structural geometry with that of the isostructural Cr^{3+} (d^3) cryolite. While in the latter compound, as in the Al and Fe cryolites, the MF_6 octahedra are nearly regular (Cr—F 1.900–1.907 Å), the MnF_6 group is elongated with $Mn—F_{ax} = 2.018$ and a mean $Mn—F_{eq} = 1.880$ Å (Table 2, Fig. 2*a*). In terms of relative bond strengths (Massa & Babel, 1988) the axial bonds are weakened by 23%. Nevertheless, this remarkable effect is the smallest among all known structures with ordered statically distorted MnF_6 groups. The reason must be the weak coupling of the quasi-isolated (MnF_6) groups in the lattice. One-, two-, three-dimensional connection leads to a stronger cooperative Jahn–Teller effect. Comparing the geometry of the (MnF_6) units to that in other sodium fluoromanganates, for instance, we find in the chain compound Na_2MnF_5 axial/mean equatorial Mn—F bond lengths of 2.109/1.849 Å (Massa, 1986) and in the layer structure of $NaMnF_4$ 2.167/1.839 Å (Molinier, Massa, Khairoun, Tressaud & Soubeyroux, 1991). The ordering of the elongated octahedra is ferrodistortive. The long axes point roughly towards the *c* axis but are inclined at about 20°, similar to the Cr compound (Fig. 1). Owing to the *n*-glide operation, the octahedra on the corners of the unit cell and at the centre are inclined to each other by 18.7° (Cr 18.5°). Na1 has a weakly distorted octahedral coordination, while the Na2 cation has an eight-coordinated surrounding of F^- ions best described as a distorted bicapped trigonal prism (Table 2, Fig. 2*c*).

We thank cand. chem. M. Geßner for his help in preparing the crystals, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

Babel, D. & Tressaud, A. (1985). *Crystal Chemistry of Fluorides*. In *Inorganic Solid Fluorides, Chemistry and Physics*, edited by P. Hagenmuller, pp. 77–203. New York: Academic Press.
Brunton, G. (1969). *Mater. Res. Bull.* **4**, 621–627.
Bucovec, P. & Siftar, I. (1975). *Monatsh. Chem.* **106**, 1333–1336
Cromer, D. T. & Mann, J. D. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Hawthorne, F. C. & Ferguson, R, B. (1975). *Can. Mineral.* **13**, 377–382.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Massa, W. (1986). *Acta Cryst.* C**42**, 644–647.
Massa, W. & Babel, D. (1988). *Chem. Rev.* **88**, 275–296.
Matvienko, E. N., Yakubovich, O. V., Simonov, M. A., Ivashchenko, A. N., Melnikov, O. K. & Belov, N. N. (1981). *Dokl. Akad. Nauk SSSR*, **257**, 105–108.
Molinier, M., Massa, W., Khairoun, S., Tressaud, A. & Soubeyroux, J. L. (1991). *Z. Naturforsch.* In the press.
Naray-Szabo, S. V. & Sasvari, K. (1938). *Z. Kristallogr.* **99**, 27–31.
Sheldrick, G. M. (1989). *SHELXTL-Plus*. Release 4.0 for Siemens *R*3 Crystallographic Research Systems. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
Siebert, G. & Hoppe, R. (1971). *Z. Anorg. Allg. Chem.* **391**, 117–125.

Acta Cryst. (1992). C**48**, 8–10

Structure of the Cyclic Barium Copper Silicate $Ba_2Cu_2[Si_4O_{12}]$ at 300 K

By Jan Janczak and Ryszard Kubiak

Institute for Low Temperature and Structure Research, Polish Academy of Science, 50–950 *Wroclaw*, *Pl. Katedralny* 1, *Poland*

(*Received* 16 *November* 1990; *accepted* 20 *February* 1991)

Abstract. Dibarium dicopper tetrasilicate, $Ba_2Cu_2Si_4O_{12}$, $M_r = 706{\cdot}1$, tetragonal, $I4/mmm$, $a = 7{\cdot}0515\,(20)$, $c = 11{\cdot}1503\,(30)$ Å, $V = 554{\cdot}4\,(4)$ Å^3, $Z = 2$, $D_x = 4{\cdot}228$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 113{\cdot}0$ cm^{-1}, $F(000) = 644$, $T = 300$ K, final $R = 0{\cdot}0300$ for 97 unique reflections [313 observed with $|F_o| > 3\sigma(|F_o|)$]. The structure contains isolated cyclic $[Si_4O_{12}]^{8-}$ groups, Si—O(1) = 1·570 (10), Si—O(2) = 1·602 (4) Å in the ring system. The copper cation is square coordinated by four O(1) atoms, Cu—O(1) = 1·925 (11) Å. The barium cation is surrouned by a square antiprism formed by eight O(1) atoms, Ba—O(1) = 2·930 (5) Å, and four O(2) atoms at 3·263 (8) Å.

Introduction. The title compound is the second barium copper silicate obtained during our studies of the chemcial reactivity of the '1-2-3' type superconductors. Results on the synthesis and crystal structure of $BaCu_2Si_2O_7$ which was obtained in the reaction of $YBa_2Cu_3O_{7-x}$ with SiO_2 in the presence of Bi_2O_3 have been published previously (Janczak,

0108-2701/92/010008-03$03.00

Kubiak & Głowiak, 1989, 1990). The present work describes a structural investigation of the cyclic dibarium dicopper tetrasilicate, $Ba_2Cu_2Si_4O_{12}$.

Experimental. Crystals of $Ba_2Cu_2Si_4O_{12}$ were obtained in the reaction of $YBa_2Cu_3O_{7-x}$ with PbO and Na_2O_2 in the molar proportion 1:2:1. The mixture was pelletized, evacuated and sealed in a quartz tube. The pellets were first heated at 873K for 1 d, and then for 4 h at 1173K and finally quenched in air. At the high temperature the mixture reacted with the tube walls and $Ba_2Cu_2Si_4O_{12}$ was formed as the major phase. A violet spherical crystal with radius 0·05 mm (density not measured) was used for intensity data collection on a Siemens diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Preliminary examination by rotation and Weissenberg photographs revealed the systematic absences *hkl*: $h + k + l = 2n + 1$. Space group *I4/mmm* was used in the structure solution and refinement. Lattice parameters were refined by a least-squares fit of 15 reflections in the range $15 \leq 2\theta \leq 25°$. 313 reflections [with $|F_o| > 3\sigma(|F_o|)$] were measured in the range $3{\cdot}5 \leq 2\theta \leq 40°$ using the ω–2θ scan technique with scan speed 1·01–9·77° $\min^{-1}$ and scan width 1·1°. The *hkl* range was $h\ 0 \rightarrow 6$, $k\ 0 \rightarrow 6$, $l\ -10 \rightarrow 10$. Two standard reflections (400 and 402) were monitored every 40 reflections. They showed no significant intensity variation. The measured intensities were corrected for Lorentz and polarization effects. A spherical absorption correction was applied, $\mu R = 0{\cdot}57$, the transmission factors were in the range 0·42–0·44. 97 independent reflections ($R_{\rm int} =$ 0·0401) were used in subsequent calculations. The structure was solved by the Patterson method (Ba and Cu atoms) (*SHELXS*86; Sheldrick, 1986), and the remaining atoms were located from $\Delta\rho$ maps. The structure was refined by the full-matrix least-squares method with anisotropic temperature factors (*SHELX*76; Sheldrick, 1976) [O(2) had an unreasonably high thermal-motion parameter for U_{33}, *viz*. 0·201 (20) $Å^2$, and this may involve some disorder of the ring]. An empirical secondary-extinction correction was applied according to the formula $F_{\rm cor} = F(1 - xF^2/\sin\theta)$, where x converged to 0·00107 (28). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 41{\cdot}9135/\sigma^2(F)$. Final $R = 0{\cdot}0300$, $wR = 0{\cdot}0347$ for 20 refined parameters, $(\Delta/\sigma)_{\max} = 0{\cdot}001$. Residual electron density in final difference Fourier map within $-1{\cdot}11$ and $1{\cdot}10\ {\rm e\ Å^{-3}}$. Scattering factors including corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Figures were drawn with *PLUTO*78 (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1965). All calculations were preformed with an IBM PC/AT.

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* $U_{\rm eq}$, *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}(Å^2)$
Ba	0	0·5	0·25	0·0160 (4)
Cu	0·5	0·5	0·1225 (3)	0·0090 (10)
Si	0·2245 (5)	0·2245 (5)	0	0·0103 (11)
O(1)	0·3070 (11)	0·3070 (11)	0·1199 (8)	0·0513 (26)
O(2)	0	0·2594 (23)	0	0·0700 (70)

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°), *with e.s.d.'s in parentheses*

Si—O(1)	1·570 (10)	Cu—Cu$^{\rm i}$	2·733 (6)
Si—O(2)	1·602 (4)	Ba—O(1)	2·940 (5)
Cu—O(1)	1·925 (11)	Ba—O(2)	3·263 (8)
		O(1)—O(2)	2·566 (9)
O(1)—Si—O(2)	108·0 (3)	O(1)—Si—O(1)$^{\rm i}$	116·8 (8)
Bond angles in the $[Si_4O_{12}]^{8-}$ ring			
O(2)—Si—O(2)$^{\rm ii}$	108·0 (3)	Si—O(2)—Si$^{\rm iii}$	162·4 (6)

Symmetry code: (i) $x, y, -z$; (ii) y, x, z; (iii) $-x, y, z$.

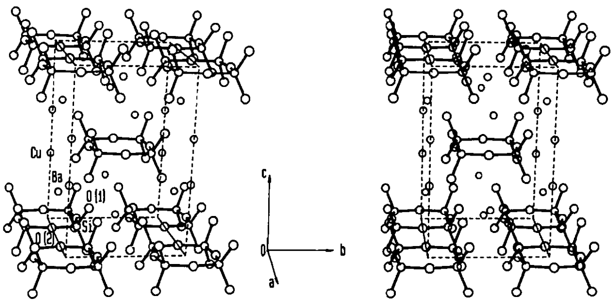

Fig. 1. A packing stereodiagram of molecules of the title compound.

Discussion. Final positional parameters and isotropic temperature factors are given in Table 1,* and interatomic distances and angles in Table 2. A stereodrawing of the contents of the unit cell is shown in Fig. 1.

The characteristic feature of the structure is the existence of isolated cyclic $[Si_4O_{12}]^{8-}$ groups. Four corner-sharing SiO_4 tetrahedra form a ring around the fourfold axis. All the bridging bonds are Si—O(2) with a bond distance of 1·602 (4) Å. The remaining eight O(1) atoms lie in planes perpendicular to the ring plane. The non-bridging Si—O(1) distance [1·570 (10) Å] is shorter than in other tetrasilicates (Simonov, 1960; Malinovskij, 1983; Jakovicz

---

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54019 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0183]

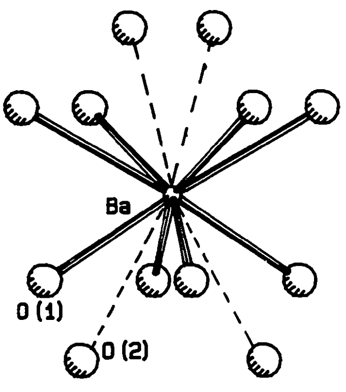

Fig. 2. View of the barium coordination by O atoms.

& Simonov, 1985). The bond angles O—Si—O and Si—O—Si in the ring are equal [107·6 (3)° and 162·4 (5)°, respectively]. Each barium and copper cation is coordinated by eight and four O(1) atoms, respectively, forming a three-dimensional network. The Cu^{2+} cation is located at site symmetry $4mm$, with four O(1) atoms (each from a different $[Si_4O_{12}]^{8-}$ group) forming a square coordination with Cu—O(1) = 1·925 (11) Å. This value is comparable to the Cu—O distances in other copper silicates (Pabst, 1959; Kawamura & Kawahara, 1976). The Ba^{2+} cation is surrounded by a regular square antiprism of O(1) atoms with Ba—O(1) = 2·940 (5) Å. There are four O(2) atoms outside this polyhedron at 3·263 (8) Å (Fig. 2.)

The authors are indebted to Professor Z. Gałdecki, Technical University of Łódź, Poland, for the opportunity to collect data in his laboratory.

References

Jakovicz, O. W. & Simonov, M. A. (1985). *Kristallografiya*, **30**(6), 1072–1076.
Janczak, J., Kubiak, R. & Głowiak, T. (1989). 12th Eur. Crystallogr. Meet., Moscow, USSR.
Janczak, J., Kubiak, R. & Głowiak, T. (1990). *Acta Cryst.* **C46**, 1383–1385.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kawamura, K. & Kawahara, K. (1976). *Acta Cryst.* **B32**, 2419–2422.
Malinovskij, Yu. A. (1983). *Dokl. Akad. Nauk SSSR*, **272**(6), 1375–1378.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Pabst, A. (1959). *Acta Cryst.* **12**, 733–739.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
Simonov W. J. (1960). *Kristallografiya*, **5**(4), 544–546.

Acta Cryst. (1992). **C48**, 10–13

$Ce_3Rh_2Ge_2$ and Isotypes with the Orthorhombic $La_3Ni_2Ga_2$ Type

By R. E. Gladyshevskii, J. T. Zhao and E. Parthé

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 *Quai E. Ansermet,*
*CH-*1211 *Geneva* 4, *Switzerland*

(*Received* 30 *March* 1991; *accepted* 25 *June* 1991)

Abstract. $Ce_3Rh_2Ge_2$, M_r = 771·35, orthorhombic, $La_3Ni_2Ga_2$ type, $oP28$, (57) $Pbcm - e^2d^2c$, a = 5·7001 (9), b = 8·099 (1), c = 13·461 (3) Å, V = 621·4 (1) $Å^3$, Z = 4, D_x = 8·244 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 35·492 mm^{-1}, F(000) = 1312, T = 293 K, wR = 0·022 for 725 contributing unique reflections. Isotypes are found for $R_3Rh_2Ge_2$ with R = Y, La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm and Lu. The structure is characterized by infinite columns of trigonal-prism blocks along the c axis, each block being rotated with respect to its two neighbours by 180° around the column axis and shifted by $\frac{1}{2}\mathbf{c}$. Every block consists of three rectangular-face-linked trigonal prisms which are centred by Rh or Ge atoms. These columns are linked to neighbouring columns in a way similar to the linkage of the trigonal-prism columns in the FeB structure. Ignoring the difference in the site occupation of the prism centres the $La_3Ni_2Ga_2$ type can be considered a slab-stacking variant of the Y_3Co_3Ga type. The geometrical relation between these types corresponds to that already described for the FeB and CrB structure types, allowing the use of the same transformation equations for the cell parameters.

Introduction. In the system Ce–Rh–Ge only orthorhombic CeRhGe with TiNiSi type was known (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982), but a comparison with the large number of phases in the rare-earth–Fe group–Si systems led us to expect

0108-2701/92/010010-04$03.00