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Fresnoite Oxides: Synthesis, Crystal Chemistry and Possible Melilite Intergrowth

*“Investigation of the impact of structural distortion on
functionalities”*

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in partial fulfillment of the requirement for the degree of
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Abstract

Fresnoites ($A_2BC_2O_8$) and melilites ($A_2BC_2O_7$) are layered oxides whose basic structures are modified by crystallographic modulation arising from the need to accommodate pentagonal oxygen rings that cannot fill space without distortion. The modulations are systematized using higher dimensional space groups ($> 3D$). Interest in these materials has focused on chemically and/or thermally induced commensurate-incommensurate phase transitions, and provided insights into the nature of interlayer bonding and polyhedral rigidity. Exploitation of this understanding to develop and tune functionality is, as yet, hardly explored. In particular, the application of these oxides as heterogeneous semiconductor photocatalysts has not been considered.

This thesis examines the drivers of crystal chemically induced commensurate-incommensurate phase transitions, their impact on defect structure at nano- and micro- scales, the influence of these changes on the band gap energy, and the possibility of moving the photocatalytic response towards visible light energies. The $(Ba_{1-x}Sr_x)_2TiSi_2O_8$ and $Ba_2Ti(Si_{1-x}Ge_x)_2O_8$ fresnoite solid solution series, and a melilite $Sr_2CoSi_2O_7$ were synthesized, and characterized with electron, X-ray and neutron diffraction. The physical properties were probed by thermogravimetric analysis and ultraviolet-visible spectroscopy. The task of unambiguously describing the modulated structures, and correlating catalytic activity with incommensuration proved challenging, with in-depth analysis only possible for $(Ba_{1-x}Sr_x)_2TiSi_2O_8$. Specifically, Rietveld refinement was restricted to large-grained products of high temperature syntheses, while catalytic testing required finely-divided powders obtained by soft chemical methods. Therefore, structure-property correlations were inferred.

A Pechini synthesis of fresnoites ($(Ba_{1-x}Sr_x)_2TiSi_2O_8$) was developed to obtain homogeneous high surface area oxides that circumvented the need for an inert atmosphere blanket. This method was adapted for the synthesis of $Sr_2CoSi_2O_7$ melilite, and can be used to prepare fresnoite-melilite intergrowths proposed as novel band gap shifted photocatalysts.

Fresnoites are tetragonal and/or orthorhombic with inflection of the a and c -axes indicating a change in symmetry at $x \sim 0.5$ in $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Si}_2\text{O}_8$ and $\text{Ba}_2\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_8$ ($1 \leq x \leq 0$). As the metal motif is almost invariant, oxygen displacements promote these phase transitions. To directly gather information on the oxygen sublattice, $\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $(\text{BaSr})\text{TiSi}_2\text{O}_8$ were examined by neutron diffraction. However, Rietveld refinement proved ambiguous due to a noticeable background arising from the diffuse scattering, together with many overlapping weak satellite reflections, that prevented convergence to physically realistic crystal parameters. Several refinement strategies were attempted for extracting the average modulated structures that were partially successful. Electron diffraction found that modulation of the mixed fresnoite $((\text{BaSr})\text{TiSi}_2\text{O}_8)$ was more complex than for the endmembers $(\text{Ba}_2\text{TiSi}_2\text{O}_8$ and $\text{Sr}_2\text{TiSi}_2\text{O}_8)$. Analytical high resolution transmission electron images revealed for the first time, the co-existent of chemically differentiated commensurate-incommensurate phases. For $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$, two distinct band gaps (~ 3.2 - 3.5 eV and ~ 2.9 - 3.1 eV) varied with composition, and for endmembers could be modeled using density functional theory methods. However, band gap tuning was not realized, as the commensurate-incommensurate phase transition is exceedingly difficult to control at nanoscales. Photocatalytic activity of fresnoites, as determined by the mineralization of methylene blue was not competitive with commercially available titania catalysts.

The significance of this work is that the unexpected complexity of fresnoite and melilite powders have been recognized and comprehensively described, but incommensurate-commensurate intergrowths are not readily controlled through adaptation of the synthesis method or composition. Nonetheless, the insights arising from this work provide a roadmap for future examination of this question. While this research confirmed the expected linkage between crystal chemistry and electronic structure, crystallographic analysis of industrially useful fine powders was not feasible and optimization of processing conditions and validation of properties is presently difficult.

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Figure 6.7. Electron diffractions of Br-fresnoite along both [001] and [010] from areas with almost homogeneous bright contrast (a) and (b), and from portions showing dark contrast (c). It is observed that the intensities for incommensurate reflections along [001] is not pronounce. Tilting off axis is necessary to bring out the weaker reflections. By capturing a larger set of diffraction spots, satellite reflections are observed in [100] direction. Insets red disks correspond to kinematical family reflections common to all fresnoite family members respectively; smaller yellow disks represent incommensurate reflections.

Figure 6.8. High resolution imaging of Ba-fresnoite powder along [001] (a)-(b) and [100] (c)-(d). Modulation along [001] perhaps are too weak to be reconstructed while strong modulation is observed along [100] with regions of commensurate (lighter contrast) and incommensurate (darker contrast). (b) and (d) is the enlargement of (a) and (c) respectively.

Figure 6.9. Electron diffractions of BaSr-fresnoite along both [001] and [010]. It is observed that the intensities for incommensurate reflections along [001] are not pronounced as Sr-fresnoite. It is observed that the diffraction captured along [100], (b) and (c), showing two different sets of diffractions spots after prolonged observation under the transmission electron microscope. Insets red disks correspond to kinematical family reflections common to all fresnoite family members respectively; smaller yellow disks represent incommensurate reflections.

Figure 6.10. High resolution imaging of BaSr-fresnoite powder along [001] (a)-(b) and [100] (c)-(d). Modulation along [001] showing co-existence of regions of commensurate (lighter contrast) and incommensurate (darker contrasts). It is observed that the incommensurate regions along [100] is changing with illumination times. (b) is the enlargement of (a), while (c) and (d) showing the change in incommensuration with illumination times with (d) being illuminated longer than (c).

Figure 6.11. On the left are reported two HRTEM images used to reconstruct Fourier Transforms (FT) from different sample areas using the program CRISP. Calculated FT from areas showing different degrees of disorder (i.e. different contrast distributions) clearly bring to evidence that incommensuration is not homogeneously distribute over the sample. (a) Beside the presence of clearly commensurate areas (a), samples portions showing different kind of darker contrast related to different degrees of structural disorder, show evidences of different of modulated incommensuration (b, c, d, e, f) as imaged by the reconstructed FT calculated from different disordered areas.

Figure 7.1. Splitting of d electrons of Ti^{4+} ions in regular and distorted square pyramidal coordination. The distortion shown by $\text{Ba}_2\text{TiGe}_2\text{O}_8$ is representative of $\text{Sr}_2\text{TiSi}_2\text{O}_8$. Taken from [19].

Figure 7.2. Absorbance spectra and extrapolation to band gap for (a) titania photocatalyst, (b) Ba-fresnoite (BTS), and (c) Sr fresnoite (STS). The weaker absorption edge nearer the visible region is readily observed in STS.

Figure 7.3. An additional absorption edge becomes more pronounced with increasing strontium content in the fresnoite structure. (a) Ba-fresnoite (BTS), (b)-(d) are mixtures with Sr atoms replacing Ba atoms in steps of 20 at%, 50 at% and 80 at% respectively, and (e) Sr-fresnoite (STS).

Figure 7.4. The change band gap determined by UV-visible spectroscopy varies with strontium replacement in Ba-fresnoite. Band gaps calculated from (a) the strongest band edge (solid line), and (b) the additional edge (dotted line), are shown.

Figure 7.5. The band gaps of (a) Ba-fresnoite, (b) Sr-fresnoite, and (c) Ba,Sr-fresnoite. In (c), the second absorption edge indicates the creation of additional band gap in the forbidden gap region as a result of Sr substitution.

Figure 7.6. Computed density of states from CASTEP. (a) BTS and (b) STS showing slight variation to the band gap change which were largely attributed to the Ti(d) orbital.

Figure 7.7. The decoloration of methylene blue is used as an indicator of catalytic activity. The plot above shows absorbance decreasing with time (0, 5, 10, 15, 20, 30, 40, 50, & 60 min.).

Figure 7.8. Baseline experiment performed in the dark showing negligible absorption of methylene blue molecules by the powdered BTS photocatalyst.

Figure 7.9. The oxidation of methylene blue treated with BTS and STS photocatalysts processed via the Pechini method. A methylene blue blank is included to provide baseline.

Abbreviations

BSTS	Barium-Strontium Titanium Silicate
BTG	Barium Titanium Germanate
BTS	Barium Titanium Silicate
DGA	Differential Gravimetric Analysis
E _{bg}	Band Gap Energy
EDX	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
NMR	Nuclear Magnetic Resonance
PCO	Photo Catalytic Oxidation
PSG	Pechini-type Sol-gel
RUM	Rigid Unit Mode
R _{wp}	Weighted R-Bragg
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
STS	Strontium Titanium Silicate
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate
TGA	Thermogravimetric Analysis
TIP	Titanium Isopropoxide
UV	Ultraviolet
XAS	X-ray Absorption Analysis
XRD	X-ray Diffraction

Part I:

*Fundamentals, Synthesis &
Characterization*

Chapter 1

Introduction

Fresnoite and melilite possess incommensurate crystal structures and contain transition metals in tetrahedral, and the less common square pyramidal oxygen coordination. Such crystal chemistry may hold potential for creating novel photocatalysts, and this hypothesis is explored by searching for structure and functionality relationships amongst these materials. The challenges in establishing such correlations are considered.

1.1 Preamble

Global warming and the role of green house gases (CO_2 , SO_3) generated by the combustion of coal and oil has provided impetus for the development of renewable power sources (i.e. wind, solar, and water) to enable sustainable growth. In addition, hydrogen can be used as a non-polluting combustible fuel produced by photocatalytic (solar) splitting of water. Moreover, photocatalysis driven by sunlight can be used for water and air purification, as reported as early as 1976 [1-2], and research to enhance catalytic activity through harnessing solar power to provide clean fuel, and for environmental remediation, is an international endeavor.

To date, the only commercially viable photocatalysts are titania-based. However, the band gap energies of both the anatase and rutile polymorphs lie in the ultraviolet, and the mobilization of electron-hole pairs to initiate catalytic activity is minimal in sunlight. Therefore, band gap adjustment of titania through the introduction of anion and cation chemical dopants has been extensively explored with mixed success, and other classes of materials, such as perovskites and perovskite-related compounds, are being screened as potential photocatalysts [3]. These semiconductors (BaFeO_3 , $\text{Sr}_2\text{Fe}_2\text{O}_5$, $\text{Ca}_2\text{Fe}_2\text{O}_5$, $\text{BaCoO}_{2.93}$, $\text{Sr}_2\text{Co}_2\text{O}_5$ [3] and Ca_2NiWO_6 [4]) can absorb visible light photons to create excitons for initiating redox reactions that decompose water or render contaminants benign [4]. However, despite initial promise, those candidates are not yet commercially developed, due to the difficulty of fabricating materials with reproducible properties.

A systematic approach for developing complex oxide semiconducting catalysts is required. One rationale is to select crystal structures that force the active ions (e.g. titanium) into unusual oxygen coordination polyhedra (i.e., TiO_4 , TiO_5) rather than TiO_6 to modify the band gap. For example, double perovskites (e.g. $\text{MIn}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ($\text{M} = \text{Ca}$, Sr , and Ba)) absorb energy in ultraviolet and visible light in a structurally systematic way and can cleave water into hydrogen and oxygen [5]. The ability of these compounds to absorb

visible light photons shows that electronic structure and band gap energy can be manipulated through crystallochemical design [6-8].

An unusual barium titanosilicate mineral from the Eastern Fresno County of California was noted in 1962 [9], and subsequently confirmed by Alfors [10] using powder X-ray diffraction. The type specimen was named fresnoite and described as “lemon or canary yellow, (with) vitreous luster, and a white streak” [10]. Although physical, optical and chemical analyses were performed, the crystallography was unsolved until Moore and Louisnathan [11-12] established that $\text{Ba}_2\text{TiSi}_2\text{O}_8$ fresnoite was a layered structure where planes of barium atoms were separated by corner-connected sheets of SiO_4 and TiO_5 polyhedra. This unique motif, especially with respect to titanium in square-pyramidal coordination, spurred research interest into its magnetic [13-15] and optical properties [16-17].

Structurally similar to fresnoite, melilite $((\text{Ca},\text{Na})_2(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_7)$ was first characterized by Warren [18] and further investigation by Smith [19] revealed slabs of corner-connected tetrahedra between which the larger cations were located. Much later, synthetic versions of this material were examined for their ionic conductivity [20], electrical conductivity [21] and photoluminescence properties [22].

In general, fresnoite ($\text{A}_2\text{BC}_2\text{O}_8$) and melilite ($\text{A}_2\text{BC}_2\text{O}_7$) type oxides possess three cation-acceptor sites (i.e. A, B and C) and flexible layers that allow the synthesis of numerous chemical analogues in powder and single crystal forms. These compounds are receiving increasing attention because their wide functionalities suggest promise as technological materials [23-41]. The properties of fresnoite and melilite can be adjusted by charge coupled substitutions to tailor ionic and electrical conductivity, photoluminescence, magnetic and optical characteristics [16, 21-22, 42]. As the possibilities for alternate substitutions are considerable, it appears feasible to tune the band gap by doping and distorting the transition metal-oxygen co-ordination, and these ideas provide the context for introducing fresnoite and melilite-types as potential heterogeneous photocatalysts. It is also noted that the local bonding

environments are comparable to those of the layered titanosilicate ($\text{Na}_4\text{Ti}_2\text{Si}_8\text{O}_{22}\cdot 4\text{H}_2\text{O}$) [43] that is constructed from double Ti-Si-O sheets, as opposed to fresnoite and melilite which contain single sheets. Significantly, reconnaissance photocatalytic investigations of this sodium titanosilicate succeeded in oxidizing phenol to quinone [43], and fresnoite/melilite may also be effective. Given the similarity of their crystallochemical motifs, it may be feasible to intergrow fresnoite and melilite to deliver new properties.

In this thesis, this hypothesis was tested by:

- (i) *modifying the ionic substitutions in fresnoite and melilite* and completely describing the crystallography including the incommensurate component;
- (ii) *developing new synthesis methods* that deliver single-phase, high surface-area products suitable for photocatalysis; and
- (iii) *attempting to blend fresnoite with melilite* crystallographically to create new materials with direct band gaps in the visible light region.

The overall goal is to correlate crystallography with property through understanding of their electronic structures, and so develop high activity catalysts with the capacity to operate in sunlight.

1.2 Hypothesis and Novelty

It is the aim of this work to establish if fresnoites ($\text{A}_2\text{BC}_2\text{O}_8$) and melilites ($\text{A}_2\text{BC}_2\text{O}_7$), by virtue of their modulated structures (i.e. characterized by more than 3 dimensions in reciprocal space), will show variations in metal-oxygen bond distances, that can be manipulated to deliver specific band gap energies that enhance photocatalytic activity (Fig. 1.1). Melilites in particular have received little attention as technological materials, and the possibility of fresnoite-melilite structural intergrowths is an entirely unexplored field of study. Potentially, the incorporation of transition metal rich melilite domains

in fresnoite could move the band gap energies far into the visible range and lead to a superior class of photocatalyst.

Figure 1.1. Rationale for the investigation of fresnoites and melilites as photocatalysts.

$A_2BC_2O_8$ and $A_2BC_2O_7$ solid solution systems were prepared using aliovalent and intervalent substitutions to correlate incommensurate order with photoactivity. The approach will include:

- (i) *controlled distortion of the small cation polyhedra* (square pyramidal and tetrahedral) by means of cationic replacements (i.e. B or C); and
- (ii) *incorporation of different inter-layer A cations* to adjust the distance between the layers while keeping the B and C chemistry fixed.

By varying these parameters independently, those structural features that most profoundly modify band gap structure and/or catalytic activity shall be identified.

1.3 Challenges

The challenges in this study are three-fold:

- (i) *Solid solutions between fresnoite and melilite have not been reported* and their synthesis may prove difficult. While previous studies focused on single crystals of the parent structure, which are relatively simple to crystallize from the melt, this study is concerned with polycrystalline powders that cannot be readily prepared phase pure.
- (ii) *Crystal chemical investigations require detailed attention due to long-range modulation* that creates many low intensity overlapping reflections. X-ray, neutron and electron diffraction shall be

employed as complementary tools to probe the crystal structures of fresnoite and melilite. These data must be interpreted entirely quantitatively as artifacts or equipment limitations could lead to false structure assignments.

- (iii) *Protocols for photocatalytic testing will require development* as these materials have not previously been evaluated for catalytic activity.

1.4 Objectives and Scope

The objectives of this research were to:

- (i) *develop methods to synthesize fresnoite and melilite* in physical forms suitable for crystallographic characterization and as fine divided reactive powders; and
- (ii) *establish relationships between crystallochemistry and electronic structure* by understanding the crystal structure and macroscopic/intrinsic defects of these materials.
- (iii) *A third goal was to employ this knowledge to design and optimize* products for environmental applications, particularly for waste water treatment. However, the difficulty of developing products with reproducible physical and chemical forms was only partially overcome in these studies.

The scope of this PhD comprises:

- (I) Comprehensive characterization
 - (I-i) Electron microscopy: Electron diffraction, due to the high coherence of the electron beam and small probe volume, can be used to differentiate the space group of the synthesized materials and observe superlattice formation. The strength of this technique is that the interaction of electrons with matter is much stronger than X-rays because the latter scatter at relatively long range. This favors the detection of weak superstructure reflections not visible by X-ray diffraction. High

resolution electron microscopy can identify atomic segregation and crystallographic modulation. The visualization of macroscopic defects, and grain size and phase segregation is best accomplished by scanning electron microscopy.

- (I-ii) Powder diffraction: X-ray and fixed wavelength neutron diffraction were employed to obtain crystallochemical information (unit cell parameters, composition, anisotropic thermal parameters, modulation and distortion of polyhedra), conduct quantitative phase analysis, and examine microstructural evolution during calcination. This method is important for understanding stress-structure relations that contribute to exciton formation and catalytic activity.

(II) Fresnoite and melilite catalyst fabrication

- (II-i) Solid state reaction: A complete solid solution of Ba,Sr-fresnoite was synthesized for detailed crystallographic analysis. High temperature fabrication with repeated grinding and heating leads to minimal impurities, but the large particles are unsuitable for technological applications.
- (II-ii) Sol-gel synthesis: A method was developed for synthesizing phase pure and finely divided polycrystalline powder suitable for photocatalytic testing. Previously reported methods which yield phase pure single crystals are not for viable large scale production.
- (II-iii) Fresnoite-melilite intergrowth: Light doping of Ti^{4+} in melilite and Co^{2+} in fresnoite is possible. These substitutions were performed using the sol-gel technique, designed in (II-ii).

(III) Developing protocols for quality control and testing

- (III-i) Photocatalytic oxidation (PCO) of methylene blue (a benchmark organic pollutant): Photocatalytic activity of the

sol-gel material was examined by monitoring the photodegradation of methylene blue as a function of illumination time using UV-visible spectroscopy.

1.5 Dissertation overview

This dissertation is divided into two parts. **Part I** describes the aims and introduces concepts in higher dimensional crystallography, characterization methodology, and preparative approaches. **Part II** contains crystal structure refinements of fresnoite primarily, together with less detailed analyses of melilites. Finally, an overview of the work performed and directions for future studies are given that could lead to visible light photocatalysts. A summary of reconnaissance experiments undertaken to this end is provided.

Part I: Fundamentals, Synthesis & Characterization

Chapter 1 gives a short review of the fresnoite-melilite structures and the rationale for pursuing this study. It also presents the hypothesis, challenges encountered, and experimental design strategies.

Chapter 2 provides the conceptual scaffold for incommensuration and an historical prospective of the crystallographic descriptions of fresnoite and melilite. The importance of defects in photocatalysis, their detection and possible influence on catalytic activity.

Chapter 3 explores the range of techniques employed to probe the modulated structures, including their limitations and complementarity, and provides insights into the synthesis methodology.

Chapter 4 collates the experimental observations concerning the evolution of fresnoite and melilite during synthesis. The optimal Pechini process for the formation of phase pure materials is established.

Part II: Crystal Structure & Functionality

Chapter 5 focuses on the structure refinement of strontium doped fresnoite compounds from powder neutron diffraction data. The polyhedral distortion with respect to cationic substitution is explored using several strategies to overcome peak overlap and weak incommensurate reflections.

Chapter 6 examines the microscopic defects formation in fresnoite and its implications for the characterization of the “modulated” structures observed by X-ray and neutron diffraction. It is suggested that the complex nanostructure prevents a simple correlation between chemistry and modulation, that in turn, will make the tuning of band gaps less straightforward.

Chapter 7 provides a first attempt to correlate photocatalytic activity and band gap with respect to fresnoite composition. It is shown that the usual methods of extracting band gap energy from absorption spectra, the calculation of partial density of states are not readily applied to these oxides.

Chapter 8 summarizes how the outcomes of this research provide guidance for designing fresnoite and melilite catalysts, developing appropriate strategies for characterization, criteria for enhancing the performance of these materials as photocatalyses are identified.

1.6 Significance and Achievements

It was hypothesized that subtle structural changes in fresnoite phases could be managed through adaptation of synthesis methodology and composition to deliver fine control of functionality. However, this study using transmission electron microscopy and neutron diffraction has shown that the crystal chemistry of these phases is far more complex than previously suspected. *The significance of this research is that incommensurate-commensurate intergrowths arising from local compositional variations are not easily eliminated, and consequently, the electronic properties could not be readily tailored due to local crystallographic relaxation propagating through the fresnoite layers.* It can be reasonably expected, on the basis of preliminary results, that the related melilite compounds show similar behavior. Therefore, the focus of this research was redirected towards developing a comprehensive understanding the nanostructure of these materials, rather mapping structure-property relationships.

Nonetheless, several objectives of the proposed study were partially met and include:

- (i) developing a novel Pechini method for synthesizing fresnoite which was subsequently used for fresnoite and melilite intergrowth;
- (ii) differentiating the fresnoite average structure and the real structure while recognizing the complexity of its macroscopic/bulk defects; and
- (iii) establishing that structural stress induced by cationic substitution allows band gap tailoring which is essential for heterogeneous photocatalytic materials design.

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Chapter 2

Derivation of Crystallographically Incommensurate Semiconductor Photocatalysts

Classical crystals show three-dimensional periodicity. Modulation of crystal structures by chemical substitution or atomic displacements lead to incommensurate order that can be described by higher dimensional superspace groups. Fresnoite and melilite are examples of modulated structures which arise from rotation of tetrahedral and square pyramidal polyhedra, and this flexibility may prove useful for band gap tuning of heterogeneous photocatalysts.

2.1 Classical Crystal Structures

2.1.1 Real Space

Single crystals possess repeated patterns where atoms are arranged in a regular fashion in three dimensional space, known as real space [1]. The arrangement of atoms adheres to fixed points that creates a network [1], and joining these points results in a mosaic or motif of atoms contained within a repeating unit cell (Fig. 2.1).

Figure 2.1. A unit cell is formed by regularly spaced objects in three dimensional space which creates a mosaic from the lines joining the points. (a) A two dimensional projection of a mosaic pattern. (b) A regular pattern representing the arrangement of atoms in three dimensional space.

The symmetry of crystals is described in one, two or three dimensions by point groups, plane groups, and space groups respectively, that systematize the relationships between chemically or structurally distinct compounds. These ‘classical’ three dimensional structures conventionally adhere to the definition of a ‘crystal’, where the constituent atoms are related by 4 fundamental operations – translation, reflection, rotation and glide that combine to create screw axes, inversion and roto-inversion operations [2]. Such materials are said to possess perfect long range order. These symmetry operators, together with the unit cells of the 14 space lattices, and coupled with translation symmetry, yields the 230 space groups [1].

2.1.2 Diffraction and Reciprocal Space

There are various techniques for “solving” crystal structures, the best known of which are related to obtaining diffraction data, where generally, an incident beam of monochromated X-rays, neutrons or electrons is directed towards the material (Fig. 2.2) [3]. These radiations propagate at wavelengths comparable to atomic spacings that scatter to create inference patterns whose characteristics are related to the positions and interaction strengths with the atoms [3]. During diffraction, crystallographic data is preserved in “coherent elastic scattering” such that constructive interference [3-4], that carries the crystallographic information and results in a “diffraction pattern” [3]. The physical “real” space crystal, yields a diffraction pattern in “reciprocal” space.

Figure 2.2. Geometry for interference of an incident wave scattered from two planes of atoms separated by a spacing, d . The dashed lines are parallel to the crests or troughs of the incident and diffracted wavefronts. The total length difference for the two rays is the sum of the two dark segments. Reproduced from [3].

Bragg’s Law provides a simple means to relate the atomic arrangement in real space to reciprocal space, whose derivation is shown in figure 2.2 where the interplanar spacing (d) fixes the difference path for scattering from the top and bottom atomic planes described geometrically as $2d\sin\theta$. A diffraction peak or line is observed only when the path difference is equivalent to the wavelength, λ [3-4], as captured in

$$2d\sin\theta = n\lambda \quad (\text{Equation 2.1})$$

This equation relates crystallographic constants to diffraction pattern information. In single crystal diffraction, data is collected as a spot pattern that is a two dimensional projection of the three dimensional crystal. Evidently, to completely understand a crystal structure, diffraction patterns must be recorded in several orientations. Each spot represents a diffraction plane in reciprocal space that is referred to as a Bragg or main reflection [3]. Bragg reflections are spaced at integral distances, possess intensities that are characteristic of the scattering power of the diffracting planes, and display a half-width which grows narrower with increasing coherent diffracting volume.

Figure 2.3. An illustration of the relationship between the arrangement of atoms in three dimensional space with the projections of the reciprocal space diffraction patterns. (a) The arrangement of atoms in a unit cell when (b) projected in two dimension yields characteristic diffraction patterns in reciprocal space.

In 3D structures, atomic ordering within the unit cell (i.e. subcell) will lead to the formation of a superlattice (i.e. supercell). A superlattice arises when the atoms are arranged in a manner that creates multiple folds of the basic unit cell to create a larger repeating unit cell (Fig. 2.4). Here, the supercell adheres to the fundamentals of a classical structure, and in reciprocal space, the supercell reflections are weaker than those of the subcell, and remain integral or commensurate.

Figure 2.4. The arrangement of atoms in three dimensional space with the reciprocal space diffraction pattern for supercell structures. (a) The ordering of atoms in a unit cell and (b) the corresponding reciprocal space diffraction pattern. The weaker reflections shown in (b) indicate the formation of a supercell arising from atomic ordering.

2.2 Higher Dimensional Symmetry

2.2.1 Introduction to Non-Classical Crystals

With the discovery of new crystalline materials and the advancement of characterization tools, the simple description of a “crystal” has increasingly been found wanting. Crystals which have long range order, but do not necessarily adhere to the definition of periodic crystals, have prompted the examination of a novel classes of materials – the incommensurate and vernier structures [2]. While essentially distinct, these groups are an extension of the “classical” definition of crystals, that differ in not possessing three dimensional translational symmetry or very long range periodicity [2,5]. Their structures are more correctly described in n-dimensional periodic space and are systematized by higher dimensional symmetry. Broadly, the three classes of aperiodic crystals [5-6] are:

- (i) incommensurately modulated structures;
- (ii) incommensurate composite crystals; and
- (iii) quasicrystals.

The distinctions between these groups of aperiodic crystals are somewhat arbitrary, as small changes in composition can lead to alternation between types (i) and (ii). Incommensurately modulated structures have long-range order without 3D symmetry. In this case, there is a basic structure which can be described by a three-dimensional symmetry, upon which is superimposed a period of modulation that renders the overall structure incommensurate. Such crystals are frequently described by a periodic average structure, but in fact the true unit cell contents are shifted systematically by a translational operation. This shift conforms to a modulation function which can be of a displacive, occupational, or thermal motion type or a combination of these.

Incommensurate composite crystals arise from the intergrowth of two periodic structures (each with their independent 3D space-group symmetry). Commonly, these examples are described as two chemically independent materials stacked as layered composites or as an interpenetrating network.

These materials can alternatively be considered as two commensurate subsystems which are mutually incommensurate, with their own principle reflections modulated due to interaction with the other subsystem.

Quasicrystals do not adhere to any crystallographic point group symmetries as they locally contain 5-fold rotational symmetry. The building principle is different to composite and modulated structures. Due to the absence of translational periodicity, main and satellite reflections are not clearly distinguished. Essentially, quasicrystals are based on pentagonal atomic motifs that are unable to fill space without the inclusion of disorder; these networks are also known as Penrose tilings.

2.2.2 Description of N-Space Crystallography

Higher dimensional space groups can systematize the absence of 3D symmetry in aperiodic crystals, while providing a chemically meaningful account of the origins of modulations [7-8]. This approach introduces one or more additional reciprocal lattice vectors, described by $(3+n)$ -dimensional, $n \geq 1$, superspace groups. Here, lattice periodicity is “restored” through the addition of lattice (q) vectors that propagate in directions derived from the basic lattices (i.e. a , b and c).

2.2.3 Incommensurate Crystal Phases - Substitutional and Displacive Modulations

In incommensurately modulated structures [9] a portion of the basic crystal is systematically altered by substitutional and displacive modulations [7,9] (Fig. 2.5) that van Smaalen [10] described as atomic displacements from the undisturbed positions in the basic unit cell. Figure 2.6 illustrates the most basic longitudinal and translational displacements possible with respect to the subcell edges that may be purely displacive, or include occupational modulations [9]. These different types of modulations can be distinguished by characteristic electron density maps (Fig. 2.7) [7].

Figure 2.5. A comparison of (a) displacive (a) and (b) occupational modulations. In (a), the atoms are displaced from the ideal positions in unit cell following a wave function, while in (b) the atoms are in ideal positions but different atomic species are ordered. Taken from [9,11].

Figure 2.6. Crystal structures with displacement modulations. (a) The basic structure, (b) supercell indicated by incommensuration rectangle, (c) in longitudinal incommensuration direction and (d) in transversal incommensuration direction. Lattices indicated by dash lines and atoms by the circles. Taken from [10].

Figure 2.7. Comparison of difference Fourier maps for (a) an ideal commensurate structure, (b) where is present occupational modulation and (c) with displacive modulations. The diagram includes the higher dimensional space lattice vector a_4 . P' indicates the intensity of reflections in reciprocal space while R_3 shows the thickened line indicating the positions of atoms in real space. Taken from [7].

2.2.4 Main and Satellite Reflections

Main reflections, as mentioned in the previous section, arise from the diffraction of classical periodic three dimensional structures, and in single crystal diffraction, are characterized by higher intensities than the surrounding subcell reflections [7]. The nature of the modulations defines the occurrence and position of those satellite reflections [7]. Often 3D superlattices and incommensurate superlattices give the superficial appearance of being similar, however, when the location of the satellite reflections is non-rational with the respect to the subcell, the structure is correctly described as modulated. In some systems, the position of the supercell reflections can alternate between rational and irrational, as a function of chemical composition.

The relationship between the real space structure and reciprocal space pattern is illustrated in Figure 2.8. Periodic structures (Fig. 2.8 (a)), have regular and intense diffraction spots, while a perturbed structure (Fig. 2.8 (b)) possessing a supercell or commensurately modulated structure, has weak satellite reflections appearing along certain directions and evenly spaced along the systematic rows. The incommensurately modulated structures (i.e. substitutional and displacive modulations) exhibit non-regularly spaced weak satellite reflections (Fig 2.8 (c-d)).

Figure 2.8. Relationship between real space and reciprocal space. The squares indicate unit cells in 2D space, circles denote similar atoms, while the black circles are the main reflections and the small grey dots are the satellite reflections, and the wave indicates modulation. (a) A regular 3D crystal, (b) a superlattice with doubled unit cell, (c) displacement (longitudinal and transversal) modulation and (d) ionic/chemical ordering represented by whole circles and broken circles. Taken from [11].

The relationship between the main and satellite reflections is readily described through vector mathematics, and illustrated as projections on the 2D reciprocal lattice of the higher dimensional superspace (Fig. 2.8) [7]. When satellite reflections/points are projected along q , the classical 3D reciprocal space lattice is observed (Fig. 2.8) [7]. Including one or more q vectors allows the satellite reflections to be directly related to the underlying 3D lattice to which the modulation is added.

Figure 2.9. The projection of satellite reflections in (a) 2D space and (b) 3D space. The reciprocal direction a_2^* is perpendicular to the a_1^* direction. The satellite reflections are aligned along an additional reciprocal lattice (a_4^*) that is a projection of spots running along a_1^* . Thus, the vector which properly describes this phenomenon is the vector q , where $q = \alpha a_1^*$ (α is rational for commensurate crystals while it is irrational for incommensurate crystals). Adapted from [7].

Figure 2.10. In 5D modulated structures satellite reflections may be difficult to observe due to the high intensity of the subcell reflections. Presented here is a hypothetical (3+2)-superspace structure (i.e. the aperiodic crystal possesses two modulation vectors).

For example, if the satellite reflections are described by the vectors q_1 and q_2 , then a (3+2)-superspace group is created that contains the reciprocal lattice vectors a_4^* and a_5^* in addition to a_1^* , a_2^* and a_3^* such that [6]

$$a_4^* = q_1 \quad (\text{Equation 2.2})$$

$$a_5^* = q_2 \quad (\text{Equation 2.3})$$

It is evident that the modulation vectors can also be expressed in terms of the underlying three dimensional lattice [7,10].

$$q_1 = \alpha_1 a_1^* + \beta_1 a_2^* + \gamma_1 a_3^* \quad (\text{Equation 2.4})$$

$$q_2 = \alpha_2 a_1^* + \beta_2 a_2^* + \gamma_2 a_3^* \quad (\text{Equation 2.5})$$

2.3 Crystal Structures of Fresnoite and Melilite

2.3.1 Fresnoite

When fresnoite was first described, crystallographic information was spare, but the structure was evidently tetragonal with chemical composition $\text{Ba}_2\text{TiSi}_2\text{O}_8$, $Z = 2$, and possible space groups of $P4/mbm$, $P4bm$ or $P-4b2$ [12]. Single crystal X-ray diffraction conclusively established the symmetry as $P4bm$ with, $a=8.52 \pm 0.01 \text{ \AA}$, $c=5.210 \pm 0.005 \text{ \AA}$ [13] (Table 2.1). The structure was described as layers of “[Si_2O_7] $^{6-}$ double groups linked to Ti-O square pyramids parallel with {001},” connected such that the tetrahedral SiO_4 and TiO_5 square pyramids formed planes of pentagonal tunnels separated by barium. At that time, fresnoite provided a unique example of five-coordinated titanium, with the result that one Ti-O and Si-O bond was slightly shorter than usual; for Si this phenomenon was believed consistent with partial nonequivalent- sp^3 hybridization (Table 2.2) [14]. An independent study by Masse et al. [15] employing Patterson and Fourier methods yielded similar results ($P4bm$, $a = 8.52 \text{ \AA}$, $c = 5.21 \text{ \AA}$), and concluded that fresnoite was adequately described as a conventional 3D crystal.

Table 2.1. Atomic coordinates of fresnoite with standard deviations in parentheses [14].

Atom	Coordinates		
	x	y	z
Ba	0.3272 (01)	$\frac{1}{2} + x$	0
Si	0.1282 (06)	$\frac{1}{2} + x$	0.5207 (30)
Ti	0	0	0.5414 (18)
O (1)	0	0.5	0.6183 (91)
O (2)	0.1236 (19)	$\frac{1}{2} + x$	0.2125 (64)
O (3)	0.2896 (23)	0.5762 (23)	0.6584 (45)
O (4)	0	0	0.2278 (91)

Table 2.2. Angles and distances for fresnoite [14].

Ti polyhedron		Si ₂ O ₇ group	
Ti-O (3)	= 2.001 (21) Å	Si-O (1)	= 1.626 (37) Å
Ti-O (4)	= 1.634 (45) Å	Si-O (2)	= 1.607 (39) Å
O (3) - O (4)	= 2.944 (43) Å	Si-O (3) [2x]	= 1.613 (25) Å
O (3) - O (3')	= 2.696 (28) Å	O (3) - O (3'')	= 2.569 (40) Å
O (4) - Ti - O (3)	= 107.74° (34)	O (3) - O (2) [2x]	= 2.750 (33) Å
O (4) - Ti - O (3')	= 144.54° (61)	O (3) - O (1) [2x]	= 2.559 (20) Å
Si - O (3) - Ti	= 135.82° (47)	O (2) - O (1)	= 2.587 (26) Å
		Si - O (1) - Si'	= 143.51° (60)

Figure 2.11. Fresnoite crystal structure determined by Moore and Louisnathan [14] in (a) [001] and (b) [010] projections. The material possesses a 2D rigidity due to the corner-connected polyhedra. The Ti-O and Si-O bonds in the (001) plane are longer than the apical metal oxygen bonds.

More than 20 years would pass before the modulated nature of synthetic fresnoite was revealed by electron diffraction, with weak satellite reflections found in the $hk\frac{1}{2}$ layers when crystals were tilted slightly off the [001] zone axis indicating a doubling of the c parameter [16]. However, details concerning the nature of the incommensuration (i.e. displacive or occupational modulation) and the origin of domains revealed by dark field imaging were not established. It was hypothesized that incommensuration relieved strain in the Si_2O_7 sorosilicate and TiO_5 groups propagating from the interlayer barium atom in ten-fold coordination [16]. Höche et al. [17] revisited this material, finding similar selected area diffraction patterns, and suggested that as the $\text{Ba}_2\text{TiGe}_2\text{O}_8$ analogue was displacively modulated, natural $\text{Ba}_2\text{TiSi}_2\text{O}_8$ fresnoite could behave similarly.

Figure 2.12. Selected area diffraction patterns of incommensurately modulated fresnoite captured in the (a) $[001]_p$ and (b) $[100]_p$ zone axes. Satellite reflections surround the subcell reflections indicative of long range order [18]. The satellite reflection are non-integral with respect to the main diffraction, and indexed in terms of 5D superspace.

Not until 2002 was fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) comprehensively characterized by Withers et al. [18], as a (3+2)-dimensional superspace group with modulation vectors $q_1 \sim 0.30[110]_p^*$ and $q_2 \sim 0.30[1-10]_p^*$ (here $_p^*$ denotes the parent cell). To satisfy superspace symmetry requirements, c_p was doubled to remove the rational component of the q_1 and q_2 modulation vectors such that $c^* = \frac{1}{2}c_p^*$. It was concluded that RUM (rigid unit mode) modeling could be employed to simplify the description, and explain the displacive modulations. This model is based on two possible deformations of the corner-connected polyhedra; first, coupled rotation of the polyhedra may take place strictly in the basal planes, or second, out-of-plane buckling of the polyhedra can be envisaged. As basal plane rotation requires less energy, this mechanism is

favoured to relieve strain in fresnoite and promote polymorphic phase transitions.

Figure 2.13. Two types of deformation in fresnoite are possible as shown by the arrows which illustrate (a) rotation/deformation of the collective polyhedra about the c-axis or (b) buckling polyhedral in the basal plane. Polyhedral rotation is energetically favourable, thus the most likely mode to reduce deformation.

With a more complete understanding of synthetic fresnoite available, the characterization of natural fresnoite was revisited [19], using single crystal X-ray diffraction to extract electron density maps that showed directly the modulation wave arose from atomic displacements. Refinement in superspace group $P4bm(\alpha, \alpha, \frac{1}{2})(-\alpha, \alpha, \frac{1}{2})0gg$ with $\alpha = 0.302(3)$ [19] showed anisotropic atomic displacement parameters, explained by the RUM rotation of polyhedra across the bridging oxygen atoms. This phenomenon was attributed to larger atoms occupying the polyhedra that increased the amplitude of Ba-O modulation distances. Consequently, the distorted structure inevitably results in a wide range of bond lengths. Interestingly, the TiO_5 polyhedra were not severely distorted but merely rotating around the c-axis. In short, refinement as a superspace group allows the quantitative analysis of the nature of fresnoite modulation.

Many chemical analogues of fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$ or BTS) have been synthesized and provide the opportunity to better understand the origin of modulations and its impact on crystal chemistry (Table 2.3). For example, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ (STS) [18, 20], is metrically similar to fresnoite but with more intense satellite reflections, attributed to greater structural misfit (i.e. Sr is smaller than Ba) giving rise to much larger strain. $\text{Ba}_2\text{VSi}_2\text{O}_8$ on the contrary

[21, 22], shows less polyhedral rotation than $\text{Sr}_2\text{TiSi}_2\text{O}_8$. Nonstoichiometric $\text{Ba}_{1.5}\text{V}^{4+}\text{OSi}_2\text{O}_7$ lead to similar observations as $\text{Ba}_2\text{VSi}_2\text{O}_8$ but with a shorter Ti-O bond (the apical oxygen) [23], however, a more comprehensive study is needed as only isotropic temperature factors were refined. When a larger atom replaces Ti, as in $\text{Ba}_2\text{MnSi}_2\text{O}_7\text{Cl}$, the Mn-Cl bond lengths are longer, distorting the square pyramid [24]. The $\text{Rb}_2\text{V}_3\text{O}_8$ analogue appears to be unique in possessing a single modulation vector, $q \sim 0.16c$, while retaining a tetragonal metric ($P4bm$, $a = 8.9229 \text{ \AA}$, $c = 5.5014 \text{ \AA}$) [25]. A later investigation of $\text{K}_2\text{V}_3\text{O}_8$ revealed a commensurate structure with $q \pm 1/3 \langle 110 \rangle_p^* + 1/2 c_p^*$ in $P4bm$, with $a = 8.8954 \text{ \AA}$, $c = 5.2472 \text{ \AA}$ and the lattice parameters are slightly smaller than $\text{Rb}_2\text{V}_3\text{O}_8$ [26]. Germanium can replace silicon in fresnoite as $\text{Ba}_2\text{TiGe}_2\text{O}_8$ but this compound is orthorhombic, $Cmm2$, $a=12.291 \text{ \AA}$, $b=12.274 \text{ \AA}$, $c=10.733 \text{ \AA}$ with $q \sim 0.3[110]_p^*$ [18,27]. Thus, distortion in fresnoite analogues is more pronounced when stress is largest, and is relieved by (001) polyhedral rotations to produce commensurate and incommensurate modulations most usually described by a (3+2)-dimensional super spacegroup.

Table 2.3. Compilation of selected modulation vectors for fresnoite and its analogues.

Compound	Modulation vector(s)	Temperature (K)	Ref
$\text{Ba}_2\text{TiGe}_2\text{O}_8$	$q \sim 0.315 \langle 110 \rangle^* + \frac{1}{2} c^*$	room temperature	18
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	$q \sim \pm 0.302 \langle 110 \rangle^* + \frac{1}{2} c^*$	room temperature	19
$\text{Sr}_2\text{TiSi}_2\text{O}_8$	$q \sim \pm 0.3 \langle 110 \rangle^* + \frac{1}{2} c^*$	room temperature	20
$\text{Ba}_2\text{VSi}_2\text{O}_8$	$q \sim \pm 0.297 \langle 110 \rangle^* + \frac{1}{2} c^*$	room temperature	22
$\text{Rb}_2\text{V}_3\text{O}_8$	$q \sim 0.16 \langle 110 \rangle c^*$	269	25
$\text{K}_2\text{V}_3\text{O}_8$	$q \sim \pm 1/3 \langle 110 \rangle^* + \frac{1}{2} c^*$	115	26

2.3.2 Melilite

The crystal structure of melilite ($(\text{Ca},\text{Na})_2(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_7$), a mineral first identified by Warren [28], is similar to fresnoite but possesses the general formula $\text{A}_2\text{BC}_2\text{O}_7$. Further investigation by Smith [29] of this mineral determined it to be tetragonal, $P-42_1m$ with $a = 7.789 \text{ \AA}$ and $c = 5.018 \text{ \AA}$.

Table 2.4. Atomic coordinates of melilite [29].

Atom	x	y	z
Ca	0.33	0.17	0.51
Si	0.14	0.36	0.95
Mg	0	0	0
O (1)	0.50	0	0.19
O (2)	0.14	0.36	0.26
O (3)	0.08	0.18	0.81

Figure 2.14. Polyhedral representation of melilite viewed along (a) [010], (b) [001] and (c) tilted to clarify the corner connectedness of the tetrahedra [29].

The melilite structure is constructed from corner-connected tetrahedra (i.e. BO_4 and CO_4) to create layers separated by the larger A cation. CO_4 tetrahedra exist as C_2O_7 dimers with the vertices directed up or down with regard to the polyhedral slabs (Fig. 2.14). Louisnathan [30] examined the synthetic melilite $\text{CaNaAlSi}_2\text{O}_7$ and provided insights into the bonding and connectivity of the BO_4 and CO_4 polyhedra, but within the context of three dimensional symmetry. The first report of modulation was a study on the solid solution of melilite-type, iron-bearing åkermanites, that underwent commensurate to incommensurate phase transitions [31].

Figure 2.15. Electron diffraction pattern of $\text{Ca}_2\text{MgSi}_2\text{O}_7$, slightly tilted from the $[001]$ orientation to accentuate the satellite. The aperture used for the dark-field imaging is also shown [31].

In synthetic Co-åkermanite [32], it was found the SiO_4 tetrahedron did not adhere to a rigid body unit, with distortion conclusively established by the wide variation in Si-O bond lengths and O-Si-O angles. This material was described in space group $P-42_1m$ with modulation vectors $q_1 = 0.2913 (a^* + b^*)$ and $q_2 = 0.2913 (-a^* + b^*)$, and polyhedral bond lengths similarly modulated. A study of a natural melilite yielded comparable results [33], with the range of bond-lengths in melilite-type structures arising from a combination of cation and anion shifts within the polyhedral layers [34]. Visualization of the anisotropic displacements revealed distortion (eg. flattening or twisting) of the structure by the bridging anions [33, 34]. Chemical analogues possess different modulation vectors, and although the changes are minimal, reflect significant atomic displacements and differences

in Fourier amplitudes [35]; discrete cationic substitutions in alternating polyhedral layers were also consistent with this observation [36]. For melilites, changes in the intensity and sharpness of the satellite reflections are pronounced as cation substitution alters, due to differing misfits between the tetrahedral sheets and the interlayer cations.

The structural modification of melilite-type materials, though subtle, leads to changes in functionality. For example, calorimetric properties are found to correlate with polyhedral sheet distortion, especially when smaller interlayer cations cause internal strain [37] relieved by polyhedral distortion and modulation. These variations result in commensurate-incommensurate phase transformations, and lattice parameter adjustments driven by changes in chemistry (i.e. cationic substitution) or temperature [37, 38].

Table 2.5. Compilation of selected modulation vectors for melilite and its analogues.

Compound	Modulation vector(s)	Temperature (K)	Ref
$\text{Ca}_2\text{CoSi}_2\text{O}_7$	$q \sim \pm 0.2913 (a^* + b^*)$	room temperature	32
	$q \sim \pm 0.292 (a^* + b^*)$	292	35
$(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.98}\text{Al}_{0.02})\text{O}_7$	$q \sim \pm 0.2815 (a^* + b^*)$	room temperature	33
$\text{Ca}(\text{Mg}_{0.55}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$	$q \sim \pm 0.295 (a^* + b^*)$	room temperature	34
$\text{Ca}_2\text{MgSi}_2\text{O}_7$	$q \sim \pm 0.280 (a^* + b^*)$	room temperature	35
	$q \sim \pm 0.280 (a^* + b^*)$	348	35
$\text{Ca}_2(\text{Mg}_{0.55}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$	$q \sim \pm 0.295 (a^* + b^*)$	297	35
	$q \sim \pm 0.290 (a^* + b^*)$	383	35

2.4 Semiconductor Photocatalysts

2.4.1 Fundamental Concepts

Mills et al. [39] explained “photocatalysis” as “the acceleration of photoreaction by the presence of a catalyst”, and involves photosensitization of the photochemical reaction due to absorption of energy (i.e. light) by a susceptible chemical (i.e. photosensitizer). There are two broad classes of photocatalysts - heterogeneous which includes interphase reactions [40], and

homogeneous photocatalysis, where only gases or liquids are involved - with typical reactions including oxidation, dehydrogenation, hydrogen transfer, metal decomposition and water detoxification. Heterogeneous photocatalysis consists of five principle stages:

- (i) *Contact* between the molecules (i.e. reactants) and catalyst;
- (ii) *Absorption* of the molecule to the surface of the catalyst;
- (iii) *Reaction* between the molecule and catalyst;
- (iv) *Desorption* of by-products; and
- (v) *Removal* of chemical residues from the catalyst surface.

Semiconductor photocatalytic reactions, which encompass heterogeneous photocatalysis, are surficial [39-42] and require a substrate to be in contact/adsorb on the catalyst leading to either:

- (i) *Photoexcitation of the adsorbed molecule* prior to reaction with the ground state of a catalyst (i.e. catalyzed photoreaction), or
- (ii) *Photoexcitation of the catalyst* and reaction with the ground state of the adsorbed molecule (i.e. sensitized photoreaction).

For the destruction of pollutants, these reactions will ideally proceed with solar energy and a semiconductor catalyst which can be excited, preferably by visible light photons. During heterogeneous photocatalysis, sunlight promotes an electron from the valence band to the conduction band to create free electrons and holes. These electron-holes pairs or excitons, are generated in significant amounts when the energy absorbed is more than the band gap energy, E_{bg} (Fig. 2.14) [39-44]. Thus the adsorbed molecules will undergo redox reactions to yield inert or environmentally friendly by-products [43] with idealized outcome summarized as:

Figure 2.16. Schematic representation of the band energy model for the overall process of semiconductor photocatalysis during water purification [40].

2.4.2 Defects and Photocatalysis

Both surface and bulk defects play important roles for enhancing photocatalysis [45]. The primary requirements are for excitons to be produced in significant numbers and long lifetimes to initiate reactions, while the surface environment simultaneously inhibits electron-hole recombination and promotes adsorption of reactants [41-42]. In principle, reactivity will be enhanced by tailoring band gaps for visible light excitation.

2.4.3 Bulk Defects

The important bulk defects in photocatalysis arising from the modification of electronic structure (i.e. polyhedral distortion or bonding) and/or crystallinity of the material [46], are commonly created by introducing interstitial anions or anionic vacancies [47] or by cationic substitution [46]. Of particular concern in this study, is the role of the polyhedral structure in photocatalysis. In MSnO_3 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$), it has been found that E_{bg} and the photogeneration of the excitons, are closely related to the polyhedral distortion [46] that

accommodates structural misfit, and these distortions then enhance electron-hole migration while minimizing the band gap of the material. Fresnoites and melilites where the polyhedra are unusually irregular offer the possibility for unique catalytic responses.

2.4.4 Surface Defects

Photocatalytic kinetics will be enhanced if surface defects favour the inhibition electron-hole recombination while enhancing the absorption of reactants and creating more active sites [48-49]. Such improvements have been achieved by photoetching [48] and annealing in oxygen [49]. However, certain defects will be undesirable should they lead to recombination and capturing free charges (e.g. lattice defects) [50]. As described in *Chapter 4*, the present research emphasized the development of synthesis routes that yield high surface area semiconductors to maximize absorption and create defects that slow exciton annihilation.

2.4.5 Rationale for Optimizing Fresnoite and Melilite Photocatalytic Activity

The preceding sections outlined the nature and description of higher dimensional structures, particularly with respect to the layered fresnoite and melilite phases. In both cases, modulation provides a means to accommodate unusual bonding environments, by rotation and distortion of polyhedra. It is postulated that incommensuration can be adjusted through chemical substitutions, to systematically modify the polyhedra, and allow tuning of semiconductor band gap energies. This may provide a means to create excitons in visible light to promote higher efficiency photocatalysis.

Within this context, research was conducted to:

- (i) Fully describe the higher dimensional symmetries of fresnoite and melilite and establish polyhedral distortion as a function of composition;

- (ii) Exploit the structural similarity of fresnoite and melilite to design hybrids or intergrowths with favorable photocatalytic band gaps;
- (iii) Create both bulk and surface defects through chemical tailoring and materials processing that enhance photocatalytic activity; and
- (iv) Correlate crystallochemical and electronic properties for fresnoite and melilite phases in sufficient detail to guide the design of novel photocatalysts, especially for wastewater treatment.

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Chapter 3

Synthesis and Characterization

The recognition and description of modulated crystal structures is challenging, especially in finely-divided materials because incommensuration is inherently difficult to detect or crystal-to-crystal variation may be present. Synthetic methods that yield technologically useful fresnoite and melilite powders of high surface area and with homogeneous distributions of band gap adjusting dopants are required.

3.1 Precepts

A fundamental requirement for correlating structure with functionality is that a material be of consistent physical form and chemically uniform. It is generally true that as the number of components increase the delivery of reproducible results requires greater control of processing parameters. A survey of fresnoite and melilite type materials shows that the majority of studies are of large crystals, often melt grown, with a focus on crystallographic descriptions rather than property-driven investigations of technologically useful forms such as nano-powders, thin films or composites (Tables 3.1 and 3.2).

Table 3.1. Compilation of studies performed on fresnoite and fresnoite-type compounds.

Composition	Powder/single crystal	Purpose of study	Ref
$(\text{Ba}_{1.962}\text{Ca}_{0.038})\text{TiSi}_2\text{O}_8$	Mineral	Crystallography	1
$\text{Sr}_2\text{TiSi}_2\text{O}_8$	Single crystal & polycrystalline glass ceramics	Crystallography	2
$\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$	Single crystal & polycrystalline glass ceramics	Crystallography	3
$\text{Ba}_2\text{TiSi}_2\text{O}_8$, and $\text{Ba}_2\text{TiGe}_2\text{O}_8$	Polycrystalline glass ceramics	Crystallography and computational study	4
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Crystallography	5
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Mineral	Crystallography	6
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Mineral	Crystallography	7
$\text{Ba}_2\text{Ti}_{1-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 0.14$)	Polycrystalline ceramic powder	Crystal chemistry	8
$\text{Ba}_2\text{TiGe}_2\text{O}_8$	Single crystal	Crystallography	9
$\text{Ba}_2(\text{Ti}_{0.95}\text{Hf}_{0.05})(\text{Ge}_{2x}\text{Si}_{2-2x})\text{O}_8$ ($0 \leq x \leq 1$)	Polycrystalline ceramic powder	Crystallography	10
$\text{A}_2\text{V}_3\text{O}_8$ ($\text{A} = \text{K}, \text{Rb}, \text{NH}_4$)	Polycrystalline ceramic powder	Crystallography & magnetic properties	11
$\text{K}_2\text{V}_3\text{O}_8$	Single crystal	Crystallography	12
$\text{Rb}_2\text{V}^{5+}\text{V}^{3+}_2\text{O}_8$	Single crystal	Crystallography	13
$\text{Ba}_2\text{MnSi}_2\text{O}_7\text{Cl}$	Single crystal	Crystallography	14
$\text{Ba}_{1.5}\text{VO}_5\text{Si}_2\text{O}_7$	Polycrystalline ceramic powder	Optical properties	15
$\text{Ba}_2\text{VSi}_2\text{O}_8$	Polycrystalline ceramic powder & single crystal	Crystallography	16
$\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$	Polycrystalline ceramic powder	Crystallography	17
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Crystallography & phase transition	18
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Mineral	Crystallography	19
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline glass ceramics	Nucleation & growth kinetics	20
$\text{Ba}_2\text{TiGe}_2\text{O}_8$	Polycrystalline glass ceramics	Formation and optical study	21
$\text{Ba}_2\text{TiSi}_2\text{O}_7\text{-SiO}_2$	Polycrystalline glass ceramics	Microstructural characterization	22
$\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$	Modeling	Optical properties	23
$\text{Sr}_2\text{TiSi}_2\text{O}_8$	Polycrystalline glass ceramics	Crystal growth	24
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Modeling	Surface-acoustic-wave	25
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline glass ceramics	Optical and luminescent properties	26
$\text{Ba}_2\text{Ge}_2\text{TiO}_8$	Polycrystalline glass ceramics	Piezoelectric study	27
$\text{K}_2\text{V}_3\text{O}_8$	Polycrystalline glass ceramics & modeling	Antiferromagnet	28
$\text{K}_2\text{V}_3\text{O}_8$	Modeling	Antiferromagnet	29
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Nanocrystallized glasses	Optical Properties	30
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline glass ceramics	Crystal chemistry	31
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Surface acoustic wave properties	32
$\text{Ba}_2\text{Ge}_2\text{TiO}_8$	Single crystal	Phase Transitions, Dielectric,	33
$\text{K}_2\text{V}_3\text{O}_8$	Polycrystalline ceramic powder	Piezoelectric and Pyroelectric Properties	34
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Crystallography	35
$\text{K}_2\text{V}_3\text{O}_8$	Single crystal	Surface-acoustic-wave characteristic	36
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline ceramic powder	Luminescence properties	37
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Piezoelectric properties	38
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Piezoelectric properties	39
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Crystallography & pyroelectric	40
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal & polycrystalline Ceramic powder	Ferroelectric property	41
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Single crystal	Growth and physical properties	42
$\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$	Polycrystalline glass ceramics	Optical property	43
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline glass ceramics	Crystallography & crystal chemistry	44
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline glass ceramics	Crystallography	45
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline glass ceramics	Morphology study	46
$\text{Ba}_2\text{Ti}_{1-x}\text{Si}_{2+x}\text{O}_8$ ($0 \leq x \leq 0.14$),	Polycrystalline ceramic powder	Crystal chemistry	47
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Thin film	Crystal growth	48
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Ferroelectric films	Crystal growth & ferroelectric property	49
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	Polycrystalline ceramic powder	Crystal growth	50
$\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$	Single crystal	IR spectroscopic	51

Table 3.2. Compilation of studies performed on melilite and melilite-type compounds.

Composition	Powder/single crystal	Purpose of study	Ref
$(\text{Ca}_{1-x}\text{Sr}_x)\text{CoSi}_2\text{O}_7$ ($0 \leq x \leq 1$)	Polycrystalline Ceramic powder	Crystallography	52
$\text{Ca}_2\text{CoSi}_2\text{O}_7$	Single crystal	Crystallography	53
$(\text{Ca}_{1-x}\text{Sr}_x)\text{CoSi}_2\text{O}_7$ ($0 \leq x \leq 0.32$)	Single crystal	Crystallography	54
$\text{Ca}_2\text{CoSi}_2\text{O}_7$, $\text{Ca}_2\text{MgSi}_2\text{O}_7$, and $(\text{Ca}_2\text{Mg}_{0.53}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$	Single crystal	Crystallography	55
$(\text{Ca}_{1-x}\text{Sr}_x)\text{MgSi}_2\text{O}_7$ ($0.04 \leq x \leq 0.32$)	Single crystal	Crystallography	56
$\text{CaMgSi}_2\text{O}_7$ - $\text{CaFeSi}_2\text{O}_7$, $\text{Fe}/(\text{Fe}+\text{Mg})=0 \sim 0.7$	polycrystalline glass ceramics	Crystallography	57
$\text{CaNaAlSi}_2\text{O}_7$	polycrystalline glass ceramics	Crystallography	58
$((\text{Ca},\text{Na})_2(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_7)$	Mineral	Crystallography	59
$(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.98}\text{Al}_{0.02})\text{O}_7$	Mineral	Crystallography	60
$\text{Ca}_2(\text{Mg}_{0.53}\text{Fe}_{0.45})\text{Si}_2\text{O}_7$	Polycrystalline Ceramic powder	Crystallography	61
$\text{X}_2\text{ZT}_2\text{O}_7$; $\text{X}=\text{Ca}, \text{Sr}, \text{Pb}, \text{Ba}, \text{Na}, \text{Y}, \text{Z}=\text{Be}, \text{Mg}, \text{Fe}^{2+}, \text{Cu}, \text{Co}, \text{Zn}, \text{Mn}, \text{Cd}, \text{Al}, \text{Fe}^{3+}, \text{Ga}, \text{Si}, \text{T}=\text{Si}, \text{Ge}, \text{Al}, \text{Fe}^{3+}, \text{Ga}, \text{Be}$	Review	Crystallography and crystal chemistry	62
$\text{Ca}_2\text{Mg}_{0.6}\text{Fe}_{0.4}\text{Al}_{0.6}\text{Si}_{1.4}\text{O}_7$, $(\text{Ca},\text{Sr},\text{Ba})_2(\text{Zn},\text{Fe})(\text{Si},\text{Ge})_2\text{O}_7$, $\text{La}_{1+x}\text{Sr}_{1-x}\text{Ga}_2\text{O}_7$, $x < 0.6$	Polycrystalline ceramic powder	Crystallography and crystal chemistry	63
$(\text{Ca}_{1.85}\text{Na}_{0.14}\text{Pb}_{0.01})(\text{Zn}_{0.85}\text{Al}_{0.07}\text{Mg}_{0.03}\text{Mn}^{3+}_{0.04}\text{Fe}^{3+}_{0.02})\text{Si}_2\text{O}_7$	Polycrystalline ceramic powder	Ion conductivity	64
$\text{La}_{1.05}\text{Sr}_{0.95}\text{Ga}_2\text{O}_7$	Single crystal	Crystallography	65
$\text{Ba}_2\text{CuGe}_2\text{O}_7$	Polycrystalline ceramic powder	Electrical conductivity	66
$\text{Ca}_2\text{Zn}_{0.97}\text{Co}_{0.03}\text{Ge}_2\text{O}_7$	Modeling	Antiferromagnet	67
$\text{Ca}_2\text{ZnGe}_2\text{O}_7$ & $\text{Ca}_2\text{ZnGe}_{1.25}\text{Si}_{0.75}\text{O}_7$	Polycrystalline glass ceramics	Crystallography	68
$(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.97}\text{Al}_{0.03})\text{O}_7$	Polycrystalline ceramic powder & Single crystal	Crystallography	69
$\text{Ba}_2\text{CoSi}_2\text{O}_7$	Mineral	Crystallography	70
$(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.98}\text{Al}_{0.02})\text{O}_7$	Polycrystalline glass ceramics	Crystallography	71
$\text{Ca}_{2.03}\text{Al}_{2.06}\text{Si}_{0.95}\text{O}_7$, $\text{Ca}_{2.03}\text{Mg}_{0.21}\text{Al}_{1.54}\text{Si}_{1.24}\text{O}_7$, $\text{Ca}_{2.03}\text{Mg}_{0.46}\text{Al}_{0.99}\text{Si}_{1.52}\text{O}_7$, $\text{Ca}_{2.04}\text{Mg}_{0.71}\text{Al}_{0.51}\text{Si}_{1.74}\text{O}_7$, $\text{Ca}_{2.05}\text{Mg}_{0.96}\text{Si}_{1.99}\text{O}_7$	Mineral	Crystallography	27
$(\text{Ca}_{1.89}\text{Sr}_{0.01}\text{Na}_{0.08}\text{K}_{0.02})(\text{Mg}_{0.92}\text{Al}_{0.08})(\text{Si}_{1.98}\text{Al}_{0.02})\text{O}_7$	Polycrystalline glass ceramics	Crystallography	73
$\text{Ln}_x\text{Ca}_{2-x}\text{Al}[\text{Al}_{1+x}\text{Si}_{1-x}\text{O}_7]$ with $0 \leq x \leq 1$ and $\text{Ln} = \text{La}, \text{Eu}, \text{Er}$	Polycrystalline ceramic powder	Crystallography	74
$(\text{Ca}_{1.70}\text{Sr}_{0.07}\text{Na}_{0.20}\text{K}_{0.03})(\text{Mg}_{0.70}\text{Fe}^{2+}_{0.04}\text{Al}_{0.25}\text{Fe}^{3+}_{0.01})\text{Si}_2\text{O}_7$	Mineral	Crystallography	75
$\text{Y}_2\text{Si}_2\text{O}_7$	Modeling	Crystallography	76
$\text{M}_2\text{MgSi}_2\text{O}_7$; Re^{3+} ($\text{M}=\text{Ba}, \text{Sr}, \text{Ca}$)	Polycrystalline ceramic powder	Photoluminescence properties	77
$\text{M}_2\text{MgSi}_2\text{O}_7$; Eu^{2+} ($\text{M}=\text{Ca}, \text{Sr}$)	Polycrystalline ceramic powder	Luminescence properties	78
$\text{Sr}_2\text{ZnSi}_2\text{O}_7$; Eu^{2+} , Dy^{3+}	Polycrystalline ceramic powder	Photoluminescence properties	79
$\text{Sr}_2\text{ZnSi}_2\text{O}_7$; Eu^{2+} , Dy^{3+}	Polycrystalline ceramic powder	Photoluminescence properties	80
$\text{Ca}_2\text{CoSi}_2\text{O}_7$	Single crystal	Crystallography	81
$\text{CaNaBeSi}_2\text{O}_7\text{F}$	Mineral	Crystallography	82
$\text{X}_2\text{ZSi}_2\text{O}_7$; $\text{X}=\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$; $\text{Z}=\text{Be}^{2+}, \text{Mg}^{2+}, \text{Fe}^{2+}$	Review	Theory	83
$\text{Y}_2\text{Si}_2\text{N}_4\text{O}_4$ (N-Melilite) & $\text{Y}_4\text{Si}_2\text{O}_7\text{N}_2$ (J-Phase)	Polycrystalline ceramic powder	Crystallography	84
$\text{La}_{1+x}\text{Sr}_{1-x}\text{Ga}_2\text{O}_{7-2x}$ ($-0.15 \leq x \leq 0.60$)	Polycrystalline ceramic powder	Electrical properties	85

In this thesis, equal weight was given to developing an understanding of the origin of structural modulations and its influence on photocatalytic activity. However, the forms of fresnoite and melilite most suitable for these studies are distinct. Higher dimensional structures are more readily, and least ambiguously, examined as large single crystals by X-ray or neutron diffraction. Ceramic powders or sintered tablets required for catalytic applications prove more demanding to describe at a fundamental level, but will deliver enhanced functionality. Therefore, the research described here used several preparative routes that allow for a range of testing, but with the limitation that structure-property correlations had then to be inferred. A particular constraint, was the inability to completely refine crystal structures using Rietveld techniques, presumably due to microdomain formation as discussed in *Chapters 5 and 6*.

3.2 Synthesis Methods

3.2.1 Solid State Reaction

The starting materials for solid state synthesis were oxides ground together homogeneously, pelletized and fired at high temperature ($>1000^{\circ}\text{C}$). Repeated grinding and compaction was needed to obtain homogeneous products and remove persistent intermediate phases to yield phase pure products. Solid state synthesis was performed as the initial part of this study for basic structural understanding, while wet chemistry was employed to produce high surface area materials as catalysts as described in *Chapter 4*.

3.2.2 Soft Chemistry

Sol-gel processes were chosen to obtain chemically homogeneous precursors. The starting materials were ethylene glycol, acetates, silicates and propoxides. A Pechini method was developed to eliminate water, permit better control of gelation rate and circumvent the need to synthesize in an inert environment.

3.3 Structural Characterization Methods

It is not the purpose of this section to describe in detail the operational aspects of the diffraction and imaging methods used, but rather, highlight their complementarity for examining modulation. As these techniques probe crystals at different scales, with distinct sensitivity to chemical constituents, and yield data of varying accuracy, drawing together these disparate results was challenging. However, taken in combination, a more complete description of fresnoite and melilite emerged, avoiding over-emphasis on the reliability of single-technique data to guide materials processing and regulate functionality.

3.3.1 Transmission Electron Microscopy (TEM)

Electron diffraction, due to the high coherence of the electron beam and small probe diameter can establish the space group of materials, or at least exclude non-conforming symmetries, and detect superlattice formation [87]. X-ray and neutron diffraction, with much poorer spatial resolution, examine the average

structure. The strength of microscopy arises because electrons strongly interact with the periodic potential of the lattice at relatively long range. This favors the detection of weak superstructure reflections that may not be readily observed by X-ray or neutron diffraction.

In the present work, selected area electron diffraction (SAED) patterns were collected with a field emission transmission electron microscope (TEM) operating at 200kV using a JEOL JEM-2100F TEM ($C_s = 0.5$ mm). Both powdered and ion beam thinned samples were examined. The powders were dispersed ultrasonically before depositing on holey carbon films, while the ion beam thinned samples were prepared as sintered pellets that were trepanned into disks (3 mm $\varnothing$) using an ultrasonic cutter. These were polished to 100 μm before gluing to a copper washer using epoxy. The mounted disks were mechanically dimpled before high precision ion milling at 5 keV with argon. A thin evaporated carbon thin film was deposited on the perforated disk to minimize charging during microscopy.

In order to observe incommensuration, crystals were usually tilted slightly off the principle axes to better excite weak modulated reflections or minimize masking by strong main reflections. In single scattering, kinematic electron diffraction is assumed for structure analysis as systematic absences will be consistent with symmetry, but dynamical scattering can complicate this analysis as secondary scattering (i.e. double diffraction) can lead to weak intensities forbidden by symmetry (Fig. 3.1).

Figure 3.1. (a) An electron diffraction pattern showing kinematic scattering where “forbidden” reflection is indicated by ‘X’ and (b) an electron diffraction pattern showing dynamical scattering can falsely lead to the observation of “forbidden” reflections.

3.3.2 High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM was employed to study atomic scale structural disorder of thin (< 10nm) crystals and is extremely beneficial for examining nano-sized particles or crystallographic domains. Direct observation of stacking faults, incommensuration and grain boundary structure is possible [88-89]. For the present work, the challenge lies in selecting crystal orientations that reveal the satellite reflections and are most intense in thicker crystals. These conditions (off-axis orientation and thick crystal) are incompatible with HRTEM, where thin samples aligned to principle zone axes are essential to produce interpretable contrast. A further limitation was the susceptibility of many fresnoite and melilite composites to electron beam damage that rapidly reduces the intensity of satellite reflections and sometimes resulted in amorphization. This effect was sometimes apparent during SAD experiments where the beam was defocused and less then intense during HRTEM imaging.

3.3.3 Scanning Electron Microscopy (SEM)

Crystal morphology was examined by secondary electron images (SEI) obtained with a scanning electron microscope (JEOL JSM 5310) equipped with an energy dispersive X-ray (EDX) operating at 10-15 keV. The samples were gold sputter coated before fixing with double sided carbon tape to an aluminum sample holder. Backscattered electron imaging (BEI) was performed on finely polished samples to reveal compositionally distinct regions. EDX point analysis and mapping were used to correlate microstructure and chemistry.

3.3.4 Powder X-ray Diffraction (XRD)

Reconnaissance crystal structure parameters were extracted from powder X-ray diffraction (Shimadzu, XRD 6000 and Bruker AXS) patterns collected with Cu- $K\alpha$ radiation and step-scanned over a 2θ range of 10-140° at intervals of 0.02° using Bragg-Brentano geometry. Accurate unit cell parameters were obtained by introducing an internal silicon standard spiked to 20 wt% (NIST SRM 640c). This approach also allowed the amorphous content of the sample to be estimated. TOPAS 3.0 (Bruker AXS) was used for phase analysis and

unit cell parameter extraction. However, a limitation of X-ray diffraction arises because the interaction with light atoms (especially oxygen in the present context) is weak, although the anion sublattice defines the symmetry and modulations. This proves especially severe when the oxygen is embedded in a structure containing high atomic number elements, such as barium $\text{Ba}_2\text{TiSi}_2\text{O}_8$ fresnoite. In addition, the angular dependence of X-ray scattering means there is limited intensity at high diffraction angles, yet this region contains information for determining anisotropic atomic displacements (ADP).

3.3.5 Neutron Diffraction

Neutron diffraction is used in conjunction with electron and X-ray diffraction to provide a more complete description of superstructure ordering. For ceramics, neutron methods are highly reliable as diffraction from oxygen is appreciable and the location of oxygen atoms and the distortion of metal-centered polyhedra determined with greater confidence. In preliminary experiments, neutron powder diffraction patterns were collected ($\lambda = 1.8854 \text{ \AA}$) over the range of $10^\circ < 2\theta < 140^\circ$ with a step scan of 0.02° on the High Resolution Powder Diffractometer (HRPD) at the Australian Nuclear Science and Technology Organization (ANSTO), Sydney, Australia. However, the intensity of the satellite reflections was not statistically reliable, and it proved impossible to conduct crystallographic refinements. To observe superstructure reflections, which are overlapped and substantially weaker than the main reflections, patterns were collected with a higher neutron flux at ECHIDNA, the high resolution diffractometer at ANSTO at the same wavelength.

3.3.6 Rietveld Refinement

Rietveld 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. This method minimizes the differences between the calculated and experimental data through variation of instrumental and crystallographic parameters to arrive at a structure refinement. However, a reliable starting model against which the experimental data can be fitted is essential, as conventionally, Rietveld refinement does not permit structure

determination. The method, which relies on a least square refinement, can arrive at false minima and unreliable structure parameters although the fit between calculated and experimental dataset is statistically excellent. Rietveld refinement is unique as peak deconvolution includes instrumental contributions (e.g. diffraction resolution), crystallographic detail (e.g. structure factor), and physical form (e.g. texture) [90], such that peak distortions arising from all these may be separated. Here, TOPAS 3.0 was used for evaluating X-ray diffraction patterns [91], while structural modulation was examined with JANA2000 [92-93].

3.3.6.1 TOPAS 3.0

Basic crystallographic (i.e. subcell) information was extracted from powder X-ray diffraction data using the fundamental parameter approach. This two step method first establishes the instrumental influences on peak position and shape with reference to the NIST SRM 640c standard. The peak shape is modeled using “equatorial convolutions” while peak asymmetry is corrected with “axial convolutions” where further adjustments of the instrumental parameters are made assuming no peak broadening arising from the sample. These parameters are then fixed during the refinement of lattice metrics, atomic positions and thermal parameters. As intensity arises primarily from the location and abundance of metals, modulations arising from oxygen displacements were not investigated in this manner.

Figure 3.2. Rietveld refinement $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (fresnoite) performed using TOPAS 3.0 with P4bm as the model structure. Bragg markers (bottom most) indicate the reflection planes. The grey trace is the difference curve, indicating the goodness of fit between the experimental (circle) and simulated (line) intensities across the whole pattern.

3.3.6.2 JANA2000

Neutron diffraction data were analyzed using JANA2000 [93], a software which supports the interpretation of modulated superstructure reflections. The basic principle for data extraction is similar to TOPAS 3 with a “profile fit” performed before structural refinement. Modulation vectors can be extracted from weak, but distinct, satellite reflections in $(\text{Ba},\text{Sr})\text{TiSi}_2\text{O}_8$ fresnoite. However, it proved impossible to convincingly establish atomic positions or anisotropic thermal displacement parameters as further discussed in *Chapter 5*.

Figure 3.3. Rietveld refinement performed using JANA2000 with markers indicating reflections from the parent (black) and modulated structures (green). The satellite reflections are extremely weak overlapping and sometimes obscured by parent reflections. The black line shows the difference curve, indicating the goodness of fit between the data and simulated pattern.

3.4 Physical Property Measurements

3.4.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TA Inst, TGA 2950) was conducted on oven-dried sol-gel precursors under flowing air at a heating rate of 10 °C/min from room temperature to 900 °C to determine the temperature of crystallization. This method was also used to monitor loss of water and volatiles.

3.4.2 Photocatalytic Activity Analysis

Photocatalytic activity was monitored by following the degradation of an aromatic dye (methylene blue). In these tests, 0.1 g of catalyst was suspended in 1 L of an aqueous solution containing 4.45 ppm of methylene blue. Prior to testing, the catalyst was hydrated overnight in 500 cm³ of deionized water in a volumetric flask of 1 L. Methylene blue was then introduced and the volume made up to 1 L, homogenized in an ultrasonic bath for 30 minutes, and loaded into the reactor. Aliquots were taken from the reactor at intervals of $t = 0, 5,$

10, 15, 20, 30, 40, 50 and 60 minutes, then centrifuged at 10000 rpm for 7 minutes to separate the suspended catalyst from the liquid. UV-visible spectra collected at wavelengths from 200-800 nm monitored the decolorization rate for an absorption band at approximately 664 nm (Shimadzu UV 2501PC). A plot of C_0/C_t vs. irradiation time (C_0 = original concentration at 664.5 nm; C_t = concentration at time t at 664.5 nm) was used to follow the kinetics of degradation.

Figure 3.4. Schematic diagram of the reactor used for catalytic testing.

3.4.3 Band Gap Estimation

The band gap was estimated from UV-visible spectra of powders of the solid state catalyst, with data collected from 200 to 800 nm (ultraviolet to visible light region). The absorption edge allows band gap energy to be estimated through the relation:

$$E_{bg} (J) = \frac{h \cdot c}{\lambda} \quad (\text{Equation 3.1})$$

where E = band gap energy (J), h = Planck's constant (6.626×10^{-34} J s), c = light speed (3×10^{17} nm s⁻¹), and λ = wavelength (nm) [94].

Figure 3.5. Representative optical absorption spectra for nanocrystalline $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ for $x = 0.7$ and 0.8 , respectively; the inset shows the related Tauc plot confirming a direct bandgap. Reprint from [95].

3.5 Integrated Synthesis and Characterization

The investigation of modulated structure even in large crystals require excellent diffraction data coupled with specialized interpretation methods that properly account for higher dimensional symmetry. The preceding discussions shows that while an appreciation of fresnoite and melilite structures has expanded substantially in the past decade, these investigations have necessarily relied upon physical forms that are of limited technological impact (at this time) or employed characterisation methods that sample crystals in overly statistical nature (e.g. neutron diffraction) or non-statistical (e.g. electron diffraction) ways. Marrying these data and specimens to obtain a comprehensive understanding is essential before tailoring of functionality will be feasible. In the case of photocatalyst, the additional requirement is that fine-grained, large surface area powders are employed; in this form, modulation can be difficult to detect, much less evaluate. The remaining *Chapters* describe progress towards developing synthesis methods for producing catalytic powders and the validation of their physical and crystallographic properties.

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Chapter 4

Crystal Chemical Evolution of Fresnoite and Melilite Photocatalytic Powders*

The crystallization of fresnoite and melilite from sol-gel and solid state precursors yields distinct products, with equilibration of the former phase requiring several days annealing. The temperature and time dependence of phase evolution during fresnoite synthesis includes several compounds (perovskites, carbonates). A reconnaissance investigation of melilite $\text{Sr}_2\text{CoSi}_2\text{O}_7$ processing proved successful.

4.1 Synthesis Needs and Barriers

The synthesis of fresnoites and melilites presents several challenges. The first reflects the chemical complexity of these systems, which are either ternary or quaternary with respect to the oxide components, and requires chemically blended precursors and/or long heat treatments to obtain homogeneous products. The second arises from the need to prepare compounds that have large coherent diffraction domains suitable for crystal structure refinement, a problem exacerbated by the inherent flexibility of these layered structures which can lead to the intergrowth of commensurate and incommensurate regions (*Chapter 6*). This chapter describes the design and validation of a novel soft chemical method for the synthesis of fresnoite that can be adopted for the preparation of fresnoite-melilite solid solutions. Presented here is a Pechini-type sol-gel (PSG) process for creating high surface area materials suitable for photocatalytic applications. In the case of fresnoite, crystallization from the PSG route was compared with conventional solid state reactions that yield materials better suited to the study of structural modulation.

4.2 Solid State Formation of Fresnoite

As described earlier, mineral and synthetic $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (BTS) fresnoites exhibit incommensuration [1-3] to relieve strain arising from structural misfit [4], and strong incommensurate satellite reflections have been observed in the $\text{Sr}_2\text{TiSi}_2\text{O}_8$ analogue (STS) [2]. However, a detailed investigation of the solid solution between BTS and STS has been lacking, although essential to completely evaluate the drivers of modulation. This approach also provides the means to detect phase boundaries, as would occur between $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (BTG) where the endmembers adopt tetragonal ($P4bm$) or orthorhombic ($Cmm2$) symmetry [2, 4]. Furthermore, a systematic study of structural integrity, within those solid solutions, and the possibility of domain formation requires investigation. To this end, two fresnoite solid solutions $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$; $1 \leq x \leq 0$, and $\text{Ba}_2\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_8$; $1 \leq x \leq 0$, were prepared and characterized by powder XRD. Detailed analysis of these materials by neutron diffraction is considered in *Chapter 5*.

4.2.1 Synthesis

The starting materials for solid state syntheses were oxides (anatase-TiO₂-Aldrich, 99+ %; GeO₂-Alfa, 99.9 %), carbonates (BaCO₃-Fisher, 99.6 %; SrCO₃-BDH, 98.5 %) and silicic acid (H₂SiO₃-Sino, 99 %). These were stoichiometrically combined by manually grinding in an agate mortar and pestle then pressed into pellets before sintering in air. Intermediate phases (BaTiO₃, BaSiO₃ and SiO₂ (cristobalite)) were persistent and repeated heating, grinding, and pelletization were needed to attain high yields. The synthesis conditions to obtain near single phase products are summarized in Table 4.1.

Table 4.1. List of compounds synthesized with the specific conditions.

Compound	Sintering temperature	Sintering period
Ba ₂ TiSi ₂ O ₈	1200 °C	3 x 12 hours
Sr ₂ TiSi ₂ O ₈	1200 °C	2 x 12 hours
	1250 °C	2 x 12 hours
(Ba _{1-x} Sr _x) ₂ TiSi ₂ O ₈ ,		
0.1 ≤ x ≤ 0.5	1200 °C	3 x 12 hours
0.6 ≤ x ≤ 0.9	1200 °C	3 x 12 hours
	1250 °C	1 x 12 hours
Ba ₂ TiGe ₂ O ₈	1100 °C	1 x 12 hours
Ba ₂ Ti(Ge _{1-x} Si _x) ₂ O ₈ ,		
0.1 ≤ x ≤ 0.5	1100°C	1 x 12 hours
0.6 ≤ x ≤ 0.9	1100°C	1 x 12 hours
	1150°C	1 x 6 hours

4.2.2 Characterization

The pellets were ground into fine powder suitable for X-ray diffraction. Crystal structure parameters were extracted from powder patterns collected with Cu-K α radiation and step-scanned over a 2 θ range of 10-140° at intervals of 0.02° using Bragg-Brentano geometry. Accurate unit cell parameters were obtained by introducing an internal silicon standard spiked to a content of 20 wt% (NIST SRM 640c). TOPAS 3.0 was used for phase analysis and unit cell parameter refinement. For these experiments, only the three dimensional

subcell was considered as structural modulation was not evident in the diffraction data.

4.2.3 Lattice Parameters

4.2.3.1 $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$; $1 \leq x \leq 0$

Lattice parameters trends suggest that cationic substitution (i.e. Ba and Sr) is homogeneous with the metrics dilating as strontium (IR = 1.36 Å, c.n. = 10) was displaced by barium (IR = 1.52 Å, c.n. = 10) (Fig. 4.1), and the expansion of a less than c . Close examination shows that the lengthening of cell edges is not strictly linear with inflection at Ba:Sr = 1:1, that may reflect order correlation and/or a change in modulation.

Figure 4.1. Unit cell trends in tetragonal $P4bm$ $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ compounds. The (a) a -parameter, (b) c -parameter and (c) volume dilate as Ba content increases. (d) However, the a/c ratio contracts as the interlayer spacing expands most rapidly. Inflection at $x = 0.5$ in $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ suggests a boundary with respect to cation disorder, modulation vector, or a combination of these. (Error bars are not shown because they are smaller than the plot. The estimated standard deviations (esds) in the cell parameter refinements can be found in Appendix I)

4.2.3.2 $\text{Ba}_2\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_8$; $1 \leq x \leq 0$

Because $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$ adopt tetragonal ($P4bm$) and orthorhombic ($Cmm2$) symmetries respectively, a phase boundary will exist at intermediate compositions [2,4]. As expected, the lattice parameters dilate as fresnoite becomes increasingly germanous because Ge^{4+} (IR = 0.39 Å, c.n. = 4) is larger than Si^{4+} (IR = 0.26 Å, c.n. = 4). While the c -axis expands in an essentially linear fashion, the a -axis ($P4bm$) or a/b -axes ($Cmm2$) clearly do not follow Vegard's Law (Fig. 4.2) indicating structural frustration that leads to a change in space group, with the phase boundary located at Si:Ge ~ 1:1. Linear segments can be fitted on either side of this chemical composition. The tetragonal and orthorhombic phases are related as [5]:

$$\begin{pmatrix} a_{\text{orth}} \\ b_{\text{orth}} \\ c_{\text{orth}} \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} a_t \\ b_t \\ c_t \end{pmatrix} \quad (\text{Equation 4.1})$$

where a_{orth} , b_{orth} , c_{orth} and a_t , b_t , c_t are orthorhombic and tetragonal lattice parameters.

Figure 4.2. Phase boundary in the $\text{Ba}_2\text{TiSi}_2\text{O}_8$ - $\text{Ba}_2\text{TiGe}_2\text{O}_8$ solid solutions appears at 50 wt%. Vegard's Law is obeyed within each phase region.

Table 4.2. Lattice parameters refined in spacegroup $P4bm$ and $Cmm2$.

Germanium Content (at %)		Lattice parameter, (Å)				
		$P4bm$		$Cmm2$		
		a	c	a	b	c
Orthorhombic	100	8.6816(1)	5.3689(0)	12.2847(0)	12.2671(1)	5.3666(0)
	90	8.6611(0)	5.3550(0)	12.2650(0)	12.2368(1)	5.3548(1)
	80	8.6373(0)	5.3362(1)	12.2277(0)	12.2077(0)	5.3369(0)
	70	8.6208(0)	5.3195(1)	12.2017(1)	12.1802(1)	5.3204(1)
	60	8.6001(1)	5.3037(1)	12.1715(0)	12.1504(0)	5.3040(0)
	50	8.5857(1)	5.2886(1)	12.1534(1)	12.1326(0)	5.2892(1)
Tetragonal	40	8.5713(1)	5.2780(0)	12.1379(1)	12.1093(0)	5.2788(1)
	30	8.5552(0)	5.2588(0)	12.1140(0)	12.0859(1)	5.2589(0)
	20	8.5378(1)	5.2394(1)	12.0926(1)	12.0641(1)	5.2412(0)
	10	8.5327(1)	5.2275(1)	12.0948(0)	12.0523(0)	5.2259(0)
	0	8.5287(0)	5.21554(1)	12.0666(0)	12.0537(1)	5.2145(1)

4.3 Pechini Processing of Fresnoite

4.3.1 Reconnaissance Studies

Sol-gel syntheses can be divided into three main categories [6]:

- (i) hydrolysis-condensation of metal alkoxides;
- (ii) gelation of metal-chelates; and
- (iii) polymerization-complex routes (PC).

These methods are especially versatile for the production of ceramics [7] and were investigated for the preparation of fresnoite and melilite because they deliver chemically homogeneous precursors with a capacity to finely control the chemical and physical properties of functional materials [6].

It has been reported that refluxing barium acetate, tetraethyl silicate and titanium isopropoxide for several hours, followed by slow hydrolysis and calcination (750°C) permitted tuning of BTS morphology [8-12]. Elsewhere, tetramethyl orthosilicate, titanium isopropoxide and barium metal in isopropanol were refluxed under nitrogen, with hydrolysis regulated by

varying the water:alcohol ratio and the rate of addition to the alkoxides. However, none of these syntheses led to fine-grained and single-phase BTS that is technologically useful in the broadest sense.

In this study, several different precursors and solvents were trialed. For example, using ethanol as a solvent for the metal alkoxides, and deionised (DI) water for metal acetates did not lead to fresnoite in high yield, but stabilized intermediates such as BaTiO_3 . Introducing citric acid as a chelating agent enhanced fresnoite formation, but the product remained far from single phase, and refluxing the final mixture did not deliver higher yields. In order to gain better control of moisture uptake, the process was performed under N_2 ; this allowed the reaction to proceed almost to completion but reproducibility was variable. Subsequently, elimination of water from the synthesis by using ethylene glycol as a solvent permitted the sol-gel process to be performed in a air and give single phase fresnoite.

This approach was developed as a simple route for synthesizing fine-grained and homogeneous $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ ($0 \leq x \leq 1.0$) fresnoite (BTS - STS) solid solutions series via *in situ* polymerization, where an esterification reaction between citric acid and ethylene glycol homogeneously immobilizes the cations in a resin that decomposes to the ternary oxide. Also known as the Pechini process [13], metal chelation proved a robust means of circumventing differential hydrolysis rates and the selective precipitation of metal ions that promote secondary phase formation [14-15]. Direct mixing of the ingredients avoids refluxing in an inert (N_2) atmosphere, while crystal growth and phase development evolves via the elimination of volatile compounds and reaction with an amorphous silica-rich intermediate.

4.3.2 Synthesis Strategy

BTS powders were synthesized using tetraethyl orthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) (Aldrich, 98 %), titanium isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (TIP) (Aldrich, 97 %), barium acetate $\text{Ba}(\text{CH}_3\text{COO})_2$ (BA) (Aesar, 99 %), anhydrous ethylene glycol $\text{OHCH}_2\text{CH}_2\text{OH}$ (EG) (Merck, 99.5 %) and citric acid monohydrate

$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (CA) (Aldrich, 98 %). Citric acid (mole ratio of CA:BTS product = 20:1) was dissolved in EG (1:100 parts by volume) and heated to 70 °C with vigorous stirring to obtain a clear solution. Titanium isopropoxide (1:70 parts by volume of TIP in ethylene glycol) was transferred to the citric acid solution and stirred for 3 h, followed by injection of tetraethyl orthosilicate in Ti:Si = 1:2 metal proportions. After aging for 1 hr, barium acetate in ethylene glycol (mole ratio 1:150) was added stoichiometrically and stirred vigorously for 2 hr to obtain the transparent sol. A brown resin containing the immobilized metals was prepared by drying the sol (150 °C / 2 d).

Similarly, STS powders were made from the same ingredients as BTS, but with the substitution of strontium acetate $\text{Sr}(\text{CH}_3\text{COO})_2$ (SR) (Aldrich, 99 %). The solid solutions of $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ (BSTS) were prepared by introducing strontium and barium acetates separately in the desired alkali earth mole ratios. To study phase development and the kinetics of crystallization the resin precursors were calcined in air as a function of temperature (650-900 °C / 12 h) and time (1-48 h / 900 °C).

The formation of BTS-STs is sensitive to the gelation temperature, rate of TIP addition and drying, and these parameters required optimization to prevent the formation of $(\text{Ba},\text{Sr})\text{TiO}_3$ perovskite and residual amorphous silica. The most favorable temperature for reaction (70 °C) should be constant, to avoid the formation of double citrates $\text{MTi}(\text{CA})_3$ (M = Sr, Ba) that are highly stable and once formed will transform to perovskite during calcination. In addition, direct injection of concentrated TIP leads to incomplete dissolution of the alkoxide in CA that is recognizable as white turbidity. To obtain a homogeneous solution, it is essential to dissolve TIP in ethylene glycol before transferal to the CA solution. Finally, the transparent sol is oven dried until a gummy brown resin forms to ensure the preservation of molecular-scale homogeneity during calcination.

4.3.3 Characterization Methods

4.3.3.1 Quantitative Phase Analysis

Powder X-ray diffraction (XRD) patterns were collected as described in section 4.2.2, with phase abundance, unit cell parameters and amorphous content extracted by the Rietveld method with reference to an internal CaF_2 standard spiked to 20 wt% (Fig. 3) [16-18]. It is noted that the amorphous content is systematically slightly overestimated, due the effects of X-ray microabsorption. Quantitative phase analysis was performed by introducing BTS/STS as the tetragonal ($P4bm$) sub-structure, together with $(\text{Ba,Sr})\text{CO}_3$ witherite-type [19] and $(\text{Ba,Sr})\text{TiO}_3$ perovskite [20] as secondary phases. The absolute CaF_2 content (20 wt%) was only approached after long calcination at higher temperatures when the non-diffracting components were near completely converted to fresnoite.

4.3.3.2 Thermal Analysis

Decomposition and crystallization of the resin was investigated by thermogravimetric analysis (TGA) and differential gravimetric analysis (DGA) (TA Instruments, TGA 2950) in flowing air at a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C .

4.3.3.3 Fourier-Transform Infra-Red Spectroscopy (FTIR)

Spectra was collected ($400\text{--}4000\text{ cm}^{-1}$) from KBr pellets (1 part fresnoite: 100 parts KBr by weight or 0.2 g of KBr mixed with 2mg of sample) with a resolution of 2 cm^{-1} in 30 cycles. Broad bands from $450\text{--}1100\text{ cm}^{-1}$ were deconvoluted into components before assignment of Ti-O and Si-O stretching and bending modes.

4.3.4 Fresnoite Crystallization Pathways

4.3.4.1 Phase Evolution

Thermal analysis showed mass loss peaked from $100\text{--}450^\circ\text{C}$ during removal of water and volatile compounds, with gradual consumption of $(\text{Ba,Sr})\text{CO}_3$ and $(\text{Ba,Sr})\text{TiO}_3$ from $450\text{--}700^\circ\text{C}$ (Fig. 4.3). X-ray diffraction patterns

collected from isochronally annealed (12 hr) powders are consistent with thermal analysis as fresnoite only forms at 650 °C with intermediates crystallizing at lower temperatures. During isochronal calcination BTS formed to near 100 % yield by 700 °C from BaTiO₃, BaCO₃ and a non-diffracting phase presumed to be silica-rich (Fig. 4.4a), while isothermal treatment (900 °C) for 1 hour yielded similar results.

Figure 4.3. TGA-DGA of the BTS fresnoite precursor obtained by the Pechini process. Strontium-rich precursors showed similar behavior during heating.

However, decomposition of BTS begins after 900 °C for 12 hours, demonstrating that both annealing time and temperature are critical. It is concluded that the optimal synthesis condition for BTS (highest yield and grain growth) should not exceed 900 °C/12 hours, and that the primary oxide reactions are:

For STS and the mixed Ba:Sr = 50:50, fresnoite phase development followed similar pathways, but required higher temperatures > 900 °C due to the

persistence of perovskite and carbonate phases (Fig. 4.5 b,c). Isothermal annealing (900 °C) confirmed that STS forms more slowly than BTS (Fig. 4.5 d,e,f). A non-diffracting residue (shaded portion of Fig. 4.5) was retained as a small fraction of all preparations even after extended annealing, and in the strontium-rich materials the high stability of this component may delay fresnoite formation.

Figure 4.4. Rietveld plots for $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ fresnoites calcined at 900 °C/12 hrs and spiked with 20 wt% CaF_2 prior to XRD collection. (a) BTS ($x = 0$) was single phase within the detection limits of XRD. (b) BSTS ($x = 0.5$) contained trace < 1 wt% $(\text{Ba,Sr})\text{TiO}_3$ perovskite. (c) STS ($x = 1$) contained < 2 wt% SrTiO_3 of small crystal size

(29 nm) suggesting it is finely dispersed. The Bragg markers from top-to-bottom are fresnoite, perovskite and CaF_2 .

Figure 4.5. Phase development during isochronal (12 hr) and isothermal (900 °C) synthesis of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (BTS), $\text{BaSrTiSi}_2\text{O}_8$ (BSTS) and $\text{Sr}_2\text{TiSi}_2\text{O}_8$ (STS) fresnoites. During isochronal treatment fresnoite crystallizes both directly from the Pechini resin and indirectly from reaction of intermediate carbonate, perovskite and a silica-rich glass (shaded region). For BTS (a and d) crystallization is essentially complete by 700 °C, but for BSTS with $x = 0.5$ (b and e) and STS (c and f) it is delayed until 900 °C. Note all weight percentages sum to 100 % inclusive of the CaF_2 spike.

4.3.4.2 Evolution of Lattice Parameters

Although BTS, STS and BSTS (Ba:Sr = 50:50) begin to crystallize at lower temperatures (Figs. 4.6 a-c) lattice parameter dimensions stabilize only after annealing for 12 hrs at 900 °C (Fig. 4.6 a), suggesting that the composition of fresnoite is varying due to reaction with the glassy phase. Such equilibrated fresnoites will be optimal for evaluating crystallographic properties. Similarly, higher annealing temperatures lead to a contraction in cell dimensions (Fig. 4.6 b). For the equilibrated $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ ($0 \leq x \leq 1$) samples Vegard's Law was obeyed across the entire compositional join (Figs. 4.6 c-e) indicating complete solid solution and the absence of a miscibility gap. The crystal domain size extracted by analysis of the Bragg peak widths after heat treatment for 12 hrs/900 °C was ~ 70 nm.

Figure 4.6. For BTS both (a) isothermal and (b) isochronal syntheses show that firing for 12 hrs at 900 °C is required to bring the material to near equilibrium and stabilize the unit cell parameters. For the equilibrated $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ (c, d, e) the lattice parameters dilate linearly as barium replaces strontium.

4.3.4.3 FTIR Analysis

Polymerization of the EG/CA resin yields symmetric and asymmetric carbonyl (COO^-) vibrations at 1630 and 1380 cm^{-1} [21], an intense band at 1725 cm^{-1} arising from C=O stretching, C-H stretching at 2950 and 2880 cm^{-1} [22], and C-C-O stretching at 1186 cm^{-1} with the latter two vibrations arising from ethylene glycol [21]. These vibrations are consistent with chelation between metal ions during polymeric reactions that lower the temperature for fresnoite formation, as compared to conventional solid state reactions. Subsequently, as the calcination temperature increases, the precursor slowly forms fresnoite by releasing volatile organics with the Ti-O and Si-O stretching and Si-O-Si bending modes at 600 °C, characteristic of BTS, becoming increasingly evident at higher calcination temperatures (Fig. 4.7) [23].

After prolonged calcination (900 °C for 12 hr) the FTIR spectra are dominated by Ti-O and Si-O stretching and Si-O-Si bending modes [23]. The bands are quite broad, and increasingly so, as strontium replaces barium indicating a

greater level of disorder and bond strain related to the inherent structural modulation. Using earlier studies as a guide, these features have been separated into distinct vibrational modes, especially for BTS (Fig. 4.8). As strontium replaces barium, the bands are displaced towards higher wavenumbers as molecular oscillations increase in frequency leading to stronger mixing of the Si-O and Ti-O vibrations.

Figure 4.7. FTIR spectra showing BTS phase evolution during isochronal (12hr) calcination. (a) precursor, (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C and (f) 900 °C.

Figure 4.8. FTIR spectra of (a-b) $\text{Ba}_2\text{TiSi}_2\text{O}_8$; (c-d) $\text{BaSrTiSi}_2\text{O}_8$; and (e-f) $\text{Sr}_2\text{TiSi}_2\text{O}_8$ show progressive broadening of the vibrational bands and their displacement to larger wavenumbers as Ba is replaced by Sr leading to higher frequency oscillations of the Ti-O and Si-O bonds.

4.3.5 Production of Photocatalytic Powders

In the present study, ethylene glycol is both the solvent and chelating agent, with the former role of particular importance, as water need not be introduced to dissolve barium and strontium acetates. This circumvented controlling the water to solvent ratio to avoid hydrolysis and low yields. Chelation of TIP is essential as previous attempts to synthesize fresnoite without citric acid were unsuccessful. Moreover, the sequence of chelation must be regulated as chelating TEOS with citric acid followed by TIP lead to incomplete fresnoite formation. Slow dissolution of TIP into ethylene glycol with moderate stirring is essential to minimize reaction with air that precipitates TIP and prevents complete chelation of the Ti-CA complex. Too little ethylene glycol solvent hinders TIP and TEOS dissolution resulting in segregation and precipitation of metal ion chelates.

In summary, $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$ ($0 \leq x \leq 1$) fresnoites were prepared by calcination (900 °C) of a resin obtained by esterification of $\text{Ba}^{2+}/\text{Sr}^{2+}\text{-Ti}^{4+}$ -citrate and Si^{4+} -citrate complexes that are resistant to accelerated hydrolysis. In this manner, metal alkoxides are immobilized in a rigid polyester framework by ethylene glycol polymerization which eliminates metal segregation during hydrolysis/pyrolysis. This inhibits the formation of perovskite, and other alkali earth titanates, as significant secondary phases. Chelation also circumvents the need for an inert atmosphere (N_2) blanket during hydrolysis. Two unsuccessful synthesis approaches should be noted. Sol-gel reaction by direct mixing of TIP, TEOS and BA ethanolic solutions in air yielded, after calcination, BaCO_3 (12.4 wt%), BaTiO_3 (10.6 wt%) and BaTi_4O_9 (24.4 wt%) as intractable secondary phases because TIP hydrolyses more rapidly than TEOS leading to a metal segregated gel. Deploying the same method in a N_2 glove box delayed the hydrolysis of $\text{Ti}(\text{OC}_3\text{H}_7)_4$, but was unable to prevent BaTiO_3 (7.1 wt%) formation.

Crystallization of fresnoite occurs, in part, via $(\text{Ba,Sr})\text{CO}_3$ and $(\text{Ba,Sr})\text{TiO}_3$ which are eliminated by reaction with a silica-rich non-diffracting phase, and at higher temperatures (> 800 °C) phase-pure BTS-STs fresnoite was obtained. To date, the development of fresnoite as a functional material has been hampered due to the difficulty of obtaining reactive single phase powders. The new Pechini process described here yields homogeneous fresnoite powders and will simplify deployment as photocatalysts, dielectric materials and ion conductors.

4.4 Pechini Synthesis of Melilite

4.4.1 Rationale

Most structural investigations of melilites involve materials synthesized as single crystals from melts [24-26], recrystallization from glass [27], and solid state reactions [28-30], whereas soft chemistry routes were employed for enhancement of functionalities [31-32]. Melilite-types have been successfully synthesized using sol-gel chemistry [33-34], and here, a method was

developed to synthesize $\text{Sr}_2\text{CoSi}_2\text{O}_7$ using a low temperature chemical route, rather than melt processing [35-36].

4.4.2 Synthesis Method

$\text{Sr}_2\text{CoSi}_2\text{O}_7$ (SCS) melilite powders were synthesized from tetraethyl orthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) (Aldrich, 98 %), strontium acetate $\text{Sr}(\text{CH}_3\text{COO})_2$ (SR) (Aesar, 99 %), cobalt nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck, 97 %), anhydrous ethylene glycol $\text{OHCH}_2\text{CH}_2\text{OH}$ (EG) (Merck, 99.5 %) and citric acid monohydrate $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (CA) (Aldrich, 98 %). Citric acid (mole ratio of CA:SCS product = 20:1) was dissolved in EG (1:100 parts by volume) and heated to 70 °C with vigorous stirring to obtain a clear solution. TEOS was then added to the solution and stirred for 3 hrs. Separately, strontium acetate and cobalt nitrate were dissolved in EG which was added to the TEOS mixture after continuous stirring for 3 hrs and the final solution aged for a further 2 hrs. A brown resin containing the immobilized metals was prepared by drying the sol (100 °C /2 d).

4.4.3 Characterization

Powdered samples were ground prior to X-ray diffraction using Cu- $K\alpha$ radiation and step-scanning from $10 < 2\theta < 140^\circ$ at intervals of 0.02° using Bragg-Brentano geometry. Cell parameters were calibrated against an internal silicon standard (20 wt%) NIST SRM 640c, and TOPAS 3.0 was used for phase analysis and unit cell parameter extraction.

4.4.4 Phase Development

The evolution of $\text{Sr}_2\text{CoSi}_2\text{O}_7$ was monitored for fixed calcination times and as a function of temperature. The formation of this compound was more direct than for BTS. Melilite powders formed easily by the gelation method, with the lattice parameters showing narrow variations with time and temperature (Fig. 4.9). Melilite is equilibrated after 18 hrs sintering at 800 °C or 5 hrs at 1000 °C. No secondary phases were observed via X-ray diffraction.

Figure 4.9. Change in lattice parameters with variation in (a) sintering times at 1000 °C, and (b) sintering temperatures with 18 hrs of dwell time.

4.5 Conclusion

This study has shown that Pechini syntheses where ethylene glycol is used as the chelating agent are appropriate for the preparation of fresnoite and melilite tectosilicates. The method is robust, controllable and results in high yields. Specifically, these ceramics are expected to be homogeneous and show well-defined functionalities. In the present context, controlling chemistry provides the means to minimize crystallographic strain, control modulation, and thereby regulate band gap energy.

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Part 2:

Crystal Structure &

Functionality

Chapter 5

Structure of Fresnoite, $M_2TiSi_2O_8$ ($M = Ba, Sr$); Strategies for Powder Neutron Refinement*

Refining the crystal structures of powdered incommensurate materials present several challenges. Most structure determinations rely on single crystal methods and while these data are usually reliable, an analysis of bond valence sums suggests these solutions may be inadequate. Furthermore, in technological fine powders of high surface area, the starting model for refinement of powder diffraction patterns may need to be quite distinct to single crystal solutions. The principle limitations are the frequent intergrowth of compositionally distinct nano-domains and the appearance of diffuse scattering. The refinement outcomes are dependent on the sequence of releasing refineable parameters, correlations between positional and compositional modulations, and ambiguous determinations of atomic displacement parameters.

5.1 Introduction

Increasing numbers of ‘common’ materials are now recognized as crystallographically incommensurate. Powder neutron diffraction can be used to refine modulated structures [1-8], including magnetic superlattices, and follow temperature dependent transformations [2]. In favorable circumstances, this method can differentiate modulation modes (i.e. displacive and occupational) [3], however, uncertainty remains concerning refinement reliability when mixtures of atoms with a range of scattering factors are present [5]. In some cases, single crystal X-ray diffraction will be superior [5], as strong satellite reflections are indicative of heavy atom modulation, while neutron diffraction tends to accentuate the light atom structure [4, 6-8]. However, modeling ‘light’ atom modulation requires a balance between highly correlated anisotropic thermal displacements and polyhedral distortions [4] while bonds remain physically reasonable [6]. In some cases, the temperature dependence of the modulation vector provides a means to solve these ambiguities [7]. In a typical example, mineral fresnoite characterized by single crystal diffraction [1] found the corner-connected oxygen atoms of the SiO_4 and TiO_5 polyhedra possessed large anisotropic ellipsoids and a range of bond lengths; but from a crystallochemical perspective significant distortion of polyhedra would not be expected. For this reason, the Rigid Unit Mode (RUM) model has offered a means to provide physically meaningful descriptions at least at the unit cell scale [9].

Table 5.1. Crystallographic data used for refinement comparison [10].

Crystallographic data for selected fresnoite crystal	
Crystal data	
Chemical formula	$(\text{Ba}_{1.962}\text{Ca}_{0.036})\text{O}_{8.000}\text{Si}_{2.000}\text{Ti}_{1.000}$
M_r	506.7
Temperature (K)	110
a, c (Å)	8.8353(6), 10.4128(7)
V (Å³)	758.59 (9)
Z	4

In this study, BTS, STS and BSTS powders were prepared via the sol-gel method and studied by powder X-ray and neutron diffraction. This low temperature synthesis is unlikely to be in thermodynamic equilibrium, but was

expected to be chemically homogenous and therefore crystallographically distinct from large crystals by showing either unique incommensuration or significant disorder. In fact, X-ray diffraction only captures reflections from the average 3D structure, although electron microscopy studies yield pronounced satellites. This difference is consistent with modulation dominated by light atoms and/or poor correlations in the modulated domains. However, when neutron diffraction was employed satellite reflections are evident, but their intensity is several orders of magnitude weaker than the subcell reflections; this is at odds with many other incommensurate oxide systems studied by powder neutron methods. Moreover, the diffraction patterns show an unusually intense background at high 2θ angles which is attributed to diffuse scattering and could be indicative of substantial disorder and deviation from the average long-range structure. Finally, severe peak overlap rendered refinements unstable.

Presented here is the culmination of several attempts to overcome these problems and obtain an average modulated fresnoite structure. The results are benchmarked against published single crystal refinements that upon close inspection, may also be incompatible with crystal chemical principles. Perturbations of STS fresnoite as barium replaces strontium are considered as a means to bridge the gap between single crystal characteristics versus finely divided sol-gel powders. Because initial analysis of powders obtained by solid state reaction (*Chapter 4*) suggested the appearance of structural frustration for $x \sim 0.5$ for $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{TiSi}_2\text{O}_8$, three samples were selected – $\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $(\text{BaSr})\text{TiSi}_2\text{O}_8$. The outcomes from Rietveld analysis are compared with the crystal determinations of Bindi et al. [10] and Höeche et al. [11] for $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and $\text{Sr}_2\text{TiSi}_2\text{O}_8$ respectively while $(\text{BaSr})\text{TiSi}_2\text{O}_8$ was compared against these endmembers.

5.2 Synthesis

$\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $(\text{BaSr})\text{TiSi}_2\text{O}_8$ powders were synthesized by the sol-gel method described in *Chapter 4*.

5.3 Characterization

The powders were first characterized by X-ray powder diffraction (Bruker AXS) collected with Cu- $K\alpha$ radiation over a 2θ range of 10-140° with a stepwidth of 0.02° using Bragg-Brentano geometry. Phase pure materials, in the sense that only Bragg reflections for fresnoite were evident, were selected and sent to ANSTO for neutron diffraction studies at the high resolution powder diffractometer (Echidna). The powders were loaded into vanadium canisters and data collected at a constant wavelength of 1.8854 Å for $\text{Ba}_2\text{TiSi}_2\text{O}_8$ and $\text{Sr}_2\text{TiSi}_2\text{O}_8$, while $(\text{BaSr})\text{TiSi}_2\text{O}_8$ pattern was obtained at 1.622 Å monochromatised using a Ge monochromator over the angular range 8-163° at a step scan of 0.05°. The experiments were conducted at room temperature over 12 hrs to improve satellite reflection signals and, for BSTS, to minimize peak overlap by working at a shorter wavelength. The average structure was refined using TOPAS 3.0 [12] where the 3D lattice parameters and atomic positions were extracted. These data were then used as the starting parameters for neutron refinement with JANA2006 [13] which supports modulated structures.

5.4 Rietveld Refinement

5.4.1 Diffraction Pattern Characteristics

X-ray diffraction patterns of sol-gel derived fresnoites display narrow diffraction peaks with full width half maxima indicative of well crystalline material. Principle reflections were adequately modeled using existing crystallographic data [14], however, the satellite reflections could not be detected, consistent with incommensuration arising from poorly scattering oxygen (Fig. 5.1). By comparison, neutron diffraction data consisted of relatively broad peaks but with an additional incommensurate superlattice (Fig. 5.2) about two orders of magnitude less intense than the main reflections. Significant peak asymmetry was observed at low 2θ angles. Devising a refinement strategy to separate the subcell from the modulated structure and yield physically meaningful crystallographic parameters was not

straightforward, due to the overlapping of satellite reflections with the principle reflections.

At higher angles, neutron diffraction patterns include a background from $\sim 80^\circ$ to 130° that is tentatively attributed to diffuse scattering; similar features were observed in some X-ray patterns. However, a physical model to account for this background was not possible and this contributed significantly to refinement instability, especially with respect to thermal parameters. Figure 5.4 provides a square root of intensity plot to enhance the visibility of the background signal.

Figure 5.1. Rietveld refinement of X-ray diffraction data collect at wavelength = $1.54 \text{ \AA}$ from sample BTS (partial; full pattern to 130°) showing goodness of fit by employing only the parent structure. Blue markers indicate Bragg reflections while the lower difference plot is shown in grey line.

Figure 5.2. Rietveld refinement of neutron diffraction data collect at wavelength = 1.8854 Å from sample BTS (partial; full pattern to 163°) showing goodness of fit; both the subcell (black) and first order satellite (green) reflections markers are shown, while the difference plot is the lower black line. Only very weak satellite reflections are observed (arrowed).

Figure 5.3. Wide angle Rietveld refinement of neutron diffraction data showing goodness of fit. Markers for the subcell (black) and first order satellite (green) reflections are shown while the difference plot is the lower black line. The centers of background features are arrowed.

Figure 5.4. Neutron powder diffractogram of $\text{Ba}_2\text{TiSi}_2\text{O}_8$, with the square root of intensity is plotted versus the 2θ angle. The grey line emphasizes the structured background.

5.4.2 Symmetry

Withers et al. [9] examined the structure of BTS using electron diffraction and concluded that the parent structure consistent with $P4bm$ symmetry. However, as discussed in *Chapter 2*, slight distortion of the corner-connected polyhedral framework when replacing Si^{4+} by larger Ge^{4+} as in $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (BTG) causes the transformation to orthorhombic $Cmm2$ (i.e. $a=12.291$ Å, $b=12.274$ Å, $c=10.733$ Å) [15] (Fig. 5.5). As the treatment of powder diffraction data to extract higher dimensional structures is challenging, it was essential in this study to have reliable benchmark structures for comparative purposes. In general, single crystal determinations are regarded as superior, and consideration of the modulated bond lengths obtained in this way appear reasonable. For example, using the starting models of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ [9] and $\text{Sr}_2\text{TiSi}_2\text{O}_8$ [10] and simulating the atomic modulations using JANA2006, it appears that at least a reasonable approximation to the structure has resulted (Fig. 5.6). However, bond valence sums show quite extreme departures from the formal oxidation states (Fig. 5.7). While this might be acceptable for the large cations (Ba/Sr), it appears highly unrealistic that Si^{4+} would show large differences given that the Si-O bond length is one of the most invariant

known. The underlying cause of these anomalous parameters remains to be understood (see *Chapter 6*), however, it was of interest to explore if Rietveld refinement could deliver results to single crystal diffraction structure determinations.

Figure 5.5. Representation of tetragonal BTS superimposed on orthorhombic BTG in [001] projection.

Figure 5.6. Si-O and Ti-O bond lengths extracted from single crystal X-ray diffraction solutions (a) BTS and (b) STS refined in higher dimensional symmetry ($P4bm(a,a,1/2)(-a,a,1/2)0gg$). The bond length modulations refined with unconstrained harmonic functions yield results within acceptable ranges. Data for the above plots retrieved from Bindi et al. [9] and Höeche et al. [10].

Figure 5.7. Cation-oxygen BVS of single crystal X-ray diffraction solutions for (a) BTS and (b) STS refined in higher dimensional symmetry ($P4bm(a,a,1/2)(-a,a,1/2)0gg$). Data for the above plots retrieved from Bindi et al. [9] and Hoeche et al. [10].

Both the tetragonal and orthorhombic crystallographic settings were used as starting points for X-ray diffraction refinements, but neither model was distinctly superior (Table 5.2). Lattice parameters transposed from *P4bm* to *Cmm2* are similar to the refined orthorhombic structure with comparable R_B ; in accord with standard practice, the final refinements were performed in *P4bm* as no conclusive differentiation could be made even with neutron data.

Table 5.2. Summary of refined X-ray diffraction data in two probable space groups.

Compound	Refined structure; Lattice parameter (Å) (<i>P4bm</i>)		Transposed from <i>P4bm</i> *; Lattice parameter (Å) (<i>Cmm2</i>)		Refined structure; Lattice parameter (Å) (<i>Cmm2</i>)			R Bragg (<i>P4bm</i>)	R Bragg (<i>Cmm2</i>)
	<i>a</i> = <i>b</i>	<i>c</i>	<i>a</i> = <i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>		
Ba₂TiSi₂O₈	8.5188	5.2245	12.0474	5.2245	12.0549	12.0332	5.2233	0.0169	0.0188
(BaSr)TiSi₂O₈	8.4260	5.1247	11.9162	5.1247	11.9230	11.9090	5.1245	0.0162	0.0149
Sr₂TiSi₂O₈	8.3221	5.0270	11.7692	5.0270	11.7681	11.7692	5.0268	0.0249	0.0266

* Note: The transposed structure is for comparison in *Cmm2* structure, but the *c*-axis was not doubled.

5.4.3 X-ray data

The powder refinements employed the fundamental parameter approach developed by Cheary and Coelho (*Chapter 4*) [16]. In this approach, the instrumental effects were first extracted using a LaB₆ standard (NIST SRM 660a). Using the starting model of Moore & Louisnathan [13] for mineral BTS, the objective of the X-ray refinements was to provide input for subsequent treatment of neutron data refinement. Initially, only the lattice parameters and zero error were refined with the atomic positions subsequently released. Site occupancy was assumed complete for all species, with no observable impurities and constraints imposed. In this way, the refinements of BTS, STS and BSTS converged directly to $R_{wp} = 3.4, 3.8$ and 4.2 respectively.

5.4.4 Neutron data

These Rietveld refinements aimed to properly model the oxygen positions and explore the strain-induced structure deformation and progress through several stages.

(i) A “profile fit” was performed before structure refinement, with a pseudo-Voigt function used for peak shape modeling while 4 terms of a Berar-Baldinozzi function was employed for asymmetry correction [17]. The initial crystallographic data (i.e. lattice parameters, atomic positions and ADPs) used for refining the endmembers and the mixed occupancy of Sr substituted Ba fresnoite were taken from Bindi et al. [9] and Höeche et al. [10].

(ii) As noted in Figure 5.4, a complex and relatively intense background made refinement difficult in comparison with X-ray patterns, thus several approaches were made to incorporate this feature. Initially, the background was modeled using higher terms of Legendre polynomials (i.e. 15 terms), and doubling of the *c*-axis by imposing the *q* vector $0.30\ 0.30\ \frac{1}{2}$ and $0.30\ -0.30\ \frac{1}{2}$. The lattice parameters, peak shape and asymmetry functions were fixed according to “profile fitting” while all atomic positions were refined isotropically.

(iii) Ti-O and Si-O bond lengths were constrained to prevent spreading to unrealistic average bond lengths. Refinement at this point was unsatisfactory with poor goodness of fit.

(iv) A subsequent refinement included anisotropic ADPs with the previously refined isotropic parameters as starting points (i.e. 2 terms of harmonic function) and 2 terms of positional sinusoidal modulation waves to allow the modeling of satellite reflections.

(v) The final refinement cycles were made with lattice parameters and “profile fitting” parameters released, and though this leads to convergence, it proved

impossible to avoid non-physical negative ADPs, that were strongly correlated with the background modeling.

In a second approach, the background intensities were selected manually with the combination of a 5-term Legendre polynomial. Though this background modeling provides a more realistic structural refinement, negative ADPs were not entirely avoided. The convergence values of R_{wp} for Ba-fresnoite, Sr-fresnoite and BaSr-fresnoite were 3.17, 3.70 and 4.02 respectively.

5.5 Crystal Structure

5.5.1 Unit Cell Analysis

The subcell parameters obtained from X-ray diffraction data showed little variation from the published values [9-10]. As noted in *Chapter 4*, there is a linear contraction of lattice parameters from BTS to STS. In BSTS, the atomic positions of Ba1/Sr1 and their displacement parameters were held identical while the occupancies were refined. The Ba:Sr occupancies invariably refined close to 1:1, while monoatomic sites were fully occupied (Table 5.3).

When the atomic displacement parameters were refined isotropically, the oxygens yielded higher values (~ 2 -3 times) than for Sr/Ba, Ti and Si atoms reflecting the true ellipsoidal nature of these movements. The largest ADPs were observed for the corner-connected oxygen atoms (i.e. O1 and O3) (Table 5.4). The bond valence sums (BVS) deviated substantially from the ideal values (Table 5.5), most significantly from distortion of the TiO_5 square pyramid that showed large excursions from ideal valance.

Table 5.3 Lattice parameters details.

Chemical formula	Ba ₂ TiSi ₂ O ₈	(BaSr)TiSi ₂ O ₈	Sr ₂ TiSi ₂ O ₈
Crystal data			
Chemical formula weight	507	457	407
Temperature (K)	297	297	297
Cell setting	Tetragonal	Tetragonal	Tetragonal
Parent spacegroup	<i>P4bm</i>	<i>P4bm</i>	<i>P4bm</i>
<i>a</i> (Å)	8.518791(83)	8.426018(94)	8.322106(56)
<i>c</i> (Å)	5.224437(53)	5.124744(72)	5.027038(42)
Z	4	4	4

Cell volume ($\text{\AA}^3$)	379.1363(85)	363.8455(96)	348.1598(55)
Theoretical density (g/cm^3)	4.438461(99)	4.1618(68)	3.885085(61)
Powder colour	white	white	white

Table 5.4 Atomic positions and B_{eq} from powder neutron refinements.

Chemical formula	Atom	Position			B_{eq}
		x	y	z	
Ba₂TiSi₂O₈	Ba1	0.326843(28)	0.826843(28)	0	0.6731(74)
	Si1	0.12959(12)	0.62959(12)	0.4945(11)	0.477(33)
	Ti1	0	0	0.53512(57)	0.064(34)
	O1	0	1/2	0.6153(12)	2.67(18)
	O2	0.12573(30)	0.62573(30)	0.22354(63)	0.818(94)
	O3	0.28994(26)	0.57849(31)	0.63603(39)	1.628(78)
	O4	0	0	0.21951(97)	0.96(13)
(BaSr)TiSi₂O₈	Ba1/Sr1	0.327453(57)	0.827453(57)	0	2.85(48)
	Si1	0.12852(19)	0.62852(19)	0.4975(17)	2.885(70)
	Ti1	0	0	0.53930(91)	1.939(71)
	O1	0	1/2	0.6094(23)	6.78(32)
	O2	0.12673(47)	0.62673(47)	0.2077(10)	3.05(17)
	O3	0.28922(47)	0.57614(51)	0.63043(74)	5.12(15)
	O4	0	0	0.1927(18)	4.11(26)
Sr₂TiSi₂O₈	Sr1	0.328501(46)	0.828501(46)	0	1.430(14)
	Si1	0.12898(12)	0.62898(12)	0.50917(80)	1.260(39)
	Ti1	0	0	0.53806(60)	0.903(37)
	O1	0	1/2	0.6092(14)	5.00(18)
	O2	0.12836(28)	0.62836(28)	0.19284(60)	0.972(92)
	O3	0.29282(30)	0.58407(33)	0.63410(46)	6.32(11)
	O4	0	0	0.1865(11)	3.51(17)

Table 5.5 Bond valence sums from powder neutron refinements.

Chemical formula	Polyhedral	Bond lengths		BV
Ba₂TiSi₂O₈	Square pyramid	Ti1 – O3	1.9817(24) x 3	0.637 x 3
		Ti1 – O4	1.6489(51) x 1	1.567 x 1
		BVS		4.115
	Tetrahedron	Si1 – O1	1.6839(25) x 1	0.888 x 1
		Si1 – O2	1.4165(33) x 1	1.830 x 1
		Si1 – O3	1.6130(34) x 2	1.076 x 2
		BVS		4.870
	Square pyramid	Ti1 – O3	1.9453(41) x 3	0.703 x 3
		Ti1 – O4	1.7762(93) x 1	1.111 x 1
		BVS		3.923
(BaSr)TiSi₂O₈	Tetrahedron	Si1 – O1	1.6352(49) x 1	1.013 x 1
		Si1 – O2	1.485(10) x 1	1.520 x 1
		Si1 – O3	1.5787(53) x 2	1.180 x 2
		BVS		4.893
	Square pyramid	Ti1 – O3	1.9224(26) x 3	0.748 x 3
		Ti1 – O4	1.7671(56) x 1	1.138 x 1
		BVS		4.130
	Tetrahedron	Si1 – O1	1.5991(24) x 1	1.117 x 1
		Si1 – O2	1.5903(50) x 1	1.144 x 1
		Si1 – O3	1.5470(30) x 2	1.286 x 2
		BVS		4.833

* Note: BV calculated from [18].

5.5.2 Modulated Structure Analysis

Neutron powder refinements for BTS, STS and BSTS gave the lattice metrics summarized in Table 5.6, while fractional coordinates and ADPs are shown in Table 5.7. It is evidently impossible to avoid convergence to false minima due to the number of correlated parameters introduced by the harmonic functions and modulation displacements that are fitted to weak satellite reflections. The use of constraints to obtain structurally plausible solutions was sometimes successful, but not advisable as neutron diffraction should have little difficulty in locating the modulated oxygen.

It is particularly instructive to compare the final powder solutions with the published single crystal data. While bond lengths generally modulated within acceptable ranges, the BVS were often unrealistic. The final neutron data are comparable and similarly flawed (Fig. 5.7-5.9). It is now believed that Rietveld refinement of fresnoite structures may be impossible by powder methods. In particular, the nanodomains and phase mixtures described in *Chapter 6* render Rietveld methods inappropriate. While, it has been found that inclusion of 2-phase mixtures during refinement notably yields superior results, this is an artifact of the approach.

Table 5.6 Crystal parameters of modulated structures from neutron refinements. The doubling of the *c*-axes for these refinements was included by modifying the *q* vectors.

Chemical formula	Ba ₂ TiSi ₂ O ₈	(BaSr)TiSi ₂ O ₈	Sr ₂ TiSi ₂ O ₈
Crystal data			
Temperature	Room	Room	Room
Cell setting	Tetragonal	Tetragonal	Tetragonal
Parent spacegroup	<i>P4bm</i>	<i>P4bm</i>	<i>P4bm</i>
<i>a</i> (Å)	8.5054(2)	8.4155(19)	8.3055(5)
<i>c</i> (Å)	5.2159(2)	5.1198(16)	5.0178(3)
q1	[0.3000,0.3000,½]*	[0.2912,0.2912,½]*	[0.3019,0.3019,½]*
q2	[-0.3000,0.3000,½]*	[-0.2912,0.2912,½]*	[- 0.3019,0.3019,½]*
Z	2	2	2
Cell volume (Å ³)	377.4(2)	362.6(16)	346.1(3)

Figure 5.8. (a) Bond lengths of Si-O and Ti-O, and (b) cation-oxygen BVS of cations and oxygens of BTS neutron diffraction data refined in higher dimensional symmetry ($P4bm(a, a, 1/2)(-a, a, 1/2)0gg$).

Figure 5.9. (a) Bond lengths of Si-O and Ti-O, and (b) cation-oxygen BVS of cations and oxygens of STS neutron diffraction data refined in higher dimensional symmetry ($P4bm(a,a,1/2)(-a,a,1/2)0gg$).

Figure 5.10. (a) Bond lengths of Si-O and Ti-O, and (b) cation-oxygen BVS of cations and oxygens of BSTS neutron diffraction data refined in higher dimensional symmetry ($P4/m(a,a,1/2)(-a,a,1/2)0gg$).

Table 5.7 Atomic positions and anisotropic displacements for Ba₂TiSi₂O₈, (BaSr)TiSi₂O₈ and Sr₂TiSi₂O₈

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ba	0.3243 (3)	0.8243 (3)	0	-0.0042 (17)	-0.0042 (17)	0.002 (4)	-0.006 (2)	-0.0099 (19)	0.0099 (19)
Ti	0	0	0.5339 (8)	0.002 (2)	0.002 (2)	0.005 (4)	0	0	0
Si	0.1297 (4)	0.6297 (4)	0.5128 (6)	-0.0118 (14)	-0.0118 (14)	0.018 (2)	-0.0127 (17)	0.0010 (16)	-0.0010 (16)
O1	0	½	0.6268 (8)	0.0333 (19)	0.0333 (19)	0.022 (4)	0.033 (3)	0	0
O2	0.1275 (3)	0.6275 (3)	0.2096 (4)	0.0232 (13)	0.0232 (13)	0.006 (2)	-0.0017 (18)	0.0007 (11)	-0.0007 (11)
O3	0.2933 (3)	0.5784 (3)	0.6402 (4)	0.0107 (14)	0.040 (2)	0.0141 (13)	-0.0128 (12)	0.0041 (13)	-0.0001 (16)
O4	0	0	0.2120 (6)	0.024 (2)	0.024 (2)	0.013 (3)	0	0	0
Ba/	0.3261 (3)	0.8261 (3)	0	0.0294 (19)	0.0294 (19)	0.026 (2)	-0.016 (2)	0.0021 (17)	0.0021 (17)
Sr									
Ti	0	0	0.529 (2)	0.026 (4)	0.026 (4)	0.016 (5)	0	0	0
Si	0.1273 (5)	0.6273 (5)	0.5015 (15)	0.032 (2)	0.032 (2)	0.020 (3)	0.021 (3)	-0.007 (3)	-0.007 (3)
O1	0	½	0.6186 (15)	0.099 (5)	0.099 (5)	-0.006 (3)	-0.074 (6)	0	0
O2	0.1273 (3)	0.6273 (3)	0.1958 (10)	0.0121 (14)	0.012 (14)	0.028 (2)	-0.004 (2)	0.0052 (14)	0.0052 (14)
O3	0.2958 (4)	0.5787 (6)	0.6407 (11)	0.021 (2)	0.090 (4)	0.0136 (18)	0.024 (2)	-0.0031 (18)	-0.025 (2)
O4	0	0	0.1950 (13)	0.038 (2)	0.038 (2)	0.024 (4)	0	0	0
Sr	0.3273 (2)	0.8273 (2)	0	0.0210 (13)	0.0210 (13)	0.007 (2)	-0.0245 (15)	-0.0038 (14)	-0.0038 (14)
Ti	0	0	0.5217 (19)	0.024 (3)	0.024 (3)	-0.002 (4)	0	0	0
Si	0.1279 (4)	0.6279 (4)	0.5021 (11)	0.0248 (19)	0.0248 (19)	0.007 (2)	0.009 (2)	-0.006 (2)	-0.006 (2)
O1	0	½	0.6196 (10)	0.094 (4)	0.094 (4)	-0.036 (2)	-0.071 (5)	0	0
O2	0.1277 (3)	0.6277 (3)	0.1964 (8)	0.0006 (12)	0.0006 (12)	0.0144 (18)	0.0035 (19)	0.0021 (13)	0.0021 (13)
O3	0.2980 (4)	0.5808 (5)	0.6514 (9)	0.042 (2)	0.150 (3)	0.0473 (19)	0.040 (2)	-0.021 (2)	-0.043 (2)
O4	0	0	0.1823 (12)	0.013 (4)	0.013 (4)	0.019 (4)	0	0	0

***Note: Negative anisotropic displacements encountered for some atoms.**

Table 5.8 Modulated wave functions for Ba₂TiSi₂O₈, (BaSr)TiSi₂O₈ and Sr₂TiSi₂O₈

	Order of modulation n	cos			sin		
		x	y	z	x	y	z
Ba	100	0.0074(15)	0.0074(15)	0	-0.0030(12)	0.0030(12)	-0.0197(14)
Ba	010	-0.0174(10)	-0.0174(10)	0	-0.0054(14)	-0.0054(14)	0
Ti	100	0	0	-0.0025(6)	-0.0023(5)	0.0026(6)	0
Ti	010	0	0	-0.0025(6)	0	0.0037(4)	-0.0037(4)
Si	100	0.00711(18)	0.00711(18)	0	0.0037(4)	-0.0037(4)	-0.0069(2)
Si	010	-0.0009(3)	-0.0009(3)	0	-0.0016(5)	-0.0016(5)	0
O1	100	0	0	0	0.0060(4)	-0.0060(4)	0
O1	010	0	0	0	-0.0019(6)	-0.0019(6)	0
O2	100	0.0002(2)	0.0002(2)	0	-0.0031(4)	0.0031(4)	-0.0068(2)
O2	010	-0.0009(4)	-0.0009(4)	0	-0.0017(5)	-0.0017(5)	0
O3	100	0.0056(3)	0.0056(3)	0.0032(5)	0.0044(4)	0.0044(4)	-0.0059(5)
O3	010	-0.0016(5)	-0.0017(5)	0.0010(5)	-0.0030(5)	-0.0014(2)	0.0027(5)
O4	100	0	0	-0.0025(6)	0	-0.003(2)	0.0035(15)
O4	010	0	0	-0.0025(6)	-0.0035(15)	-0.003(2)	0
Ba/ Sr	100	0.0042	0.0042	0.0058	-0.0053	-0.0053	-0.0006
Ba/ Sr	010	-0.0027(15)	-0.0027(15)	-0.005(5)	0.0041(19)	0.0041(19)	0
Ti	100	0	0	-0.006(6)	0	0.005(4)	-0.005(4)
Ti	010	0	0	-0.006(6)	0	0	0
Si	100	-0.0005(3)	-0.0005(3)	-0.0028(16)	0.0006(3)	0.0006(3)	0.0037(15)
Si	010	-0.000001(12)	-0.000001(12)	0.00000(2)	0.000000(7)	0.000000(7)	0
O1	100	0	0	0	0	0	0
O1	010	0	0	0.00000(9)	-0.0015(10)	0.0015(10)	0
O2	100	0.0002(3)	0.0002(3)	0.0014(17)	0.0007(3)	0.0007(3)	0.0044(14)
O2	010	0.01689(8)	0.01689(8)	0.00001(2)	0.01688(8)	-0.01688(8)	0
O3	100	-0.0008(2)	-0.0008(2)	-0.0045(14)	0.0002(3)	0.0002(3)	0.0012(17)
O3	010	-0.0115(7)	-0.0278(7)	0.012(3)	-0.0103(7)	0.0111(18)	0.0442(7)
O4	100	0	0	0.005(6)	0	-0.005(3)	-0.005(3)
O4	010	0	0	0.005(6)	-0.005(3)	-0.005(3)	0
Sr	100	-0.0114(9)	-0.0114(9)	-0.015(3)	0.0011(12)	0.0011(12)	0.009(4)
Sr	010	0.0042(13)	0.0042(13)	-0.009(4)	0.0026(13)	-0.0026(13)	0
Ti	100	0	0	0.006(3)	0.0009(7)	0.0020(13)	0
Ti	010	0	0	0.006(3)	0.0020(13)	-0.0009(7)	0
Si	100	-0.0001(3)	-0.0001(3)	0.015(3)	0.0074(3)	0.0074(3)	0.0019(19)
Si	010	0.00000(2)	0.00000(2)	0.00000(2)	0.00000(18)	0.00000(18)	0
O1	100	0	0	0.010(3)	0.0073(5)	0.0073(5)	0
O1	010	0	0	0.00000(14)	-0.0017(10)	0.0017(10)	0
O2	100	0.0060(3)	0.0060(3)	0.010(2)	0.0043(3)	0.0043(3)	-0.011(2)
O2	010	-0.01432(9)	-0.01432(9)	0.00006(2)	-0.01431(13)	0.01431(13)	0
O3	100	0.0002(3)	-0.0022(14)	-0.004(2)	0.0048(9)	-0.0037(5)	0.005(3)
O3	010	0.0001(2)	0.0004(2)	0.0000(5)	0.0000(2)	0.0000(3)	0.0000(5)
O4	100	0	0	-0.003(6)	0.008(2)	0.028(2)	0
O4	010	0	0	-0.003(6)	0.028(2)	-0.008(2)	0

5.6 Conclusions

There is a substantial literature concerning the crystal structure of modulated materials. In general, the variation of BVS across the modulation is not routinely published, but the present study suggests this may not be best practice. It is clear that a re-examination of benchmark BTS and STS structures contain cause for concern with respect to bonding and polyhedral distortion. Indeed, from this perspective, neither single crystal X-ray nor powder approaches seem satisfactory. Clearly, the small probe size of electron diffraction allows unambiguous examination of modulation at the submicron scale, but the results may not be representative of the bulk. In future, time-of-flight diffraction analysis, followed by point distribution analysis may allow better correlations of local and global structure and disorder.

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Chapter 6

Microstructural Features and Domain Formation in Fresnoite*

The photocatalytic efficiency of semiconductor oxides is impacted by the atomic scale distribution of band gap shifting dopants, the presence of secondary phases, and the formation of chemically or crystallographically discrete domains. The direct observation of these features by electron microscopy exposes the limitations of X-ray and neutron diffraction, and suggests that tuning the electronic structures of fresnoite and melilite through adjustments of the “average” incommensuration observed by the latter techniques may not be feasible.

6.1 Observation of Defects

The development of crystallochemical models for fresnoite and melilite has relied heavily on electron diffraction to unequivocally define the superspace groups and modulation vectors. However, several studies have revealed that incommensuration can vary between crystals, even when preparative methods are notionally identical. Höche et al. [1] using a combination of single crystal X-ray and electron diffraction reported a range of satellite reflection patterns, even within the same ‘crystal’, that unequivocally indicates domain formation. The appearance of domains will impact upon the reliability of the Rietveld refinements, and prevent the investigation of anisotropic thermal parameters and possible cation ordering. These limitations were extensively canvassed in *Chapter 5*. Presented here is a microstructural, electron diffraction and high resolution electron microscopy study of Ba-fresnoite (BTS), Sr-fresnoite (STS) and a mixed of Ba,Sr-fresnoite (BSTS). It is found that incommensurate modulations are stoichiometrically dependent and moreover, it is suggested that Sr-fresnoite, previously described as a homogeneous single crystal, may be better visualized as nanometric intergrowths of commensurate and incommensurate domains. The formation and co-existence of these regions is examined in (i) powdered and ion-milled STS, and (ii) powdered BTS and BSTS.

Figure 6.1. Fresnoite crystal structure projections. (a) View along [001] emphasizes, the corner connected Ti-square pyramids (yellow) and Si-(Ge)-tetrahedra (light blue) (110) slabs. Basal and apical oxygens (red dots) (b) and (c) are separated by 10-fold coordination to alkaline-earth cations (green spheres).

Historically, BTS was not immediately suspected of being incommensurate, even though some unusual atomic displacement parameters were extracted by X-ray diffraction [2-3]. However, selected area electron diffraction (SAED) conducted at room temperature readily revealed modulated satellite reflections along $\langle 100 \rangle$ at $h\ k\ l\ \frac{1}{2}$ levels and a doubling of the parent c axis [4]; incommensurate modulations were found along the a^* and the b^* directions. Specifically, a transition between commensurate and incommensurate modulated BTS was reported at 160°C, with the suggestion that the phase boundary migrates through distortion (buckling and tilting) of the corner connected polyhedral network [5], rather than compositional variation.

Electron microscopy confirmed that STS is also modulated [1, 6], and while metrically similar to BTS, STS has two families of satellite reflections observed at $0.4a^*$, $0.4b^*$, $0.6a^*$ and $0.6b^*$ and additionally at $0.43a^*$, $0.43b^*$, $0.57a^*$ $0.57b$. The origin of the latter satellites suggests that correlations between the polyhedral layers become stronger because strontium is smaller than barium [6]. Single crystal X-ray analysis of STS found a super-space group $P4bm$ ($-\alpha, \alpha, \frac{1}{2}; \alpha, \alpha, \frac{1}{2}$) with $\alpha = 0.3$ with $a = 8.312\ \text{\AA}$, $c = 10.07\ \text{\AA}$ [1].

Withers et al. [5] has demonstrated that satellite reflections in fresnoite type structures can arise from prescribed Rigid Unit Mode (RUM) model movements of the corner connected polyhedra. This analysis assumes the polyhedra are difficult to deform, and it is energetically preferable to rotate these units about $[001]$ to relieve stress within the sheets. In this manner, rigid body displacements lead to phase transitions and polymorphism.

As discussed in *Chapter 2*, most observations concerning synthetic incommensurate fresnoite and natural analogues were from single crystals produced from melts [4-6] or large mineral species [7]. It was assumed that melting produces chemically homogeneous and thermodynamically stable materials [5], and that commensurate-incommensurate phase transitions could be promoted by adjusting annealing time and temperature [8]; indeed, given the subtle changes in the oxygen sublattice involved, different degrees of order-disorder might be expected simultaneously at nanometer and

macrometer scales of nominally single crystals. Further investigation revealed the correlation of phase transformations on ionic ordering [9], while another study found geometrical charge frustration could lead to modulation [10]. Alternatively, a collective nucleation mechanism has been proposed to explain the coexistence of both commensurate and incommensurate phases suggesting a continuous transition [11].

In this chapter, STS produced via the solid state method (see *Chapter 4*) was re-examined by high resolution transmission microscopy (HRTEM), SAED, and analytical electron microscopy (AEM), to better understand if the satellite reflections revealed by electron diffraction [1, 6], are peculiar to the whole sample structure as suggested by bulk volume investigations, or are spatially localized as non-equilibrated crystal domains. It will be demonstrated that compositionally distinct commensurate and incommensurate domains co-exist in STS, and to a lesser extent in BTS. The complexity of BSTS is also revealed.

6.2 Experimental methods

6.2.1 Sample Preparation

In brief, the starting materials for solid state synthesis were oxides (anatase-TiO₂-Aldrich), carbonates (BaCO₃-Fisher, 99.6%, SrCO₃-BDH, 98.5%) and silicic acid (H₂SiO₃-Sino, 99%). These were manually mixed in stoichiometric proportions using an agate mortar and pestle, before preparing pellets and sintering in air. Table 6.1 compiles the different temperatures for the formation of fresnoite compounds. XRD (*Chapter 4*) showed that intermediate phases were removed by repeated cycles of grinding, pelletizing and sintering to obtain (nearly) single phase products (Fig. 6.2).

Table 6.1. Synthesis of fresnoite-type compounds.

Compound	Sintering temperature	Sintering period
$\text{Ba}_2\text{TiSi}_2\text{O}_8$	1200°C	3 x 12 hours
$\text{Sr}_2\text{TiSi}_2\text{O}_8$	1200°C	2 x 12 hours
	1250°C	2 x 12 hours
$(\text{BaSr})_2\text{TiSi}_2\text{O}_8$	1200°C	3 x 12 hours

Figure 6.2. X-ray diffraction pattern of Sr-fresnoite (STS) powder obtained after multiple firing cycles. Rietveld analysis suggests a high degree of homogeneity.

After final annealing, two sample sets were prepared for TEM: a collection of powdered materials deposited on holey-carbon coated copper-grids, and a set of argon ion milled portions of sintered pellets. For milling, 3 mm Ø disks were trepanned using an ultrasonic cutter (Gatan 601). These were finely polished with diamond paste before gluing onto a copper washer using epoxy, mechanically dimpled (dimple grinder; Gatan 656), and finally perforated using high precision ion milling (Gatan 691). To minimize charging during electron microscopy, the samples were coated with a thin film of evaporated carbon.

6.2.2 Electron Microscopy

TEM was conducted at 200 kV using a JEOL JEM-2100F TEM ($C_s = 0.5$ mm) as detailed in *Chapter 3*. High-resolution images were collected using a high contrast objective aperture of 20 μm , corresponding to a nominal point-to-point resolution of 0.17 nm. In order to verify the stoichiometry, all crystals

were analyzed semi-quantitatively in TEM-EDS mode, with a live counting time of 100 s and a nominal beam diameter < 5 nm. Recalculation and normalization of the AEM analyses were performed assuming the thin-film approximation, using experimental calibrations from oxide standards. Image processing and simulations for TEM images were carried out using CRISP [12] and JEMS [13] respectively. X-ray maps were collected from the ion milled samples using a low vacuum scanning electron microscope (JEOL JSM 5410LV) operating at 20 keV, while backscattered electron (BSE) images were collected using a scanning electron microscope (SEM) (JEOL JSM 5310) working at 15 keV.

6.3 Electron Crystallography and Microstructure

6.3.1 Sr-Fresnoite (STS)

6.3.1.1 Powdered Sample

SAED patterns collected in [001] and [010] zones contain the features observed by Höche et al. [1], but under identical instrumental parameters (*i.e.* SAED aperture, spot size, sample thickness, illumination conditions), the intensity of the satellite reflections varied regionally from very weak (Figs. 6.3a and 6.3c) to very intense (Figs. 6.3b and 6.3d), while the subcell (parent) reflections showed no such effects (beyond those expected from curvature of the Ewald sphere).

Figure 6.3. Selected area electron diffraction patterns of Sr-fresnoite (STS) along both [001] and [010] from areas with almost homogeneous bright contrast (a) and (c), and from portions showing dark contrast (b) and (d) respectively. The (200) and (001) reflections with $d = 4.28 \text{ \AA}$ and $5.26 \text{ \AA}$ are readily indexed. For volumes where high intensities of incommensurate reflections are observed figure insets are presented (b, d). For both insets red disks and open red circles correspond to kinematical and dynamical family reflections common to all fresnoite family members respectively; smaller yellow disks represent incommensurate reflections showing the same geometrical distribution already described by Höche et al. [1].

Figure 6.4. (a) [001] TEM images of the Sr-fresnoite powder sample where irregularly shaped dark contrast areas are bounded by wider areas where the contrast is more homogeneous and brighter. (b) [001] HRTEM image clearly showing the higher degree of structural disorder characterizing the dark contrast volumes compared to areas where the Sr-fresnoite structure is ordered (bright parts).

When HR electron imaging was used, it became clear that incommensurate reflections were stronger for crystal areas containing dark contrast (Fig. 6.4a), while the satellites were near absent in areas with homogeneous bright contrast. Overall, darker areas were much less abundant compared to bright regions; image analyses from several crystals found about 10-15 % of the former vs. 90-85 % of the latter. Figure 6.4b shows a crystal where differences in contrast delineate volumes with considerable structural disorder (dark contrast) and portions where the STS is unaffected by defects, stacking faults, or twinning (bright contrast). AEM analyses found the defective portions to be depleted in strontium and silicon, and relatively enriched in titanium compared to unmodulated bright contrast areas. The Sr- and Si-deficits are in the range of 0.6-0.8 apfu and 0.2-0.4 apfu respectively, while titanium shows an excess of about 0.3-0.5 apfu, with respect to the nominal $\text{Sr}_2\text{TiSi}_2\text{O}_8$ composition. Together with these dominant contrast distributions were a few percent (~ 1-3 %) of homogeneous and very bright contrast areas, that SAED showed were poorly crystalline as indicated by a diffuse diffraction rings and the absence of Bragg spots. The ring positions were variable and could not be indexed to published crystallographic data for oxides of Sr, Si, and Ti in any combination.

6.3.1.2 Ion-Milled Sample

TEM images of the ion milled fresnoites contain intriguing structures where areas of bright uniform contrast (*i.e* hereafter named crystal-1), were separated by a herringbone structure (Fig. 6.5a). More rarely idiomorphic crystalline material with darker contrast (hereafter named crystal-2) is embedded in the non crystalline ground mass revealed by SAED (Fig. 6.5b). AEM analyses indicate that all three crystal morphologies correspond to Sr-fresnoite, while the amorphous regions are extremely poor in Ti and therefore enriched in Sr and Si. Chemical analyses of crystal-2, as was already observed for dark contrast areas of the powder samples, show the same deficits in Sr and Si contents and Ti-enrichments.

SAED of crystal-1 show the characteristics of the powder samples, with the skeletal and/or idiomorphic crystals invariably containing strong satellite reflections (Fig. 6.5c). In general, TEM images of crystal-2 appear to have uniform contrast (Fig. 6.5c) but, enhancing diffraction contrast clearly provides evidence of mottled bright and dark areas (Fig. 6.5d), that were too small to be examined by SAED and proved exceedingly electron beam sensitive while attempting convergent beam electron diffraction (CBED). Another common observation for the idiomorphic crystal-2 is that, curved and irregular contrast bands run through the thinnest regions and change in both intensity and position as the diffraction conditions are altered (Fig. 6.5b).

SEM-EDS analysis of the ion milled material shows that the structures observed by TEM are part of a larger scale growth phenomenon (Fig. 6.6a), where most of the volumes between the micrometric-sized Sr-fresnoite grains contain amorphous regions in which STS skeletal crystals are embedded. BSE images (Fig. 6.6b) together with EDS analyses and X-ray elemental mapping (Fig. 6.6c-6.6e) are consistent with AEM. In particular, X-ray elemental mapping confirmed the non crystalline volumes are significantly depleted in titanium and slightly enriched in strontium and silicon.

Figure 6.5. Low magnification TEM images of an ion mill sample. (a) Skeletal crystals (crystal-2) growth within a glassy ground mass separating volumes with the same bright uniform contrast (crystal-1). (b) Idiomorphic darker contrast crystalline material (crystal-2) is present within a lighter contrast non crystalline ground mass as revealed by SAED (inset). (c) Electron diffractions reveal that both skeletal and idiomorphic crystals within the glassy ground mass are characterized by the constant presence of incommensurate reflections testifying that almost the entire structure is characterized by a high degree of disorder. (d) The high degree of structural disorder is evident for higher magnification images where a very fine and patchy distribution of contrast appear within both skeletal and small idiomorphic crystals.

Figure 6.6. SEM images and EDX elemental maps of ion mill samples. Both secondary (a) and BSE images (b) clearly show the presence of intra-crystalline domains (light grey) where a quenched structure characterized by the presence of skeletal crystals plunged with a glassy matrix (mesostasis) are visible. X-ray EDS mapping of intra-crystalline areas reveal that the glassy matrix is slightly enriched in both Si (c) and Sr (d) while clearly depleted in Ti (e).

6.3.2 Powdered Ba-Fresnoite

Because STS powders and ion-milled sections revealed unexpected spatial and chemical features of incommensurability, BTS was examined to establish if these phenomena were generic. The satellite reflections of BTS are similar to those of STS during SAED [5] but less intense than in single crystal X-ray diffraction (Fig. 6.7) [1]. The strength of the satellites could be enhanced by the standard method of tilting slightly off the [001] axis (Fig. 6.7b). Moreover, HRTEM imaging of BTS exhibits the same variable regional contrast as STS due to intergrowth of commensurate and

Figure 6.7. Electron diffractions of Ba-fresnoite along both [001] and [010] from areas with almost homogeneous bright contrast (a) and (b), and from portions showing dark contrast (c). It is observed that the intensities for incommensurate reflections along [001] is not pronounce. Tilting off axis is necessary to bring out the weaker reflections. By capturing a larger set of diffraction spots, satellite reflections are observed in [100] direction. Insets red disks correspond to kinematical family reflections common to all fresnoite family members respectively; smaller yellow disks represent incommensurate reflections.

incommensurate domains (Figs. 6.8c-6.8d). These features are readily observed in [100] but are not so apparent in [001] (Figs. 6.8a-6.8b).

Figure 6.8. High resolution imaging of Ba-fresnoite powder along [001] (a)-(b) and [100] (c)-(d). Modulation along [001] perhaps are too weak to be reconstructed while strong modulation is observed along [100] with regions of commensurate (lighter contrast) and incommensurate (darker contrast). (b) and (d) is the enlargement of (a) and (c) respectively.

6.3.3 Powdered Ba,Sr-Fresnoite

The electron diffraction patterns of BSTS suggest a more complex modulation than the fresnoite endmembers; although [001] was similar, the [100] zones are distinct. The material was noticeably electron beam sensitive and SAED intensity changed after a few minutes observation. Further work is needed to determine if displacive (mainly oxygen) and occupational (barium-strontium) modulations are occurring concurrently. Similar to the fresnoite endmembers, BSTS patterns can be indexed as a combination of commensurate and

incommensurate reflections. However, as shown in Figure 6.9, extracting reliable information from HRTEM without artifacts is

Figure 6.9. Electron diffractions of BaSr-fresnoite along both $[001]$ and $[010]$. It is observed that the intensities for incommensurate reflections along $[001]$ are not pronounced as Sr-fresnoite. It is observed that the diffraction captured along $[100]$, (b) and (c), showing two different sets of diffractions spots after prolonged observation under the transmission electron microscope. Insets red disks correspond to kinematical family reflections common to all fresnoite family members respectively; smaller yellow disks represent incommensurate reflections.

problematic, and it is evident that the strength and distribution of satellite spots changed after prolonged observation (Fig. 6.10).

Figure 6.10. High resolution imaging of BaSr-fresnoite powder along [001] (a)-(b) and [100] (c)-(d). Modulation along [001] showing co-existence of regions of commensurate (lighter contrast) and incommensurate (darker contrasts). It is observed that the incommensurate regions along [100] is changing with illumination times. (b) is the enlargement of (a), while (c) and (d) showing the change in incommensuration with illumination times with (d) being illuminated longer than (c).

6.4 Discussion

6.4.1 The Role of Sr/Si and Ti Occupancy in Modulation

HRTEM of powdered and ion mill STS found incommensurate and commensurate domains at nano- to micro-metric scales (Fig. 6.4). Fourier reconstruction from different regions shows the satellite reflections and distributions are variable (Fig. 6.11), and because this heterogeneity extends to a fine scale, the reconstruction of the real structure is challenging. It is evident that incommensuration and contrast arising from stress are correlated (Fig. 6.4b), and the intensity and position of the bands vary

Figure 6.11. On the left are reported two HRTEM images used to reconstruct Fourier Transforms (FT) from different sample areas using the program CRISP. Calculated FT from areas showing different degrees of disorder (i.e. different contrast distributions) clearly bring to evidence that incommensuration is not homogeneously distribute over the sample. (a) Beside the presence of clearly commensurate areas (a), samples portions showing different kind of darker contrast related to different degrees of structural disorder, show evidences of different of modulated incommensuration (b, c, d, e, f) as imaged by the reconstructed FT calculated from different disordered areas.

as the diffraction conditions change (*i.e.* sample tilting). It is presumed strain arises to relieve mismatch induced by the co-existing 3D and higher dimensional volumes; the modulated parts are strontium-poor which induces local changes in cation-anion bond lengths. These re-arrangements will be accompanied by polyhedral tilting and/or rotation [5] as the mechanism for stress propagation. Most probably in tandem, Ti-rich fresnoite will co-exist with the Ti-poor intergranular groundmass accompanied by the substitution of Si by Ti in tetrahedral coordination.

The bright, undifferentiated contrast of commensurate regions suggests stress is minimal, although bound between incommensurate contoured domains (Fig. 6.5). This phenomenon may be analogous to the incommensurate walls [14]

observed in high temperature superconductors that is postulated to arise from misfit dislocations appearing near the stress bands [15]. In STS, similar defects may be necessary to relieve the stress induced by atomic modulation that accompanies Sr depletion. As observations from powdered BTS and BSTS are similar to STS, the role of Sr/Ba, Ti and Si occupancy/displacement in modulation may be inferred to broadly correspond.

6.4.2 Ionic Ordering in Modulated Phases

It can be concluded that regional differences in satellite reflection intensity for the [100]/[010] zones (Fig. 6.3) of STS probably originated from the disordered intergrowth of compositionally differentiated incommensurate regions within the parent structure; for the ion milled samples (Fig. 6.5b-6.5f) variations in satellite reflection intensity could be observed in the same “crystal”. This suggests different degrees of polyhedral distortion, tilting and/or rotation (RUM mode) [5] induce stresses that create pronounced and/or diffuse boundaries between modulated phases. As significant stoichiometric anomalies are common, more complex phase combinations cannot be excluded of the form of $\text{Sr}_{2-x}\text{Ti}_{1+y}\text{Si}_{2-y}\text{O}_{8-x}$. For example, matsubaraite ($\text{Sr}_4\text{Ti}_5\text{Si}_4\text{O}_{22}$) [S.G $C2/m$; $a = 13.850 \text{ \AA}$, $b = 5.631 \text{ \AA}$, $c = 11.892 \text{ \AA}$, $\beta = 114.143^\circ$] [16] contains structural elements in common with fresnoite and incorporation of trans-structural regions may provide a mechanism to relieve strain.

Although materials were prepared via solid state reaction, the skeletal crystal morphology (Fig. 6.5) within glass suggests incipient melting occurred, as is typical of high temperature systems quenched very rapidly such as glass mesostasis in chondritic meteorites [17-18]. In such systems, kinetics rather than thermodynamics controls the reaction products as the temperature drops. In the first stage, when cooling rates are very high, only a few crystal germs attain the critical mass to continuously grow; simultaneously, the crystal structure relaxes to eliminate strain (i.e. removal of ionic disorder, crystal defects, etc.). As the temperature diminishes ionic migration rates tend to zero which captures the skeletal structures within the amorphous titanium poor

matrix, and the capability to eliminate structural strain within incommensurate domains. This scenario is in agreement with early observations of BTS where incommensurate domains present at room temperature are removed by heating to $> 160\text{ }^{\circ}\text{C}$ [5]. The presence of irregularly shaped modulated domains within crystal-1 and, moreover, the strong incommensuration shown by late-formed skeletal crystal-2 shows that for STS, and probably BTS and BSTS, the first stage crystallization of incommensurate structures is followed by a partial reorganization that continues until ion mobility slows and freezes the domains. In the last stage, the system retains sufficient energy to nucleate numerous crystallites (the skeletal crystals) but not to sustain crystal growth and structural reorganization that would lead to homogeneous crystal modulation.

Although single crystal melt growth yields improved crystal homogeneity, microscopy suggests that even here domains exist, although these may not be linked to compositional variation. In syntheses conducted near-solidus the phase evolution is more clearly seen from the morphology of the skeletal crystals which is comparable to metastasis in meteorites.

6.5 Conclusion

For the barium and strontium fresnoites studied here, chemical inhomogeneities were characteristic of incommensurate regions while, commensurate regions displayed a stoichiometry less perturbed from $\text{A}_2\text{BC}_2\text{O}_8$. Evidence for these phenomena is directly visible in selected area electron diffraction (SAED) and also captured via high-resolution transmission electron microscopy (HRTEM) images, but would not be detected by bulk diffraction methods (i.e. X-ray and neutron diffraction) where an “average” structure is recognized; it is unlikely that modeling algorithms can be devised to better extract microstructural content from these latter techniques. Incommensurate and commensurate areas are readily separated by their different degrees of modulation. Fourier reconstructions of HRTEM images captured in the modulated regions showed distinct variations in incommensurability, while SAED patterns from areas without structural disorder do not show satellite reflections. To summarize, in STS a mechanism

is proposed to explain the co-existence of both commensurate and non-commensurate phases. HRTEM clearly shows the formation of these domains with AEM analysis supporting stress induced domain formations in Sr depleted regions. These conclusions can be extended to BTS and BSTS that have similar HRTEM images and SAD patterns.

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Chapter 7

Structural Modification and Band Gap Adjustment

Band gap tailoring is fundamental for designing novel heterogeneous photocatalysts. Visible light activation is desirable to enhance the economy of operation, efficiency of exciton production and simplify reactor design. Many photocatalysts operate in blue or ultraviolet light, and cationic and anionic substitutions are one means to reduce band gap energy sufficiently for electron-hole pairs to be created in sunlight. Chemical doping is accompanied by crystallographic adjustments, that can also modify the catalytic response, and in the case of fresnoite and melilite, promote topological distortion and modulation. However, computational methods, that have been successfully applied to III-V semiconductors, are not readily extended to these complex structures.

7.1 Band Gap Manipulation

Cationic and anionic replacements are commonly used to manipulate functionalities in parent crystals [1-2]. This approach also provides a means for band gap engineering, as for example, in the BiVO_4 - CeVO_4 join where exciton creation energy changes linearly (i.e. band gap decreases with lattice expansion; ionic radii $\text{Bi}^{3+} \sim 1.52 \text{ \AA}$ while $\text{Ce}^{3+} \sim 1.034 \text{ \AA}$ [3]) from 1.8 eV in CeVO_4 to $\sim 1.5 \text{ eV}$ in $\text{Ce}_{0.6}\text{Bi}_{0.4}\text{VO}_4$ and $\text{Ce}_{0.5}\text{Bi}_{0.5}\text{VO}_4$ [4], though the band gap of BiVO_4 is $\sim 2.8 \text{ eV}$. While this observation is peculiar to this series, it is often found that the band gap decreases in tandem with lattice dilation [5-7]. Generally, band gap manipulation is most effective when relatively stronger electronegative elements such as Bi (i.e. ~ 2.02 Pauling scale [3]) replace less electronegative elements including In (i.e. ~ 1.78 Pauling scale [3]) [5]. Ionic substitution can extend exciton lifetime by reducing pair formation energy [8], or as in the superconductor BaFe_2As_2 , structural distortions modify the Fermi surface to alter the electronic structure/band structure [9]. For Bi_2MTaO_7 ($\text{M} = \text{In, Ga and Fe}$) each structural analogue possesses different band gaps that correlate with lattice distortion arising from deformation of the corner-linked MO_6 octahedra [10]. The best performing composition, $\text{Bi}_2\text{InTaO}_7$ displayed enhanced electron and hole migration to the surface that increased the probability of pollutant mineralization [10].

Besides the fundamental requirement for the excitation of free electrons and holes, a viable catalyst should have sufficient surface activity to inhibit exciton recombination and readily adsorb pollutant molecules. In addition, a host of factors including charge carrier trapping, quantum size effects, photocatalyst loading, organic pollutant concentration, oxygen activity, light intensity, temperature, and pH must be considered during catalytic optimization [11-12]. Only a few “ideal” pollutants - stearic acid, methylene blue and ink [13-15] - have been widely used for screening photocatalytic activity. A final challenge is that mineralization is pollutant-dependant and in real wastes, containing a mixture of hazardous compounds, the creation of stable, but toxic intermediate mineralization products, may “poison” the catalyst by surface absorption.

This chapter considers the effect of cation substitution in fresnoite and demonstrates that performance is primarily controlled by the physical form of the catalyst, with the band gap playing secondary role. The difficulties in using computational methods to guide the selection of suitable compositions are also discussed.

7.2 Band Gap Measurements and Photocatalytic Testing

The band gap and catalytic activity were estimated using UV-visible spectrometry as described in *Chapter 3*. Briefly, absorption spectra were collected from 200 to 800 nm (ultraviolet to visible light region) from powdered catalyst. Extrapolation of the slope of the absorption edge to zero allowed an estimation of the band gap, however, the method is unreliable in doped systems where several edges overlap. Photocatalytic activity was investigated by following decoloration (assumed equivalent to mineralization) of an aromatic dye (methylene blue).

7.2.1 Band Gap of (Ba,Sr)TiSi₂O₈

The band gap of a material is controlled by its electronic structure [16], and it follows that modification of atomic symmetry and disorder lead to changes in electronic state (i.e. degeneracy in energy levels) that alter the conduction and valence bands [17]. In the extensively studied III-V quaternary alloys, modeling studies found the band gap increases with superlattice period [18], and established correlations with structural analyses as a prerequisite for band gap engineering.

Electron loss-spectroscopy (EELS) of Ba₂TiGe₂O₈ (BTG) fresnoite found TiO₅ square pyramidal distortion induced splitting of the Ti(3d) orbitals and a probable change in band gap, while Ba₂TiSi₂O₈ has regular TiO₅ square pyramidal polyhedra [19-20]. Employing the same method to probe Sr₂TiSi₂O₈ (STS) suggests that this compound is akin to BTG [21], and bond length modification that results from substituting Ba by Sr will change the crystallographic and electronic structures. In present study, the absorption

edges of Ba and Sr-fresnoite are distinct (Fig. 7.2) and the band gaps are estimated as 3.27 eV and 3.43 eV respectively (see Equation 3.1).

Figure 7.1. Splitting of d orbitals of Ti^{4+} ions in regular and distorted square pyramidal coordination. The distortion shown by $\text{Ba}_2\text{TiGe}_2\text{O}_8$ is representative of $\text{Sr}_2\text{TiSi}_2\text{O}_8$. Taken from [19].

The fresnoite band gaps are larger than for the benchmark anatase photocatalyst (~ 2.99 eV). However, the replacement of strontium with barium not only shifts the band gap, but also creates an additional absorption edge (i.e. 409 nm/3.03 eV). It is proposed that this secondary feature may arise from the structural modulation that accompanies strontium substitution for barium, while the stronger common absorption edge is determined by the parent structure. Adjustments of modulation to tune the band gap could not be unequivocally established due to the complexity of nanostructure (*Chapter 6*) and the intergrowth of domains, which play an unknown role in modifying electronic structure through strain fields.

Figure 7.2. Absorbance spectra and extrapolation to band gap for (a) titania photocatalyst, (b) Ba-fresnoite (BTS), and (c) Sr fresnoite (STS). The weaker absorption edge nearer the visible region is readily observed in STS.

Figure 7.3. An additional absorption edge becomes more pronounced with increasing strontium content in the fresnoite structure. (a) Ba-fresnoite (BTS), (b)-(d) are mixtures with Sr atoms replacing Ba atoms in steps of 20 at%, 50 at% and 80 at% respectively, and (e) Sr-fresnoite (STS).

Figure 7.4. Band gaps determined by UV-visible spectroscopy varies with strontium replacement in Ba-fresnoite. Band gaps calculated from (a) the strongest band edge (solid line), and (b) the additional edge (dotted line), are shown.

The two absorption edges of mixed Sr and Ba-fresnoites vary independently; the less energetic (~ 3.00 eV) decreases with increasing Ba content, while the band gap of the parent structure (~ 3.60 eV) is relatively constant over much of the solid solution series. It is believed that cationic substitution creates an additional energy level due to splitting of orbitals that accompanies polyhedral distortion (Fig. 7.5). It is then feasible, in principle, to select a Ba and Sr mixtures to reduce the energy for exciton production sufficiently to permit a light sensitized photocatalysis.

Figure 7.5. The band gaps of (a) Ba-fresnoite, (b) Sr-fresnoite, and (c) Ba,Sr-fresnoite. In (c), the second absorption edge indicates the creation of additional band gap in the forbidden gap region as a result of Sr substitution.

Band gap modification of the BTS-STs join were modeled using a density functional theory approach with CASTEP [23], with the aim of establishing a relation between structural lattices and electronic structure for fresnoite-type compounds in a manner analogous to the III-V semiconductor and vanadates. These calculations were performed using the subcell rather than incommensurate supercell. The simulated subcell band gaps of the endmembers were observed to be BTS ~ 3.00 eV and STS ~ 3.40 eV. However, it was not possible to model (Ba,Sr)TiSi₂O₈ mixed subcells or the modulated cell as the simulation package did not support (3+n)-superspace symmetry; the influence of modulation could not be confirmed. Figure 7.6 shows that the band gap of the simulated subcell was attributed to the d orbital, consistent with EELS (i.e. splitting of Ti(d) orbital) [19-20], and suggests that the electronic structure of these materials could be manipulated by distortion of square pyramids.

Figure 7.6. Computed density of states from CASTEP. (a) BTS and (b) STS showing slight variation to the band gap change which were largely attributed to the Ti(d) orbital.

7.2.2 Photocatalytic Degradation of Methylene Blue

Following the procedure in *Chapter 3*, the degradation of methylene blue as a function of time under UV illumination time at 25 °C was monitored (Fig. 7.7); this experiment is representative of several fresnoite compounds. Experiment performed in dark (i.e. without any irradiation) shows no trapping of methylene blue molecules which produce artifact (i.e. implying mineralization) under UV irradiation. Employing Beer-Lambert's Law [24], a plot of relative concentration shows that oxidation of methylene blue with titania is far superior to powdered Ba and Sr-fresnoite (Fig. 7.9). There is little distinction in the activities of these two fresnoites though the band gap is vastly different, confirming that surface activity is the controlling parameter.

Figure 7.7. The decoloration of methylene blue is used as an indicator of catalytic activity. The plot above shows absorbance decreasing with time (0, 5, 10, 15, 20, 30, 40, 50, & 60 min.).

Figure 7.8. Baseline experiment performed in the dark showing negligible absorption of methylene blue molecules by the powdered BTS photocatalyst.

Figure 7.9. The oxidation of methylene blue treated with BTS and STS photocatalysts processed via the Pechini method. A methylene blue blank is included to provide baseline.

7.3 Conclusion

The expected dependence of band gap on fresnoite composition is confirmed, however it is not feasible at this time to correlate chemistry with photocatalytic activity, as is possible in structurally simpler systems. This remains a major impediment to the development of these compounds as functional materials. UV-visible spectrometry shows changes in absorption, but given the structural complexity explored in *Chapters 5 and 6*, it would be speculative to attribute variations in band gap to modulation properties. Although the band gap energy is in the ultra-violet region, it can be tuned by varying the Ba/Sr content. This is related to polyhedral deformation (i.e. square pyramid and tetrahedron), but the influence of crystal strain is yet to be established. While fresnoite and its analogues absorb energy in the ultra-violet region, their catalytic activities as probed by methylene blue decolorization remain inferior to commercially available titania. Further investigation of the surface activity of fresnoite and fresnoite-type compounds is required to enhance catalytic activity.

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Chapter 8

Fresnoite and Melilite Photocatalysts: Conclusions and Future Prospects

Fresnoite and melilite-type compounds are crystallographically and chemically complex at the nanoscale, and while the appearance of incommensuration is related to composition, the link is not always direct. Structural studies, especially of nanosized powders, are feasible by electron diffraction, but irradiation artifacts are often introduced after short observation. Powder neutron diffraction also provides ambiguous results because of the low intensity of incommensurate reflections and the intergrowth of domains. A wider strategy is necessary to establish an integrated understanding of crystallographic defects, optimize synthesis routes and tune the band gap. Solid solutions between fresnoite and melilite appear feasible and may be beneficial in creating a superior visible-light photocatalysts.

8.1 Feasibility of a Fresnoite-Melilite Photocatalyst

This research was designed to test the hypothesis that fresnoite and melilite-type compounds could be tuned through crystallochemical tailoring to deliver enhanced photocatalytic materials. This aim proves ambitious. Nonetheless, several objectives were partially met and include:

- (iv) developing a novel Pechini method for synthesizing fresnoite which was subsequently used for fresnoite and melilite intergrowth;
- (v) differentiating the fresnoite average structure and the real structure while recognizing the complexity of its macroscopic/bulk defects; and
- (vi) establishing that structural stress induced by cationic substitution allows band gap tailoring which is essential for heterogeneous photocatalytic materials design.

This re-examination of fresnoite-type crystallography has led to a deeper understanding of the differences between average ‘modulated’ structures and the nanostructure observed directly by microscopy. While incommensuration, especially of large single crystals can be described in terms of higher dimensional symmetries, the nature and concentration of defects remains controversial. X-ray and electron single crystal diffraction probe different volumes and demonstrate that in many materials an absolute description of atomic motifs might not be possible. Incommensurate fresnoite-melilite usually contain nanoscale variations in chemical composition leading to the promulgation of domains whose intergrowth induces strain. The nature of the domains is dependant on the synthesis method, providing an opportunity to compare crystals produced by melting, solid state reaction or sol-gel syntheses. It was found, for the first time, that in $(\text{Ba,Sr})\text{TiSi}_2\text{O}_8$ fresnoite commensurate and incommensurate regions co-exist, leading to framework strain relaxation and deformation. Consequently, attempts to solve neutron powder diffraction patterns remains difficult, and perhaps impossible, as several parameters are strongly correlated, and at a fundamental level a

‘unique’ structure may not exist. Indeed, the very extreme departure in BVS observed in single crystal determinations and powder diffraction refinements, suggest the crystallographic models for fresnoite may be far from satisfactory. While a systematic change in band gap across the solid solution of Sr and Ba-fresnoite was demonstrated, systematizing and controlling the electronic structure remains elusive. Photocatalytic activity of fresnoite is presently inferior to commercial titania products however, with both physical and chemical limitations as contributing factors.

While this study of fresnoites and melilites was inconclusive with respect to their photocatalytic potential, a better understanding of the flexible framework composed of rigid body polyhedra was achieved. It is perhaps significant that there is no systematic change in the incommensurate vectors (q_1 and q_2) as a function of composition in $(\text{Ba,Sr})\text{TiSi}_2\text{O}_8$ fresnoite. This is in contrast to $\text{CeNbO}_{4+\delta}$ fergusonite [1] where there is a clear change in the position of the satellite reflections with oxygen content, and a continuum between commensurate and incommensurate superstructures is observed. It is reasonable to speculate that in fergusonites, nonstoichiometry is distributed homogeneously at the atomic scale, rather than in compositionally discrete domains as in fresnoite. Therefore, for $\text{CeNbO}_{4+\delta}$ [1] the structure solution and higher dimensional structures show great validity. Finally, a more comprehensive protocol is needed for evaluating photocatalytic activity.

8.2 Roadmap for Future Research

8.2.1 Integrated Structural Studies

This thesis has shown that crystallographic modulation and the rationalization of unsatisfactory crystal structure refinements, not only requires in-depth understanding of higher dimensional symmetry but also an appreciation of the probe used (i.e. electrons, neutrons, X-rays). Primarily, synthetic single crystals have been used in solving fresnoite and melilite structures, but these descriptions require critical analysis, because although the individual metal-oxygen bond lengths appear reasonable, the BVS can deviate substantially from expected values. This may be indicative of domain intergrowth.

Furthermore, while single crystal materials are the ideal form for solving higher dimensional structures, powder samples are often required for technological applications. In *Chapter 5*, it was pointed out that single crystal and powdered materials may not be comparable, as they contain variable proportions of commensurate and incommensurate regions. An integrated approach is essential to ‘solve’ incommensurately modulated powder structures, or at least recognize their primary crystallographic features, and will span:

- macroscopic investigations (e.g. phase assemblage, growth domains) to microscopic characterization (nonstoichiometry and domain formation); and
- surface defect studies to assess the impact on the average structure, and to complement the observation of polymorphic transformations.

While electron microscopy has the advantage of directly measuring higher dimensional features, the location of oxygen is necessarily ambiguous, although anions may be the ‘modulating’ species. Neutron diffraction is essential for locating weakly diffracting atoms, and ideally, should be combined with chemical analysis, surface defect descriptions, and electron diffraction to produce a comprehensive structural solution.

However, for the materials studied here, several persistent issues pertaining to neutron powder diffraction are unresolved, including broad background features at high angles, and weak satellite reflections overlapping main reflections that cannot be satisfactorily modeled. It proved impossible to establish a convincing refinement strategy that does not lead to improbable fractional coordinates and/or negative anisotropic displacement parameters. The most pressing issues are to avoid reaching false minimum while deconvoluting background from Bragg diffraction, and separating subcell reflections and satellite reflections.

8.2.2 Co-existence of Incommensurate and Commensurate Domains

The co-existence of incommensurate and commensurate domains is thought to be ubiquitous whatever the synthesis method; an analysis of independent structural studies suggests this is generally true in $A_2BC_2O_8$ and $A_2BC_2O_7$ oxides. The co-existence of chemically distinguishable nanodomains is not usually commented upon, but not an unexpected outcome given the quaternary nature of these systems. Clearly, a more comprehensive approach to correlate structural disorder with band gap is needed, and thereby customize and manipulate materials for visible light exciton production. In particular, the higher dimensional structures should be homogeneous at atomic scale. This approach remains feasible in principle, but in fresnoite-melilite structures direct and simple band gap tuning proved impossible.

Several experimental issues require attention. A reliable method to measure the electronic band gap is essential, to establish the linkage between polyhedral deformation and composition. It is unclear how deformation through layer flexing influences the electronic structure. This intricate issue may be intractable when materials contain 3D and higher dimensional domains in various proportions. To date, little solid state nuclear magnetic resonance (NMR) spectroscopy has been undertaken, but together with X-ray absorption spectrometry (XAS) would provide insights into the local environment of the metal ions.

8.2.3 Catalytic Activity

Fresnoite powders showed limited potential as photocatalysts compared to commercial titania. This sub-optimal performance is not intrinsically linked to the band gap, but rather poor control of surface area and manipulation of surface defects; a large surface area is required to produce more active sites, while defects reduce the frequency of electron hole recombination. It would be of interest to prepare fresnoites and melilites as three dimensional macroporous (3DOM) materials using the Pechini synthesis; this approach has proved beneficial for the performance of titania [2].

A more comprehensive method is required for gauging the catalytic activity of these materials and should include:

- broadening the type of pollutants used as standard measures of activity to better mimic surface absorption and poisoning in ‘real’ chemically complex wastes;
- developing a prescribed method to assess performance under a range of controlled conditions (e.g. pH, temperature, amount of absorbed light); and
- adopting, as routine, the examination of durability and recyclability.

8.2.4 Fresnoite – Melilite Solid Solutions as Photocatalysts

The preliminary synthesis of a fresnoite-melilite intergrowth (i.e. $\text{Sr}_2(\text{Ti}_{1-x}\text{Co}_x)\text{Si}_2\text{O}_{7+\delta}$, $0 \leq x \leq 0.05$) found Co^{2+} could be incorporated to some extent in fresnoite, or alternatively, Ti^{4+} into melilite. The change in color from white (in fresnoite) to light green suggests a substantial adjustment in band gap towards the visible. However, a thorough study is needed as $\text{A}_2\text{BC}_2\text{O}_{7+\delta}$ compounds may prove especially complex as framework structures. The most significant questions to be addressed include:

- establishing the solid solution limits of intergrowth structures;
- monitoring changes in symmetry as a function of doping;
- tuning valance to optimize electronic structure; and
- examining the influence of localized strain.

8.3 Conclusion

In conclusion, this thesis proved to be challenging experimentally, especially with respect to synthesis and characterization, and theoretically, as modeling approaches are not readily extended to higher dimensional crystals. Nonetheless, several new insights into the nature of modulation were developed, including the intergrowth of chemically distinct regions at nano and microscales, and the probable need to reexamine contemporary

crystallochemical descriptions. In addition, progress was made towards a viable soft chemical route for synthesizing homogenous products. While the outcomes were not always complete or unambiguous these studies can underpin tailoring fresnoite-melilite functionality to maximize the efficiency of these materials for the photocatalytic oxidation of pollutants.

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Appendix I

Refinement of Cell Parameters in Spacegroup $P4bm$ ($\text{Ba}_{1-x}\text{Sr}_x$) $_2\text{TiSi}_2\text{O}_8$ with estimated standard deviations in bracket.

Lattice parameters in space group $P4bm$		
at % Ba	a	c
100	8.531252(59)	5.214354(51)
90	8.505982(45)	5.193905(38)
80	8.484955(43)	5.175506(36)
70	8.464900(61)	5.156634(50)
60	8.442743(55)	5.136449(44)
50	8.422857(56)	5.117985(42)
40	8.403335(67)	5.099494(51)
30	8.383467(73)	5.080869(55)
20	8.362353(62)	5.061625(47)
10	8.342848(71)	5.043625(55)
0	8.322927(73)	5.025604(48)

Appendix II

Diffractograms as a function of d-spacing collected from (a) X-ray and (b) neutron diffraction.

(a) Blue markers indicate Bragg reflections while the lower difference plot is shown in grey line and (b) markers for the subcell (black) and first order satellite (green) reflections are shown while the difference plot is the lower black line.