Synchrotron X-ray powder diffraction study on synthetic Sr-Fresnoite.

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The Sr analogue of the mineral fresnoite ($Sr_2TiSi_2O_8$) is of interest as a potential storage medium for radioactive Sr from nuclear waste. No high or low temperature crystal structure information is known on this phase. Therefore high-resolution synchrotron X-ray powder diffraction measurements have been done on a synthetic sample of Sr-fresnoite in the temperature range 87-1223K. This was done as a test experiment using the HRPD beamline P02.1 at PETRA-III, DESY. Synchrotron X-ray wavelengths of 0.2067(3)Å (293K and 573-1223K) and 0.2079(3)Å (87-499K) were used. Powder diffraction data were collected with a counting time of 30s using a PerkinElmer XRD 1621 flat panel image plate detector. CeO_2 was included as an internal standard to calibrate the sample to detector distance. The *P4bm* tetragonal crystal structure of fresnoite ($Ba_2TiSi_2O_8$) was used as a starting model for Sr-fresnoite. Small amounts of $SrTiO_3$ and $SrSiO_3$ were also found as impurities in this sample; therefore four-phase Rietveld refinements were done. The *P4bm* fresnoite structure is retained over the temperature range 87-1223K.

Key words**:** Rietveld refinement, minerals, synchrotron radiation.

I. Introduction.

The Sr analogue of the mineral fresnoite ($Sr_2TiSi_2O_8$) is of interest as a potential storage medium for radioactive Sr from nuclear waste (Park and Navrotsky, 2010). A synthetic sample of Sr-fresnoite was made by melting a stoichiometric mixture of $SrCO_3$, TiO_2 and SiO_2 to form a glass. This glass was then quenched to 293K, reground and then heated for 7 days at 1323K.

We have recently refined (Bell and Henderson, 2013) the 293K crystal structure of Sr-fresnoite from high-resolution synchrotron X-ray powder diffraction data. At room temperature this material is *P4bm* tetragonal with lattice parameters a = 8.3218(2) and c = 5.0292(2)Å, PDF 39-228 (ICDD, 1989). These lattice parameters, in conjunction with the crystal structure of fresnoite ($Ba_2TiSi_2O_8$, Ochi, 2006), were used as a starting model for this 293K Rietveld (Rietveld, 1969) refinement.

No non-ambient temperature crystal structure information is known on this material.

II. Data collection and analysis.

A. Data collection

Synchrotron X-ray powder diffraction data have been collected on this Sr-fresnoite sample using the High-Resolution Powder Diffraction (HRPD) beamline P02.1 at PETRA-III, DESY, in Hamburg. This beamline operates with fixed energy photons of 60 keV ($\lambda \approx 0.207$Å) that exhibit low divergence, small energy bandwidth, and relative high flux. The photon energy of 60 keV enables high angular resolution experiments as well as the characterisation of nanocrystalline and disordered materials through the access of Q ~ 25 $Å^{-1}$.

In order to evaluate the performance of the beamline, two powder diffraction data collection runs were performed. For the first run the sample was loaded into a 0.7mm diameter quartz capillary and mounted on the diffractometer; a synchrotron X-ray wavelength of 0.2067(3)Å was used and data were collected at 293K with a counting time of 30s using a PerkinElmer XRD 1621 flat panel image plate detector. A small amount of CeO_2 (NIST Standard Reference Material 674a) was added to the sample as an internal standard to calibrate the sample-detector distance of approximately 1.4m providing access to 11.7°2θ (minimum d-spacing = 1.01Å). The sample was then heated up to 1223 K with the Cyberstar hot air gas blower attachment. From 573 to 1223K diffraction data were collected in 50K steps as indicated in Figure 1.

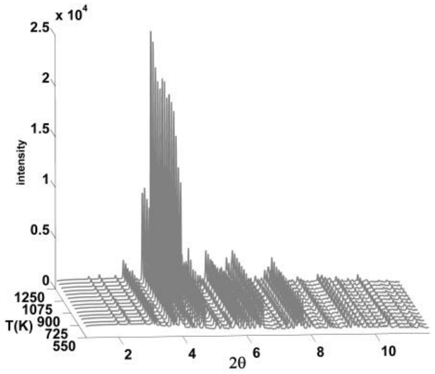

Figure 1. Sr-fresnoite powder diffraction data, 573-1223K, λ = 0.2067(3)Å.

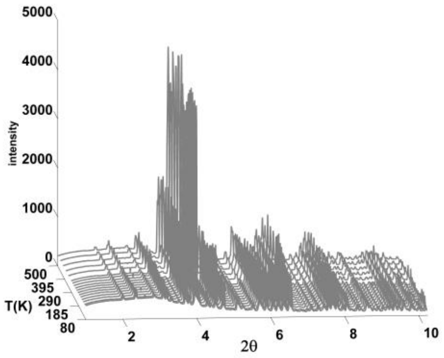

Figure 2. Sr-fresnoite powder diffraction data, 87-499K, λ = 0.2079(3)Å.

For the second data collection run the same sample was loaded into a 0.5mm diameter quartz capillary. Data were collected out to 10.4˚2θ (minimum d-spacing = 1.14Å) with a wavelength of 0.2079(3)Å and with a counting time of 30s. Data were collected over the temperature range 87-499K with a LN3 (Cryo Industries of America) cryo-streamer used to control the sample temperature. The temperature steps were approximately 20K below 300K and 40K above 300K. Figure 2 shows a plot of these powder diffraction data 87-499K.

B. Data analysis

Most of the Bragg reflections in the 293K powder data set could be indexed with the *P4bm* tetragonal lattice parameters for $Sr_2TiSi_2O_8$ (Bell and Henderson, 2013). However, Bragg reflections could also identified for the CeO_2 (Goldschmidt and Thomassen, 1923) internal standard and two other impurity phases, $SrTiO_3$ (Mitchell *et al*, 2000) and $SrSiO_3$ (Machida *et al*, 1982).

A four-phase Rietveld refinement was done with FULLPROF (Rodriguez-Carvajal, 2001) using the 293K data set. Full structural parameters were only refined for the Sr-fresnoite phase, the closest Ti-O and Si-O distances were soft constrained to those for $Ba_2TiSi_2O_8$. For the other three phases only lattice parameters (no atomic co-ordinates) were refined. 81(1)wt.% of Sr-fresnoite was present in this sample with 4.6(3)wt.% CeO_2, 7.0(6)wt.% $SrTiO_3$ and 7.4(8)wt.% of $SrSiO_3$ present as impurities. The results of this 293K refinement were used as a starting model for the refinements using higher and lower temperature datasets. Figure 3 shows a Rietveld difference plot from the 293K data.

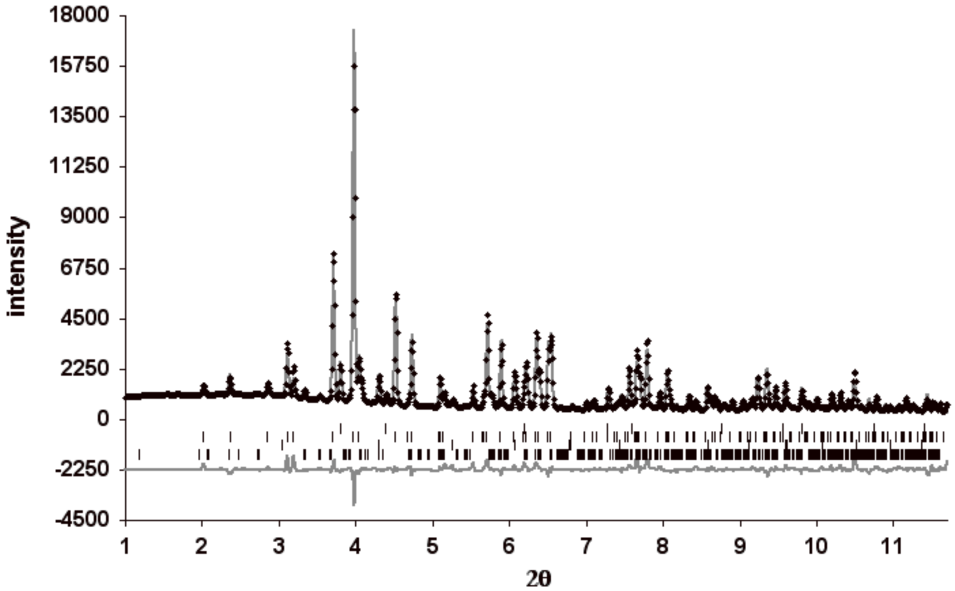

Figure 3. Rietveld difference plot using 293K powder diffraction data. Black dots are observed powder diffraction data points, upper grey line is the calculated powder diffraction profile. Lower grey line is the observed-calculated difference curve. Bragg reflection positions for the 4 phases present are indicated by black vertical lines. The uppermost line is for CeO_2, the next lowest is for Sr-fresnoite, the next lowest is for $SrTiO_3$ and the lowest is for $SrSiO_3$.

III. Discussion.

The 293K crystal structure of Sr-fresnoite consists of a layer structure with corner-sharing TiO_5 and SiO_4 polyhedra sandwiched between distorted SrO_6 octahedra. Figure 4 shows VESTA (Momma and Izumi, 2008) plots of this crystal structure in the *ac* and *ab* planes. This crystal structure is isostructural with fresnoite (Ochi, 2006) and mixed Ba/Ca fresnoites ($Ca_xBa_{2-x}TiSi_2O_8$, $0.0 \leq x \leq 1.0$) (Barbar and Roy, 2012)

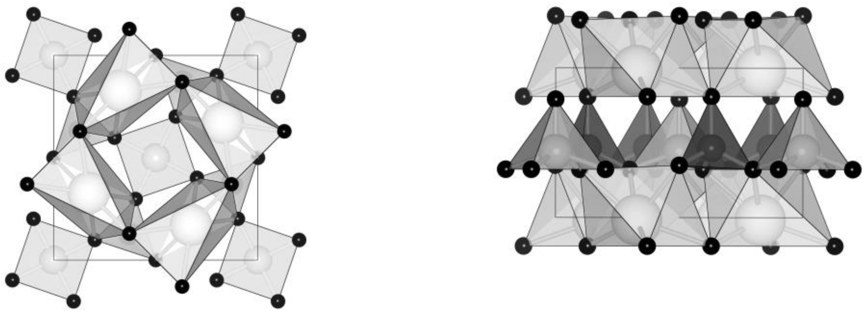

Figure 4. Plots of the Sr-fresnoite crystal structure in the ab plane (left) and bc plane (right). Black spheres represent O, light grey represents Ti and TiO_5 polyhedra, dark grey represents Si and SiO_4 polyhedra and white represents Sr and SrO_6 octahedra. Outlines of the unit cell are given as black lines.

Rietveld refinements showed that the 293K starting model could be used successfully for refinements using all powder diffraction datasets collected over the temperature range 87-1223K. No phase transition(s) could be observed in any of the 4 phases present in this sample. Apart from thermal expansion of the unit cell with increasing temperature, there were no significant changes in the Sr-fresnoite crystal structure over this temperature range. Figure 5 shows how the lattice parameters for Sr-fresnoite vary with temperature.

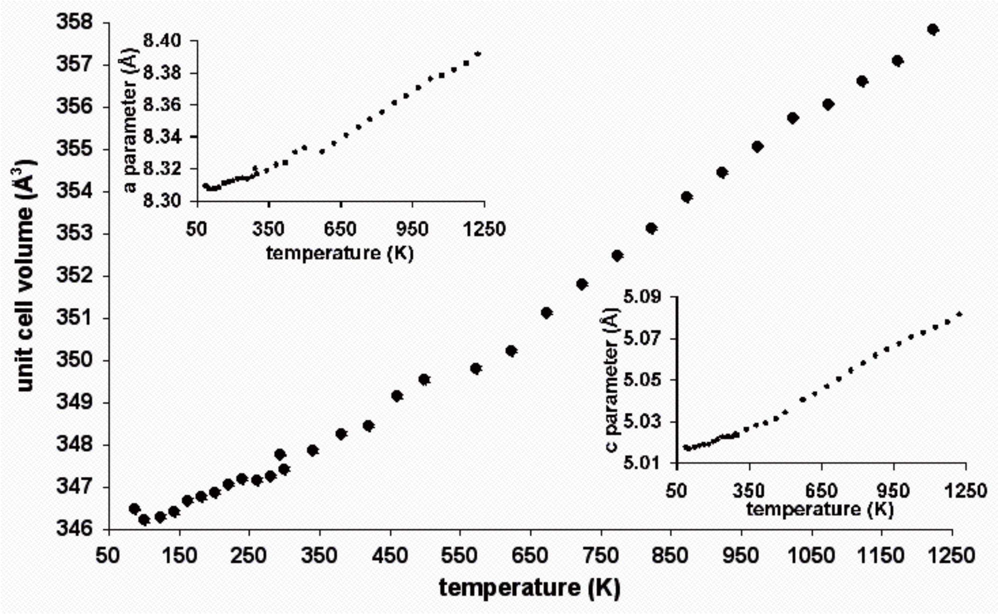

Figure 5. Plots of the variation of Sr-fresnoite lattice parameters over the temperature range 87-1223K.

Thermal expansion coefficients (TEC) have been determined, from the variation of lattice parameters with temperature, for all 4 phases present in this sample. Table I shows the TEC for each phase. Unit cell volume TEC are given for the three minor phases (CeO_2, $SrTiO_3$ and $SrSiO_3$). For Sr-fresnoite TEC are given for the tetragonal *a*- and *c*-axes and for the unit cell volume. The Sr-fresnoite unit cell expands more along the *c*-axis than along the *a*-axis with increasing temperature.

Table I. thermal expansion coefficients, 87-1223K.

Phase	thermal expansion coefficient (K^{-1})
CeO_2 – cell volume	3.6(1) x 10^{-5}
Sr-fresnoite – a axis	0.90(2) x 10^{-5}
Sr-fresnoite – c axis	1.19(2) x 10^{-5}
Sr-fresnoite – cell volume	3.01(6) x 10^{-5}
$SrTiO_3$ – cell volume	2.88(6) x 10^{-5}
$SrSiO_3$ – cell volume	3.16(6) x 10^{-5}

IV. CONCLUSION.

The new PETRA-III P02.1 HRPD beamline has been used to collect powder diffraction data on a sample of Sr-fresnoite ($Sr_2TiSi_2O_8$) over the temperature range 87-1223K. The data collection time for each powder data set was only 30s. However, these data were good enough for high quality four-phase Rietveld refinements at each temperature. Full structural parameters could be refined for Sr-fresnoite, the *P4bm* 293K fresnoite structure is retained over the temperature range 87-1223K. Lattice parameters could also be refined for 3 impurity phases and thermal expansion coefficients determined for all 4 phases.

This experiment describes the current performance of beamline P02.1 and that it may be used to collect high quality powder diffraction data with short data collection times.

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