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REFINEMENT OF THE CRYSTAL STRUCTURE OF BaSi₄O₉ IN THE BENITOITE FORM†

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Abstract—The crystal structure of BaSi₄O₉ with the benitoite structure, synthesized at 4 GPa and 1000°C, has been refined using the method of Rietveld. This framework structure contains mixed four- and six-fold coordination for silicon and consists of double layers of three-membered tetrahedral rings that are cross linked by the octahedra. Barium atoms are situated in the channels of this framework. The relationship between this phase and another polytype with the higher density barium tetragermanate structure is not known; however, we favor a mechanism in which the transformation is induced by grinding at room pressure and temperature.

Keywords: A. oxides, C. X-ray diffraction, D. crystal structure.

1. INTRODUCTION

The development of the techniques of determination and refinement of crystal structures from accurate powder patterns is one of the exciting recent advances in solid-state physics and chemistry. It is now possible to study those materials that do not form large single crystals, or those systems in which the conditions and/or time needed to grow large crystals change the nature of the product. High-resolution powder diffractometers on synchrotron sources are an important component of such developments. One of the finest examples of such instruments, located at Beamline X7A at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory has been built and operated by Dr D. E. Cox, who is being honored in this special issue. We present an example where this instrument was used to analyse a portion of the products of a single synthesis experiment in which two polymorphs were generated. One of these phases was present as relatively large single crystals, the other as a powder.

The study of crystal chemistry of silicon in six-fold coordination is important to understanding high-pressure mineralogy [1]. Although most such studies involve chemical systems that approximate the deep Earth, it is frequently possible to learn new principles

from compositions that do not occur naturally. In the present study, samples obtained during an investigation of moderately low-pressure, mixed-coordination compounds [2] became available for high-resolution powder X-ray diffraction studies.

2. EXPERIMENTAL PROCEDURES

The sample of BaSi₄O₉ was synthesized at Novosibirsk from a near stoichiometric mixture of BaCO₃ + 4SiO₂. Reagent grade BaCO₃ was dried in a vacuum at 300°C for 6 h and mixed with amorphous SiO₂. A small excess (≈ 5 wt %) of the latter reagent was used to prevent the formation of a complicated mixture of Ba-Si phases along with BaSi₄O₉. Synthesis was performed in a split-sphere, multi-anvil, high-pressure device. The prepressed sample was placed into a cylindrical graphite heater without a capsule. Pressure was raised to 4 GPa, then the sample was heated to 1000°C. These pressure-temperature conditions were maintained for 10 h, and the run was quenched in temperature by turning the heater power supply off. Finally the pressure was released.

The cylindrical run product, which had a diameter of 5 mm and a height of 6 mm, was divided into two sub-equal cylinders. One of these was split into two half cylinders, one of which was ground in a tungsten carbide mortar. Preliminary powder X-ray diffraction studies for phase identification were conducted in Novosibirsk, then the samples were transferred to Washington. The powdered

†Contributed in honor of D. E. Cox, on the occasion of his retirement as Editor.

¶A U.S. National Science Foundation Science and Technology Center.

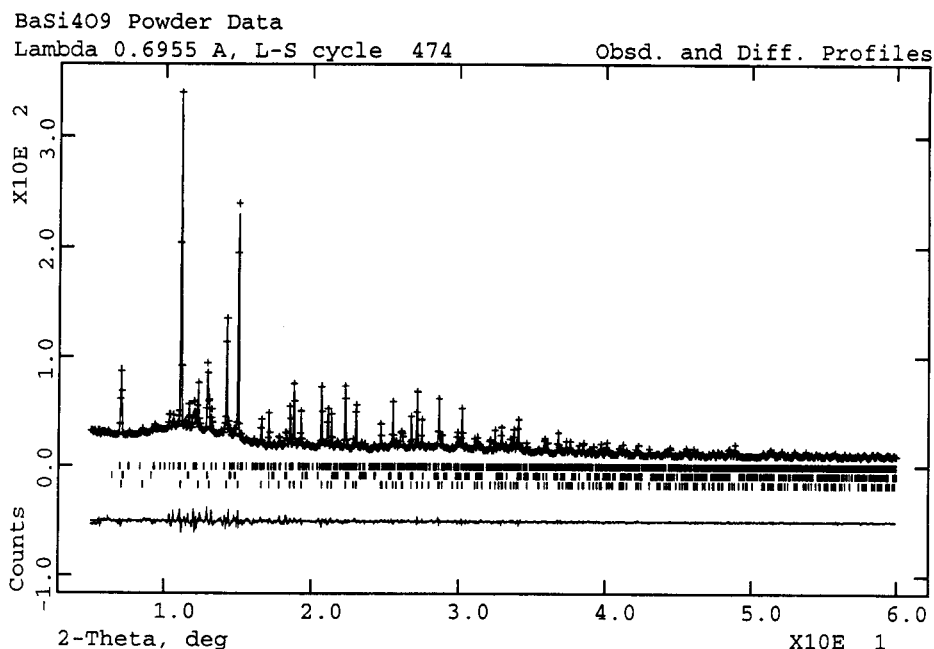


Fig. 1. Fitted pattern for BaSi₄O₉. The observed counts are indicated by crosses and the calculated pattern by a smooth line. The bottom trace indicates the difference between observed and calculated values. From bottom up, the short vertical ticks between the difference plot and the data show the positions of reflections in the benitoite form of BaSi₄O₉, coesite, and the unknown contaminant, respectively.

portion was used in the present study. The remaining half cylinder portion, which will be described later, did not undergo any further processing.

High-resolution powder diffraction studies were conducted at the NSLS beamline X7A. A sample of the powdered material was formed into a ball of roughly 0.15 mm diameter, using an organic polymer as a binder. The sample, mounted on a glass fiber, was irradiated with radiation of 0.6955 Å obtained from a triangular, asymmetrically-cut Si(220) crystal bent into a cylindrical shape [3, 4]. This arrangement will focus approximately 1.25 mrad (20 mm at 16 m) of horizontal fan from the bending magnet into an 0.2 mm spot. The beam is not focussed in the vertical direction.

Diffracted X-rays were observed with a linear position sensitive detector (PSD), which is a multiwire proportional counter [5–7], operated with a 90% Kr–10% CO₂ gas mixture at 4 bar. Pulse-height discrimination of the anode signal was used to accept only those events arising from escape peaks—a procedure that gives the highest detector resolution. The detector was calibrated from the diffractogram of CeO₂ ($a = 5.4113$ Å). Although detectors of this type have linear resolution below 0.1 mm, which should translate into an angular resolution of 0.01° at a sample to detector distance of 450 mm, peak widths in the present experiment are broadened by the convergent geometry and the $\Delta\lambda/\lambda$ characteristics of the monochromator. Actual

resolution of the system, as determined from the diffractogram of LaB₆ (NIST SRM660), was 0.05° full-width at half maximum. The diffraction pattern of the barium silicate was collected with 0.5° step-scans of the detector with the center angle ranging from 7 to 60° 2θ . The central 4° segment of each PSD frame was corrected for dead time and beam decay, and combined into a single diffractogram with equal step sizes [8] for input into a standard Rietveld refinement program such as GSAS [9].

3. STRUCTURE REFINEMENT

Preliminary X-ray diffraction studies in Novosibirsk had suggested that this sample consisted of BaSi₄O₉ with the benitoite lattice [2, 10], along with minor amounts of coesite. Confirmation of this result was obtained by fitting the profiles of individual reflections, and preliminary refinement of the unit-cell constants ($a = 6.495$ Å, $c = 9.346$ Å) with program NBS*AIDS83 [11].

Although this form of BaSi₄O₉ was assumed to have the benitoite structure, based on both lattice parameters and intensities, it was decided to solve the structure independently from the powder data. Program GSAS [9] was used to extract intensities using a whole-pattern fitting technique [12]. Unit-cell and profile parameters were refined at this stage. The resulting data were used to confirm the space group

Table 1. Refined structural parameters for the benitoite form of BaSi₄O₉†

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Ba	2/3	1/3	0	1.14(2)‡
Si 1	1/3	2/3	0	0.59(9)
Si 2	0.0877(5)	0.3008(7)	1/4	0.70(7)
O 1	0.9213(11)	0.7377(11)	1/4	0.47(9)§
O 2	0.1041(8)	0.4387(7)	0.1032(6)	0.47(9)§

†Space group $P\bar{6}c2$, $a = 6.4953(1)$ Å, $c = 9.3465(1)$ Å, $V = 341.50(1)$ Å³, $\rho_x = 3.829$ g/cm³.

‡Ba refined with uniaxial temperature factor: $B_{||} = 1.22(4)$ Å² and $B_{\perp} = 1.10(3)$ Å².

§Isotropic temperature factors for O1 and O2 are constrained to be equal.

as $P\bar{6}c2$ and to determine the Ba position from a Patterson synthesis. The positions of all Si and O atoms could then be determined from successive difference Fourier maps. As expected, the material is isostructural with benitoite, pabstite and bazirite [10].

Besides barium silicate, the powder pattern shows

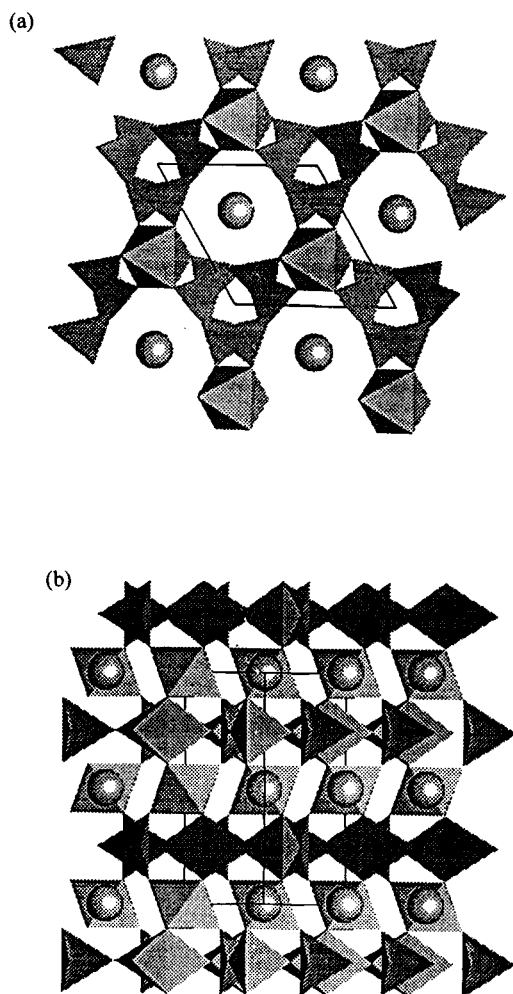


Fig. 2. The structure of the benitoite form of BaSi₄O₉, viewed along (a) [001] and (b) [110]. Barium ions are represented by spheres, silicon occurs at the centers of tetrahedra and octahedra, and oxygen is at the vertices of the polyhedra.

Table 2. Bond distances for the benitoite form of BaSi₄O₉

Bond	Distance (Å)
Ba —O1 [6x]	3.279(4)
Ba —O2 [6x]	2.743(4)
Si 1 —O2 [6x]	1.770(5)
Si 2 —O1	1.626(7)
Si 2 —O1	1.651(7)
Si 2 —O2 [2x]	1.613(5)

diffraction peaks belonging to coesite, which arises from the excess silica in the charge. Lattice constants and profile parameters were adjusted for this phase; however, the structural parameters were fixed at the published values [13].

The diffraction pattern also contains intensity arising from one or more additional phases, which do not match the patterns in the powder diffraction database [14] for known phases in the Ba–Si–O system, BaSi₄O₉ in barium germanate form [15, 16], or from tungsten carbide, the most likely contaminant. Attempts to determine a unit cell for these extra peaks using program TREOR90 [17] have not been satisfactory. One triclinic cell, which explains most of the extra lines, has been included in the refinement with integrated intensity extraction [12] to decrease the effects of interference with the barium silicate phase. Work is continuing on the problem of identification of the minor phase or phases in the pattern.

A total of 41 parameters were refined in this study, including 12 lattice constants among the three phases, 10 background coefficients using four radial distribution functions to account for the amorphous scattering from the glass fiber and the binder, an absorption correction coefficient for Debye–Scherrer geometry, a diffractometer zero point, scale factors for the two known structures and profile parameters for all three phases. Each of these has a pseudo-Voigt peak shape [18] with the Gaussian component fixed to that of the instrument as determined on LaB₆, and the Lorentzian component corresponding to Scherrer broadening is refined. An asymmetry coefficient [19] is also included for each phase. The statistics for the fit are as follows: $R_{wp} = 0.052$, $R_p = 0.039$, expected $R_{wp} = 0.019$, reduced $\chi^2 = 7.5$, and R_{Bragg} for BaSi₄O₉ = 0.03. The observed, calculated and residual patterns are shown in Fig. 1.

The refined structural parameters for the benitoite form of BaSi₄O₉ are listed in Table 1. The structure (Fig. 2) consists of three-membered rings of SiO₄ tetrahedra linked to SiO₆ octahedra such that each tetrahedron shares corners with two tetrahedra and two octahedra. Each octahedron shares corners with six tetrahedra. In addition, the oxygens at the vertices of the octahedra are bonded to the Ba ion

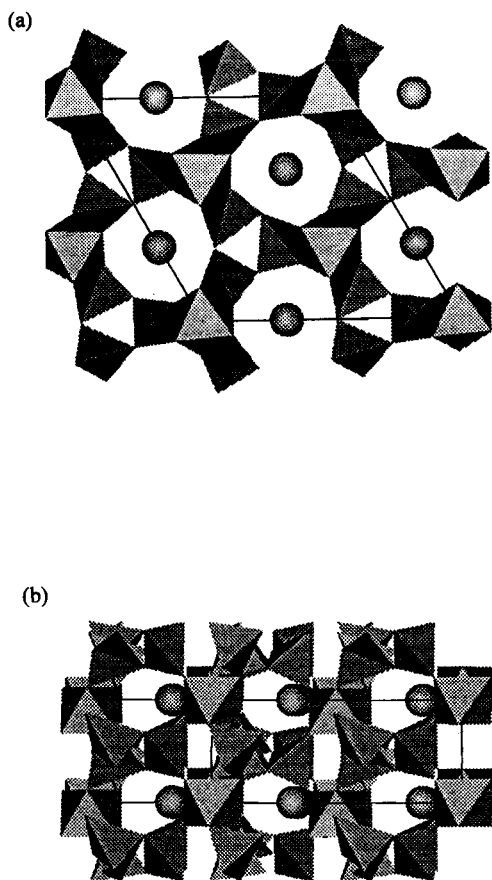


Fig. 3. The structure of the barium germanate form of BaSi_4O_9 , viewed along (a) [001] and (b) [110], using the previous conventions.

situated in the channels parallel to the c axis. Bond distances for this phase are shown in Table 2.

4. DISCUSSION

This study has shown that it is possible to obtain a high-quality refinement of the crystal structure of a phase even though the sample contains an impurity of unknown composition and structure, as long as the resolution of the diffractometer is relatively high, and the shapes of the diffraction peaks are well defined.

One unusual feature of this study is the presence of two different polymorphs of BaSi_4O_9 . The portion of the run product that had been crushed, but not ground, contains 50–60 μm crystals isostructural with BaGe_4O_9 [14, 15, 20], which is shown in Fig. 3. This form crystallizes with space group $P321$ and an a -axis length approximately $\sqrt{2}$ times that of the benitoite form and a c -axis length shorter by a factor of 2. The barium tetragermanate form is roughly 4% more dense. It is possible that the two phases are each stable in a different portion of the run products because of the temperature differential across the

sample assembly of the high-pressure apparatus. Alternatively, one of them could have formed metastably and was in the process of transforming to the stable form when the experiment terminated. We feel, however, that both of these explanations are unlikely because no trace of the barium tetragermanate form was found in the powdered sample of the benitoite form. A more likely explanation is that the grinding process transformed the sample from the denser barium tetragermanate form to the benitoite form. A mechanism for such a transformation can be seen by comparing Figs 2(a) and 3(a). The two structures are equivalent if there is a rotation of silicon octahedra by 30° around the c -axis and a counter rotation of half of the connections between the octahedra and tetrahedra. The shearing action involved in grinding would facilitate such a transformation.

Whatever the structural relationship between the two polymorphs, it must be emphasized that both are high-pressure phases because each contains silicon in six-fold coordination [1]. Many systems have back transformation of high-pressure structures to a less dense crystal, or an amorphous phase, upon grinding and/or heating at low pressure. This study is the first known case of an induced transformation between high-pressure forms taking place at low pressure.

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REFERENCES

1. Finger L. W. and Hazen R. M., *Acta Crystallogr.* **B47**, 561 (1991).
2. Fursenko B. A., *Acta Crystallogr.* **A40**, C248 (abstract) (1984).
3. Lemonnier M., Fourme R., Rousseaux F. and Kahn R., *Nucl. Instrum. Methods* **152**, 173 (1978).
4. Jephcoat A. P., Finger L. W. and Cox D. E., *High Press. Res.* **8**, 667 (1992).
5. Boie R. A., Fischer J., Inagaki Y., Merritt F. C., Radeka V., Rogers L. C. and Xi D. M., *Nucl. Instrum. Methods* **201**, 93 (1982).
6. Fischer J., Radeka V. and Smith G. C., *IEEE Trans. Nucl. Sci.* **NS-33**, 136 (1986).
7. Smith G. C., *Synch. Rad. News* **4**, 24 (1991).
8. Toby B. C., Personal communication to L. W. Finger (1993).
9. Larson A. C. and Von Dreele R. B., *GSAS: General Structure Analysis System*. Unpublished Computer Program Manual, Los Alamos National Laboratory (1994).
10. Hawthorne F. C., *N. Jb. Miner. Mh.* **1987**, 16 (1987).
11. Mighell A. D., Hubbard C. R., Stalick J. K. and Holomany M. A., Unpublished manual for computer

- program NBS*AIDS83, JCPDS-International Centre for Diffraction Data, Swarthmore, PA (1983).
12. Le Bail A., Duroy H. and Fourquet J. L., *Mater. Res. Bull.* **23**, 447 (1988).
 13. Levien L. and Prewitt C. T., *Am. Mineral.* **66**, 324 (1981).
 14. *Powder Diffraction Data File*, JCPDS-International Centre for Diffraction Data, Swarthmore, PA.
 15. Robbins C., Perloff A. and Block S., *J. Res. Natl Bur. Stand.* **A70**, 385 (1968).
 16. Smolin J. I., *Sov. Phys.—Dokl.* **13**, 641 (1968).
 17. Werner P.-E., Eriksson L. and Westdahl L., *J. Appl. Crystallogr.* **18**, 367 (1985).
 18. Thompson P., Cox D. E. and Hastings J. B., *J. Appl. Crystallogr.* **20**, 79 (1987).
 19. Howard C. J., *J. Appl. Crystallogr.* **15**, 615 (1982).
 20. Finger L. W., Hazen R. M., Downs R. T. and Fursenko B. A., in preparation.