

LETTER

BaCuSi₂O₆: A new cyclosilicate with four-membered tetrahedral rings

L. W. FINGER, R. M. HAZEN, R. J. HEMLEY

Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton Street N.W., Washington, D.C. 20008-3898, U.S.A.

ABSTRACT

Single-crystal X-ray diffraction and Raman spectroscopy were used to characterize the crystal structure and vibrational properties of BaCuSi₂O₆, a new silicate structure type with isolated 4-rings of tetrahedra and square-plane-coordinated Cu. This new phase, synthesized inadvertently in the search for high-temperature superconductors, possesses only seven variable structure parameters and thus is one of the simplest of all known cyclosilicates. A Raman peak at 506 cm⁻¹, which results from an in-plane breathing mode of the Si₄O₁₂ ring, provides a marker for 4-rings in other silicate crystals and glasses.

INTRODUCTION

The search for high-temperature superconductors has focused attention on the crystal chemistry of Cu in square-planar coordination, a common feature of all known superconductors with T_c above 40 K. A new cyclosilicate, distinguished by a unique arrangement of isolated four-member tetrahedral rings cross-linked by square-plane-coordinated Cu, has been synthesized as a by-product in the search for superconductors in the Tl-Ba-Ca-Cu-O system. In their first attempts to prepare Tl-bearing oxide superconductors, Sheng and Hermann (1988a, 1988b) heated oxide mixes in open silica boats. The resulting polyphase samples consisted primarily of two new 100-K superconducting phases (Hazen et al., 1988): Tl₂Ba₂Ca₁Cu₂O_{10+δ} and Tl₂Ba₂Ca₂Cu₃O_{12+δ}. Reaction between the oxide mixture and the silica sample container, however, produced a thin coating of two silicate phases. In transmitted light, one is striking magenta and the other is turquoise. Both of these insulating phases are alkaline-earth Cu silicates with new structure types. The turquoise phase, Ba₃CuCaSi₂O₁₇, is orthorhombic (space group *B2mb*, $a = 14.405 \text{ \AA}$, $b = 16.077 \text{ \AA}$, $c = 7.088 \text{ \AA}$). Its structure, which will be described elsewhere, features chains of 6-tetrahedra silicate rings, similar to those of pellyite (Ba₂CaMg₂Si₆O₁₇) (Meagher, 1976). Here we describe the new crystal structure and Raman spectra of the magenta phase, BaCuSi₂O₆.

CRYSTAL STRUCTURE

Several single crystals up to 300 μm in diameter were studied by electron-probe microanalysis, X-ray diffraction, and Raman spectroscopy. Microanalyses were done on a JSM model 35 scanning electron microscope, operated at 20 kV and 0.01-μA beam current with a 2.5-μm spot size. Standards included pure Cu metal, Ba-bearing glass, and a diopside₆₅-jadeite₃₅ pyroxene glass. Only Cu,

Ba, and Si were detected; several different grains gave the same stoichiometric composition: BaCuSi₂O₆.

A single crystal of BaCuSi₂O₆ with approximate dimensions 50 × 60 × 80 μm was selected for X-ray study. This magenta phase is body-centered tetragonal with $a = 7.042(3)$ and $c = 11.133(3) \text{ \AA}$. An octant of intensity data was collected to $\sin \theta/\lambda = 0.7$ on a Rigaku AFC-5 diffractometer with monochromated MoK α_1 radiation ($\lambda = 0.7093 \text{ \AA}$). A total of 1529 intensity data was measured. The Laue class is *4/mmm* with no systematic absences beyond the lattice centering. The space group is therefore restricted to *I422*, *I4mm*, *I4m2*, *I42m*, or *I4/mmm*. The structure solution was attempted with direct methods in the common subgroups, which are *I4* or *I4*; a topologically plausible solution was found that conformed to space group *I4/mmm*. Preliminary refinements in the centrosymmetric space group converged, but unreasonably large oxygen temperature factors and significant difference-map features near oxygen positions precluded that high-symmetry structure. Subsequent refinements in the noncentric subgroup, *I4m2*, yielded a well-behaved solution with reduced residuals. After reflection averaging, there were 443 unique observations, of which 427 had $I \geq 2\sigma_I$. The structure was refined with anisotropic temperature factors to an unweighted residual of 4.2%. Refined structural parameters and conditions of refinement are given in Table 1; structure factors have been deposited.¹

The structure of BaCuSi₂O₆ (Fig. 1) consists of isolated 4-rings of silicate tetrahedra. Tetrahedral parameters are typical of other silicates, with Si-O-Si angles of 151.2°

¹ A copy of observed and calculated structure factors may be ordered as document AM-89-414 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 1. Crystallographic data for BaCuSi₂O₆

Atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃	B _{eq}
Ba1	1/2	0	1/4	1.29(8)	= B ₁₁	1.18(10)	0	0	0	1.25(4)
Ba2	0	1/2	1/4	1.29(8)	= B ₁₁	0.59(10)	0	0	0	1.08(3)
Cu	0	0	0.1225(1)	0.97(20)	0.14(16)	1.04(5)	0	0	0	0.72(3)
Si	0.2759(2)	= x	0	0.33(6)	= B ₁₁	1.04(10)	-0.05(6)	0.3(2)	= -B ₁₃	0.59(3)
O1	0.2185(10)	0.1645(12)	0.1190(5)	1.7(3)	2.4(4)	1.4(2)	-1.5(3)	-0.1(2)	0.5(2)	2.1(2)
O2	0.7429(13)	0	0.5300(7)	1.4(3)	0.5(3)	1.9(4)	0	0.2(3)	0	1.3(2)

Note: Diffraction experiments with Rigaku AFC-5 diffractometer, rotating anode generator, MoK α radiation, graphite monochromator, $\lambda = 0.7093$ Å, scan mode $\omega - 2\theta$, ambient temperature and pressure. Space group $I4m2$; $Z = 4$; $a = 7.042(3)$ Å; $c = 11.133(3)$ Å; $V = 522.1(4)$ Å³; $\rho_{\text{calc}} = 4.49$ g·cm⁻³; $\mu = 120.0$ cm⁻¹; formula weight = 353.06 g. Temperature factors are given by $\exp[-\sum \sum h_i h_j B_j / (4a_i a_j)]$. Numbers in parentheses indicate estimated standard deviations.

and a mean Si-O distance of 1.610 Å. Cu atoms are almost ideally planar-coordinated to four oxygens (Cu-O = 1.926 Å; opposite O-Cu-O = 177.7°). The four oxygens deviate significantly from a square, however, with adjacent O-Cu-O = 74.5° and 105.5° instead of the ideal 90° values. Two Cu atoms link each set of four adjacent 4-rings to form (001) layers. These CuSi₂O₆ layer units, a unique feature of the structure, are interconnected parallel to the *c* axis by eight-coordinated Ba1 atoms (Ba1-O = 2.728 Å) and twelve-coordinated Ba2 atoms (mean Ba2-O = 3.107 Å) halfway between the Cu-Si-O layers. Each Ba is coordinated to four 4-rings—two in the layer above and two below. Selected interatomic distances and angles appear in Table 2.

Silicates with isolated tetrahedral 4-rings are rare, with fewer than ten documented structure types (Liebau, 1985). Of these, BaCuSi₂O₆ stands out for at least three reasons. First, the 4-rings of this phase have 2*mm* point symmetry; all other known 4-ring cyclosilicates have lower ring-point symmetries of 2 or *m*. Second, all of the other struc-

tures are either hydrated or possess additional anions not coordinated to Si. Third, the BaCuSi₂O₆ structure has only six symmetrically distinct atoms and only seven variable atomic coordinates, making it by far the simplest of 4-ring structures.

The observed BaCuSi₂O₆ structure deviates from centric *I4/mmm* symmetry by relatively minor shifts of the two distinct oxygen atoms. A transition to this supersymmetry might occur at high temperature, but our samples are untwinned, suggesting that the acentric form is stable at least to the 880 to 910 °C temperature range employed by Sheng and Hermann. The centric *I4/mmm* structure, which features 4-rings of maximal 4/*mmm* point symmetry, has only five symmetrically distinct atoms and five variable atomic coordinates. Idealized atomic coordinates for this postulated BaCuSi₂O₆ parent structure are given in Table 3.

The structure of the new 4-ring silicate, though quite different from any other cyclosilicate, is closely related to the rare mineral gillespite (BaFeSi₄O₁₀) and its synthetic isomorphs including BaCuSi₄O₁₀ (Pabst, 1959; Hazen and Finger, 1983). In *c*-axis projection (Fig. 2A), the two barium copper silicates seem to be topologically identical. In the BaCuSi₄O₁₀ structure, however, each 4-ring is linked to four others in the adjacent layer (Fig. 2B), forming a unique 4-ring silicate layer instead of a structure with isolated 4-rings.

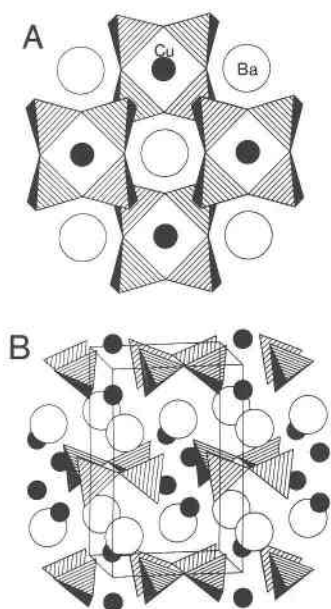


Fig. 1. The structure of BaCuSi₂O₆. (A) (001) projection. (B) View with tetragonal *c* axis vertical.

TABLE 2. Selected interatomic distances (Å) and angles (°) for BaCuSi₂O₆

Cu square plane			Si tetrahedron		
Cu-O1	[4]	1.926(7)	Si-O1	[2]	1.589(6)
O1-O1	[2]	2.331(19)	Si-O2	[2]	1.630(2)
			mean Si-O		1.610
O1-Cu-O1	[2]	177.7(4)	O1-O1		2.699(11)
O1-Cu-O1	[2]	74.5(7)	O1-O2	[2]	2.561(9)
O1-Cu-O1	[2]	105.5(7)	O1-O2	[2]	2.647(9)
			O2-O2		2.642(13)
			O1-Si-O1		116.2(5)
			O1-Si-O2	[2]	105.4(5)
			O1-Si-O2	[2]	110.6(5)
			O2-Si-O2		108.3(7)
			Si-O1-Cu		121.2(4)
			Si-O2-Si		151.2(6)
			O2-O2-O2		86.3(2)
Ba1 polyhedron					
Ba1-O1	[8]	2.728(9)			
Ba2 polyhedron					
Ba2-O1	[8]	3.166(10)			
Ba2-O2	[4]	2.988(8)			

Note: Square-bracketed values represent bond or angle multiplicities.

TABLE 3. Idealized coordinates for *I4/mmm* hypothetical parent structure of BaCuSi₂O₆

Atom	x	y	z
Ba	1/2	0	1/4
Cu	0	0	0.125
Si	0.275	0.275	0
O1	0.195	0.195	0.120
O2	0.740	0	1/2

RAMAN SPECTROSCOPY

The BaCuSi₂O₆ structure, because of its high symmetry and simple topology, makes an ideal candidate for documenting the distinctive vibrational characteristics of its structural constituents, including the 4-ring and square-plane Cu. We have therefore measured the Raman spectrum of ~50- μ m crystals of this phase using single-crystal micro-optical techniques (Mao et al., 1987; Hemley and Mao, 1987). The signal levels were low because of the small size of the crystal and the high absorption of the laser light, which required the use of laser powers of less than ~25 mW to prevent heating and photodecomposition. Although these limitations precluded a complete polarization study, high-quality spectra were obtained for the polarized scattering components (Fig. 3). The structure refinement indicates that the deviation from centrosymmetric space group *I4/mmm* is small. A factor group analysis for this space group indicates that the Raman active vibrations should transform as $5A_{1g} + 5B_{1g} + 2B_{2g} + 8E_g$ symmetry species. Polarization measurements are consistent with the assignment of the prominent bands at 268, 454, 506, 579, and 976 cm⁻¹ as the five totally symmetric *A_{1g}* modes (in *I4/mmm*).

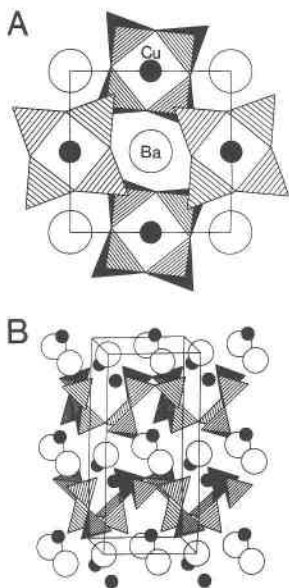


Fig. 2. The gillespite (BaFeSi₄O₁₀) structure, represented by the synthetic isomorph BaCuSi₂O₆. (A) (001) projection. (B) View with tetragonal *c* axis vertical. Note the close relationship between this structure and that of BaCuSi₂O₆.

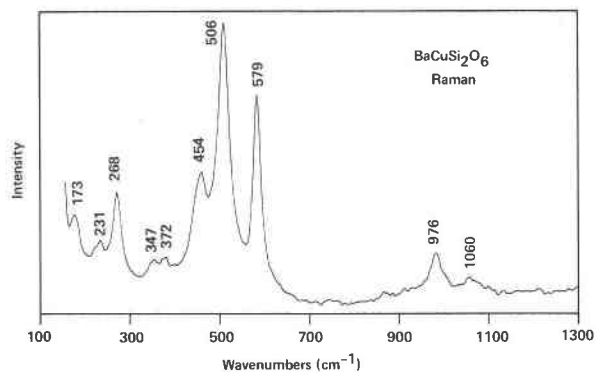


Fig. 3. Raman spectrum of BaCuSi₂O₆ measured with 514.5-nm Ar-ion excitation. Bands at 500–600 cm⁻¹ are assigned to oxygen breathing modes of the 4-membered tetrahedral rings and square-planar Cu (see text). The high-frequency bands at 900–1100 cm⁻¹ are assigned to symmetric Si–O stretching vibrations; low-frequency bands arise from SiO₄ tetrahedral bending motions, bending modes of the square-planar Cu, and Ba–O stretching motions.

The bands at 500–600 cm⁻¹ are of particular interest in detailing the vibrational dynamics of tetrahedral ring configurations and square-planar Cu. The 579 cm⁻¹ band is likely to be associated with in-plane Cu–O stretching motions, by analogy with Cu–O breathing modes measured for the high *T_c* cuprates (e.g., Rosen et al., 1988; Weber et al., 1988). The 506 cm⁻¹ peak is enhanced by polarized scattering with the phonon propagation direction along the *c* axis (α_{xx}). A strongly polarized peak in this region is observed in the Raman spectra of other silicates having four-membered Si₄O₁₂ rings. The spectrum of coesite, a high-pressure silica polymorph, is dominated by a strongly polarized band at 521 cm⁻¹, which is identified as the symmetric Si–O–Si stretching mode; in contrast, the principal band in α -quartz (effectively a 6-ring structure) appears at the significantly lower frequency of 464 cm⁻¹ (Sharma et al., 1981). The strong bands in other silicates with 4-ring structures have frequencies that are close to those observed here in BaCuSi₂O₆: orthoclase (KAlSi₃O₈), 513 cm⁻¹; low albite (NaAlSi₃O₈), 506 cm⁻¹; and anorthite (CaAl₂Si₂O₈), 503 cm⁻¹ (White, 1975). The frequency is independent of cross-linking of the ring structures; this fact indicates that the mode is largely localized within the ring structure. Our polarization measurements are consistent with the vibration being an in-plane 4-ring breathing mode involving displacements principally of oxygen (Sharma et al., 1981; Galeener, 1982; Hemley et al., 1986). This assignment supports the use of Raman bands at ~500 cm⁻¹ as signatures for ring configurations in amorphous silicates.

ACKNOWLEDGMENTS

We thank F. C. Hawthorne, H. K. Mao, and C. T. Prewitt for helpful reviews. The work was supported in part by National Science Foundation Grants EAR87-08192 (R.M.H. and R.J.H.) and EAR86-18649 (L.W.F.) and by the Carnegie Institution of Washington.

REFERENCES CITED

- Galeener, F.L. (1982) Plane rings in glasses. *Solid State Communications*, 44, 1037–1040.
- Hazen, R.M., and Finger, L.W. (1983) High-pressure and high-temperature crystallographic study of the gillespite I–II phase transition. *American Mineralogist*, 68, 595–603.
- Hazen, R.M., Finger, L.W., Angel, R.J., Ross, N.L., Hadidiacos, C.G., Heaney, P.J., Veblen, D.R., Sheng, Z.Z., El Ali, A., and Hermann, A.M. (1988) 100-K superconducting phases in the Tl-Ca-Ba-Cu-O system. *Physical Review Letters*, 60, 1657–1660.
- Hemley, R.J., and Mao, H.K. (1987) Single-crystal micro-Raman spectroscopy of phases in the Y-Ba-Cu-O superconductor. *Physical Review Letters*, 58, 2340–2342.
- Hemley, R.J., Mao, H.K., Bell, P.M., and Mysen, B.O. (1986) Raman spectra of SiO₂ glass at high pressure. *Physical Review Letters*, 57, 747–750.
- Liebau, F. (1985) *Structural chemistry of silicates*. Springer-Verlag, New York.
- Mao, H.K., Hemley, R.J., and Chao, E.C.T. (1987) The application of micro-Raman spectroscopy to analysis and identification of minerals in thin section. *Scanning Microscopy*, 1, 495–501.
- Meagher, E.P. (1976) The atomic arrangement of pellyite: Ba₂Ca(Fe,Mg)₂Si₄O₁₇. *American Mineralogist*, 61, 67–73.
- Pabst, A. (1959) Structures of some tetragonal sheet silicates. *Acta Crystallographica*, 12, 733–739.
- Rosen, H.J., MacFarlane, K., Engler, E.M., Lee, V.Y., and Jacowitz, R.D. (1988) Systematic Raman study of effects of rare-earth substitution on the lattice modes of high-T_c superconductors. *Physical Review B*, 38, 2460–2465.
- Sharma, S.K., Mammone, J.F., and Nicol, M.F. (1981) Raman investigation of ring configurations in vitreous silica. *Nature*, 292, 140–143.
- Sheng, Z.Z., and Hermann, A.M. (1988a) Superconductivity in the rare-earth-free Tl-Ba-Cu-O system above liquid-nitrogen temperature. *Nature*, 332, 55–58.
- (1988b) Bulk superconductivity at 120 K in the Tl-Ca/Ba-Cu-O system. *Nature*, 332, 138–139.
- Weber, W.H., Peters, C.R., Wanklyn, B.M., Chen, C., and Watts, B.E. (1988) Evidence for anisotropic excitonlike enhancement of the Raman scattering from La₂CuO₄. *Physical Review B*, 38, 917–920.
- White, W.B. (1975) Structural interpretation of lunar and terrestrial minerals by Raman spectroscopy. In C. Karr, Jr., Ed., *Infrared and Raman spectroscopy of lunar and terrestrial minerals*, p. 325–358. Academic Press, New York.

MANUSCRIPT RECEIVED APRIL 13, 1989

MANUSCRIPT ACCEPTED MAY 5, 1989