca at the $6h$ position; however there is a clear preference to the $4f$ site. All samples were annealed a similar way ($1500^\circ\text{C}/24\text{hr}$) and it is possible that complete partitioning of Ca to the $4f$ site could be achieved with extended treatment as found in $(\text{Ca}_5\text{Pb}_5)(\text{VO}_4)_6\text{F}_2$ apatites [68]. The Pr phase uniquely showed no evidence of $4f$

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vacancies; however, it is possible that $\text{Pr}^{3+}/\text{Pr}^{4+}$ mixed valency could modify the structure and perturb the refinement strategy. An unusual observation is that although synthesised in the same manner as the other REE britholites, the Pr sample gave the lowest overall count rate during XRD and the highest standard uncertainties in the refined parameters. This may reflect structural disorder induced by $\text{Pr}^{3+}/\text{Pr}^{4+}$ disproportion, but confirmation would require X-ray photoelectron spectroscopy.

Table 4.4a: PXRD refinements for $[\text{Ca}_2\text{REE}_8][(\text{SiO}_4)_6][\text{O}_2]$ with REE = Pr, Nd, Sm, Eu, Gd and Tb.

Composition <i>REE</i>	Pr	Nd	Sm	Eu	Gd	Tb
<i>A^I</i> (1), 4 <i>f</i> (1/3, 2/3, <i>z</i>)						
<i>Z</i>	0.9885(11)	0.9997(5)	0.9975(6)	0.0007(9)	0.9985(10)	0.0001(6)
Occ. Fac. (Ca)	0.500	0.358	0.320	0.345	0.390	0.365
<i>Beq</i>	0.5(1)	0.2(1)	0.3(1)	0.3(1)	0.2(1)	0.4(1)
<i>A^{II}</i> (2), 6 <i>h</i> (<i>x</i> , <i>y</i> , 1/4)						
<i>x</i>	0.2330(3)	0.2323(1)	0.2334(2)	0.2326(2)	0.2328(2)	0.2326(2)
<i>y</i>	0.9889(5)	0.9893(2)	0.9921(2)	0.9911(3)	0.9919(4)	0.9929(2)
Occ. Fac. (Ca)	0	0.094(1)	0.119(2)	0.104(5)	0.074(4)	0.091(3)
<i>Beq</i>	0.5(1)	0.2(1)	0.3(1)	0.5(1)	0.3(1)	0.1(1)
<i>Si</i> , 6 <i>h</i> (<i>x</i> , <i>y</i> , 1/4)						
<i>x</i>	0.410(2)	0.4002(6)	0.4011(7)	0.4001(8)	0.4015(10)	0.3992(6)
<i>y</i>	0.382(2)	0.3720(6)	0.3711(7)	0.3707(9)	0.3726(10)	0.3728(6)
<i>Beq</i>	2.3(4)	0.5(1)	0.3(1)	0.3(1)	0.2(1)	0.4(1)
<i>O</i> (1), 6 <i>h</i> (<i>x</i> , <i>y</i> , 1/4)						
<i>x</i>	0.351(4)	0.3210(11)	0.3232(13)	0.321(2)	0.315(2)	0.3157(12)
<i>y</i>	0.517(4)	0.4923(12)	0.4895(14)	0.488(2)	0.484(2)	0.4890(12)
<i>Beq</i>	0.5(4)	0.4(1)	0.3(1)	0.5(2)	0.3(1)	0.7(1)
<i>O</i> (2), 6 <i>h</i> (<i>x</i> , <i>y</i> , 1/4)						
<i>x</i>	0.591(4)	0.5952(12)	0.6011(15)	0.597(2)	0.603(2)	0.5989(13)
<i>y</i>	0.477(4)	0.4671(12)	0.4666(14)	0.471(2)	0.447(2)	0.4687(12)
<i>Beq</i>	0.5(4)	0.4(1)	0.3(1)	0.5(2)	0.3(1)	0.7(1)
<i>O</i> (3), 12 <i>i</i> (<i>x</i> , <i>y</i> , <i>z</i>)						
<i>x</i>	0.330(2)	0.3487(7)	0.3401(9)	0.3399(12)	0.3393(12)	0.3379(7)
<i>y</i>	0.245(2)	0.2627(8)	0.2516(9)	0.2518(13)	0.2488(13)	0.2474(8)
<i>z</i>	0.076(2)	0.0666(8)	0.0666(9)	0.0673(14)	0.0665(14)	0.0672(9)
<i>Beq</i>	0.5(4)	0.4(1)	0.3(1)	0.5(2)	0.3(1)	0.7(1)
<i>O</i> (4), 2 <i>a</i> (0, 0, 1/4)						
<i>Beq</i>	0.5(4)	0.4(1)	0.3(1)	0.5(2)	0.3(1)	0.7(1)

*Due to the strong scattering by *REE*, the oxygen occupancies are not possible to be refined; hence fixed as full occupancy, 1.

Table 4.4b: PXRD refined atomic positions for $[\text{Ca}_2\text{RE}_8][(\text{SiO}_4)_6][\text{O}_2]$ with RE = Dy, Ho, Er, Tm, Yb and Lu.

Composition <i>REE</i>	Dy	Ho	Er	Tm	Yb	Lu
$A^{\text{I}}(1), 4f \ (1/3, 2/3, z)$						
<i>z</i>	0.9993(6)	0.0012(6)	0.9973(19)	0.9998(13)	0.0038(13)	0.0058(9)
Occ. Fac. (Ca)	0.288	0.395	0.413	0.388	0.388	0.388
<i>Beq</i>	0.15(4)	0.63(5)	0.7(1)	1.8(1)	0.2(1)	0.4(1)
$A^{\text{II}}(2), 6h \ (x, y, 1/4)$						
<i>x</i>	0.2331(2)	0.2336(2)	0.2345(5)	0.2348(3)	0.2357(3)	0.2369(2)
<i>y</i>	0.9943(3)	0.9956(3)	0.3772(8)	0.9994(5)	0.0021(5)	0.0040(4)
Occ. Fac. (Ca)	0.142(2)	0.071(1)	0.053(2)	0.075(1)	0.075(1)	0.075(1)
<i>Beq</i>	0.1(1)	0.26(3)	0.1(1)	1.1(1)	0.1(1)	0.1(1)
$\text{Si}, 6h \ (x, y, 1/4)$						
<i>x</i>	0.3997(6)	0.3997(5)	0.4026(17)	0.4020(11)	0.3950(12)	0.3998(11)
<i>y</i>	0.3731(6)	0.3722(5)	0.4947(17)	0.3687(11)	0.3747(13)	0.3761(11)
<i>Beq</i>	0.3(1)	0.4(1)	0.3(1)	0.2(2)	0.4(1)	0.8(2)
$\text{O}(1), 6h \ (x, y, 1/4)$						
<i>x</i>	0.3110(12)	0.3106(11)	0.315(3)	0.314(2)	0.326(2)	0.3215(19)
<i>y</i>	0.4841(12)	0.4827(11)	0.495(3)	0.487(2)	0.489(2)	0.4843(18)
<i>Beq</i>	0.5(1)	0.9(1)	0.5(3)	0.7(2)	0.1(2)	0.1(2)
$\text{O}(2), 6h \ (x, y, 1/4)$						
<i>x</i>	0.5996(13)	0.5971(11)	0.594(3)	0.593(2)	0.604(2)	0.605(2)
<i>y</i>	0.4677(12)	0.4700(11)	0.594(3)	0.474(2)	0.475(2)	0.4814(17)
<i>Beq</i>	0.5(1)	0.9(1)	0.5(3)	0.7(2)	0.1(2)	0.1(2)
$\text{O}(3), 12i \ (x, y, z)$						
<i>x</i>	0.3392(7)	0.3370(7)	0.3470(16)	0.3454(12)	0.3344(12)	0.3310(10)
<i>y</i>	0.2483(8)	0.2464(7)	0.2537(18)	0.2578(13)	0.2486(14)	0.2442(12)
<i>z</i>	0.0623(8)	0.0655(8)	0.070(2)	0.0630(15)	0.0608(15)	0.0677(13)
<i>Beq</i>	0.5(1)	0.9(1)	0.5(3)	0.7(2)	0.1(2)	0.1(2)
$\text{O}(4), 2a \ (0, 0, 1/4)$						
<i>Beq</i>	0.5(1)	0.9(1)	0.5(3)	0.7(2)	0.1(2)	0.1(2)

*Due to the strong scattering by *REE*, the oxygen occupancies are not possible to be refined; hence fixed as full occupancy, 1.

Table 4.5: Selected bond lengths and angles from the powder XRD refinements.

Bond	Distance (Å)					
	Pr	Nd	Sm	Eu	Gd	Tb
A ^I -O(1)	2.39(3)	2.381(9)	2.396(10)	2.372(15)	2.390(15)	2.338(9)
A ^I -O(2)	2.50(3)	2.455(1)	2.392(12)	2.449(18)	2.369(18)	2.401(11)
A ^I -O(3)	2.92(2)	2.794(7)	2.823(8)	2.821(12)	2.808(12)	2.810(7)
A ^{II} -O(1)	2.98(3)	2.712(9)	2.724(10)	2.689(15)	2.643(15)	2.663(9)
A ^{II} -O(2)	2.41(3)	2.483(10)	2.461(11)	2.425(17)	2.453(17)	2.431(9)
A ^{II} -O(3)	2.43(2)	2.397(6)	2.363(7)	2.355(10)	2.345(10)	2.338(6)
	2.47(2)	2.605(7)	2.490(8)	2.488(11)	2.456(11)	2.427(7)
A ^{II} -O(4)	2.282(4)	2.266(1)	2.249(2)	2.240(2)	2.231(3)	2.2171(18)
Si-O(1)	1.64(5)	1.657(15)	1.620(18)	1.62(3)	1.61(3)	1.631(16)
Si-O(2)	1.51(4)	1.609(11)	1.641(13)	1.610(18)	1.65(2)	1.624(12)
Si-O(3)	1.68(2)	1.572(7)	1.608(8)	1.595(11)	1.618(11)	1.615(7)

Angle	°					
	Pr	Nd	Sm	Eu	Gd	Tb
O(1)-Si-O(3)	114.6(6)	111.0(3)	111.1(3)	110.9(4)	110.4(4)	111.9(7)
O(1)-Si-O(2)	105.7(2)	114.1(7)	114.7(8)	113.0(9)	118.1(9)	115.9(7)
O(3)-Si-O(3)	94.2(8)	109.9(6)	104.9(3)	104.8(5)	102.7(5)	101.7(3)
O(3)-Si-O(2)	113.9(6)	105.2(4)	107.3(3)	108.4(4)	107.0(4)	107.2(3)

Bond	Distance (Å)					
	Dy	Ho	Er	Tm	Yb	Lu
A ^I -O(1)	2.353(9)	2.343(8)	2.29(2)	2.315(16)	2.309(16)	2.314(14)
A ^I -O(2)	2.380(10)	2.408(9)	2.38(3)	2.436(19)	2.396(18)	2.434(16)
A ^I -O(3)	2.789(7)	2.802(6)	2.726(16)	2.741(11)	2.813(12)	2.840(9)
A ^{II} -O(1)	2.625(9)	2.621(8)	2.69(2)	2.678(16)	2.772(16)	2.745(13)
A ^{II} -O(2)	2.431(9)	2.403(9)	2.41(2)	2.357(16)	2.334(16)	2.274(13)
A ^{II} -O(3)	2.305(6)	2.314(6)	2.361(15)	2.305(10)	2.261(11)	2.296(9)
	2.434(7)	2.403(9)	2.412(16)	2.440(11)	2.366(12)	2.296(10)
A ^{II} -O(4)	2.2105(19)	2.204(2)	2.267(6)	2.188(4)	2.182(3)	2.182(3)
Si-O(1)	1.624(15)	1.617(14)	1.66(4)	1.67(3)	1.49(3)	1.51(2)
Si-O(2)	1.623(11)	1.597(10)	1.55(3)	1.54(2)	1.68(2)	1.651(19)
Si-O(3)	1.633(7)	1.615(6)	1.573(17)	1.544(11)	1.624(12)	1.614(11)

Angle	°					
	Dy	Ho	Er	Tm	Yb	Lu
O(1)-Si-O(3)	110.9(2)	110.5(2)	113.1(6)	109.0(9)	113.4(4)	111.5(4)
O(1)-Si-O(2)	118.1(7)	116.8(7)	117.0(2)	111.5(1)	113.2(1)	113.8(1)
O(3)-Si-O(3)	103.3(2)	101.8(2)	101.2(7)	109.2(5)	102.3(5)	97.8(4)
O(3)-Si-O(2)	106.5(2)	108.1(2)	105.5(6)	109.1(4)	106.8(4)	110.6(4)

Figure 4.3: Rietveld profiles of PXRD patterns, showing the observed pattern (blue), the calculated pattern (red) and the difference profile (grey), (a) $\text{Ho}_8\text{Ca}_2(\text{SiO}_4)_6\text{O}_2$ and (b) $\text{Yb}_8\text{Ca}_2(\text{SiO}_4)_6\text{O}_2$ with upper tick marks for britholite and the lower for $\text{Yb}_2\text{Si}_2\text{O}_7$.

4.4.2 Crystal Chemistry – Powder Neutron Diffraction

Using the refined cation distributions determined from the powder XRD study all the TOF neutron data could be refined in the hexagonal space group $P6_3/m$ to yield excellent fits. The refined atomic positions and anisotropic displacement parameters are shown in Tables 4.6 and 4.7, with selected bond lengths and angles also collated (Table 4.8). A typical refinement profile is shown in Figure 4.4.

The diffractometer at the ISIS facility UK is currently the highest resolution instrument of its type in the world, and therefore, significant deviations from hexagonal symmetry should be easily detected. Inspection of the diffraction patterns showed no obvious splitting of the Bragg reflections or anisotropic broadening indicative of a reduction in symmetry. The clearest evidence for symmetry change comes from the anisotropic displacement parameters of the Yb/Ca-britholite, which gave non-positive definitive values for the A^{II} (6h) and Si sites. However, without further evidence for a reduction in symmetry, refinements in lower symmetry space groups would be inconclusive, as R values will appear to improve simply due to the greater number of refineable parameters. Nonetheless, these unusual ADPs do warrant further investigation, possibly via electron diffraction which could probe smaller volumes for evidence of disequilibrium, nanodomains or incommensuration.

Figure 4.4: Rietveld profile of TOF PND backscattering pattern (pattern shown - $\text{Ca}_2\text{Tb}_8(\text{SiO}_4)_6\text{O}_2$) with the observed pattern shown as black crosses, the background in green, the calculated pattern in red and the difference profile in blue.

Table 4.6: PND crystallographic data for $[\text{Ca}_2\text{REE}_8][(\text{SiO}_4)_6][\text{O}_2]$ with REE = Pr, Nd, Tb, Ho and Yb.

Composition REE	Pr	Nd	Tb	Ho	Yb
Ca(1), $4f$ (1/3, 2/3, z)					
z	0.0018(4)	-0.0003(2)	0.00062(16)	0.00095(18)	0.0016(2)
Occ. Fac. (Ca)	0.50	0.358	0.365	0.395	0.388
<i>Uiso</i>	0.011*	0.009*	0.001*	0.011*	0.007*
Ca(2), $6h$ (x , y , 1/4)					
x	0.2320(3)	0.23190(12)	0.23291(9)	0.23344(9)	0.23444(9)
y	0.9886(3)	0.98929(15)	0.99410(12)	0.99586(12)	0.00036(13)
Occ. Fac. (Ca)	0	0.095	0.091	0.071	0.075
<i>Uiso</i>	0.009*	0.005*	0.0005*	0.005*	0.0003*
Si, $6h$ (x , y , 1/4)					
x	0.4019(3)	0.4010(2)	0.39936(18)	0.3977(2)	0.3976(3)
y	0.3737(3)	0.3706(2)	0.37128(15)	0.37130(16)	0.3707(2)
<i>Uiso</i>	0.002*	0.010*	0.004*	0.007*	0.003*
O(1), $6h$ (x , y , 1/4)					
x	0.3242(2)	0.32304(17)	0.31753(13)	0.31715(15)	0.3180(2)
y	0.4893(2)	0.48856(17)	0.48687(12)	0.48693(14)	0.4888(2)
<i>Uiso</i>	0.008*	0.013*	0.011*	0.015*	0.011*
O(2), $6h$ (x , y , 1/4)					
x	0.5966(2)	0.59778(19)	0.59823(13)	0.60013(15)	0.6007(2)
y	0.4709(3)	0.47106(19)	0.47302(12)	0.47436(14)	0.4746(2)
<i>Uiso</i>	0.011*	0.015*	0.008*	0.012*	0.010*
O(3), $12i$ (x , y , z)					
x	0.34100(18)	0.34151(13)	0.33923(10)	0.33819(11)	0.33775(15)
y	0.25310(16)	0.25251(14)	0.24974(10)	0.24845(11)	0.24828(16)
z	0.06772(13)	0.06687(11)	0.06234(8)	0.06104(9)	0.05996(14)
<i>Uiso</i>	0.017*	0.020*	0.012*	0.016*	0.011*
O(4), $2a$ (0 , 0 , 1/4)					
<i>Uiso</i>	0.016*	0.023*	0.010*	0.014*	0.001*

* see tables of anisotropic displacement parameters

*Due to the strong scattering by REE, the oxygen occupancies are not possible to be refined; hence fixed as full occupancy, 1.

*Britholite Apatites for the Incorporation of Rare Earth Fission Products Chapter 4***Table 4.7:** Refined anisotropic displacement parameters for $[\text{Ca}_2\text{REE}_8][(\text{SiO}_4)_6][\text{O}_2]$ with REE = Pr, Nd, Tb, Ho and Yb.

Pr/Ca	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A^{I}	0.0121(10)	0.0121(10)	0.0095(10)	0.0060(5)	0	0
A^{II}	0.0106(10)	0.0077(15)	0.0081(10)	0.0052(10)	0	0
Si	0.0016(15)	0.0018(15)	0.0042(15)	-0.0015(13)	0	0
O(1)	0.0150(13)	0.0045(14)	0.0082(12)	0.0081(10)	0	0
O(2)	0.0072(13)	0.0067(12)	0.0192(13)	0.0040(10)	0	0
O(3)	0.0349(12)	0.0112(11)	0.0070(9)	0.0129(8)	-0.0092(6)	-0.0038(5)
O(4)	0.0121(10)	0.0121(10)	0.0095(10)	0.0060(5)	0	0

Nd/Ca	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A^{I}	0.0076(4)	0.0076(4)	0.0110(4)	0.00379(19)	0	0
A^{II}	0.018(4)	0.0046(7)	0.0052(4)	0.0001(4)	0	0
Si	0.0101(10)	0.0028(11)	0.0118(10)	0.0004(9)	0	0
O(1)	0.0180(9)	0.0123(11)	0.0121(9)	0.0121(8)	0	0
O(2)	0.0121(9)	0.0088(7)	0.0246(9)	0.0048(8)	0	0
O(3)	0.0377(8)	0.0163(6)	0.0114(4)	0.0165(5)	-0.0088(5)	-0.0048(4)
O(4)	0.0143(8)	0.0143(8)	0.0409(16)	0.0071(4)	0	0

Tb/Ca	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A^{I}	0.0035(5)	0.0035(5)	-0.0038(5)	0.0018(2)	0	0
A^{II}	0.0008(5)	0.0022(6)	-0.0012(5)	0.0011(4)	0	0
Si	0.0016(9)	0.0028(9)	0.0065(9)	0.0005(7)	0	0
O(1)	0.0180(8)	0.0104(8)	0.0100(7)	0.0120(6)	0	0
O(2)	0.0054(8)	0.0068(7)	0.0112(7)	0.0015(6)	0	0
O(3)	0.0222(6)	0.0099(6)	0.0062(5)	0.0090(4)	-0.0077(3)	-0.0040(3)
O(4)	0.0035(7)	0.035(7)	0.0232(12)	0.0017(4)	0	0

Ho/Ca	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A^{I}	0.0106(3)	0.0106(3)	0.0105(3)	0.00528(15)	0	0
A^{II}	0.0036(3)	0.0020(3)	0.0035(3)	0.0020(3)	0	0
Si	0.0040(8)	0.0047(8)	0.0114(9)	0.0020(7)	0	0
O(1)	0.0199(7)	0.0159(8)	0.0155(7)	0.0140(6)	0	0
O(2)	0.0073(7)	0.0065(6)	0.0188(7)	0.0018(6)	0	0
O(3)	0.0294(5)	0.0124(5)	0.0082(3)	0.0116(4)	-0.0067(4)	-0.0034(4)
O(4)	0.0036(3)	0.0076(4)	0.0035(3)	0.0020(3)	0	0

Yb/Ca	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
A^{I}	0.0072(4)	0.0072(4)	0.0063(4)	0.0036(2)	0	0
A^{II}	0.0006(4)	0.0006(5)	-0.0003(4)	-0.0017(4)	0	0
Si	-0.0017(12)	-0.0025(12)	0.0089(13)	-0.0043(10)	0	0
O(1)	0.0231(11)	0.0090(12)	0.0143(11)	0.0171(10)	0	0
O(2)	0.0087(10)	0.0017(10)	0.0168(12)	0.0012(9)	0	0
O(3)	0.0194(8)	0.0086(7)	0.0051(6)	0.0077(6)	-0.0089(5)	-0.0069(5)
O(4)	0.0006(4)	0.0006(5)	0.0254(17)	0.0004(4)	0	0

Table 4.8: Selected bond lengths and angles derived from powder neutron diffraction data.

Bond	Distance (Å)				
	Pr	Nd	Tb	Ho	Yb
A ^I -O(1)	2.408(2)	2.4107(15)	2.3542(10)	2.3348(11)	2.2995(15)
A ^I -O(2)	2.493(3)	2.4666(16)	2.4338(11)	2.4176(12)	2.3973(16)
A ^I -O(3)	2.8528(15)	2.8323(11)	2.8006(8)	2.7914(8)	2.7802(12)
A ^{II} -O(1)	2.728(4)	2.716 (2)	2.6779(16)	2.6770(16)	2.713(2)
A ^{II} -O(2)	2.462(3)	2.4534(17)	2.3959(12)	2.3687(12)	2.3494(17)
A ^{II} -O(3)	2.3976(13)	2.3848(9)	2.3118(6)	2.2877(7)	2.2657(10)
	2.550(3)	2.5325(16)	2.4526(11)	2.4214(11)	2.3752(15)
A ^{II} -O(4)	2.275(2)	2.2625(10)	2.2151(7)	2.2003(6)	2.1777(6)
Si-O(1)	1.611(3)	1.628(3)	1.6131(18)	1.595(2)	1.602(3)
Si-O(2)	1.613(3)	1.624(3)	1.6173(18)	1.638(2)	1.636(3)
Si-O(3)	1.6284(19)	1.6128(16)	1.6217(11)	1.6234(12)	1.6099(17)

Angle °					
	Pr	Nd	Tb	Ho	Yb
O(1)-Si-O(3)	111.22(10)	110.94(8)	110.98(7)	111.59(8)	111.72(11)
O(1)-Si-O(2)	113.59(17)	113.00(13)	113.60(9)	113.50(10)	112.78(13)
O(3)-Si-O(3)	104.33(14)	105.50(12)	104.90(8)	104.48(9)	104.52(14)
O(3)-Si-O(2)	107.99(11)	108.06(9)	107.97(6)	107.59(7)	107.84(11)

4.4.3 Metaprism Twist Angle Diagnostics

Using the techniques described in Chapter 3, the metaprism twist angle has been used to interrogate the britholite refinements. The twist angles for the XRD and PND are somewhat similar for the light rare earth britholites, but diverge substantially for REE heavier than Dy. However, neutron diffraction is expected to be more accurate because of the greater sensitivity to oxygen, and the high resolution of the data. Unfortunately, because of substantial neutron absorbance for several lanthanides there are a limited number of points for this series, however inspection of the twist angle trends (Figure 4.5) shows it reaches a maximum of $\sim 23.4^\circ$ before decreasing; previous work suggests this value of ϕ is near the highest observed in $P6_3/m$ apatites, after which there is distortion to lower symmetry variants. Typically, hexagonal apatites are reduced to triclinic symmetry via rotation of the BO_4 tetrahedra that is accompanied by tetrahedral distortions. To date, triclinic symmetry has only been found in apatites containing As, V, Ge and P [69], but a Si analogue has never been observed, possibly due to SiO_4 rigidity and its reluctance to vary its coordination sphere. It is however possible, that Si apatites lower their symmetry via alternative routes, for example, by forming a supercell such as that described for Cd containing

phosphates [70], which contain twist angles of a similar magnitude to the britholites. An unrecognised supercell may explain the unusual ADPs for the Yb britholite. Selected area electron diffraction or single crystal X-ray diffraction would be required to confirm the existence of such a supercell. If Si apatites cannot readily change symmetry, this may explain why the Er, Tm, Yb and Lu compounds co-exist with secondary phases. These $\text{REE}_2\text{Si}_2\text{O}_7$ appear increasingly as the framework and tunnel mismatch grows larger, possibly because the silicate apatites cannot adopt twist angles $> 23.4^\circ$ to relieve internal stress by distortion. The XRD data give twist angles $> 25^\circ$ for the Dy, Ho, Er and Tm members, however these results are considered unreliable, structural distortion is expected, and inspection of the standard uncertainties in the Si-O bond lengths are unacceptably high. The most extreme deviation between the twist angles for the XRD and neutron data is found for the Pr member and may reflect mixed valency of $\text{Pr}^{3+}/\text{Pr}^{4+}$. X-rays will be more sensitive to the Pr coordination sphere as neutrons are point scatterers whereas X-rays diffract from the electron potential; if there is mixed $\text{Pr}^{3+}/\text{Pr}^{4+}$ valence the X-ray form factors will vary significantly. This would also be consistent with the higher standard uncertainties in the Pr-O bond lengths compared to other britholites studied by XRD. Table 4.9 compares the calculated metaprisim twist angles from XRD and ND.

Table 4.9: Calculated metaprisim twist angles derived from both powder XRD and neutron diffraction data, together with partitioning coefficients.

	XRD		PND
	ϕ ($^\circ$)	ϕ ($^\circ$)	k_{REE}^*
Pr	14.1 ₅	21.9 ₉	0.33
Nd	23.6 ₈	22.0 ₃	0.47
Sm	21.8 ₀		
Eu	22.9 ₄		
Gd	23.5 ₉		
Tb	24.2 ₉	23.3 ₆	0.47
Dy	25.5 ₅		
Ho	25.8 ₉	22.9 ₆	0.43
Er	25.6 ₄		
Tm	25.4 ₃		
Yb	19.6 ₀	22.5 ₈	0.44
Lu	19.9 ₀		

$$*k_{\text{REE}} = \frac{2}{3} \times (\text{occ.REE in 4f} / \text{occ. REE in 6h})$$

Figure 4.5: Twist angles derived from powder XRD (blue diamonds) and neutron diffraction (red squares) where the region highlighted in red is where secondary $REE_2Si_2O_7$ phases occur and where structural distortion is observed.

4.5 Conclusions and Implications for HLW Stabilization

It has been found that $[Ca_2REE_8][(SiO_4)_6][F_2]$ britholites were prepared with ease by solid state reactions, except for erbium, thulium, ytterbium and lutetium where $REE_2Si_2O_7$ becomes increasingly prevalent for heavier REEs. Generally, rare earth britholites are hexagonal $P6_3/m$ with REEs preferentially partitioned to the $6h$ site regardless of the ionic radii. However, a change in symmetry for the small REEs cannot be discounted. From the point of view of tailoring apatite wasteforms, it is significant that substantial vacancies in the framework are common (i.e. $[Ca_2REE_{1.66}\square_{0.33}][REE_6][(SiO_4)_6][O_{1.33}]$ ideally). In mixed fission product wasteform apatites such departures in stoichiometry must be corrected for during development of precursors. In particular, care will be needed to avoid the formation of non durable secondary phases.

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Chapter 5

Thorium Britholite as an Analogue for a Tetravalent Transuranic Wasteform

Investigation of the solid state chemistry of the actinides uranium, neptunium and plutonium is strictly regulated and can only be conducted in hot cell facilities or glove boxes. Uranium, neptunium and plutonium are commonly tetravalent (U^{4+} , Np^{4+} , Pu^{4+}) and their behaviour is mimicked by Th^{4+} , which although radioactive, is far less hazardous. As Th^{4+} ($0.94\text{\AA}$) is larger than U^{4+} ($0.89\text{\AA}$), Np^{4+} ($0.87\text{\AA}$) and Pu^{4+} ($0.86\text{\AA}$), its incorporation in britholite provides a conservative estimate of the solid solubility of tetravalent transuranic elements.

5.1 Actinide Simulants for Ceramic Wasteforms

Commonly, transuranic nuclides are trivalent (esp. Cm^{3+} , Am^{3+}) or tetravalent (Np^{4+} , Pu^{4+}) in oxides. However, investigating the mechanisms for incorporating these species in HLW ceramics requires hot cell facilities or glove boxes and strict safeguards. These factors necessitate that wasteform prototyping is conducted with non-radioactive, or slightly radioactive, simulants to validate synthesis and processing procedures. In Chapter 4, the mechanisms for trivalent rare earth fixation in britholites were explored, and while principally concerned with fission product incorporation, these materials also serve as analogues for the small, heavy trivalent transuranics.

Detailed crystallochemical studies of britholite-type apatites are quite limited, however, as the collation in Table 5.1 shows the available data suggest that distortion from hexagonal may be common. While $P2_1$, $P2_1/m$ and $P-1$ are the maximal isomorphic subgroups available, it appears that the former is commonly adopted, although this is concluded from only two investigations. However, these structure determinations are expected to be reliable as all twist angles – three per distorted metaprisms – are within acceptable ranges. Within the context of nuclear waste management, it would be valuable to expand these studies across extended solid solution experiments. For example, Obert *et al.* [15] examined $(\text{Y}_{8.96}\text{Ca}_{0.40}\text{Lu}_{0.64})(\text{SiO}_4)_6\text{F}(\text{OH})$ and $(\text{Y}_{9.26}\text{Ca}_{0.46}\text{Lu}_{0.28})(\text{SiO}_4)_6\text{F}(\text{OH})$, but the synthesis and structural characterisation of $[\text{Y}_x\text{Ca}_{10-(x+x/10)}\text{Lu}_{x/10}][(\text{SiO}_4)_6][\text{F}_{2-(x+x/10)}\text{O}_{x+x/10}]$, $x < 2$ compounds would be most instructive.

Table 5.1: Britholites crystallochemical properties.

Composition	A ^I	A ^{II}	B	X	Sym.	Volume ($\text{\AA}^3$)	ϕ ($^\circ$)	Ref.
$\text{Ce}_{6.76}\text{Ca}_{2.24}\text{Sr}(\text{SiO}_4)_6\text{OF}_{0.76}$	Ce, Ca, Sr	Ce, Ca	Si	O, F	$P6_3/m$	569.64	22.3 ₄	[12]
$\text{Ca}_9\text{Nd}_1(\text{PO}_4)_5(\text{SiO}_4)\text{F}_{1.50}\text{O}_{0.25}$	Ca, Nd	Ca, Nd	P, Si	O, F	$P6_3/m$	527.41	23.9 ₁	[13]
$\text{Na}_{1.45}\text{La}_{8.55}(\text{SiO}_4)_6\text{F}_{0.9}\text{O}_{1.1}$	La, Na	La, Na	Si	O, F	$P1_12_1$	581.04	23.2 ₉ , 23.8 ₀ , 24.0 ₃	[14]
$\text{Na}_{1.19}\text{Gd}_{8.81}(\text{SiO}_4)_6\text{F}_{0.38}\text{O}_{1.62}$	Na, Gd	Na, Gd	Si	O, F	$P1_12_1$	527.25	23.5 ₂ , 23.5 ₈ , 23.8 ₁	[14]
$\text{Ca}_{4.30}\text{Ce}_{5.70}(\text{SiO}_4)_6\text{F}(\text{OH})$	Ca, Ce	Ca, Ce	Si	O, H, F	$P1_12_1$	554.96	21.9 ₄ , 22.3 ₁ , 22.3 ₁	[15]
$\text{Ca}_{4.86}\text{Ce}_{5.14}(\text{SiO}_4)_6\text{F}(\text{OH})$	Ca, Ce	Ca, Ce	Si	O, H, F	$P1_12_1$	541.51	22.7 ₃ , 23.0 ₃ , 23.0 ₄	[15]
$\text{Y}_{8.96}\text{Ca}_{0.40}\text{Lu}_{0.64}(\text{SiO}_4)_6\text{F}(\text{OH})$	Y, Ca, Lu	Y, Ca, Lu	Si	O, H, F	$P1_12_1$	519.39	22.1 ₁ , 22.3 ₃ , 23.1 ₀	[15]
$\text{Y}_{9.26}\text{Ca}_{0.46}\text{Lu}_{0.28}(\text{SiO}_4)_6\text{F}(\text{OH})$	Y, Ca, Lu	Y, Ca, Lu	Si	O, H, F	$P1_12_1$	510.9	22.1 ₆ , 22.2 ₀ , 22.2 ₃	[15]

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In this chapter, thorium is used to simulate the behaviour of U^{4+} , and the tetravalent transuranic elements (Np^{4+} , Pu^{4+}) [1]. Both uranium and thorium are found in natural britholite [2], and their content widely distributed from 0.15-12.5ppm and 0.18-32.2 ppm respectively [3]. In addition, Th-U thermochronology has been studied extensively in natural Th-bearing apatite [4-6]. However, there is little work concerning synthetic Th-bearing apatites and the saturation concentration of thorium, unlike uranium-bearing analogues [7, 8]. Fully-silicated $(Ca_6Th_4)(SiO_4)_6O_2$ was reported by Engel [9] and more recently, the synthesis and characterization of thorium-bearing britholites $[Ca_{10-x}Th_x][(PO_4)_{6-2x}(SiO_4)_{2x}][F_2]$ were studied by Terra *et al.* [10], who focussed on dissolution kinetics during static and dynamic leaching in the Ca-Nd-Th system [11]. Here, the investigation of Terra *et al.* [10] is replicated, and the reliability of structural refinement assessed using the metaprisim twist angle (ϕ). The solid solution limit for Th^{4+} is established and the implications for wasteform design considered.

5.2 Experimental Methods

5.2.1 Synthesis

A high temperature route was selected for producing well crystalline apatites of nominal formula $[Ca_{10-x}Th_x][(PO_4)_{6-2x}(SiO_4)_{2x}][F_2]$ with $x \leq 3$. Using $Ca_{10}(PO_4)_6F_2$ as the parent, charge balance was assumed via the altermvalent substitution.

The raw materials were reagent grade calcium carbonate, thorium oxide, calcium dihydrogen phosphate ($Ca(HPO_4)_2$) or calcium pyrophosphate ($Ca_2P_2O_7$), silicic acid, silica and calcium fluoride. Stoichiometric proportion of the dry powders were mechanically ground for 15 or 30 minutes, then heated at 1400°C for at least 6 hours in air.

5.2.2 Characterization

Powder X-ray diffraction (PXRD) patterns of the britholites were collected on a Bruker AXS D8 Advance diffractometer using $CuK\alpha$ radiation ($\lambda = 1.5418\text{\AA}$) fitted

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with a Vantec detector. The 2θ collection range was $10-130^\circ$ with a step size of 0.01° and a time per step of 0.5s. Rietveld refinements were carried out with TOPAS V3.0 for crystallographic and quantitative phase analysis. Structural refinements commenced with models based on fluorapatite [16] and appropriate chemical substitutions. Secondary phases were included as needed to determine their weight fractions, and a single broad peak inserted as needed to model the glassy silica. As the principle aim was to establish the crystallographic location of Th^{4+} in fluoroapatite, and its distribution across the $4f$ and $6h$ cation acceptor sites, oxygen was initially fixed at the reported fractional co-ordinates of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and refined in the final step once the distribution of Ca and Th had been determined. However, given the dominant X-ray scattering power of thorium, highly accurate oxygen positions are not expected. In addition, the isotropic atomic displacement parameters for the oxide and fluoride ions were fixed at $1 \text{ \AA}^2$ and the P/Si ratio inferred from charge balance once the Ca/Th content had been refined.

5.3 Results and Discussion

In general, $[\text{Ca}_{10-x}\text{Th}_x][(\text{PO}_4)_{6-2x}(\text{SiO}_4)_{2x}][\text{F}_2]$ thorium britholite formed the major phase together with 4-10 wt% of thorium phosphate ($\text{Th}(\text{PO}_3)_4$) or thorium oxide (ThO_2), depending on the calcium source (see section 5.3.2). The britholites were all consistent with hexagonal symmetry $P6_3/m$, in agreement with Terra *et al.* [10].

5.3.1 Effect of Precursor Grinding

Mechanical grinding improved raw materials reactivity, increasing the yield of britholite and reducing the formation of secondary phases, and was employed in all preparations. Table 5.2 shows that 30 minutes mechanical grinding is required to minimize ThO_2 content, and although not attempted here, even longer homogenization would have proved beneficial.

Table 5.2: Comparison of samples via different mixing methods.

Mixing method	Sintering conditions		Phase %	
	temperature ($^\circ\text{C}$)	duration (hr)	Apatite	ThO_2
manual	1400	6	82.83	17.17
mechanical 15 mins	1400	6	92.54	7.46
mechanical 30 mins	1400	6	96.23	3.77

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Figure 5.1: X-ray pattern of samples using (a) calcium pyrophosphate and (b) calcium dihydrogen phosphate as starting materials; with different secondary phase, ThO_2 and $\text{Th}(\text{PO}_3)_4$.

5.3.2 Effect of Calcium Reagent

The choice of calcium phosphate reagent - calcium dihydrogen phosphate ($\text{Ca}(\text{HPO}_4)_2$) and calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$) - affected the type of secondary phases formed [11]. The pyrophosphate resulted in $\text{Th}(\text{PO}_3)_4$ as a co-existing minor compound, whereas $\text{Ca}(\text{HPO}_4)_2$ yielded ThO_2 . Calcium carbonate was treated at 900°C for 3 hours to yield calcium oxide (CaO) and calcium dihydrogen phosphate was oxidized to calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$) at 1000°C for 3 hours. Overall, the ideal reactions for $x = 1$ using the two precursors were:

Figure 5.2 illustrates the powder X-ray diffraction patterns of two samples ($x = 2$) using the same sintering conditions but using different Ca precursors. It is supposed that thorium oxide, being a refractory oxide, is the last precursor to join the reaction, and so relic ThO_2 persisted (Figure 5.2(a)). Whereas if $\text{Ca}(\text{HPO}_4)_2$ is included then $\text{Th}(\text{PO}_3)_4$ appears as an intermediate product, which requires additional time for incorporation in britholite. It was concluded that calcium pyrophosphate was a superior reagent that reduced sintering time and improved crystallinity.

5.3.3 Crystallographic studies

All the $[\text{Ca}_{10-x}\text{Th}_x][(\text{PO}_4)_{6-2x}(\text{SiO}_4)_{2x}][\text{F}_2]$ britholites produced in this work were successfully refined as hexagonal $P6_3/m$ and the solid solution limit was $x \sim 1$. Table 5.3 shows the lattice parameters of the Th doped samples compared to those obtained for the undoped material $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.

Table 5.3: Crystallographic data for $\text{Ca}_{10-x}\text{Th}_x(\text{PO}_4)_{6-2x}(\text{SiO}_4)_{2x}\text{F}_2$, $0 \leq x \leq 3$.

Composition x	0	1	2	3
Space Group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	9.3672(2)	9.4467(3)	9.4972(9)	9.5112(7)
c (Å)	6.8844(2)	6.9482(3)	6.9633(10)	6.9771(6)
V (Å ³)	523.14(2)	536.99 (4)	543.90(2)	546.62(9)
ThO_2		4.75%	10.18%	22.92%

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Figure 5.2: Rietveld refinement of the $x = 2$ using $\text{Ca}(\text{HPO}_4)_2$ (upper) and $\text{Ca}_2\text{P}_2\text{O}_7$ (lower) as reagents. Higher ThO_2 content was simultaneous with the appearance of a broad amorphous region (probably silica) modelled by a single broad peak centred at approximately $66-68^\circ$ 2θ .

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For $x = 1$ there is a significant increase in volume compared to the undoped material, indicating that the incorporation of Th^{4+} into the britholite was successful. However, small quantities of ThO_2 are also present. For $x > 1$, there is a modest increase in cell volume combined with increased formation of secondary phases. The refined XRD patterns for $x = 2$ and 3 show ThO_2 and a broad feature centred at $66\text{--}68^\circ 2\theta$, presumably associated with amorphous unreacted silicate (Figure 5.2). Therefore, the real reaction can be approximated as

Higher thorium contents also lead to slightly broader reflections indicating reduced crystallinity compared to $x = 1$, and combined with the increased formation of secondary phases, the apparent small increase in refined lattice parameters/volume should be treated with caution. In addition, the intensity of the Bragg reflections is dominated by ThO_2 for higher values of x due to its large X-ray form factor.

To investigate the distribution of Th^{4+} across the $4f$ and $6h$ sites refinements were carried out on the $x = 1$ sample. With all other atomic positions fixed a statistical distribution of Th^{4+} was added to the cation acceptor sites with fixed 100% occupancy in each case and the Ca/Th distribution refined. It was clear from this procedure that Th^{4+} was only present at the $6h$ position, which was anticipated due to the higher charge compared to Ca^{2+} , as discussed in Chapter 3. The atomic positions of the remaining sites were then refined to yield an excellent fit to the diffraction pattern.

Table 5.4 shows the refined atomic positions, cation distributions and selected bond lengths and angles for $x = 1$ britholite. The Ca/Th content determined at the $6h$ site leads to the chemical content $\text{Ca}_{8.98}\text{Th}_{1.02}$, that within error, and assuming no halide loss, is in good agreement with the ideal composition $[\text{Ca}_9\text{Th}][(\text{PO}_4)_4(\text{SiO}_4)_2][\text{F}_2]$. Due to the presence of large quantities of secondary phases and/or amorphous content satisfactory refinement of britholite was not possible for $x = 2$ and 3.

*Thorium Britholite as an Analogue for Tetravalent Transuranic Wasteform Chapter 5***Table 5.4** Refined atomic positions, selected bond lengths and angles for $[\text{Ca}_9\text{Th}][(\text{PO}_4)_4(\text{SiO}_4)_2][\text{F}_2]$.

S.G.	$P6_3/m$	$a = 9.4444(5) \text{ \AA}$	$c = 6.9451(4) \text{ \AA}$	$R_{wp} = 7.3 \%$	$R_{Bragg} = 4.1 \%$
Site	x	y	z	B	Occ.
Ca/Th(1)	1/3	2/3	0.013(2)	0.4(2)	1
Ca/Th(2)	0.2395(5)	-0.0127(6)	1/4	0.6(2)	0.83(1)/0.17(1)
P/Si	0.3964(12)	0.3656(13)	1/4	0.3(2)	1
O(1)	0.320(3)	0.489(3)	1/4	1	1
O(2)	0.587(2)	0.470(3)	1/4	1	1
O(3)	0.3309(16)	0.2467(18)	0.0529(17)	1	1
F	0.00000	0.00000	1/4	1	1

(a)	Bond	Distance ($\text{\AA}$)
	Ca(1)-O(1)	2.31(2)
	Ca(1)-O(2)	2.55(2)
	Ca(1)-O(3)	2.89(2)
	Ca/Th (2)-O(1)	2.64(2)
	Ca/Th(2)-O(2)	2.38(2)
	Ca/Th(2)-O(3)	2.22 (1)
	P/Si-O(1)	1.65(3)
	P/Si-O(2)	1.57(2)
	P/Si-O(3)	1.68 (1)
	Ca/Th(2)-F	2.324(6)

(b)	Angle	$^\circ$
	O(1)-P/Si-O(3)	109.2(9)
	O(1)-P/Si-O(2)	109.2(13)
	O(3)-P/Si-O(3)	110.1(9)
	O(3)-P/Si-O(2)	109.1(11)

5.3.4 Twist Angles

Using the refined structural information the metaprism twist angle for $[\text{Ca}_9\text{Th}][(\text{PO}_4)_4(\text{SiO}_4)_2][\text{F}_2]$ was calculated to be 25.1_3° , and shows the expected increase compared to $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ with a twist angle of 24.3_5° , since the framework must dilate slightly as Th^{4+} ($0.94 \text{ \AA}$) resides exclusively in the channel and is smaller than Ca^{2+} ($1.00 \text{ \AA}$). The value of 25.1_3° is towards the upper limit of twist for a hexagonal apatite after which the structure must distort to monoclinic or triclinic symmetry. To date, no triclinic silicate apatite has been reported, presumably due to the rigidity of SiO_4 tetrahedra and its reluctance to distort as considered in Chapter 4 for the REE analogues. However, should Th be introduced to the $6h$ site to $x > 1$, the twist angle will increase further. Although under the present synthesis conditions Th

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content was limited, the imposition of higher temperatures and/or pressures may stabilize pseudomorphs with larger twist angles. In chemically complex britholites, internal stresses may be relieved through cation ordering and the adoption of monoclinic distortions (see Table 5.1).

5.4 Conclusion

For britholite solid solution $[\text{Ca}_{10-x}\text{Th}_x][(\text{PO}_4)_{6-2x}(\text{SiO}_4)_{2x}][\text{F}_2]$, $0 \leq x \leq 3$ prepared by sintering and using $\text{Ca}_2\text{P}_2\text{O}_7$ as a precursor the upper limit for Th is $x \sim 1$. The doping of Th for $x > 1$ increased the amount of secondary phases. This incorporation can be rationalized in terms of the inability to adopt $\phi > 25.13^\circ$, which appears to the maximum twist angle supported by apatites of hexagonal symmetry.

Unlike the trivalent actinides (Cm^{3+} , Am^{3+}) where extensive solid solubility has been demonstrated, this study suggests the incorporation of tetravalent actinides in britholites may be more restrictive. However, Th^{4+} is an imperfect stimulant for U^{4+} , Pu^{4+} and Np^{4+} as it is larger and possibly more covalent in nature. From a practical synthesis viewpoint, it is likely real actinide-bearing leach liquids will mix well with precursor chemicals and be readily adsorbed / precipitated within a chemically homogenous powder. Finally, this study adopted solid state synthesis, which may not be truly indicative of the capacity of britholites to incorporate tetravalent actinides. While no vacancies were observed on the A^I (as in the case of rare earth apatites) this question should be investigated further.

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Chapter 6

Crystal Structure of Deuterated Calcium-Strontium Hydroxyapatites

The role of protons in apatites, either associated with hydroxyl groups or as delocalized entities, continues to be the subject of speculation, with insights gained by combining crystallographic and spectroscopic methods. In nuclear wasteform apatites, the conversion of hydroxyl- $[A_{10}][(BO_4)_6](OH)_2$ to oxy- $[A_{10}][(BO_4)_6]O$ compounds will play an important role in primary immobilisation, and subsequently, in radiation resistance, due to creation of tunnel vacancies.

6.1 Introduction

Strontium exists as four naturally occurring isotopes - ^{83}Sr (abundance 82.6%), ^{86}Sr (9.9%), ^{87}Sr (7.0%) and ^{84}Sr (0.6%) - with an additional 35 synthetic nuclides [1]. Of particular concern is ^{90}Sr , which is a by-product of uranium and plutonium fission and accounts for 2 wt% of all nuclear waste generated by power reactors [2]. ^{90}Sr has a half-life of 29 years and decays to ^{90}Y via beta emission [3]. Chemically, strontium is analogous to calcium, and therefore its immobilisation is possible via isovalent substitution in hydroxyapatite $[\text{Ca}_{1-x}\text{Sr}_x]_{10}[(\text{PO}_4)_6][(\text{OH})_2]$. Because strontium can reduce dental caries, most studies have focussed on physio-chemical properties and correlating the extent of replacement with functionality [4-6]. Kikuchi *et al.* [7] reported that strontium occupies both the $A^{\text{I}}(4f)$ and $A^{\text{II}}(6h)$ sites at low strontium concentrations with slight preference for the A^{I} site. However, for samples containing > 10 at% Sr, a strong preference for the A^{II} site is found [7]; similar observations have been reported by other workers [8-9]. This conclusion is also broadly analogous to $[(\text{Sr}_{1-x}\text{Ca}_x)_{10}][(\text{PO}_4)_6][\text{F}_2]$ considered in Chapter 3. Strontium hydroxyapatite has been synthesized by various routes – precipitation [7, 10-11], hydrothermal reaction [11-13], sol-gel method [14] and conventional solid state fusion [15] – but there has been limited exploitation of deuterated analogues to better understand the structural detail of the tunnel anion.

Deuteration involves exchanging hydrogen ions ($^1\text{H}^+$) with the non-radioactive isotope deuterium ($^2\text{D}^+$). This procedure is often used in conjunction with neutron diffraction to locate the crystallographic position of hydrogen ions in solids [16-18]. The basis for this technique is that hydrogen and deuterium have coherent scattering lengths of opposite sign i.e. ^2D has a scattering length of 6.671 compared with of -3.7406 for ^1H [19], and the incoherent scattering of ^2D is substantially less than ^1H and that reduces the background in neutron diffraction patterns (Table 6.1). It is the incoherent scattering from the H that impact upon neutron diffraction. By carrying out comparative structural refinements of analogues containing H and D, their location can be determined from positive or negative scattering volumes in Fourier maps at the same crystallographic sites. This chapter describes the first powder neutron diffraction investigation of the $[(\text{Ca}_{1-x}\text{Sr}_x)_{10}][(\text{PO}_4)_6][(\text{OH})_2]$ compounds after exchange with D.

Table 6.1: Neutron scattering lengths and cross sections for H and D.

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
^1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
^2D	0.015	6.671	4.04	5.592	2.05	7.64	0.000519

6.2 Experimental methods

6.2.1 Synthesis

Preparation of the $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_2]$ series used a modified double decomposition synthesis first described by Collin [10, 11]. The starting materials were strontium nitrate $[\text{Sr}(\text{NO}_3)_2]$, Acros, 99%, calcium nitrate tetrahydrate $[\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$, Merck, 99%, ammonium hydrogen phosphate $[(\text{NH}_4)_2\text{HPO}_4]$, Aldrich, 99% and ethylene diamine $[\text{C}_2\text{H}_8\text{N}_2]$, Merck, 85%. The nitrates were dissolved in 400ml of deionized water in stoichiometric amounts and heated at 85°C . Ethylene diamine was subsequently added to adjust the $\text{pH} > 11$. Ammonium hydrogen phosphate (0.5408g) was dissolved in 15 ml (0.27M) of hot deionized water and the pH again adjusted to > 11 with ethylene diamine. The hot ammonium phosphate was added drop-wise to the Ca-Sr solution with heat and stirring and the total volume made up to 460ml. The precipitate and solution were maintained at 85°C while stirring for 6 hours and then allowed to settle overnight, before repeated washing with deionized water using vacuum filtration until the filtrate reached a pH of 7. The cake was dried (100°C / 5 hours) then calcined in an alumina crucible (700°C / 12 hours).

6.2.2 Deuteration

The chemical exchange of H for D in hydroxyapatite is a two step reaction using established methodology [18]. First, 0.1g of apatite immersed in 10ml of D_2O and treated hydrothermally (150°C / 24 hours). Second, the powders were filtered and dried (100°C / 2 hours) under nitrogen to remove excess D_2O .

6.2.3 Characterization

Fourier transform infrared (FTIR) spectra were collected from $400\text{--}4000\text{cm}^{-1}$ using a Perkin Elmer FTIR Spectrum GX instrument with a resolution of 2.0 cm^{-1} .

Translucent pellets were prepared by mixing the apatite powders with oven dried KBr. The number of scan cycles for each sample was set at 40.

Powder X-ray diffraction (PXRD) patterns of the apatites were collected using a Shimadzu LabX XRD-6000 with $\text{CuK}\alpha$ radiation and step-scanned over the 2θ range $10\text{--}140^\circ$ at intervals of 0.02° , and a total collection time of 12 hours. The patterns were analyzed by Rietveld refinement using TOPAS Version 3 [20] and the fundamental parameters approach [21]; further details can be found in Section 3.3.

Time-of-flight (TOF) powder neutron diffraction patterns were collected at ISIS, Rutherford Appleton Laboratory, United Kingdom from the GEM and Polaris beamlines. Approximately $1\text{--}2\text{ cm}^3$ of each apatite powder was loaded into 8mm diameter vanadium cans. For GEM and Polaris, two data sets were used for the refinement; the backscattering detector bank (average $2\theta \approx 145^\circ$ for Polaris and average $2\theta \approx 154^\circ$ for GEM) and the second from the 90° detector bank. Collections were conducted at room temperature and 4.2K; with the latter temperature chosen to minimise the Debye-Waller scattering associated with ^1H , and to encourage the proton to reside at one crystallographic site, rather than thermally disorder. Rietveld refinements were performed with GSAS [22] using the instrumental resolution files provided by ISIS to model the Bragg reflection peak shapes.

6.3 Results and Discussion

6.3.1 Quantitative Phase Analysis

All the apatites were highly crystalline and obtained single phase as confirmed by PXRD (Figure 6.1). Rietveld analyses [23] were conducted in $P6_3/m$ (176) using accepted models for calcium hydroxyapatite [24] and strontium hydroxyapatite [25] as described in Chapter 3.

Figure 6.1: A typical analysis of the PXRD pattern of $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$. Observed and calculated patterns are shown in dots and lines respectively, while the difference profile is plotted beneath and vertical lines indicate Bragg reflections.

6.3.2 Fourier Transformed Infrared Spectroscopy

6.3.2.1 Pre-deuteration

The vibrational modes of anions with the same site symmetry are related to i) mass, ii) ionic radius, iii) coordination number, iv) polarizing power, v) type of cation-anion bonding, and vi) electronic configuration of the cation. As strontium is more massive than calcium, it is expected that the wavenumbers observed by FTIR will generally be shorter for strontium apatites compared with the calcium analogues. Symmetric stretching (ν_1) and bending (ν_4) bands of phosphate ranged from 960cm^{-1} (pure Ca-apatite) to 947cm^{-1} (pure Sr-apatite) for ν_1 , and from 601cm^{-1} (pure Ca-apatite) to 593cm^{-1} (pure Sr-apatite) for ν_4 . These changes in peak frequencies are consistent with Fowler [26, 27].

Oxyapatite can be differentiated from hydroxylapatite by examining the $-\text{OH}$ libration and stretching frequencies at $535\text{--}630\text{ cm}^{-1}$ and $3572\text{--}3592\text{ cm}^{-1}$ respectively. For pure calcium apatite these bands are distinct, but as the strontium content increases, the libration band diminishes and the stretching band attenuates. These changes are interpreted as adjustments within the apatite tunnel which subsequently alter the O-H bond strength [8]. FTIR revealed that only calcium apatite contains surface hydroxyl groups; however, the mixed Ca-Sr and pure strontium apatites are characterised by an outer shell of oxyapatite, at least to the depth resolution of FTIR. Within the shell, charge balance will be through the introduction of tunnel vacancies.

6-1

Figure 6.2: Fourier-transformed infrared spectra for $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_2]$. (a) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, (b) $\text{Ca}_{7.50}\text{Sr}_{2.50}(\text{PO}_4)_6\text{O}$, (c) $\text{Ca}_{5.0}\text{Sr}_5(\text{PO}_4)_6\text{O}$, (d) $\text{Ca}_{2.50}\text{Sr}_{7.50}(\text{PO}_4)_6\text{O}$, and (e) $\text{Sr}_{10}(\text{PO}_4)_6\text{O}$.

6.3.3.2 Post-deuteration

After deuteration FTIR again could not detect hydroxyl for any compositions except $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and even minor Sr resulted in the formation of the oxyapatite layer. To confirm the pure calcium apatite contains surficial OH partial exchange with deuterium was conducted (Figure 6.3); as the stretching and libration bands for OD and OH are distinct [16], and can be used to monitor progression of the substitution. The exchange of H for D may be completed during experiment stage, however the storage environment (glove box) had some level of humidity (RH: 18%) that may have caused D species exchanged out of the tunnel. Hence, the sample had approximately 70-80% of OH, confirmed by comparing the intensities of both bands.

Figure 6.3: Fourier-transformed infrared spectra for with (a) deuterated calcium apatite, where OD and OH libration and stretch bands are observed and (b) non-deuterated calcium apatite which has OH libration and stretch bands.

6.3.3 Structural Analysis

The lattice parameters derived from X-ray and neutron diffraction refinement for identical samples (Figure 6.4) found the expected linear unit cell dilation with increasing substitution of calcium ($1.00\text{\AA}$) by strontium ($1.18\text{\AA}$) [28] in agreement with Vegard's law. Crystallographic refinements of all materials confirm that strontium prefers the A^{II} tunnel site ($6h$), consistent with numerous reports [29, 30] (Table 6.2).

Table 6.2: Lattice parameters, crystallographic data, anisotropic displacement parameters, bond lengths and angles from neutron diffraction data for pre-deuterated $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2-2y}\text{O}_y]$, $0 \leq x \leq 10$.

Nominal Composition x	0	2.50	5.00	7.50	10
Refined composition x	0	2.48	5.00	7.56	10
Space Group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	9.4091 (1)	9.4974 (1)	9.5878 (1)	9.6801 (2)	9.7665 (1)
c (Å)	6.8819 (1)	6.9782(1)	7.0801 (1)	7.1866 (2)	7.2807 (1)
V (Å ³)	527.64 (1)	545.11 (1)	563.65 (1)	583.20 (2)	601.43 (1)
φ (°)	23.55	22.98	22.56	23.19	23.72
P-O bond length (Å)	1.53	1.53	1.53	1.53	1.53
R_p	0.02	0.02	0.02	0.20	0.02
DWd	0.30	0.37	0.37	0.29	0.17
Ca/Sr(1), $4f$ (1/3, 2/3, z)					
z	0.0025 (2)	0.0027 (2)	0.0014 (1)	0.0010(2)	0.0007 (1)
Occ. Fac. (Ca/Sr)	1/0	0.77/0.23 (18)	0.56/0.44(4)	0.28/0.72(2)	0/1
U_{iso}	0.0073 (3)	0.0081 (5)	0.0070 (3)	0.0088(5)	0.0075 (2)
Ca/Sr(2), $6h$ (x , y , 1/4)					
x	0.2553 (2)	0.2563 (2)	0.2601 (1)	0.2434(2)	0.2442 (2)
y	0.0082 (2)	0.0115 (2)	0.0102 (1)	-0.0146(2)	-0.0145 (1)
Occ. Fac. (Ca/Sr)	1/0	0.74/0.26 (14)	0.46/0.54(3)	0.26/0.74(2)	0/1
U_{iso}	0.0074 (3)	0.0069 (4)	0.0092 (2)	0.0087(4)	0.0070 (2)
P, $6h$ (x , y , 1/4)					
x	0.3989 (2)	0.3992 (2)	0.4012 (1)	0.4008(2)	0.4013 (1)
y	0.3693 (1)	0.3695 (2)	0.3711 (1)	0.3696(2)	0.3683 (1)
U_{iso}	0.0084(2)	0.0053(2)	0.0091(2)	0.0079(4)	0.0042(2)
O(1), $6h$ (x , y , 1/4)					
x	0.3282 (1)	0.3311 (1)	0.3339 (5)	0.3343(2)	0.3328 (1)
y	0.4837 (1)	0.4845 (2)	0.4850 (1)	0.4836(2)	0.4810 (2)
U_{iso}	0.0117(2)	0.0077(2)	0.0149(3)	0.0120(5)	0.0073(3)
O(2), $6h$ (x , y , 1/4)					
x	0.5863 (1)	0.5851 (2)	0.5845 (1)	0.5830(2)	0.5814 (1)
y	0.4641 (1)	0.4624 (2)	0.4601 (1)	0.4604(2)	0.4612 (2)
U_{iso}	0.0042(2)	0.0165(3)	0.0227(2)	0.0205(6)	0.0104(4)
O(3), $12i$ (x , y , z)					
x	0.3435 (1)	0.3450 (2)	0.3464 (1)	0.3456(2)	0.3457 (1)
y	0.2584 (1)	0.2606 (2)	0.2633 (1)	0.2623(2)	0.2622 (1)
z	0.0707 (1)	0.0729 (1)	0.0758 (1)	0.0776(2)	0.0793 (1)
U_{iso}	0.0176(3)	0.0204(4)	0.0235(2)	0.0231(4)	0.0146(2)
O(4), $4e$ (0, 0, z)					
z	0.1923 (5)	0.1858 (6)	0.183 (2)	0.1776(13)	0.1806 (5)
Occ. Fac.	0.51(2)	0.53(2)	0.51(1)	0.48(1)	0.25
U_{iso}	0.0127(2)	0.0190(2)	0.0470(2)	0.0287(2)	0.0496
H(1), $4e$ (0, 0, z)					
z	0.0599 (11)	0.065(4)	0.0525(1)	0.058(2)	0.0584 (9)
Occ. Fac. (H)	0.45 (2)	0.53 (2)	0.35(2)	0.39(3)	0.47 (2)
U_{iso}	0.030 (3)	0.048 (4)	0.026(3)	0.020(3)	0.026 (2)

*oxygen occupancies yield values ~ 1 when refined, hence it is implied throughout that oxygen occupancies to be 1.

x = 0	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
P	0.0062(5)	0.0034(5)	0	0.0042(5)	0	0.0032(4)
O(1)	0.0164(5)	0.0107(5)	0	0.0082(6)	0	0.0067(5)
O(2)	0.0035(5)	0.0020(5)	0	0.0064(5)	0	0.0247(7)
O(3)	0.0355(6)	0.0157(4)	-0.0159(3)	0.0142(4)	-0.0090(3)	0.0075(3)
O(4)	0.0070(10)	0.0035(5)	0	0.0070(10)	0	0.0242(21)
x = 2.5	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
P	0.0066(6)	0.0062(6)	0	0.0049(7)	0	0.0085(7)
O(1)	0.0194(7)	0.0122(6)	0	0.0047(7)	0	0.0072(6)
O(2)	0.0042(7)	0.0012(6)	0	0.0066(7)	0	0.0367(12)
O(3)	0.0450(9)	0.0191(6)	-0.0188(5)	0.0135(5)	-0.0102(4)	0.0088(4)
O(4)	0.0115(15)	0.0057(7)	0	0.0115(15)	0	0.034(5)
H	0.045(4)	0.0225(21)	0	0.045(4)	0	0.052(16)
x = 5.0	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
P	0.0185(7)	0.0137(5)	0	0.0097(5)	0	0.0079(6)
O(1)	0.0339(7)	0.0232(6)	0	0.0132(10)	0	0.0129(10)
O(2)	0.0037(2)	-0.0024(9)	0	0.0066(4)	0	0.0510(9)
O(3)	0.0507(7)	0.0206(4)	-0.0167(4)	0.0184(9)	-0.0104(8)	0.0055(6)
O(4)	0.0125(10)	0.0063(5)	0	0.0125(10)	0	0.116(11)
x = 7.5	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
P	0.0123(8)	0.0072(7)	0	0.0043(8)	0	0.0111(8)
O(1)	0.0279(9)	0.0189(7)	0	0.0086(7)	0	0.0122(8)
O(2)	0.0064(9)	0.0006(7)	0	0.0072(8)	0	0.0442(14)
O(3)	0.0519(11)	0.0200(8)	-0.0180(5)	0.0154(6)	-0.0107(5)	0.0060(4)
O(4)	0.0054(14)	0.0027(7)	0	0.0054(14)	0	0.075(8)
x = 10	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
P	0.0065(5)	0.0041(5)	0	0.0038(5)	0	0.0045(5)
O(1)	0.0142(5)	0.0107(5)	0	0.0074(5)	0	0.0075(5)
O(2)	0.0034(5)	0.0005(4)	0	0.0040(5)	0	0.0221(7)
O(3)	0.0298(6)	0.0132(4)	-0.0114(3)	0.0122(4)	-0.0067(3)	0.0054(3)
O(4)	0.0055(9)	0.0027(5)	0	0.0055(9)	0	0.0313(22)

Bond	Distance (Å)				
	x = 0	x = 2.5	x = 5.0	x = 7.5	x = 10.0
A ^I -O(1)	2.405(2)	2.437(2)	2.478(2)	2.522(2)	2.565(2)
A ^I -O(2)	2.457(2)	2.482(2)	2.494(2)	2.534(2)	2.574(2)
A ^I -O(3)	2.802(2)	2.825(2)	2.849(2)	2.884(2)	2.910(2)
A ^{II} -O(1)	2.686(2)	2.708(2)	2.755(2)	2.755(2)	2.760(2)
A ^{II} -O(2)	2.357(2)	2.411(2)	2.411(2)	2.486(2)	2.495(2)
A ^{II} -O(3)	2.342(2)	2.383(9)	2.433(3)	2.477(2)	2.519(2)
A ^{II} -O(4)	2.522(2)	2.579(2)	2.613(2)	2.655(2)	2.676(2)
	2.397(2)	2.426(3)	2.492(2)	2.485(2)	2.511(2)
P-O(1)	1.523(2)	1.522(2)	1.521(2)	1.530(2)	1.538(2)
P-O(2)	1.527(2)	1.529(2)	1.522(2)	1.526(2)	1.533(2)
P-O(3)	1.530(2)	1.526(2)	1.524(2)	1.532(2)	1.533(2)

Angle °					
	x = 0	x = 2.5	x = 5.0	x = 7.5	x = 10.0
O(1)-P-O(3)	111.26(6)	111.44(2)	111.16(2)	111.04(2)	110.81(5)
O(1)-P-O(2)	111.79(9)	111.58(2)	115.55(2)	111.45(2)	110.93(9)
O(3)-P-O(3)	107.60 (9)	108.16(2)	108.03(2)	108.04(2)	108.36(9)
O(3)-P-O(2)	107.35(6)	106.99(2)	106.84(2)	107.55(9)	107.91(6)

Figure 6.4: Fitted lines of lattice parameters for $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2(1-y)}\text{O}_y]$ from neutron diffraction collected at room temperature and 4K, and deuterated samples as a function of x.

6.3.4 Metaprism twist angle

As already enunciated (Chapter 3), the metaprism twist angle can critically evaluate the refined structures of apatite and assess if they are crystallographically realistic. This investigation omitted the consideration of D influence in metaprism twist angle, as deuteration was employed as a tool to confirm the formation of hydroxyapatite instead of oxyapatite. In addition to, the D-exchanged apatite is not stable in the air; hence the conclusion should be drawn towards hydroxyapatite and oxyapatite. The twist angle pattern across $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2(1-y)}\text{O}_y]$, with increasing atomic percentage of strontium was calculated from X-ray and neutron diffraction experiments, with the latter more accurate due to the greater sensitivity toward oxygen (Figure 6.5). The parabolic variation in the twist angle as x increases in $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2(1-y)}\text{O}_y]$ arises from the non-statistical distribution of Sr across the 4f and 6h sites and is analogous to observations of $[\text{Sr}_{10-x}\text{Ca}_x][(\text{PO}_4)_6][\text{F}_2]$. At low strontium content the Sr^{2+} ions ($1.18\text{\AA}$) initially occupy the 6h site, causing the tunnel to expand, through smaller metaprism twisting. However, when the 6h sites are saturated with Sr^{2+} , the twist angle begins to increase as Sr^{2+} tenants the 4f site. The

general observation is that the tunnel size is inversely proportional to metaprisism twist angle [31] and this trend is confirmed here (Figure 6.5b). The A^I/A^{II} partitioning coefficient for strontium, is given by

$$k_{Sr} = \frac{2}{3} \text{ (occ. Sr in 4f / occ. Sr in 6h)} \quad 6.2$$

As all coefficients are below $k_{Sr} = \frac{2}{3}$, this is a measure of the site preference of Sr^{2+} for the 6h position (Figure 6.5c).

Figure 6.5: (a) Twist angles trend, (b) ionic radii ratio (framework/tunnel) and (c) partition coefficient of strontium for $[Ca_{10-x}Sr_x][(PO_4)_6][(OH)_{2-2y}O_y]$. The diamonds and triangles are derived from X-ray and neutron diffraction respectively.

6.3.4 Fourier mapping

Following Rietveld refinement in $P6_3/m$, difference Fourier maps were generated with oxygen ions situated at the usual $4e$ $(0, 0, z)$ position to confirm the position of H/D in the apatite channels. Room temperature collection is a standard procedure to examine H in apatites, while collection at 4.2 K minimizes disorder associated with thermal motion of H/D [32], and encourages the proton to locate at one crystallographic site. Partially deuterated samples are particularly valuable to aid the identification, location and possible ordering of OH in apatite. By convention, negative nuclear density is shown by dashed contours and positive density by solid lines.

6.3.4.1 Pre-deuteration

From Fourier mapping carried out at room temperature and 4.2K it was evident that excess negative nuclear density was centred at $(0, 0, 0)$ (Figures 6.6 and 6.7), and that H is present in all samples, but in greater concentration in the pure calcium hydroxyapatite; the difference is especially evident at 4.2K.

Figure 6.6: [100] difference-Fourier map at $x = 0$ from refinement of neutron diffraction pattern collected at room temperature to show hydrogen positions in pre-deuterated $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2(1-y)}\text{O}_y]$ with (a) $x=0$, (b) $x=5$ and (c) $x=10$. Hydrogen is most abundant in the pure Ca-apatite and becomes progressively less abundant as strontium content increases.

Figure 6.7: [100] difference-Fourier maps at $x = 0$ from refinements of neutron diffraction patterns collected at 4.2K showing the hydrogen positions in pre-deuterated $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2-2y}\text{O}_y]$ (a) $x = 0$, (b) $x = 5$ and (c) $x = 10$.

The greater concentration of H in pure calcium hydroxyapatite is confirmed by the higher density of contour lines in the Fourier map from this material. The lower contour density in the mid-member $\text{Ca}_5\text{Sr}_5(\text{PO}_4)_6(\text{OH})_{2-2y}\text{O}_y$ and pure strontium phase is consistent with these materials being oxy-hydroxyapatites. Although the negative contour lines are centered in the same positions at RT and 4.2K, the contour shapes are more regular and spherical in the latter since thermal motion is reduced. The Fourier mapping of the Sr containing phases may appear contradictory to FTIR, which failed to identify the expected OH stretches. However, this would be consistent with the core-shell model suggested earlier, or alternatively, may suggest disorder of O and OH groups in the apatite channel perturbs the vibrational modes. Although no firm conclusion on this effect can be drawn from this study, the contrasting results of neutron and FTIR techniques warrants further investigation.

6.3.4.2 Post-deuteration

The scattering lengths of hydrogen and deuterium are -3.7390 and 6.671 respectively [19], and co-substitution of these ions at equivalent site would on average cancel scattering. Figure 6.8 shows the Fourier maps for the deuterated apatites, which were prepared in an identical manner to the H containing samples, all show excess continuous contour lines in the same position as for the H in the apatite channel. For the pure calcium phase there are very few solid lines, compared to dashed contours indicating negative nuclear density dominates which suggests the H/D substitution was partial (H:D ratio 2:1). For the $x = 5$ and 10, solid contours indicate positive nuclear density and that the H/D substitution was more complete (H:D ratio 1:1.5). As all samples were synthesised identically the origin of the differences in H/D contents are presently unclear. Nevertheless, Fourier mapping shows that for all samples deuteration was partially successful, and confirmed the protonation in the apatite channel, rather than the framework as has been reported for electrolyte apatite.

Using the information from the Fourier maps, H and D were added to the neutron refinements of the deuterated samples to determine H:D ratio (see Table 6.3). While these compositions apply to the bulk materials, the outer layer of the $x = 5$ and $x = 10$ apatites are OH/OD poor.

Table 6.3: The ratio of H:D within the deuterated apatites $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH}, \text{OD})_2]$.

x	H	D
0	0.66	0.34
5	0.40	0.60
10	0.38	0.62

Figure 6.8: [100] difference-Fourier map at $x = 0$ from refinement of neutron diffraction pattern collected on deuterated apatites to show potential positions of H/D in $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2(1-y)}\text{O}_y]$ (a) $x = 0$, (b) $x = 5$ and (c) $x = 10$. For $x=0$, the H is slightly in excess of D, but for $x = 5$ and $x = 10$ the reverse is observed.

6.4 Conclusions and Significance

These results confirm the synthesis of $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_{2(1-y)}\text{O}_y]$ solid-solution series. Fourier transform infrared spectroscopy found hydroxyl-oxyapatite occurs at the surface of the powder in the Sr doped samples. Neutron diffraction data with subsequent Fourier mapping showed that in the bulk, all samples contain H and or D to a certain extent. This reflects the surface sensitivity of FTIR versus the bulk sampling of PND. The identification of hydroxyapatite and oxyapatite is possible by deuteration; from the HLW perspective, this would be potentially unfavourable for radiation resistance as vacancies in oxyapatite may form nanopores that can migrate and accumulate microscopically, leading to void swelling and possible deterioration of mechanical stability [33].

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Chapter 7

Fabricating Apatite HLW Ceramics by Uniaxial Hot Pressing

The ultimate performance of HLW ceramics is limited by microstructural features including pores, glassy and soluble grain boundaries, and crystal size. These features directly influence dissolution and radiation damage ingrowth. In addition, volatile nuclides including cesium and iodine must be retained quantitatively during and after solidification. Hot pressing is an established method for producing fully dense solids in a closed system and is suitable for the stabilization of radioactive waste in apatite ceramics.

7.1 Hot Pressing HLW Ceramics

Hot pressing employs temperature and pressure simultaneously to drive chemical reactions and densification, with the pressure applied isostatically (all directions) or uniaxially (monodirectional). Graphite is frequently used in uniaxial pressing as the dies are inexpensive and show improved strength at high temperatures [1]. These techniques are well established for the fabrication of ceramics and glasses with superior physical, chemical and mechanical performance compared to sintered bodies [2-3] and prove effective for near net shape production [4]. Michie *et al.* [5] concluded hot pressing may be a viable option for solidifying wastes at significantly lower temperature than sintering.

Ceramics fabricated by hot pressing are distinct from sintered materials in terms of grain shape, pore size and geometry, and interparticle contact area [6]. According to Helle *et al.* [7] six consolidation mechanisms may be operative: (i) instantaneous densification by plastic yielding (dislocation movement), (ii) climb-controlled glide of dislocations, (iii) transport of matter from interparticle boundaries to voids by grain boundary diffusion, (iv) transport of matter from interparticle boundaries to voids by lattice diffusion, (v) Nabarro-Herring creep, and (vi) Coble creep; the latter two apply where grain size is much smaller than particle size. In these models, it is assumed that the powder consists of uniform spheres, and compaction begins at an initial fractional density (green density) of $D_0 = 0.64$, while D is the observed density. In general, hot pressing proceeds in two steps: first, where $D_0 \leq D \leq 0.9$ the pores are ‘cusp-shaped’ and interconnected; and second, for $0.9 < D \leq 1$ the pores are small and isolated along the grain boundaries. In general, hot pressing optimisation focuses on applying high pressure and lower temperature for grain size control [8].

The objectives of the present studies were threefold:

- i) The possibility of cesium incorporation in wasteform apatites has been conjectural. The fundamental issue to resolve is whether cesium (Cs^+) is too large for incorporation in apatite, although it is well established that smaller alkalis (Na^+ , K^+ , Rb^+) strongly partition into the framework [9-11].
- ii) While aluminate [2] and titanate [12] ceramic waste forms have been prepared using hot pressing and the improvement in mechanical and physical properties

well documented, far less attention has been given to phospho-silicate apatites. Therefore, demonstrating the viability of hot pressing for complex simulated wastes is a key aspect of assessing the viability of apatite wasteforms.

- iii) A variety of methods are required to confirm the incorporation of waste in ceramic materials over a range of loadings, including microanalysis, electron microscopy and diffraction. Here, a key goal is to demonstrate that a single PXRD experiment and Rietveld analysis, will be sufficient to confirm successful immobilization in apatite.

7.2 Selection of Simulated Waste

The selection of suitable trial wastes for consolidation by hot pressing focussed on the range of elements present to test specific aspects of apatite performance. First, cesium was chosen. Although numerous publications have described the successful retention of smaller alkali metals (Na, K, Rb) in apatite, little evidence was available for cesium, which is a major omission in a study of nuclear waste. Campayo *et al.* [13] reported that cesium incorporation in neodymium-bearing britholite of nominal composition $[\text{Ca}_7\text{Nd}_2\text{Cs}][(\text{PO}_4)_5(\text{SiO}_4)_1][\text{FO}_{0.5}]$ was feasible through sintering oxides, carbonates and fluorides. However, the products were always multiphase with $\text{CsCaNd}(\text{PO}_4)_2$ as a major impurity. Boughzala *et al.* [14] investigated the analogous $[\text{Sr}_7\text{La}_2\text{Cs}][(\text{PO}_4)_5(\text{SiO}_4)_1][\text{FO}_{0.5}]$ and again failed to synthesise single phase britholite which invariably co-existed with $\text{CsSrLa}(\text{PO}_4)_2$. These results suggest that a closed system may be essential to retain highly volatile cesium during crystallisation. Second, the feasibility of solidifying by hot pressing a simulated multi-element nuclear waste arising from a UK weapons program was investigated. This waste was chosen as only a limited number of HLW compositions are available in the open literature, and because this particular stream is rich in halides (fluorine and chlorine) so other ceramic and vitreous systems are unsuitable for high waste loadings. In contrast, apatite wasteforms can readily accommodate halides.

7.3 Experimental Methods

7.3.1 Simulated Waste Compositions

Because homogenous and highly reactive precursor powders that rapidly densify are required, sol-gel methods are often preferred for preparing the tailored wastefrom additives. However, in this study, a non-alkoxide method was adopted to synthesize the cesium precursor for hot pressing. The starting materials (reagent grade) were phosphorus pentoxide, calcium nitrate, cesium carbonate, cesium acetate, cesium nitrate and absolute ethanol. Phosphorus pentoxide was dissolved in absolute ethanol to a concentration of 0.5M. Separately, a stoichiometric proportion of calcium nitrate and cesium acetate were dissolved in 9 ml of absolute ethanol. These solutions were stirred at room temperature for 1 day, after which the sol was oven-dried (80°C / 5 hours) to form a gel, before calcination (200°C / 2 hours) to yield powder.

The composition of the non-radioactive simulated wastestream is given in Table 7.1. The oxides were weighted and mixed manually using a mortar and pestle. A waste loading of 5.8 wt% was chosen. Tailoring was simplified by gathering together waste species expected to show similar crystal chemical properties in apatite; A-type Ca, Hf, Sm, K; B-type Ga, Al; and X-type F, Cl. The simulated waste and starting materials were mixed in these tailored proportions, then hot pressed (800°C / 30MPa) with heating and cooling rates of 10°C/min.

Table 7.1: Chemical composition of the calcined non-radioactive simulant waste, corresponding to defense waste Type III (Donald *et al.* [14]).

Component	Content %	Simulations
<u>Fission & Actinide</u>		
HfO ₂	62.2	Pu ⁴⁺
Sm ₂ O ₃	11.7	Am ³⁺
<u>Processing Contaminant</u>		
Ga ₂ O ₃	9.4	-
Al ₂ O ₃	1.7	-
CaF ₂	5	-
KCl	10	-
Total	100	-

7.3.2 Hot Pressing Protocols

For the present experiments, a uniaxial vacuum hot press (Centorr Vacuum Industries) was used; the key operating parameters include a maximum temperature of 2200°C, maximum heating and cooling rates 50°C/min, and applied pressures to 50MPa. Prior to hot pressing, a thin film of boron nitride was applied to the walls of the graphite die to reduce diffusion between the die (internal diameter 10mm/ length 50mm) and the calcine. The powder specimen (1.5g) was loaded into the die, then compacted at room temperature (4 kbar) to green density. The loaded graphite die was introduced to the furnace and the processing parameters programmed to automate the hot pressing. In addition to temperature and pressure, other parameters included waste loading (wt%), ramp rates, and holding time.

7.3.3 Materials Characterization

After hot pressing, the ceramic pellets were polished to a mirror finish using diamond paste 1µm and deionized water for scanning electron microscopy (SEM), with porosity analysis and phase segregation monitored by backscattered electron imaging (BEI). Energy dispersive X-ray spectroscopy (EDS) was used to quantitatively assess composition. Powder X-ray diffraction (PXRD) was employed for phase identification and the derivation of crystallochemical parameters, including site occupancy, lattice parameters and twist angle via Rietveld refinement. The relative density was determined by the Archimedean method in water [15]. With the use of graduated cylinder filled with known amount of water, the difference in water level would be the volume of pellet when pellet was placed inside the cylinder. The relative density is calculated via dividing the weight of pellet by volume. As the phase proportions are derived from quantitative Rietveld refinement, the theoretical density and densification ratio can be determined.

Figure 7.1: General temperature and pressure profile for uniaxial hot pressing. Solid and dashed lines are temperature and pressure respectively.

7.4 Retaining Volatile Species – Cesium

Cesium is a significant fission product in both proportion and activity with a half-life of 30.1 years and decay by beta emission. To date, cesium immobilization has been demonstrated in zeolite [16-18], hollandite [19, 20], borosilicate glass [21] and other oxides [22-28]. Here, the aim was to verify that cesium can be incorporated in apatite, as suggested from ab-initio calculations [29], via partitioning into the A^I framework position according to the precepts developed in Chapter 3. The compatibility of lighter alkalis in apatite is well established, with numerous reports of sodium- and potassium-bearing apatites [30], and some concerning rubidium-doped apatite [31]. Computational studies suggest cesium immobilization is possible in apatite with Cs^+ ions showing a slight preference for the site A^I over A^{II} [25]. Cs^+ ($1.67\text{\AA}$) has an ionic radii much larger than Ca^{2+} ($1.00\text{\AA}$), and would be expected to occupy A^I , despite A^{II} sites being larger [32]. Here, the synthesis of apatites of nominal composition $[Ca_{4-x}Cs_x][Ca_6][(PO_4)_6][(OH)_{2-x}\square_x]$, $x=1$ was attempted. The notional charge balance mechanism is

Earlier studies have shown that apatite formation takes place at high temperatures (1100-1400°C) and pressures (20-30MPa) [34-36]. However, with sol-gel techniques,

the temperature can be lowered to 700-900°C using a pressure of 30-50MPa in vacuum based hot-pressing. Heating and cooling rates play a part in yielding a fracture-free pellet; in this study, both rates were maintained at 10°C/min.

Ideally, the hot-pressed products will be single phase apatite of near theoretical density. Minimization of porosity is of paramount importance as this directly impacts upon leaching performance due to the accumulation of cesium vapours in pores [2]. It was determined that >700°C was required to obtain apatite at high yield (Table 7.2) and for all pressures, 800°C proved optimal. Conversely, pressure is less significant in terms of apatite development, but controls densification, and 30MPa proves optimal (Table 7.2). For > 90% density, porosity is constant across all samples (Figure 7.2). The abbreviations used: HA – hydroxyapatite and TCP – tricalcium phosphate.

Table 7.2: Characteristics of hot pressed $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. (a) Quantitative phase analysis, and (b) density relative to theoretical (HA - 3.156 gcm^{-3} , β -TCP – 3.07 gcm^{-3} and CaO – 3.35 gcm^{-3})

(a)		Pressure (MPa)		
		30	40	50
Temperature (°C)	700	1.1%CaO, 98.9% TCP	44.3%HA, 55.7%TCP	71.7%HA, 28.3%TCP
	800	97.1%HA, 2.9%TCP	83.3%HA, 16.7%TCP	42.0% HA, 58.0% TCP
	900	17.2%HA, 82.8%TCP	12.8%HA, 87.2%TCP	13.8%HA, 86.2%TCP

(b)		Pressure (MPa)		
		30	40	50
Temperature (°C)	700	86.6%	84.0%	75.3%
	800	98.6%	95.5%	84.8%
	900	72.1%	64.9%	71.7%

Table 7.3: EDX of cesium doped apatite with normalization of oxygen, collected over 6 sites.

Element	Element %	Sigma %	Atomic %	Measured	Ideal
P K	14.9	0.4	12.2	5.2	6
Ca K	44.6	0.6	28.2	12.0	9
Cs K	3.2	0.7	0.6	0.3	1
O K	37.3	0.6	59.0	25.0	25

Figure 7.2: Microstructure of hot pressed $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, prepared at 800°C at 30MPa for 2 hours (a) & (b) SEI and (c) & (d) BEI where the dark regions are porosity.

In accordance to the atomic density of phase, BEI(s) are often used to estimate the number of phases exists in a sample through different contrast between areas with difference chemical compositions; heavy elements scatter electrons more strongly than light elements, hence appear brighter. In Figure 7.2c and 7.2d, the back-scattered electron images did not exhibit significant contrast, this served as indication of nearly single phase in the sample. The optimum conditions from hot pressed hydroxyapatite were employed directly for the cesium doped ceramics. Although the standardless EDX analyses are semi-quantitative, it appears only 30-40% of cesium is retained in the ceramic after hot pressing at all temperatures. Moreover, based on the quantitative Rietveld refinement, cesium was not incorporated principally in apatite, but in the unusual compound cesium phosphohydride (CsPH_2) (Figure 7.3). Previously, CsPH_2 has been synthesized through a complex organo-metallic synthesis [38] that surprisingly has been obtained via hot pressing. It can be presumed that the reducing conditions within the graphite die favour its crystallization. Hence, it is concluded that cesium immobilization cannot be promoted in calcium hydroxylapatite through mechanism 7-1. This outcome is consistent with a study of calcium-barium-cesium

apatite [13]. Alternatively, cesium may solidify in apatite in presence of trivalent REE (e.g. Nd^{3+}) [13] with charge balance as

Figure 7.3: Rietveld profile of cesium bearing ceramic, showing the observed pattern (blue), the calculated pattern (red) and the difference profile (grey) # = CaO and * = CsPH₂.

The more complex replacement of Boughzala *et al.* [39] that were tested by sintering could also be beneficial.

These workers succeed in preparing single phase $[\text{Sr}_7\text{La}_2\text{Cs}][(\text{PO}_4)_5(\text{SiO}_4)][\text{F}_2]$.

7.5 Solidification of Simulated Defense Waste

Donald *et al.* [14] earlier found, that Type III simulated waste, when sintering with appropriate precursors yielded chlorapatite $\text{Ca}_{10}(\text{PO}_4)_3\text{Cl}_2$ and spodiosite $\text{Ca}_2(\text{PO}_4)\text{Cl}$. Hence, the present investigation focused on improving apatite yield. The principle tailoring reactions are:

Table 7.4: Composition of 5.8 wt% waste loaded apatite.

Additives Chemical	wt%	Additives oxide	wt%
CaCO_3	28.14	CaO	40.59
$\text{Ca}_2\text{P}_2\text{O}_7$	56.23	P_2O_5	31.41
H_2SiO_3	3.13	SiO_2	2.41
CaF_2	3.08	CaF_2	3.08
CaCl_2	4.36	CaCl_2	4.36

81.85 wt%

Waste oxide	wt%
HfO_2	3.15
Ga_2O_3	0.48
Al_2O_3	0.09
Sm_2O_3	0.59
CaF_2	0.26
KCl	0.51

5.08 wt%

WL = $5.08 / 86.93 \times 100\%$
= 5.84 wt%

*WL denotes waste loading

$$\text{Waste loading} = \text{waste oxide} / (\text{waste oxide} + \text{addictive oxide}) \times 100\% \quad 7-9$$

A waste loading of 5.8 wt% was selected in this reconnaissance study (Table 7.4).

The hot pressed (800°C / 30 MPa) wasteform was near single phase apatite, with waste incorporation evident through dilation in the unit cell and changes in occupancy factors. The ideal composition of the britholite will be $[\text{Ca}_{9.64}\text{Hf}_{0.17}\text{Sm}_{0.04}\text{K}_{0.08}][(\text{PO}_4)_{5.47}(\text{SiO}_4)_{0.45}(\text{AlO}_4)_{0.02}(\text{GaO}_4)_{0.06}][\text{F}_{0.96}\text{Cl}_{0.96}]$. Rietveld occupancy of the A^{I} and A^{II} sites are 109 % and 101% respectively; this is indicative of simulated cationic species that are heavier than Ca (Hf and Sm). It would be expected that Hf^{4+} and Sm^{3+} would show a preference for the tunnel site, according to the precepts developed in Chapter 3, 4 and 5, but this is not evident. However, the waste loading is low and the sample may not be equilibrated. Contrarily, the occupancy of phosphorus is low at 96%, which can be explained by substitutions of lighter elements like silicon and aluminium, and a small extent of gallium. Fluorine is

sharing the anion site with chlorine which is one of waste constituents. As expected, the twist angles are comparable given that the average A^I/A^{II} cation size is almost identical. A side-by-side comparison of lattice parameters and X-ray diffraction profiles of undoped and doped apatite via hot-pressing in Table 7.5 and Figure 7.4.

Table 7.5: Lattice parameters and partitions for hot pressed undoped fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ [37] and hot pressed apatite doped with 5wt% of simulated non-radioactive waste.

	undoped fluorapatite	5 wt% waste doped apatite
$a(\text{\AA})$	9.414(4)	9.450(2)
$c(\text{\AA})$	6.879(3)	6.835 (2)
$V(\text{\AA}^3)$	527.96(2)	528.6 (3)
Occ. A^I (Ca)	1	1.094 (7)
Occ. A^{II} (Ca)	1	1.015 (6)
Occ. P	1	0.962 (8)
Occ. F	1	0.745 (5)
Occ. Cl	0	0.255 (5)
Second phase	β -TCP 2.9wt%	-
$\phi(^{\circ})$	23.5	23.6

Figure 7.4: Rietveld profiles of (a) hot pressed undoped hydroxyapatite with β -TCP (green ticks) and Al metal from sample holder (pink ticks), and (b) 5 wt% waste incorporated apatite, showing the observed pattern (blue), the calculated pattern (red) and the difference profile (grey).

7.6 High Temperature Decomposition of Hydroxyapatite to TCP

Understanding materials degradation is an essential aspect of radioactive wasteforms. This investigation is devoted to the effect of temperature induced decomposition of hydroxyapatite.

7.6.1 Synthesis

The raw materials were reagent grade calcium nitrate, ethylene diamine and ammonium hydrogen phosphate with a double decomposition reaction used to produce hydroxyapatite powder. Calcium nitrate was dissolved in 100ml of deionized water, while maintaining a cation concentration of 0.2M and heated at 85°C. Ammonia was added to raise the pH > 10. Ammonium hydrogen phosphate 1.6007g (0.2M) was dissolved in 60ml of deionized water and the pH adjusted by ammonia to be > 10. The phosphorus containing solution was added drop-wise to the Ca solution with heating and stirring to a total volume approximately 200ml. The precipitate and solution were maintained at 85°C with stirring for 3 hours and filtered while warm. The precipitate was then dried overnight at 100°C before calcination from 500-1500°C.

7.6.2 Quantitative Phase Analysis

Powder X-ray diffraction (PXRD) patterns were collected with a Bruker AXS D8 Advance diffractometer system using CuK α rays ($\lambda = 1.5418\text{\AA}$) from 10-130° 2 θ with a step 0.01° and dwell time per step of 0.5s. Rietveld refinement using TOPAS V3.0 was employed for quantitative phase and crystallographic analysis. Diffraction data was collected from samples with an internal calcium fluoride (20 wt%) spike to estimate the amorphous phase content.

The apatite phase conformed to hexagonal $P6_3/m$ symmetry and decomposes to tricalcium phosphate above 900°C. As the sintering temperature is raised (500°C to 1100°C), the apatite crystallite size steadily increases, but from 1100°C to 1300°C this trend reverses, shrinking as tricalcium phosphate transforms from β -tricalcium phosphate, β -TCP ($R3c$) to α -tricalcium phosphate, α -TCP ($P12_1/a1$). The content and crystallite size of TCP increases steadily (Table 7.5). The ideal reactions are:

At 500-1100°C,

At > 1100°C,

At 1300°C,

Quantitative phase analysis found amorphicity increased in tandem with tricalcium phosphate (TCP) crystallization. This is expected as transformation from hydroxyapatite to TCP will be reconstructive or semi-reconstructive, leading to the appearance of an intermediate disordered phase (See Table 7.6 and Figure 7.5). The crystallite size of apatites was calculated using Topaz software based on Scherrer formula.

Table 7.6: Quantitative phase analysis.

Sintering temperature	500	900	1100	1300	1500
Space Group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
a (Å)	9.4160 (4)	9.4236 (1)	9.4225 (1)	9.4205 (2)	9.4231 (4)
c (Å)	6.8836 (3)	6.8844 (1)	6.8837 (1)	6.8900 (2)	6.8853 (4)
V (Å ³)	528.55 (4)	529.46 (2)	529.29 (1)	529.53 (3)	529.47 (6)
Apatite Cry Size L (nm)	28.4 (2)	97.0 (7)	271.6 (9)	146.5 (9)	173.0 (9)
R_b (%)	2.38	4.92	5.06	4.03	4.98
Apatite (wt%)	100	100	85.2	84.7	46
TCP (wt%)	0	0	13.5(β)	10.1(α)	40.3(α)
Amorphous (wt%)	5.38	14.4	20.4	31.0	30.7

Figure 7.5: Phase development as a function of sintering temperature.

Table 7.7: Amorphous content analysis of samples with spikes, CaF₂.

500°C spike					
Normalised Cryst. components		Normalised Cryst. & Amorp. components		Quantitative phase analysis	
Apatite	79.1	Apatite	75.69	Apatite	94.62
TCP	0	TCP	0.00	TCP	0.00
Fluorite	20.9	Fluorite	20.00	Amorphous	5.38
		Amorphous	4.31		
total	100	total	100.00	total	100.00
900°C spike					
Normalised Cryst. components		Normalised Cryst. & Amorp. components		Quantitative phase analysis	
Apatite	77.4	Apatite	68.5	Apatite	85.6
TCP	0	TCP	0	TCP	0
Fluorite	22.6	Fluorite	20.0	Amorphous	14.4
		Amorphous	11.5		
total	100.0	total	100.0	total	100.0
1100°C spike					
Normalised Cryst. components		Normalised Cryst. & Amorp. components		Quantitative phase analysis	
Apatite	63.3	Apatite	52.9	Apatite	66.1
TCP	12.9	TCP	10.8	β-TCP	13.5
Fluorite	23.8	Fluorite	20.0	Amorphous	20.4
		Amorphous	16.3		
total	100.0	total	100.0	total	100.0
1300°C spike					
Normalised Cryst. components		Normalised Cryst. & Amorp. components		Quantitative phase analysis	
Apatite	62.7	Apatite	47.1	Apatite	58.9
TCP	10.7	TCP	8.1	α-TCP	10.1
Fluorite	26.6	Fluorite	20.0	Amorphous	31.0
		Amorphous	24.8		
total	100.0	total	100.0	total	100.0
1500°C spike					
Normalised Cryst. components		Normalised Cryst. & Amorp. components		Quantitative phase analysis	
Apatite	30.7	Apatite	23.2	Apatite	29.0
TCP	42.8	TCP	32.2	α-TCP	40.3
Fluorite	26.5	Fluorite	20.0	Amorphous	30.7
		Amorphous	24.6		
total	100.0	total	100.0	total	100.0

7.7 Conclusions

7.7.1 Cesium Fixation

This study, when combined with the earlier work of Campayo *et al.* [13] and Boughzala *et al.* [14] has shown that the incorporation of cesium in apatite, is feasible but requires careful control of synthesis conditions, and possibly, very specific tailoring that will control the framework to tunnel size ratio and charge balance.

When sintering is employed with altermultivalent substitution including REE and alkali earth elements (AE) then $\text{CsAEREE}(\text{PO}_4)_2$ is often a secondary phase that proves difficult to minimize. Alternatively, the reducing conditions found during hot pressing in graphite dies promotes the crystallisation of cesium phosphohydride. In this case, minor cesium may have entered the apatite structure, but not a level appropriate for waste stabilisation. It would be instructive to combine hot pressing with the charge balancing and tunnel dilation mechanisms of Campayo

The question of cesium partitioning over the A^{I} and A^{II} positions also remains unclear, but could be resolved by preparing single phase powders containing substantial cesium, or through growing large single crystals. Computational methods may be useful to seek minimum energy configurations for cesium distributions, but it may prove difficult to provide experimental confirmation if equilibrated samples are not readily synthesized due to cesium evaporation.

7.7.2 Weapons Waste Type III Fixation

The reconnaissance investigation of the consolidation of the simulated UK defense waste into phase pure apatite is promising. The general conditions for solidification by hot pressing are established, but further investigation is needed to design a homogeneous and highly reactive precursor to further reduce the hot pressing temperature. The decomposition of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ into tricalcium phosphate (TCP) dimorphs may be limiting in terms of eliminating porosity, and durability may be compromised if reactive CaO is eliminated, subsequently rehydrates and swells. The swelling that accompanies conversion of CaO to $\text{Ca}(\text{OH})_2$ could lead to disintegration of the ceramic. It has been shown here, in confirmation of earlier studies, that TCP can be avoided through reaction at lower temperatures.

It was demonstrated that that a single PXRD experiment and Rietveld analysis to be suffice in confirming successful immobilization in apatite.

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Chapter 8

Conclusion: Development of Apatite for the Crystallochemical Immobilization of HLW

Apatite-based materials possess three key attributes to warrant their development as HLW ceramic nuclear wasteforms. First, the numerous cation and anion acceptor sites and structural adaptability make apatites fundamentally suitable to incorporate the entire gamut of fission products and actinides, including challenging species such as cesium and iodine. Second, in nature, apatite can quantitatively retain uranium and thorium, and synthetic analogous will be similarly durable in appropriate geological repositories. Third, the retention of volatile species and pore closure of ceramics is best achieved by hot pressing which proves to be a viable means for fabricating apatite wasteforms.

Appendix

The hypothesis put forward in this thesis is that apatite-type structures, particularly the phosphate, silicate and phosphor-silicate varieties, are sufficiently adaptable to incorporate the complete gamut of high level waste species produced during nuclear fission and subsequently released by reprocessing of spent nuclear fuel.

In this study, it was not possible to work with radionuclides, but rather, non-radioactive chemical analogues were used as proxies. The approach taken was first to investigate simplified systems containing simulated fission products, actinides and processing metals. In this manner, solid solution limits were established, and the metaprisim twist angle (ϕ) developed as a tool for confirming waste incorporation. Finally, uniaxial hot pressing was used to immobilize a high level waste analogue derived from reprocessing fuel for weapon production.

8.1 Apatite as a HLW Host

The structural flexibility of apatite in accommodating elements of variable charge and size has been comprehensively demonstrated through the synthesis and characterisation of

as simplified ceramic wasteforms. In detail, the incorporation of nuclides will often be accompanied by the creation of vacancies. Trivalent REEs, when introduced to britholites invariably produce framework A^{I} vacancies such that the ideal formula is best written as $[\text{REE}_{9.33}\square_{0.67}][(\text{SiO}_4)_6][\text{O}_2]$. Similarly, oxidation of the central tunnel anion leads to deficiencies of the type $[\text{Ca}_{10}][(\text{PO}_4)_6][(\text{F/Cl/OH})_{2-x}\square_x]$. The role of these defects with respect to radiation resistance of apatites has not yet been explored experimentally or computationally, and remains an area requiring significant investigation. From the point of view of tailoring, framework sub-stoichiometry

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could be eliminated through the introduction of monovalent ions, as for example in $[\text{REE}_{8.1}\text{K}_{1.9}][(\text{SiO}_4)_6][\text{O}_2]$, since alkali metals invariably enter the A^{I} position. It is however, more challenging to avoid tunnel anion (X-site vacancies) as halides and hydroxyls typically occupying this position are highly volatile. In any event, this essential aspect of nonstoichiometry can be probed directly by crystal structure refinement diagnosed through analysis of the $\text{A}^{\text{I}}\text{O}_6$ metaprism twist angle. When these results are combined with microanalysis (via energy dispersive X-ray spectrometry) and spectroscopy (using Fourier transform infrared spectrometry) the nature of intrinsic defects will be well established.

Although the incorporation of vacancies may compromise radiation resistance, this tendency could also prove beneficial as unexpected departures in waste stream composition may be accommodated without further tailoring of the precursor. It is perhaps significant that this work found hot-pressed apatite with 5 wt% waste was a single phase. In addition, the appearance of polymorphs and pseudomorphs introduces a further level of flexibility; however, this was not extensively explored in this study. Nonetheless, there is evidence to suggest that small heavy rare earth fission products can promote changes in apatite symmetry. These effects may not be apparent with mixed fission products, or where the waste loading is relatively low (say less than 30 wt%) and these details require study by transmission electron microscopy. In this thesis, TEM was conducted sparingly due to the electron beam sensitivity of the samples; however damage may be mitigated by *in situ* cooling or heating.

Uniaxial hot pressing in graphite dies is a viable option to fabricate apatite HLW ceramics. The key advantages are that:

- (i) ceramic bodies are produced near theoretical density to avoid the accumulation of volatile and leachable nuclides on pore surfaces and along grain boundaries;
- (ii) the system is essentially closed to minimize losses of high vapour pressure species and after solidification the die acts as a secondary barrier to mobilization; and
- (iii) providing the precursor is tailored and finely divided, and the waste liquor homogeneous, it is feasible to drive the reaction to near 100% yield of apatite.

Taken together, these findings provide strong evidence that apatite and britholite ceramic pellets can be synthesised as single phase wasteforms. This is in contrast to other materials such as Synroc or supercalcine where multiple phases coexist, accumulate different nuclides, and undergo differential swelling during damage in-growth. In the worst case, this could lead to fracture or decrepitation and inferior durability. Therefore, a monophasic apatite ceramic may deliver superior results for some classes of HLW, especially those in which the nuclides have not been partitioned.

8.2 Thesis Novelty

The research reported in this thesis is novel in several respects:

- (i) In *Chapter 3*, the proposal by White & Dong [1] that the A^1O_6 metaprism twist angle ϕ can be used to monitor crystallochemical changes is fully exploited for the first time. Whether substitution takes place over the A, B or X sites characteristic trends in ϕ can be used to monitor the reliability of structure solutions, validate nuclide uptake, and identify compositionally-driven changes in symmetry. In addition, for the first time a comprehensive assessment of published apatite solid solution series is presented to illustrate the challenges in synthesising homogeneous products and obtaining reliable crystallographic data.
- (ii) In *Chapter 4*, the crystallochemical principles developed for apatite electrolytes are extended to REE^{3+} britholites used to simulate immobilization of fission products and smaller transuranic species (Cm^{3+} , Am^{3+}). High concentrations of framework vacancies have not to date been considered in assessing the relative chemical and radiological stability of HLW apatites. Here, only fundamental questions concerning the formation of vacancies could be thoroughly investigated, but future work should include examination of chemical and radiological durability with varying degrees of non-stoichiometry.
- (iii) In *Chapter 5*, thorium was inserted into britholite to mimic the crystallochemical partitioning of U^{4+} and Pu^{4+} . While broadly in agreement with Terra *et al.* [2], it was additionally found that the final

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product was dependent upon the precursor used. This suggests that for this refractory apatite equilibrium is reached slowly, and clearly a soft chemical route to enhance homogeneity is required. Thorium solubility in $[\text{Ca}_{10-x}\text{Th}_x][(\text{PO}_4)_{6-2x}(\text{SiO}_4)_{2x}][\text{F}_2]$ ($x \sim 1$) appears quite limited, but longer firing at higher temperatures may improve the yield and thorium uptake.

- (iv) In *Chapter 6*, the first report of time-of-flight neutron diffraction of deuterated $[\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][(\text{OH})_2]$, $0 \leq x \leq 10$ is described. In this instance, a comparative study by FTIR showed that for the calcium endmember, the surface was substantially hydroxylated, but for strontium-bearing apatites the surface was oxidized and a shell of oxyapatite resulted $([\text{Ca}_{10-x}\text{Sr}_x][(\text{PO}_4)_6][\text{O}])$, $1 \leq x \leq 10$. In the bulk, neutron diffraction clearly revealed the location of OD^- , and by cooling to 4.2 K thermal motion was substantially reduced to improve the reliability of the refinement. The implications of an hydroxyl-oxy apatite core-shell structure with respect to wasteform durability are presently unknown.
- (v) In *Chapter 7*, an apatite ceramic containing a simplified waste simulate that mimics the crystal chemistry of reprocessed waste from the United Kingdom was prepared by uniaxial hot pressing in a graphite die. The temperature and pressure required to obtain a single phase product were established. While high temperatures lead to the formation of tricalcium-phosphate as a second phase, it was demonstrated that monophasic apatite could be prepared, inclusive of all waste species. These pilot results demonstrate that an apatite wasteform of high density and chemical complexity can be fabricated in this way.

The central hypothesis proposed in *Chapter 1*, and expounded upon in *Chapter 2*, that the apatite structural family possesses sufficient crystallochemical flexibility for exploitation in HLW management has been realized.

8.3 Roadmap for Future Research

The crystallographic engineering of apatite requires a deep appreciation of structural accommodation, and this thesis through design and necessity, was primarily concerned with developing a fundamental understanding of simulated wasteforms.

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Clearly, the work should be broadened substantially to provide complete assurance of apatite performance, and evidentially, this is beyond the current scope. However, the path towards future implementation is clear and would encompass experimental and theoretical studies including:

- (i) The immobilization of more complex wastestreams where a full suite of nonradioactive stimulants are used to demonstrate that precursor tailoring will yield phase pure products;
- (ii) An examination of the ultimate waste loading for a given waste stream to ensure that in actual use the wasteform is over-engineered to accommodate unexpected variability in waste composition;
- (iii) Comprehensive leach testing over a range of temperatures and pH to map those conditions under which dissolution accelerates and wasteform integrity is compromised. These experiments should include the examination of re-precipitates as well as solubilised species;
- (iv) Accelerated radiation damage testing by exposure to neutrons, alpha particles or ions with a particular emphasis on amorphization as a function of ceramic composition, energy and dose, and temperature. The rate and nature of structural recovery is also important, and should be linked to changes in leachability as described in (iii);
- (v) Scale-up of the hot pressing process to create monoliths would validate the method and allow complete investigation of physical-mechanical properties;
- (vi) Laboratory-scale production of apatites containing active waste so that the effects of self-radiation damage on durability and mechanical integrity can be assessed; and
- (vii) Selection and testing of geological repository materials at small scale and full site assessment to evaluate worst case dispersion scenarios should the wasteform package fail.

In conclusion, while this research proved challenging, the insights gained into the synthesis and characterization of apatite-based ceramics provides a scientific basis for developing a disposal protocol to permanently isolate high level nuclear waste from the biosphere.

Appendix

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Appendix**Table A1:** Calculations of the 5wt% waste incorporation in apatite structure (page 124).

to produce 0.001 mole of apatite with 5wt% waste,
amount of waste needed = $0.0161 \times 5 - 0.0423 = 0.0382\text{g}$
amount of waste
adjusted(g) 0.057
waste percentage (wt%) 5.058434174

Waste	Waste %	weight(g)	mole	Starting mat	mole	weight(g)
HfO ₂	62.2	0.0355	0.1684	CaCO ₃	3.1684356	0.317129
Ga ₂ O ₃	9.4	0.0054	0.0286	Ca ₂ P ₂ O ₇	2.7743407	0.633637
Al ₂ O ₃	1.7	0.0010	0.0095	H ₂ SiO ₃	0.4513	0.035239
Sm ₂ O ₃	11.7	0.0067	0.0191	CaF ₂	0.4443845	0.034698
CaF ₂	5	0.0029	0.0365	CaCl ₂	0.4426567	0.049129
KCl	10	0.0057	0.0765	total		1.069831
Total	100	0.0570				

	Ca	(PO ₄)	(SiO ₄)	F/Cl
Before	10	6	0	2
Hf	-0.1684	-0.33687111	0.33687111	0
Ga	-0.057170294	-0.057170294	0.05717029	0
Al	-0.019006708	-0.019006708	0.01900671	0
Sm	-0.038270401	-0.038270401	0.0382704	0
Ca	-0.0365	0	0	0
K	-0.0765	0	0	-0.0765
F				-0.0730
Cl				-0.0765
Total	9.6042	5.5487	0.4513	1.9235

Apatite produced = $\text{Ca}_{9.64}[\text{Hf}_{0.17}\text{Ga}_{0.06}\text{Al}_{0.02}\text{Sm}_{0.04}\text{K}_{0.08}](\text{PO}_4)_{5.55}(\text{SiO}_4)_{0.45}\text{F}_{0.96}\text{Cl}_{0.96}$