Investigating the Structural Behaviour and Phase Transitions of the $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ Series of Compounds

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We have synthesised powder samples across the $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ (x = 0.0 - 1.0) composition range. At ambient temperature, the x = 0 end member ($Sr_2TiSi_2O_8$) crystallised as a mixture of tetragonal *P*4*bm* and orthorhombic *Cmm*2 structures with a transformation to a pure *Cmm*2 phase at approximately 480 K. However, all other samples in the $0.1 \leq x \leq 1.0$ range formed with only the *P*4*bm* phase.

1. Introduction

At ambient temperature, the fresnoite family of compounds with the general formula $A_2BM_2O_8$ (*A* = Ba, Sr; *B* = Ti, *M* = Si, Ge) crystallises in a tetragonal structure with space group *P*4*bm* and can be described from corner-linked TiO_5 square pyramids and M_2O_7 groups that form flat sheets perpendicular to the [001]-direction and are interconnected by 10-fold coordinated *A*-cations (Fig. 1). The fresnoite structure type is one of several possible alternatives currently being investigated to replace PZT and other lead-based ferroelectric materials because of their potential to exhibit excellent piezoelectric properties [1-2]. Understanding the structural chemistry of these materials is critically important for the development of new materials with optimised physical properties that are comparable to or better than the currently available lead-based compounds.

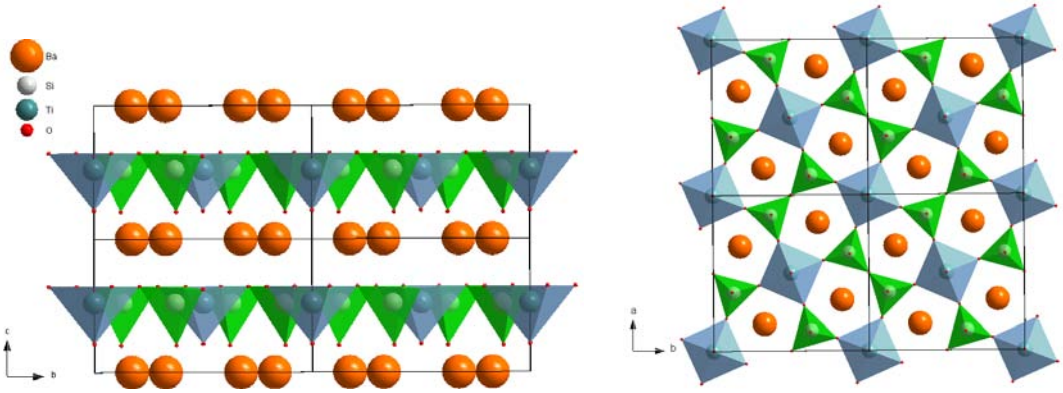

Fig 1. The fresnoite $Ba_2TiSi_2O_8$ structure projected along the a (left) and c (right) directions. The large barium cations exist in cavities formed between (001) sheets of corner-linked TiO_5 and SiO_4 polyhedra.

The $Ba_2TiSi_2O_8$ (BTS), $Ba_2TiGe_2O_8$ (BTG), and $Sr_2TiSi_2O_8$ (STS) family members are structurally well characterised [3-6]. Recent research efforts have been directed towards the study of incommensurate modulations in these structures along the a* and b* directions using quantitative high resolution transmission electron microscopy and rigid unit mode analysis [7-8]. It has been reported that the formation and nature of the incommensurate modulations in fresnoite and structurally similar compounds is highly dependent on the chemical composition. Höche *et al*. commented that the ratio of ionic radii of the atoms on the *A* and *M* sites determines the likelihood of the formation of specific solid solutions in the series [3, 9]. Based on X-ray diffraction data, complete miscibility across the $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ series was suggested, but no detailed results have been published. This paper reports the synthesis and

structural phase transitions of members of the fresnoite family within the compositional range $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ (x = 0.0 – 1.0).

2. Experimental Method

Samples of $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ (x = 0.0 – 1.0 in x = 0.1 steps) were prepared via conventional high temperature solid state reactions. Powders of pre-dried $BaCO_3$ (99.98 %), $SrCO_3$ (99.9 %), TiO_2 (99.9 %), and SiO_2 (99.95 %) were weighed in the stoichiometric ratio 2:1:2 taking into account the Ba/Sr ratio of each specific composition. Samples were ground thoroughly under acetone and heated in multiple stages according to their composition. All samples were heated at 1000 °C, 1100 °C, 1200 °C for 20 hours in powder form with periodic regrinds. Samples in the x = 0.0 - 0.4 range were then heated at 1200 °C and 1250 °C in pellet form with periodic regrinds to avoid the formation of a secondary $SrTiO_3$ phase. Samples in the x = 0.5 - 1.0 range were heated as above with an additional heating step at 1275 °C in pellet form for one week.

Synchrotron X-ray diffraction (XRD) data were collected on the powder diffraction beamline, 10-BM [10], at the Australian Synchrotron using the MYTHEN microstrip detector [11] and a Si (111) monochromator that accepts the beam directly from a bending magnet source. The samples were housed in 0.3 mm diameter capillaries that were aligned concentric to the rotation axis of the three-circle diffractometer. The wavelength was refined to 0.826108 Å using LaB_6 (NIST standard 660a). Data were collected over the angular ranges $1.0 < 2\theta < 81.5^o$ in two frames, shifted by 0.5^o in order to cover the 0.2^o gaps which are inherent in the detector and occur every 5^o. Structure refinements were carried out by the Rietveld method using Jana2006 [12]. The diffraction peaks were described by a pseudo-Voigt function and the background was estimated from 15 terms of Chebyshev polynomials.

3. Results

3.1 Structure of the $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ series

The unit cell parameters a, c and cell volume of the $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ series are plotted in Fig. 2. The linear x-dependence of each parameter across the series indicates that a solid solution is formed across the entire $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ composition range as barium ions are substituted for strontium ions.

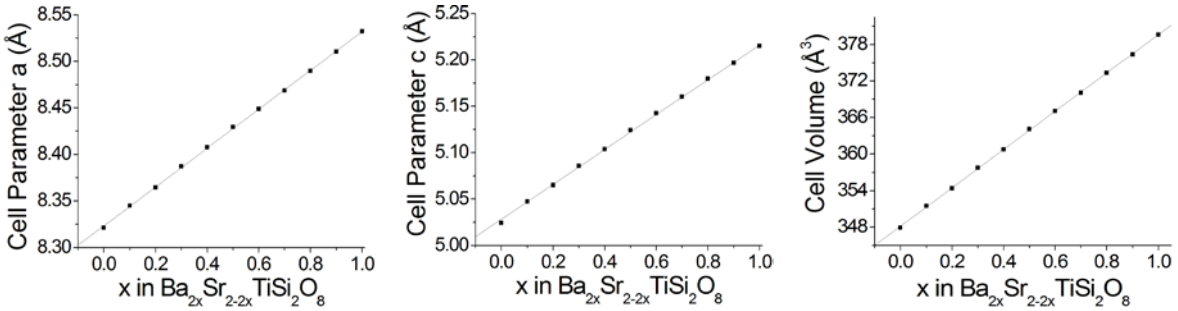

Fig. 2. Unit cell parameters a, c and unit cell volume as a function of composition for the series $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ ($0.0 \leq x \leq 1.0$) at ambient temperature.

3.2. New evidence of phase transition in $Ba_2TiSi_2O_8$

XRD data have been collected on $Ba_2TiSi_2O_8$ between 125 – 1223 K. The unit cell parameters and cell volume for $Ba_2TiSi_2O_8$ are provided in Fig. 3. There exists a change in gradient of the unit cell parameters at ~433 K, which is consistent with a reported transition that coincides with an unusual maximum in the pyroelectric and dielectric coefficients of $Ba_2TiSi_2O_8$ [13]. Further studies explained the disappearance of satellite reflections in

transmission electron micrographs from $Ba_2TiSi_2O_8$ on heating above 433 K, suggesting that the transition involves the removal of the structural modulation on heating. The correlation between this structural transition and anomaly in the physical properties demonstrates the high importance of understanding the subtle structural changes in fresnoite and related compounds for the identification of specific compositions and temperatures for materials with the maximum possible piezoelectric and dielectric response coefficients.

This new evidence of the change in gradient of the unit cell parameters a and c builds on the work of Markgraf *et al*. [13] to provide further structural evidence of the transition involving the removal of the modulation above 433 K.

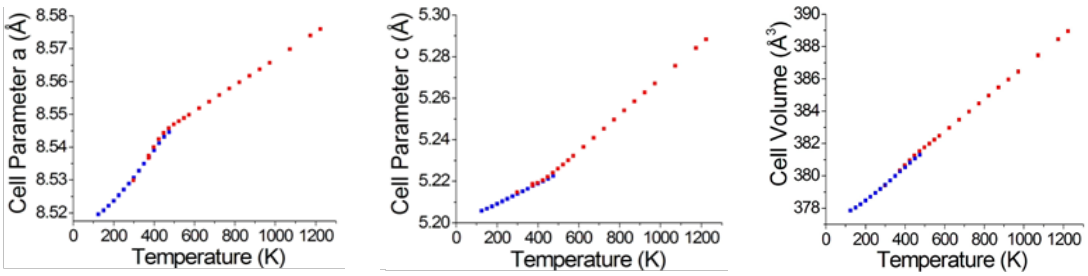

Fig. 3. Unit cell parameters a, c and cell volume as the temperature of $Ba_2TiSi_2O_8$ is increased from 125 K to 1223 K. Blue and red data points indicate data collected using a low-temperature and high temperature attachment, respectively.

Interestingly, the change in the gradient of change of the unit cell parameters a and c at 433 K cancel each other out such that a linear change in the unit cell volume between 125 – 1223 K results.

3.3 Unusual Phase Behaviour of $Sr_2TiSi_2O_8$

Variable temperature synchrotron X-ray diffraction data were collected on $Sr_2TiSi_2O_8$ between 125 – 1273 K. Structural refinements against the room temperature data confirmed that two different $Sr_2TiSi_2O_8$ phases coexist at room temperature as first suggested by electron diffraction [4]. The unit cell parameters for the tetragonal *P*4*bm* and orthorhombic *Cmm*2 $Sr_2TiSi_2O_8$ phases are provided in Fig. 4.

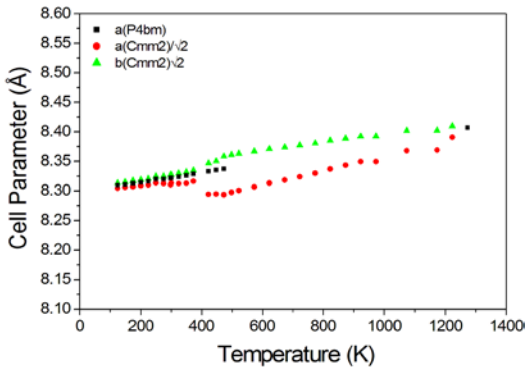

Fig 4: The change in unit cell parameters a and b in the *Cmm*2 phase (red and green, respectively) overlayed with unit cell parameter a for the *P*4*bm* phase (black) between 125 - 1273 K.

Fig. 4 shows a discontinuity in the unit cell parameters on heating at 480 K, corresponding to a structural phase transition of the *P*4*bm* to *Cmm*2 phase. The onset of the phase transition occurs at approximately 400 K and is complete at approximately 480 K. Analysis of the unit cell parameters above 1000 K in Fig. 4 suggests that a second phase transition is also present at approximately 1273 K, where the orthorhombic cell axes a and b converge back to a tetragonal setting. It is uncommon for a structure to undergo a symmetry

lowering transition on heating. However, several examples have been published for a variety of different structure types, including Rochelle salt, a well understood piezoelectric material [14]. Further XRD data at higher temperatures will be collected to confirm the existence of this transition.

Conclusions

X-Ray diffraction data have been collected on members of the fresnoite family of compounds to compile evidence for temperature-dependent structural phase transitions. Firstly, it was established that the $Ba_{2x}Sr_{2-2x}TiSi_2O_8$ range of compositions is a solid solution with a linear trend in unit cell parameters between the two end members. Secondly, a discontinuity in the unit cell parameters of $Ba_2TiSi_2O_8$ provided additional evidence of a structural phase transition that involves the removal of a structural modulation on heating above 433 K. Finally, evidence for a new structural transition in $Sr_2TiSi_2O_8$ was reported where the symmetry unusually changes from *P*4*bm* to *Cmm*2 on heating at approximately 480 K.

Acknowledgments

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