Sr–fresnoite determined from synchrotron X-ray powder diffraction data

BELL, Anthony and HENDERSON, C Michael B

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Sr–fresnoite determined from synchrotron X-ray powder diffraction data

Anthony M. T. Bell* and C. Michael B. Hendersonb

*HASYLAB/DESY, Notkestrasse 85, 22607 Hamburg, Germany, and bSchool of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 9PL, England

Correspondence e-mail: tony.bell@desy.de

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Key indicators: powder synchrotron study; T = 293 K; mean σ(Si–O) = 0.020 Å; R factor = 0.052; wR factor = 0.073; data-to-parameter ratio = 1.8.

The fresnoite-type compound Sr₂TiO(Si₂O₇), distrontium oxidotitanium disilicate, has been prepared by high-temperature solid-state synthesis. The results of a Rietveld refinement study, based on high-resolution synchrotron X-ray powder diffraction data, show that the title compound crystallizes in the space group P4bnm and adopts the structure of other fresnoite-type mineral samples with general formula A₂TiO(Si₂O₇) (A = alkaline earth metal cation). The structure consists of titanosilicate layers composed of corner-sharing SiO₄ tetrahedra (forming Si₂O₇ disilicate units) and TiO₅ square-based pyramids. These layers extend parallel to the ab plane and are stacked along the c axis. Layers of distorted SrO₆ octahedra lie between the titanosilicate layers. The Sr²⁺ ion, the SiO₄ tetrahedron and the bridging O atom of the disilicate unit are located on mirror planes whereas the TiO₅ square-based pyramid is located on a fourfold rotation axis.

Related literature

For the crystal chemistry of fresnoites, see: Barbar & Roy (2012); Höche et al. (2002); ICDD (1989). For properties of Sr–fresnoites, see: Park & Navrotsky (2010). Atomic coordinates as starting parameters for the Rietveld refinement (Rietveld, 1969) of the present phases were taken from Ochi (2006); Goldschmidt & Thomassen (1923); Machida et al. (1982); Mitchell et al. (2000). For related strontium titanosilicates, see: Miyajima et al. (2002). For synchrotron data analysis, see: Miyajima (1997); Hammersley et al. (1996).

Exp

Crystal data

Sr₂TiSi₂O₈
Mᵣ = 407.31
Tetragonal, P4bm
a = 8.3200 (3) Å
c = 5.0239 (2) Å
V = 347.77 (2) Å³
Z = 2
Synchrotron radiation,
λ = 0.207549 Å
µ = 0.43 mm⁻¹
T = 293 K
Cylinder, 20 × 0.7 mm

Data collection

In-house design diffractometer
Specimen mounting: capillary
Data collection mode: transmission
Scan method: continuous
2θmin = 0.053°, 2θmax = 11.915°,
2θstep = 0.008°

Refinement

R = 0.052
Rwp = 0.073
Rexp = 0.031
Rfactor = 0.052

Data collection: local software; cell refinement: local software; program(s) used to solve structure: program(s) used to refine structure: FULLPROF (Rodriguez-Carvajal, 2001); molecular graphics: VESTA (Momma & Izumi, 2008); software used to prepare material for publication: publCIF (Westrip, 2010).

Thanks to Dr Hans-Peter Liermann for help with data collection on P02.1.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2699).

References


supplementary materials


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Comment
The title compound, Sr₂TiO(Si₂O₇), is the Sr analogue of the mineral fresnoite, Ba₂TiO(Si₂O₇). It is of interest as a potential storage medium for radioactive strontium from nuclear waste (Park & Navrotsky, 2010). An incommensurately modulated structure of Sr-fresnoite has been determined from room-temperature single crystal data and refined in the 5D superspace group P4bm (-α, α, 1/2; α, α, 1/2) with α = 0.3 and with lattice parameters a = 8.312 (2) Å and c = 10.07 (1) Å (Höche et al., 2002). However, ICDD PDF card 39–228 (ICDD, 1989) states that at room temperature this material is tetragonal with space group P4bm and lattice parameters a = 8.3218 (2) Å and c = 5.0292 (2) Å. The crystal structure of the mineral fresnoite has been described in the same space group with lattice parameters a = 8.5159 (6) Å and c = 5.2184 (4) Å. Solid solutions with composition Ba₂₋ₓCaₓTiO(Si₂O₇) (x = 0.0, 0.2, 0.4, 0.8, 1.0; Barbar & Roy, 2012) adopt the same structure. The ordered crystal structure of Sr₂TiO(Si₂O₇) in space group P4bm and a halved c parameter in comparison with the single crystal study is reported in the present communication.

The mean Si—O and Ti—O distances in the titanosilicate layer of Sr-fresnoite are respectively 1.64 Å and 1.92 Å. The corresponding Si—O and Ti—O distances are 1.64 Å and 1.93 Å in fresnoite. The respective distances in the structures of the solid solutions Ba₂₋ₓCaₓTiO(Si₂O₇) are: 1.59 Å and 2.01 Å (x = 0.2); 1.65 Å and 2.03 Å (x = 0.4); 1.66 Å and 2.02 Å (x = 0.8); 1.71 Å and 1.95 Å (x = 1.0) (Barbar & Roy, 2012). Due to the distortion of the crystal structures by the partial replacement of Ba by Ca these distances are less comparable with those in Sr-fresnoite.

The mean Sr—O distance in the title structure is 2.62 Å, which is comparable with the mean Sr—O distance of 2.61 Å in Sr₃Ti₅O₁₄(Si₂O₇)₂ (Miyajima et al., 2002).

The O—Si—O angles deviate significantly from the ideal tetrahedral angle of 109.5°, indicating a strong distortion due to the presence of the TiO₅ polyhedra in the titanosilicate layer.

Fig. 1 shows the Rietveld difference plot for the present refinement. The crystal structure of Sr₂TiO(Si₂O₇) is displayed in Fig. 2 and consists of layers of corner-sharing SiO₄ and TiO₅ polyhedra extending parallel to the ab plane. These layers are separated along the c axis by layers of distorted SrO₆ octahedra.

Experimental
A synthetic sample of Sr-fresnoite was made by melting a stoichiometric mixture of SrCO₃, TiO₂ and SiO₂ to form a glass. This glass was then quenched to 293 K, reground and then heated for 7 days at 1323 K. A small amount of CeO₂ (NIST SRM 674a) standard was added to this powdered sample to act as an internal standard.

Refinement
The powdered sample was loaded into a 0.7 mm diameter quartz capillary, prior to synchrotron X-ray powder diffraction data collection using the P02.1 high resolution powder diffraction beamline at the PETRA-III synchrotron. The beam on the sample was 0.8 mm wide and 1.27 mm high. Powder diffraction data were collected using a PerkinElmer XRD 1621
A flat panel image plate detector, which was approximately 1.4 m from the sample. One powder diffraction dataset was collected at 293 K out to approx. 11.9°/2θ, the data collection time was 30 s. Powder diffraction data were converted to a list of 2θ and intensity using FIT2D (Hammersley et al., 1996, Hammersley, 1997). Powder diffraction data in the range 1–11.7°/2θ were used for the Rietveld refinement. Data below 1°/2θ were excluded due to scatter from the beam stop and as there were no Bragg reflections in this region. Data above 11.7°/2θ were excluded as this corresponded to the edge of the image plate detector where the Bragg peaks were weaker.

The main Bragg reflections of the powder diffraction pattern could be indexed in space group P4bm with similar lattice parameters to those of PDF card 39–228 (ICDD, 1989). The unit cell of the incommensurately modulated structure (Höche et al., 2002) corresponds to a doubled c axis compared to that given on the PDF card. The doubled c axis does not match with some of the low-angle Bragg reflections for the Sr₃TiO(Si₂O₇) sample used in the present study, therefore this incommensurate structure was not used for Rietveld refinement. Bragg reflections for three impurity phases could also be identified in the powder diffraction data. SrTiO₃ and SrSiO₃ were formed as by-products during preparation.

Initial lattice parameters for the three Sr-containing phases were refined using local software. The CeO₂ (NIST SRM 674a) standard was used to calibrate the sample to detector distance. The CeO₂ lattice parameter was fixed at 5.4111 Å so as to calibrate the wavelength as 0.207549 Å.

The P4bm crystal structure of the mineral fresnoite (Ba₂TiO(Si₂O₇); Ochi, 2006) was used as a starting model for the Rietveld refinement (Rietveld, 1969) of the structure of Sr₃TiO(Si₂O₇). The crystal structures of SrSiO₃ (Machida et al., 1982), SrTiO₃ (Mitchell et al., 2000) and CeO₂ (Goldschmidt & Thomassen, 1923) were used for the impurity phases in the refinement. Isotropic atomic displacement parameters were used for all phases. For the Sr₃TiO(Si₂O₇) phase the Si—O and Ti—O distances in the SiO₄ and TiO₅ polyhedra were soft-constrained to those for Ba₂TiO(Si₂O₇) (Ochi, 2006). The Uiso factors for all O sites were constrained to be the same. 81 (1) wt.% of Sr-fresnoite was present in this sample with 4.6 (3) wt.% CeO₂, 7.0 (6) wt.% SrTiO₃ and 7.4 (8) wt.% of SrSiO₃ present as impurities.

**Computing details**

Data collection: local software; cell refinement: local software; data reduction: local software; program(s) used to solve structure: coordinates taken from a related compound; program(s) used to refine structure: FULLPROF (Rodriguez-Carvajal, 2001); molecular graphics: VESTA (Momma & Izumi, 2008); software used to prepare material for publication: publCIF (Westrip, 2010).
Figure 1
Rietveld difference plot for the multi-phase refinement of Sr$_2$TiO(Si$_2$O$_7$), CeO$_2$, SrTiO$_3$ and SrSiO$_3$. The blue crosses, and red and black lines show respectively the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by triangles for the four phases.
Figure 2
The crystal structure of Sr₂TiO(Si₂O₇). Purple polyhedra show TiO₅ units, blue polyhedra show SiO₄ units, green polyhedra show distorted SrO₆ units. Green spheres represent Sr atoms, pink spheres represent Ti atoms, blue spheres represent Si atoms and red spheres represent O atoms.

Distrontium oxidotitanium disilicate

Crystal data
Sr₂TiSi₂O₈
Mₒ = 407.31
Tetragonal, P4 bm
Hall symbol: P 4 -2ab
a = 8.3200 (3) Å
c = 5.0239 (2) Å
V = 347.77 (2) Å³
Z = 2
Dₓ = 3.890 (1) Mg m⁻³

Synchrotron radiation, λ = 0.207549 Å
µ = 0.43 mm⁻¹
T = 293 K
Particle morphology: powder
white
cylinder, 20 × 0.7 mm
Specimen preparation: Prepared at 1323 K and 100 kPa

Data collection
In-house design
diffractometer
Radiation source: Synchrotron
Laue DCM diamond(111) & Si(111)
monochromator
Specimen mounting: capillary
Data collection mode: transmission
Scan method: continuous
2θ₁₀₀ = 0.053°, 2θₓₓₓ = 11.915°, 2θₛₑₚ = 0.008°
supplementary materials

Refinement

\[ R_p = 0.052 \]
\[ R_{wp} = 0.073 \]
\[ R_{exp} = 0.031 \]
\[ R_{Bragg} = 0.093 \]
\[ \chi^2 = 31.068 \]
1476 data points

Excluded region(s): 0-1 and 11.7-12.0 degrees

Profile function: T-C-H Pseudo-Voigt function

71 parameters

5 restraints

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
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<td>0.8282 (2)</td>
<td>0.017 (2)</td>
<td>0.0070 (8)*</td>
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<tr>
<td>Ti1</td>
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<td>0.00000</td>
<td>0.558 (3)</td>
<td>0.007 (2)*</td>
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<tr>
<td>Si1</td>
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<td>0.6305 (6)</td>
<td>0.535 (3)</td>
<td>0.019 (2)*</td>
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<tr>
<td>O1</td>
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<td>0.50000</td>
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<td>0.017 (3)*</td>
</tr>
<tr>
<td>O2</td>
<td>0.1292 (15)</td>
<td>0.6292 (15)</td>
<td>0.191 (3)</td>
<td>0.017 (3)*</td>
</tr>
<tr>
<td>O3</td>
<td>0.2985 (12)</td>
<td>0.5984 (15)</td>
<td>0.678 (3)</td>
<td>0.017 (3)*</td>
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<tr>
<td>O4</td>
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<td>0.00000</td>
<td>0.209 (3)</td>
<td>0.017 (3)*</td>
</tr>
</tbody>
</table>

Geometric parameters (Å, º)

Sr1—O1\(^{-}\) 2.733 (18)  
Sr1—O2 2.499 (13)  
Sr1—O2\(^{-}\) 2.676 (13)  
Sr1—O2\(^{ii}\) 2.676 (13)  
Sr1—O3\(^{iv}\) 2.572 (14)  
Sr1—O3\(^{v}\) 2.572 (14)  
Ti1—O3\(^{vi}\) 1.961 (12)  
Ti1—O3\(^{vii}\) 1.961 (13)  

O3\(^{ii}\)—Ti1\(^{vi}\)—O3\(^{vii}\) 84.6 (9)  
O3\(^{iii}\)—Ti1\(^{vi}\)—O3\(^{viv}\) 144.2 (10)  
O3\(^{ivv}\)—Ti1\(^{vi}\)—O3\(^{xv}\) 84.6 (8)  
O3\(^{xvi}\)—Ti1\(^{vi}\)—O4\(^{ui}\) 107.9 (12)  
O3\(^{xv}\)—Ti1\(^{vi}\)—O3\(^{x}\) 84.6 (8)  
O3\(^{xvi}\)—Ti1\(^{vi}\)—O3\(^{x}\) 144.2 (11)  
O3\(^{xvii}\)—Ti1\(^{vi}\)—O4\(^{x}\) 107.9 (12)  
O3\(^{xvi}\)—Ti1\(^{vi}\)—O3\(^{x}\) 84.6 (9)  

Symmetry codes: (i) −\(y\)+1, \(x\)+1, \(z\); (ii) −\(y\)+1, \(x\)+1, \(z\); (iii) \(y\), −\(x\)+1, \(z\); (iv) \(x\), \(y\), \(z\); (v) \(y\)+1/2, \(x\)+1/2, \(z\); (vi) −\(x\)+1/2, \(y\)+1/2, \(z\); (vii) −\(y\)+1/2, \(x\)+1/2, \(z\); (viii) \(x\)+1/2, −\(y\)+1/2, \(z\); (ix) −\(y\)+1/2, −\(x\)+1/2, \(z\); (x) \(y\)+1/2, \(x\)+1/2, \(z\); (xi) −\(x\)+1/2, \(y\)+1/2, \(z\); (xii) \(x\), \(y\), \(z\); (xiii) −\(y\)+1/2, −\(x\)+3/2, \(z\); (xiv) \(x\)+1/2, −\(y\)+3/2, \(z\).