Crystal chemistry of high-pressure $BaSi_4O_9$ in the trigonal ($P3$) barium tetragermanate structure

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ABSTRACT

Crystals of $BaSi_4O_9$ synthesized at 4 GPa and 1000 °C were determined to be isostructural with barium tetragermanate [trigonal, space group $P3$, $a = 11.2469(11)$ and $c = 4.4851(6)$ Å, $V = 491.3(1)$ Å^3]. The structure ($R = 2.4\%$) features a corner-linked framework of three-member silicate tetrahedral rings, which are cross-linked by isolated silicate octahedra. Ba cations occupy tenfold-coordinated sites in channels defined by the silicate framework. This structure is 4.2% denser than the topologically similar benitoite form of high-pressure $BaSi_4O_9$, which was produced by grinding the barium tetragermanate-type crystals described in this report.

INTRODUCTION

Crustal silicate minerals containing Si in tetrahedral coordination typically transform to denser modifications with octahedrally coordinated Si at pressures of several GPa (e.g., Birch 1952; Stishov and Popova 1961). Examination of the growing number of documented high-pressure silicates with octahedral Si reveals useful systematic structural trends that facilitate classification of known phases, as well as prediction of new ones (Finger and Hazen 1991). In this letter we report the structure of $BaSi_4O_9$ in the trigonal (space group $P3$) barium tetragermanate structure, which is a new representative of high-pressure silicate framework structures with corner-linked arrays of fourfold- and sixfold-coordinated Si (Hazen et al. 1996).

The polymorphism of high-pressure $BaSi_4O_9$ is of special interest. Finger et al. (1995) described a barium tetrasilicate with the hexagonal ($P\bar{6}c2$) benitoite structure. The polycrystalline material used in that study was produced by grinding single crystals from the sample described in the present study. At the time, the structure of the single crystals had not been determined, but was known to be trigonal and thus different from the benitoite form. Previous workers have described at least two alkaline earth tetragermanate structures that are topologically similar to benitoite—the trigonal ($P3$) $BaGe_4O_9$ structure (Robbins et al. 1966) and the trigonal ($P321$) $BaGe_4O_9$ (Smolin 1968) and $SrGe_4O_9$ (Nishi 1996) structure. We thus suspected that our crystals were isomorphs of one of these previously reported structures. All three of these structures feature corner-linked frameworks of alternating Si or Ge octahedra and Si_3O_9 or Ge_3O_9 three-tetrahedra rings. A principal objective of this study, therefore, is to understand the relative stability of these polymorphs as a function of pressure.

EXPERIMENTAL METHOD

Single crystals of $BaSi_4O_9$ up to 50 µm in diameter were synthesized at the Novosibirsk high-pressure facility from near-stoichiometric mixtures of $BaCO_3 + 4SiO_2$, as described by Finger et al. (1995). Synthesis conditions were 4 GPa and 1000 °C for 10 h, followed by a rapid temperature quench and then a gradual pressure release.

A portion of the sample was ground and studied by a high-resolution powder diffraction at the National Synchrotron Light Source (beamline X7A), Brookhaven National Laboratory (Finger et al. 1995). A single-crystal fragment ($0.05 \times 0.05 \times 0.04$ mm) showing sharp diffraction profiles was selected from unground material for the present study. All X-ray diffraction measurements were conducted on a Rigaku AFC-5R diffractometer with monochromatic MoK_1 radiation ($= 0.7093$ Å), operated at 45 kV and 180 ma. Unit-cell parameters were determined from positions of 22 reflections with $20° < 2 < 35°$: $a = 11.2469(11)$, $c = 4.4851(6)$ Å, and $V = 491.3(1)$ Å^3. X-ray diffraction intensity data from a hemisphere of reciprocal space with $0° \leq 2 \leq 60°$ were collected using step scans. Procedures of data reduction and structure refinement were similar to those described by Hazen et al. (1997). We observed 2110 reflections with $I > 2_I$; an average of symmetry-equivalent reflections based on Laue group $\bar{3}$ yielded $R_{merge} = 0.019$. The initial structural model was taken from Robbins et al. (1966). The anisotropic refinement for all atoms resulted in $R_w = 0.018$ and $R = 0.024$. Note that a model based on the $P321$ symmetry was also attempted, but it resulted in $R_{merge} = 0.036$ and negative anisotropic displacement factors for two out of five oxygen atoms. Thus, the $P3$ symmetry was adopted for all refinements.

RESULTS

Refined atomic positional coordinates and isotropic displacement parameters of high-pressure $BaSi_4O_9$ are listed in

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TABLE 1. Atomic positional coordinates and isotropic displacement parameters of BaSi$_4$O$_9$

Atom	x	y	z	B_{iso}
Ba	0.3333(1)	0.3323(1)	0	0.82(1)
Si1	0	0	0.9055(10)	0.54(9)
Si2	2/3	1/3	0.1012(10)	0.39(9)
Si3	1/3	2/3	0.0027(13)	0.43(8)
Si4	0.8162(3)	0.8142(3)	0.4148(8)	0.55(6)
Si5	0.6688(3)	0.5195(3)	0.5911(8)	0.40(6)
Si6	0.5144(3)	0.6671(3)	0.5012(12)	0.52(4)
O1	0.9349(6)	0.0817(6)	0.1324(13)	0.69(13)
O2	0.5921(7)	0.4080(7)	0.3279(14)	0.77(14)
O3	0.8046(6)	0.6666(6)	0.5048(16)	0.85(13)
O4	0.5465(6)	0.5546(6)	0.6750(14)	0.70(13)
O5	0.4827(7)	0.7446(6)	0.7694(13)	0.69(13)
O6	0.8519(6)	0.9261(6)	0.6779(13)	0.48(12)
O7	0.6584(6)	0.7776(7)	0.3338(14)	0.85(14)
O8	0.4040(6)	0.5879(6)	0.2373(12)	0.59(12)
O9	0.7306(6)	0.4808(6)	0.8720(13)	0.66(13)

Note: Mo$K_{\alpha 1}$ radiation, $\lambda = 0.7093$ Å; data collection from $0° < 2\theta < 60°$; $a = 11.2469(11)$ and $c = 4.4851(6)$ Å, $V_{cell} = 491.3(1)$ Å^3. Space group $P3$, $Z = 3$, $\rho_{calc} = 3.991$ g/cm^3, $\mu = 68.100$ cm^{-1}. Hemisphere of reciprocal space measured, $R_{merge} = 0.019$. Full-matrix least squares refinement on F with $R_w = 0.018$ and $R = 0.024$ for 738 reflections with $I > 2\sigma_I$. The weighting factor $\omega = 1/\sigma^2_F$. The goodness of fit = 1.17 with anisotropic displacement parameters for all atoms; the z coordinate of Ba fixed during the refinement.

TABLE 2. Selected interatomic distances (Å) in BaSi$_4$O$_9$

Ba-O1	2.735(6)	Si3-O5 ×2	1.793(7)
Ba-O2	2.980(7)	Si3-O5'	1.792(7)
Ba-O3	3.116(7)	Si3-O8	1.797(7)
Ba-O3	3.147(7)	Si3-O8' ×2	1.796(7)
Ba-O4	2.851(6)	Avg.	1.795
Ba-O5	2.778(6)		
Ba-O6	2.972(6)	Si4-O1	1.616(7)
Ba-O7	2.881(7)	Si4-O3	1.649(7)
Ba-O8	2.783(6)	Si4-O6	1.622(7)
Ba-O9	2.739(6)	Si4-O7	1.649(7)
Avg.	2.898	Avg.	1.634
Si1-O1 ×3	1.758(6)	Si5-O2	1.621(7)
Si1-O6 ×3	1.767(6)	Si5-O3	1.641(7)
Avg.	1.763	Si5-O4	1.653(7)
		Avg.	1.629
Si5-O9	1.601(7)		
Si2-O2	1.774(7)	Si6-O4	1.672(7)
Si2-O2' ×2	1.774(7)	Si6-O5	1.626(7)
Si2-O9 ×2	1.770(6)	Si6-O7	1.649(7)
Si2-O9'	1.769(6)	Si6-O8	1.622(7)
Avg.	1.772	Avg.	1.642

Table 1; interatomic distances and angles are in Tables 2 and 3, respectively.

The structure is isomorphous with the previously reported trigonal structure (space group $P3$) of barium tetragermanate (Robbins et al. 1966). In BaSi$_4$O$_9$ three-member rings of three symmetrically distinct silicate tetrahedra (Si4, Si5, and Si6) are cross-linked by isolated silicate octahedra (three symmetrically distinct octahedral cations are designated Si1, Si2, and Si3) to form a three-dimensional corner-linked framework. Mean Si-O tetrahedral and octahedral bond distances (1.63 and 1.78 Å, respectively) are typical of high-pressure framework silicates.

The barium cation occupies an irregular tenfold-coordinated site, with Ba-O bond distances ranging from 2.735 to 3.147 Å (mean Ba-O distance 2.898 Å). The Ba site in isostructural BaGe$_4$O$_9$ (Robbins et al. 1966) also has irregular tenfold-coordination, but the mean Ba-O distance in the germanate is longer (2.960 Å), and the coordination spheres differ slightly in the two isomorphs. The two longest Ba-O bonds in BaSi$_4$O$_9$ are to O3 atoms, while a single Ba-O7 bond is shorter than the mean. In BaGe$_4$O$_9$, by contrast, the Ba site is more distorted, with Ba-O distances ranging from 2.66 to 3.28 Å; the two longest Ba-O bonds are to O7 atoms, while the single Ba-O3 bond is relatively short.

DISCUSSION

The trigonal BaSi$_4$O$_9$ structure described above is strikingly similar in topology to its benitoite polymorph (Finger et al. 1995), as well as to the trigonal ($P321$) structure of BaGe$_4$O$_9$ (Smolin 1968) and SrGe$_4$O$_9$ (Nishi 1996). All of these framework structures contain three-membered silicate or germanate tetrahedral rings, with each ring linked to six individual silicate or germanate octahedra. Each isolated octahedron, in turn, is corner-linked to six three-membered tetrahedral rings. The result is a distinctive layering perpendicular to c of alternating tetrahedral and octahedral units (Fig. 1). This feature is common to several high-pressure alkali and alkaline earth framework silicates (Hazen et al.

TABLE 3. Selected bond angles (°) in BaSi$_4$O$_9$

O1-Si1-O1	89.8(3)	O1-Si4-O3	98.8(3)
O1-Si1-O6	92.3(3)	O1-Si4-O6	119.5(3)
O1-Si1-O6	177.0(3)	O1-Si4-O7	115.2(4)
O1-Si1-O6	88.0(3)	O3-Si4-O6	117.9(4)
O6-Si1-O6	90.0(3)	O3-Si4-O7	105.6(4)
		O6-Si4-O7	99.9(4)
O2-Si2-O2	90.4(3)		
O2-Si2-O9	87.5(3)	O2-Si5-O3	118.4(4)
O2-Si2-O9	92.6(3)	O2-Si5-O4	99.6(4)
O2-Si2-O9	176.4(3)	O2-Si5-O9	119.9(4)
O2-Si2-O2	90.4(3)	O3-Si5-O4	106.2(3)
O2-Si2-O9	176.3(3)	O3-Si5-O9	98.5(4)
O2-Si2-O9	87.5(3)	O4-Si5-O9	114.3(4)
O2-Si2-O9	92.6(3)		
O2-Si2-O9	92.6(3)	O4-Si6-O5	104.4(4)
O2-Si2-O9	176.4(3)	O4-Si6-O7	106.3(3)
O2-Si2-O9	87.5(3)	O4-Si6-O8	108.7(3)
O9-Si2-O9	89.6(3)	O5-Si6-O7	109.2(4)
O9-Si2-O9	89.7(3)	O5-Si6-O8	121.4(4)
		O7-Si6-O8	106.0(4)
O5-Si3-O5	89.4(3)		
O5-Si3-O5	89.3(3)	Si1-O1-Si4	132.5(4)
O5-Si3-O8	92.6(3)	Si2-O2-Si5	126.1(4)
O5-Si3-O8	88.9(3)	Si4-O3-Si5	129.6(4)
O5-Si3-O8	177.4(3)	Si5-O4-Si6	126.5(4)
O5-Si3-O8	92.6(3)	Si3-O5-Si6	125.0(4)
O5-Si3-O8	89.0(3)	Si1-O6-Si4	126.5(4)
O5-Si3-O8	88.9(3)	Si4-O7-Si6	128.1(4)
O5-Si3-O8	177.3(3)	Si3-O8-Si6	124.2(4)
O5-Si3-O8	92.6(3)	Si2-O9-Si5	133.2(4)
O8-Si3-O8	89.2(3)		

1996). In all of these structures, the alkali or alkaline earth cations occupy large sites (eightfold or greater coordination) in the framework.

The principal crystal chemical differences between the barium tetragermanate-type and benitoite-type polymorphs of BaSi$_4$O$_9$ are associated with framework distortions, as measured by Si-O-Si angles. These distortions, in turn, influence the size of the Ba site. In the denser barium tetragermanate-type structure, ten Ba-O distances are within 3.2 Å with a mean Ba-O distance of 2.898 Å. This mean distance is shorter than the 2.92 Å value predicted by bond distance tabulations (Shannon 1976). The average of three tetrahedral ^{IV}Si-O-^{IV}Si angles within the three-membered ring is 128.1°, whereas the average ^{VI}Si-O-^{IV}Si

*P*3 structure
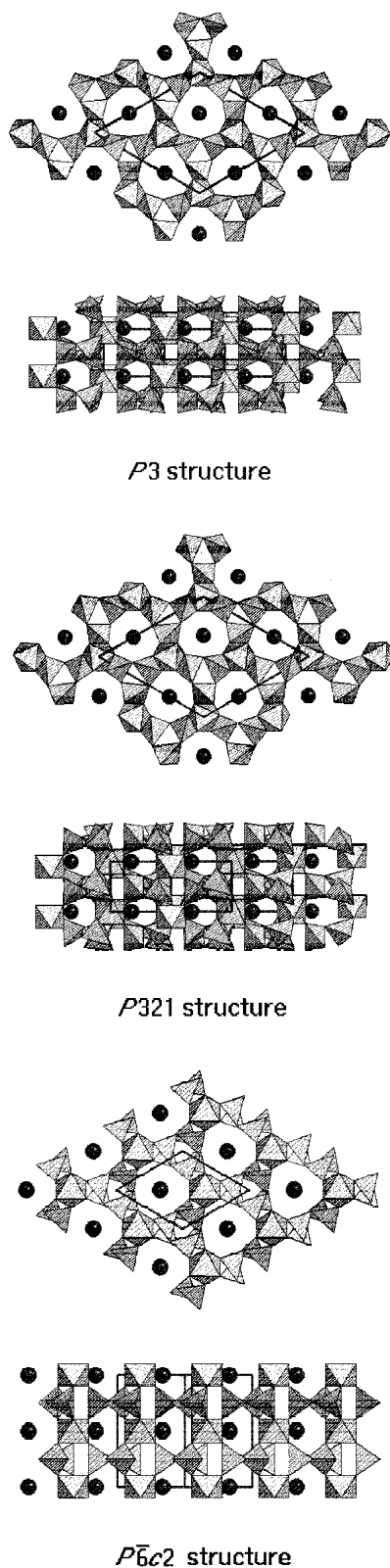

*P*321 structure

*P*6̄*c*2 structure

FIGURE 1. Comparison of the crystal structures of BaSi$_4$O$_9$ in the barium tetragermanate structure (trigonal, *P*3), BaSi$_4$O$_9$ in the benitoite structure (hexagonal *P*6̄*c*2), and the SrGe$_4$O$_9$ (trigonal *P*321) structure.

angle is 127.9°. In the benitoite-type polymorph, which is 4.2% less dense, only six Ba-O distances are within 3.2 Å and the mean Ba-O distance of 12-fold-coordinated barium is 3.011 Å; the ^{IV}Si-O-^{IV}Si and ^{VI}Si-O-^{IV}Si angles are 133.6° and 136.1°, respectively. The lower density of benitoite polymorph thus arises from the more open framework, with significantly larger Si-O-Si angles. This conclusion is supported by studies on CaSiO$_3$ pseudowollastonite polymorphs, which all contain Si$_3$O$_9$ three-member rings. The average Si-O-Si angle within a ternary ring is 134.6° in the high-temperature structure with a density of 2.90 g/cm^3 (Yang and Prewitt 1999) and only 123.4° in the high-pressure phase with a density of 3.07 g/cm^3 (Trojer 1969). The relatively short Ba-O bonds observed in the present study suggest that the Ba site in the barium tetragermanate form of BaSi$_4$O$_9$ quenched to room pressure is, in effect, compressed and thus energetically unfavorable. Grinding thus induces a martinsitic transition to the benitoite form, as observed by Finger et al. (1995).

Comparisons of the *P*3 structure of BaSi$_4$O$_9$ with the *P*321 structure of SrGe$_4$O$_9$ (Nishi 1996) are also instructive. The mean ^{IV}Ge-O-^{IV}Ge and ^{VI}Ge-O-^{IV}Ge angles in the latter structure are 122.1 and 118.6°, respectively (Nishi 1996). These values are significantly smaller than those of the trigonal *P*3 structure. Although direct comparisons of silicates and germanates must be made with caution, these differences in framework angles suggest that the trigonal *P*321 structure may be intrinsically more distorted and thus denser than the trigonal *P*3 structure. We suggest, therefore, that BaSi$_4$O$_9$ in the barium tetragermanate structure (synthesized in this study at 4 GPa) may transform to the denser SrGe$_4$O$_9$ structure at higher pressure.

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