The Structure of Lead 'Orthosilicate', 2PbO.SiO2

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Abstract

Crystal structure analysis of M'-2PbO.SiO2 shows that it contains Si_4O_{12} rings and oxide ions, not SiO_4 groups. Synthetic material is monoclinic, $A2$, $a = 19\cdot43$ (1), $b = 7\cdot64$ (2), $c = 12\cdot24$ (1) Å, $\beta = 99\cdot33$ (3)°, $d_o = 7\cdot62$ (5), $d_c = 7\cdot44$ Mg m^{-3}, $Z = 16$; cell contents: $Pb_{32}(Si_4O_{12})_4O_{16}$. $R = 0\cdot086$ for 571 reflexions with k even. Disorder, indicated by streaking of reflexions with k odd, limits the accuracy of the structure determination, but the results accord well with chemical evidence for the presence of $Si_4O_{12}^{8-}$ rings. Compounds such as this, which although of composition M_xSiO_4 do not contain isolated SiO_4 groups, should not be called 'orthosilicates'. The present compound is properly termed 'basic lead metasilicate' or 'lead oxide metasilicate'.

Introduction

A number of different crystalline phases of composition 2PbO.SiO2 can be prepared by heating glass or a mixture of the oxides at various temperatures. Earlier work on these phases and the names given to them has been summarized by Smart & Glasser (1974), whose nomenclature is used here.

Chromatographic studies (Smart, 1974) with the trimethylsilylation technique of Götz & Masson (1970) show that three polymorphs, M, M' and H, all contain rings of four silicate tetrahedra (Si_4O_{12}). Götz, Hoebbel & Wieker (1975a,b), with paper chromatography, also find Si_4O_{12} rings in one modification, which appears from the method of preparation to correspond to Smart & Glasser's M type. However, in the form that apparently corresponds to M' they find a mixture of rings and polysilicate (highly condensed silicate) and in H type they find mainly polysilicate.

More recently, Calhoun, Masson & Jansen (1980) have pointed out that the short-chain linear Si_4O_{13} unit readily cyclizes to Si_4O_{12} in acid solution during the trimethylsilylation procedure. However, Dent Glasser & Lachowski (1980) have shown that such cyclization

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does not occur when the modified procedure introduced by Tamás, Sarkar & Roy (1976) is used, and have thus confirmed the presence of Si_4O_{12} rings in the compound described here.

Experimental

Crystals of the M' polymorph are readily prepared by undercooling melts of composition 2PbO.SiO2, but are invariably disordered and often twinned. The least disordered crystals were produced by slowly cooling a melt containing 63 mol% PbO from just above the liquidus (1022 K) to 1012 K and maintaining the latter temperature for a further 24 h.

From the small, platy crystals so produced, the crystal data (Table 1) were determined. However, reflexions with k odd were still relatively weak, diffuse, and somewhat streaked parallel to **a***. Selected-area electron diffraction patterns showed that a substantial amount of disorder was present; electron micrographs sometimes showed fringes, about 20 or 40 Å apart, perpendicular to **a**.

The presence of so much disorder, combined with the pronounced pseudosymmetry, complicated the structure determination, and made it difficult even to establish the correct space group. The diffraction symmetry was $2/m$; piezo-electric tests were inconclusive. The space group was assumed to be $A2$, and this led to a reasonably satisfactory refinement.

A lath-shaped crystal $0\cdot05 \times 0\cdot4 \times 0\cdot1$ mm was selected and mounted about **b**, the longest dimension. Data were collected on a Hilger & Watts Y190 linear diffractometer with Mo $K\alpha$ radiation and balanced filters; each reflexion was measured four times. Empirical absorption corrections were applied and the data

Table 1. *Crystal data for M'-2PbO.SiO2*

reduced to structure amplitudes. After averaging equivalent reflexions 1435 non-zero reflexions remained, of which 571 had k even and 864 k odd. Calculations were mainly performed on an ICL 4/50 computer with programs supplied by F. R. Ahmed of the National Research Council of Canada, and modified for use on this machine by Mr J. S. Knowles and Dr R. A. Howie of this University.

The structure was solved using the Patterson function to locate the Pb atoms. Initially only those reflexions corresponding to the pseudocell were used, to give atomic positions averaged over the two halves of the true cell. True coordinates were then assigned from the weak reflexions with k odd, with the aid of partial Patterson maps (Takeuchi, Kudoh & Haga, 1973).

The pronounced pseudosymmetry, and the diffuseness of the reflexions with k odd, caused difficulties during refinement. The final parameters (Table 2) correspond to an R of 0·086 for the 571 reflexions of the pseudocell.* Individual agreement for the weak (k odd) reflexions is much poorer, and R for these is about 0·20; this is hardly surprising in view of the difficulty of obtaining accurate intensities for them. However, the bond lengths and angles (Table 3) seem reasonable, and this, together with the chemical evidence, gives us confidence that the structure is essentially correct.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35699 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic parameters for 2PbO.SiO$_2$

Figures in parentheses give the e.s.d. corresponding to the least significant digit. The e.s.d.'s for the temperature factors are abnormally high due to the refinement problems discussed in the text.

	x	y	z	B_{iso} (Å^2)
Pb(1)	0·0904 (2)	−0·0065 (8)	0·2274 (3)	
Pb(2)	0·0904 (2)	0·5061 (9)	0·2672 (3)	
Pb(3)	0·2446 (2)	0·0024 (9)	0·1240 (3)	
Pb(4)	0·2447 (2)	0·5065 (10)	0·1227 (3)	
Si(1)	0·415 (2)	0·530 (4)	0·501 (3)	1 (1)
Si(2)	0·417 (2)	0·966 (3)	0·501 (3)	1 (1)
O(1)	0·293 (4)	0·268 (7)	0·227 (4)	1 (1)
O(2)	0·298 (4)	0·768 (7)	0·224 (4)	<1 (1)
O(3)	0·379 (4)	0·469 (6)	0·375 (6)	4 (4)
O(4)	0·376 (4)	0·025 (7)	0·378 (6)	3 (3)
O(5)	0·381 (4)	0·475 (7)	0·609 (4)	4 (4)
O(6)	0·381 (4)	0·024 (8)	0·609 (4)	4 (4)
O(7)	0·405 (4)	0·747 (7)	0·501 (4)	2 (2)
O(8)	$\frac{1}{4}$	0·487 (7)	$\frac{1}{4}$	2 (3)
O(9)	$\frac{1}{4}$	0·014 (8)	$\frac{1}{4}$	1 (2)

Anisotropic temperature factors for Pb ($\times 10^4$)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pb(1)	3 (1)	59 (8)	33 (4)	−50 (14)	−9 (3)	2 (7)
Pb(2)	3 (1)	49 (7)	20 (3)	21 (13)	−8 (3)	24 (8)
Pb(3)	10 (1)	43 (7)	19 (3)	4 (13)	−8 (3)	24 (9)
Pb(4)	9 (1)	59 (8)	20 (3)	2 (13)	−7 (3)	26 (9)

Table 3. Summary of bond lengths (Å) and angles (°)

(1) Pb—O polyhedra (see Fig. 2 for angles)

Pb(1)—O(2)	2·15 (7)		Pb(2)—O(1)	2·25 (7)
O(3)	2·56 (6)		O(3)	2·53 (6)
O(4)	2·65 (6)		O(4)	2·66 (7)
O(5)	2·66 (5)		O(5)	2·64 (5)
O(6)	2·60 (5)		O(6)	2·56 (6)
Pb(3)—O(1)	2·49 (6)		Pb(4)—O(1)	2·34 (6)
O(2)	2·33 (6)		O(1')	2·09 (6)
O(2')	2·16 (6)		O(2)	2·49 (6)
O(5)	2·69 (7)		O(6)	2·69 (7)

Bond angles at the isolated oxide ions (e.s.d.'s ~4°)

O(1)	106, 111, 118, 106, 105, 110
O(2)	124, 106, 113, 107, 104, 101

(2) Si—O tetrahedra

Si(1)—O(3)	1·64 (7)		O(3)—Si(1)—O(5)	121 (4)
O(5)	1·64 (7)		O(7)	104 (4)
O(7)	1·68 (6)		O(8)	102 (3)
O(8)	1·68 (3)		O(5)—Si(1)—O(7)	101 (3)
			O(8)	119 (3)
			O(7)—Si(1)—O(7)	109 (3)
Si(2)—O(4)	1·64 (8)		O(4)—Si(2)—O(6)	117 (4)
O(6)	1·64 (7)		O(7)	103 (4)
O(7)	1·69 (6)		O(9)	105 (3)
O(9)	1·66 (4)		O(6)—Si(2)—O(7)	101 (3)
			O(9)	119 (3)
			O(7)—Si(2)—O(9)	110 (3)

Si(1)—O(7)—Si(2)	166 (4)
Si(1)—O(8)—Si(1')	158 (3)
Si(2)—O(8)—Si(2')	155 (3)

Discussion

Fig. 1 shows the structure, somewhat idealized and viewed slightly obliquely. The Si is present in Si$_4$O$_{12}$ rings, in agreement with Smart's (1974) chromatographic results, and there are also isolated oxide ions, each coordinated tetrahedrally to four Pb atoms. The formula should therefore be written Pb$_8$O$_4$Si$_4$O$_{12}$, not Pb$_2$SiO$_4$. Bond lengths and angles (Table 3) are normal, although the positions of the light atoms are poorly determined.

The coordination of the Pb atoms is interesting (Table 3 and Fig. 2). Pb(1) and Pb(2) are bonded to O atoms that occupy five corners of a distorted octahedron, the sixth corner being empty. Pb(3) and Pb(4) are bonded to four O atoms at the basal corners of a distorted pyramid, the apex of which is vacant. Both configurations are consistent with the presence of a stereochemically active lone pair of electrons on the Pb^{2+}. In each polyhedron there is also always one bond between Pb and an oxide ion (as opposed to O atoms attached to Si) that is much shorter than the others.

The observed disorder is readily explained in terms of this structure. Fig. 3(a) shows the structure determined here, in which adjacent rows of rings are related by vectors V_1 and V_2, in regular alternation. If

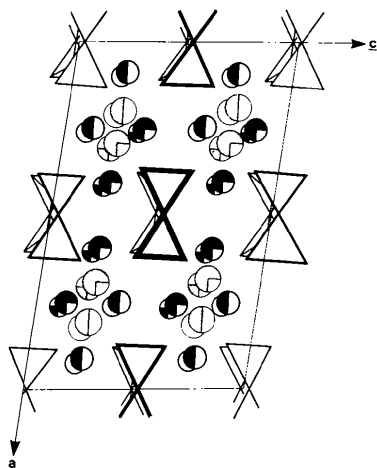Fig. 1. Idealized structure of $Pb_8O_4Si_4O_{12}$ viewed at a slight angle to **b**. Si_4O_{12} rings are shown as groups of tetrahedra; they are centred on 0, $b/4$, $b/2$ and $3b/4$ as indicated by the increasing thickness of the topmost lines. Large light circles are O atoms, smaller dark circles Pb atoms; the degree of filling of the circles shows the approximate heights (0, $b/4$, $b/2$, $3b/4$, as for the ring centres).
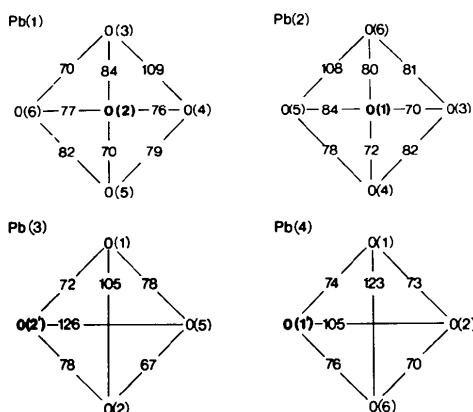

Fig. 2. Coordination of the Pb atoms, giving O—Pb—O angles (°). The O atoms connected to Pb by short bonds are indicated by bold type. E.s.d.'s of angles are $\sim 3°$.

adjacent rows were all related by V_1, the regular structure shown in Fig. 3(b) would result; this would be a triclinic modification, which has not yet been identified. Random or semi-random sequences of V_1 and V_2 give disorder corresponding to the observed streaking parallel to **a*** for reflections with k odd.

A third possibility is shown in Fig. 3(c). In this, one half of each ring in a column is translated through $b/2$ relative to the other, and the result is a continuous silicate chain parallel to **b**. This possibility is interesting in the light of the discrepancies between the chromatographic findings of Smart (1974) and of Götz et al. (1975a,b). If the amount of chain anion introduced is sensitive to the method of preparation, chromatographic study of material prepared under apparently the same conditions might yield quite different results.

In any case, one must consider whether or not such a compound should be called an 'orthosilicate', and, if not, how it should be named. If 'orthosilicate' refers to the presence of isolated SiO_4 tetrahedra (rather than to the formula), plainly these compounds are not ortho-silicates; perhaps they should be called 'basic meta-silicate', or 'metasilicate oxide'. Similar problems arise with β-Mg_2SiO_4 (Moore & Smith, 1970) and β-Co_2SiO_4 (Morimoto, Tokonami, Watanabe & Koto, 1974), both of which have the structure $M_4OSi_2O_7$, which might be termed a 'basic pyrosilicate'. Where the structure of such compounds is not known, the use of oxide formulae ($2MO.SiO_2$) is preferable to writing M_2SiO_4. Although most compounds of this ratio do, in fact, contain orthosilicate groups, the above exceptions show that one ought not to assume this is so.

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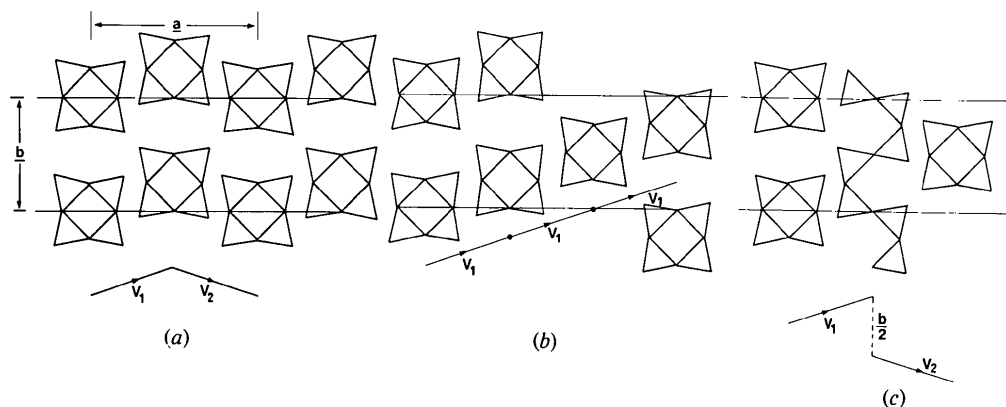DENT GLASSER, L. S. & LACHOWSKI, E. E. (1980). J. Chem. Soc. Chem. Commun. pp. 973–974.

Fig. 3. Possible arrangements of a single silicate layer in the *ab* plane. (*a*) The ordered sequence observed in the crystal used for the structure determination. (*b*) Possible triclinic variant. (*c*) Variant with mixed rings and chains.

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Zirconolite, CaZr$_x$Ti$_{3-x}$O$_7$; Structure Refinements for Near-End-Member Compositions with x = 0·85 and 1·30

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Abstract

Zirconolite, nominally CaZrTi$_2$O$_7$, exhibits a wide variation in its [Ti]/[Zr] ratio as a function of preparation temperature. Single crystals with compositions close to the solid-solution limits, i.e. Ca$_{0.993}$Zr$_{1.304}$Ti$_{1.700}$O$_7$, [Ti]/[Zr] = 1·31, and Ca$_{0.961}$Zr$_{0.850}$Ti$_{2.169}$O$_7$, [Ti]/[Zr] = 2·55, have been prepared and their structures refined with data collected on an automatic diffractometer using Mo Kα radiation. Cell parameters (space group C2/c, Z = 8) are: a = 12·445 (4), b = 7·288 (2), c = 11·487 (3) Å, β = 100·39 (1)° and a = 12·444 (2), b = 7·266 (1), c = 11·341 (2) Å, β = 100·59 (1)°, respectively. Atomic positions, anisotropic temperature factors and metal-atom occupancies were refined by full-matrix least squares to yield R = 0·045 and 0·054 (R$_w$ = 0·055 and 0·046) for 2011 and 1126 independent structure factors. The results generally support an earlier powder X-ray diffraction structure determination, but are more precise and reveal new structural features. The structure has (001) sheets of Ti(Zr)O$_6$ octahedra sharing corners in the three- and six-membered-ring arrangement found in {110} planes in pyrochlore. These sheets

are interleaved by planes containing Ca and Zr(Ti) atoms ordered into alternating [110]-type rows with Ca and Zr(Ti) eight- and seven-coordinated by O respectively. A Ti atom close to the centre of a six-membered ring of octahedra is not in trigonal-prismatic coordination by O as originally proposed, but instead this atom randomly occupies one of a pair of sites which are ~0·6 Å apart for [Ti]/[Zr] = 1·31 and 0·8 Å apart for [Ti]/[Zr] = 2·55, so as to achieve fivefold trigonal-bipyramidal coordination by O. This unusual behaviour as well as structural aspects associated with the change of [Ti]/[Zr] ratio in zirconolite are discussed.

Introduction

In the CaO–ZrO$_2$–TiO$_2$ system, the existence of a stable phase with the molar ratio 1:1:2, i.e. CaZrTi$_2$O$_7$, was first established by Coughanour, Roth, Marzullo & Sennet (1955).

From a single-crystal X-ray diffraction study on CaZrTi$_2$O$_7$, Pyatenko & Pudovkina (1964) proposed that it was an anion-deficient superstructure phase