Table 2. *Distances* (Å) *and angles* (°)

PO_4 tetrahedra

P(1)	O(2^{i})	O(2^{ii})	O(6)	O(6^{iii})
O(2^{i})	1·519 (5)	2·486 (7)	2·490 (6)	2·438 (6)
O(2^{ii})	109·8 (3)	1·519 (5)	2·438 (6)	2·490 (6)
O(6)	110·1 (2)	106·7 (2)	1·520 (4)	2·543 (6)
O(6^{iii})	106·7 (2)	110·1 (2)	113·5 (2)	1·520 (4)

P(2)	O(3^{iii})	O(4)	O(5^{iv})	O(7)
O(3^{iii})	1·507 (5)	2·534 (6)	2·543 (6)	2·422 (5)
O(4)	114·7 (3)	1·503 (4)	2·443 (6)	2·506 (7)
O(5^{iv})	115·2 (3)	108·6 (3)	1·506 (4)	2·509 (6)
O(7)	102·3 (3)	107·7 (3)	107·7 (3)	1·601 (3)

$MoNbO_6$ octahedra

MoNb	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1·908 (1)	2·816 (6)	4·012 (7)	2·814 (7)	2·778 (6)	2·832 (6)
O(2)	92·1	2·004 (5)	2·902 (6)	4·031 (7)	2·805 (6)	2·884 (6)
O(3)	177·7 (2)	89·8 (2)	2·105 (4)	2·843 (6)	2·886 (6)	2·889 (6)
O(4)	91·2 (2)	176·0 (2)	86·9 (2)	2·030 (4)	2·846 (6)	2·875 (6)
O(5)	90·0 (2)	88·4 (2)	88·8 (2)	89·3 (2)	2·020 (4)	4·036 (7)
O(6)	92·3 (2)	91·7 (2)	89·0 (2)	90·5 (2)	177·7 (2)	2·017 (4)

KO_8 polyhedra

K—O(7^{v})	2·753 (8)	K—O(6^{vii})	3·042 (6)
K—O(2^{ii})	2·825 (6)	K—O(3^{i})	3·187 (6)
K—O(2^{vi})	2·825 (6)	K—O(3^{viii})	3·187 (6)
K—O(6)	3·042 (6)	K—O(1^{ii})	3·278 (8)

Symmetry code: (i) $-x, -y, -z$; (ii) $-x, 0·5+y, z$; (iii) $x, 0·5-y, -z$; (iv) $1-x, 0·5+y, z$; (v) $-x, y-0·5, z$; (vi) $-x, 0·5-y, 0·5-z$; (vii) $x, y, 0·5-z$; (viii) $-x, -y, 0·5+z$.

The K ions are surrounded by eight O atoms, with distances less than 3·35 Å (Table 2).

It is worth pointing out that the metallic elements in octahedral coordinations exhibit a mean oxidation state of 4·125 compared with 4 for $KMo_2P_3O_{12}$. Because of the difficulty of niobium being in the tetravalent state in phosphates, unlike molybdenum which can be presumed to be Mo^{IV}, a mean valency of 4·25 is suggested for niobium which coincides with that observed in $Na_{0·5}Nb_2P_3O_{12}$ (Leclaire *et al.*, 1990).

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Structure of Barium Copper Pyrosilicate at 300 K

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Abstract. Barium dicopper disilicate, $BaCu_2Si_2O_7$, $M_r = 432·6$, orthorhombic, $Pnma$, $a = 6·866$ (2), $b = 13·190$ (3), $c = 6·909$ (2) Å, $V = 625·7$ (3) Å^3, $Z = 4$, $D_x = 4·592$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 137·47$ cm^{-1}, $F(000) = 792$, $T = 300$ K, final $R = 0·031$ for 1039 independent reflections. The structure solution and refinement established the crystal stoichiometry as $BaCu_2Si_2O_7$. The structure contains isolated groups of $[Si_2O_7]^{6-}$ with the Si—O distances ranging from 1·610 (4) to 1·662 (2) Å. The barium and copper cations have irregular coordination polyhedra. Ba^{2+} is coordinated by 7 O atoms, and Cu^{2+} by 4 + 1 O atoms.

Introduction. The '1-2-3'-type superconductors have the ability to interact with oxygen. This interaction is very important because superconducting properties depend on the oxygen stoichiometry (Pietraszko,

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

$$U_{\rm eq} = 1/3\sum U_{ii}.$$

	x	y	z	$U_{\rm eq}$
Ba	−0·0130 (1)	0·25	0·9570 (1)	0·0081 (1)
Cu	0·2223 (1)	0·0042 (1)	0·7936 (1)	0·0061 (2)
Si	0·0024 (2)	0·1340 (1)	0·4729 (2)	0·0051 (5)
O1	0·09660 (7)	0·25	0·4828 (8)	0·0080 (12)
O2	−0·1718 (5)	0·1338 (2)	0·6309 (5)	0·0097 (7)
O3	−0·0589 (5)	0·1121 (2)	0·2519 (5)	0·0107 (8)
O4	0·1828 (5)	0·0597 (2)	0·5340 (5)	0·0067 (5)

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

		O1—O2	2·605 (5)
Si—O1	1·662 (2)	O1—O3	2·645 (5)
Si—O2	1·619 (4)	O1—O4	2·603 (3)
Si—O3	1·610 (4)	O2—O3	2·746 (5)
Si—O4	1·635 (3)	O2—O4	2·708 (5)
		O3—O4	2·652 (5)
Cu—O4	1·956 (3)	Ba—O1$^{\rm viii}$	2·713 (5)
Cu—O4$^{\rm i}$	1·973 (3)	Ba—O2	2·932 (3)
Cu—O3$^{\rm i}$	2·789 (4)	Ba—O2$^{\rm iv}$	2·932 (3)
Cu—O2$^{\rm ii}$	1·930 (3)	Ba—O3$^{\rm v}$	2·749 (3)
Cu—O3$^{\rm iii}$	1·926 (3)	Ba—O3$^{\rm vi}$	2·749 (3)
		Ba—O2$^{\rm ii}$	2·863 (3)
		Ba—O2$^{\rm vii}$	2·863 (3)
O1—Si—O2	105·2 (2)	O2$^{\rm ii}$—Cu—O4$^{\rm i}$	88·2 (2)
O1—Si—O3	107·8 (2)	O3$^{\rm iii}$—Cu—O4	93·9 (2)
O1—Si—O4	104·0 (2)	O3$^{\rm iii}$—Cu—O4$^{\rm i}$	89·3 (2)
O2—Si—O3	116·4 (2)		
O2—Si—O4	112·8 (2)		
O3—Si—O4	109·6 (2)	O1$^{\rm viii}$—Ba—O2$^{\rm vii}$	147·3 (2)
Si—O1—Si	133·4 (1)	O1$^{\rm viii}$—Ba—O2$^{\rm ii}$	147·3 (2)
O3$^{\rm i}$—Cu—O4	103·1 (2)	O1$^{\rm viii}$—Ba—O2	75·6 (2)
O3$^{\rm i}$—Cu—O4$^{\rm i}$	65·0 (2)	O1$^{\rm viii}$—Ba—O2$^{\rm iv}$	75·6 (2)
O3$^{\rm i}$—Cu—O2$^{\rm ii}$	101·8 (2)	O1$^{\rm viii}$—Ba—O3$^{\rm v}$	76·8 (2)
O3$^{\rm i}$—Cu—O3$^{\rm iii}$	91·5 (2)	O1$^{\rm viii}$—Ba—O3$^{\rm vi}$	76·8 (2)
O2$^{\rm ii}$—Cu—O4	91·7 (2)	O2—Ba—O3$^{\rm v}$	100·5 (2)
		O2—Ba—O2$^{\rm iv}$	62·8 (2)
		O2—Ba—O3$^{\rm vi}$	150·6 (2)

Symmetry code: (i) $0·5 - x, -y, 0·5 + z$; (ii) $0·5 + x, y, 1 + 0·5 - z$; (iii) $-x, -y, 1 - z$; (iv) $x, 0·5 - y, z$; (v) $x, y, 1 + z$; (vi) $x, 0·5 - y, 1 + z$; (vii) $0·5 + x, 0·5 - y, 1·5 - z$; (viii) $-0·5 + x, y, 1·5 - z$.

Wołcyrz, Horyń, Bukowski, Łukaszewicz & Klamut, 1988; Welch, Emery & Cox, 1987). Heating of the '1-2-3' compounds results in reversible loss of oxygen, which indicates a high chemical activity. Therefore, one could expect these compounds to be not only potentially superconducting but also chemically reactive materials. In this work we present the crystal structure of the title compound, obtained as a product of the reaction between $YBa_2Cu_3O_{7-x}$ and SiO_2 in the presence of Bi_2O_3.

Experimental. Crystals were obtained in the reaction of $YBa_2Cu_3O_{7-x}$ with Bi_2O_3 taken in the molar proportion 1:1·5. The mixture was heated in a quartz tube at 1073 K for one day and quenched in air. At high temperature the mixture reacted with the tube walls. $BaCu_2Si_2O_7$ was formed as the major phase (Janczak, Kubiak & Głowiak, 1989).

A blue rectangular crystal with dimensions 0·13 × 0·15 × 0·12 mm (density not measured) was used for the data collection on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The space group was determined from Weissenberg photographs; the systematic absences $0kl$: $k + l = 2n + 1$ and $hk0$: $h = 2n + 1$ limited the possible space groups to $Pnma$ and $Pn2_1a$; $Pnma$ was used in the structure solution and refinement. The lattice parameters were refined by least-squares fit of 15 reflections in the range $15 < 2\theta < 25°$. 1988 [1967 with $|F_o| > 3\sigma(F_o)$] reflections were measured using $\theta/2\theta$ scan technique; $2\theta \leq 60°$, hkl range: h, 0 to 10; k, −18 to 18; l, 0 to 10. Two standard reflections were monitored every 50 reflections. They showed no significant intensity variation. The measured intensitites were corrected for Lorentz, polarization and absorption effects, absorption using the program *DIFABS* (Walker & Stuart, 1983), min. and max. absorption correction 0·829 and 1·246, respectively. 1039 independent reflections ($R_{\rm int} = 0·028$) were used in subsequent calculations.

The structure was solved by the Patterson method and subsequent difference Fourier syntheses (*SHELXS*86; Sheldrick, 1986). The structure was refined by the full-matrix least-squares method with

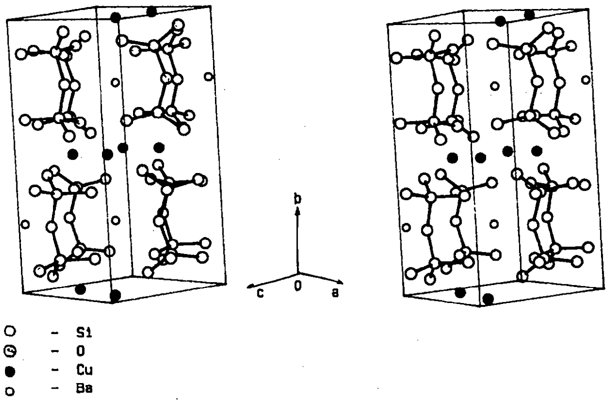

Fig. 1. A stereoview of the unit-cell contents of the title compound.

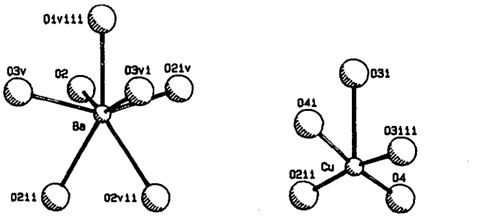

Fig. 2. Views of the copper and barium–oxygen coordination polyhedra.

anisotropic temperature factors (*SHELX76*; Sheldrick, 1976). Empirical secondary-extinction correction applied according to the formula $F_{cor} = F(1 - xF^2/\sin\theta)$ where x converged to 0·00121 (6). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 3{\cdot}6713/\sigma^2(F_o)$. Final $R = 0{\cdot}031$, $wR = 0{\cdot}037$ for 59 refined parameters, $(\Delta/\sigma)_{max} = 0{\cdot}001$. Minimum and maximum heights in the final $\Delta\rho$ map were $-1{\cdot}41$ and 2·85 e Å^{-3}, near the barium positions. Scattering factors including corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). Figures were drawn with *PLUTO*78 (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1965). All calculations were performed with an IBM PC/AT.

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1,* while details of interatomic distances and bond angles are given in Table 2. The structure of $BaCu_2Si_2O_7$ is shown in Fig. 1.

The characteristic feature of the structure is the existence of isolated anions of $[Si_2O_7]^{6-}$. The interatomic Si—O distances ranging from 1·610 (4) to 1·662 (2) Å are typical of this group and comparable with distances for other pyrosilicates (Batalieva & Patenko, 1967; Betechtin, 1950), and, especially $Ba_2CuSi_2O_7$ (Malinovskij, 1984). However, the angle Si—O—Si [133·4 (1)°] is smaller than in $Ba_2CuSi_2O_7$. This difference is a consequence of the smaller distance between barium and the bridging oxygen. The coordination polyhedra of barium and copper are also different from those in $Ba_2CuSi_2O_7$. The cations Ba^{2+} and Cu^{2+} coordinated by O atoms from $[Si_2O_7]^{6-}$ groups form irregular polyhedra (Fig. 2). The Ba^{2+} is coordinated by seven O atoms with distances ranging from 2·713 (6) to 2·932 (4) Å. The Cu^{2+} is coordinated by 4 + 1 O atoms. The nearest four O atoms and copper cation [with distances ranging from 1·926 (3) to 1·973 (3) Å] do not lie on the same plane and with the fifth oxygen [with Cu—O distance 2·789 (4) Å] the coordinated O atoms form an irregular pyramid.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52778 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Pentakis(methylammonium) Undecabromodibismuthate

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Abstract. $[NH_3(CH_3)]_5[Bi_2Br_{11}]$, $M_r = 1457{\cdot}3$, orthorhombic, $Pca2_1$, $a = 13{\cdot}405$ (3), $b = 14{\cdot}462$ (3), $c = 16{\cdot}006$ (3) Å, $V = 3102{\cdot}9$ (7) Å^3, $Z = 4$, $D_x = 3{\cdot}119$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 257{\cdot}7$ cm^{-1}, $F(000) = 2584$, $T = 297$ K, refinement based on 1976 diffractometric data with $I > 3\sigma(I)$

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