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Time-of-Flight Powder Neutron Diffraction Study of the Structure of Ba₂PbO₄

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Abstract. Dibarium lead(IV) tetraoxide, $M_r = 545.88$, tetragonal, $I4/mmm$, $Z = 2$. $T = 5$ K: $a = 4.29650$ (2), $c = 13.2285$ (1) Å, $V = 244.196$ (4) Å³, $D_x = 7.424$ g cm⁻³. $T = 298$ K: $a = 4.30241$ (1), $c = 13.26070$ (5) Å, $V = 245.466$ (2) Å³, $D_x = 7.386$ g cm⁻³. Rietveld refinement using time-of-flight powder neutron diffraction data [TOF 30000–103000 μs, 184 contributing reflections, 5 K; TOF 35000–110000 μs, 122 contributing reflections, 298 K] resulted in $R_{wp} = 2.6$ ($R_{exp} = 2.1$), $\chi^2 = 1.5$ at 5 K and $R_{wp} = 5.1$ ($R_{exp} = 3.0$), $\chi^2 = 3.0$ at 298 K. Our results confirm the room-temperature structure determined earlier by X-ray work and show the lack of structural distortions down to 5 K. They also permit a very precise determination of the geometry of the PbO₆ octahedra, showing that the tetragonal distortion had been overestimated before by at least a factor of 10. The implication of this result for recent band-structure calculations is stressed.

Introduction. The barium lead bismuthate system was one of the first superconducting oxide systems with $T_c = 12$ K for BaPb_{0.75}Bi_{0.25}O₃ (Sleight, Gillson & Bierstedt, 1975). The parent oxide BaPbO₃ is a black perovskite whose semimetallic properties are due to overlap of the Pb 6s band with the non-bonding O 2p states, arising from the 2p orbitals perpendicular to the Pb—O bonds (Mattheiss & Hamann, 1982). BaPbO₃ may be considered as the $n = \infty$ member of the homologous series of oxides Ba _{$n+1$} Pb _{n} O _{$3n+1$} . The $n = 1$ member of this series Ba₂PbO₄ is known (Weiss

& Faivre, 1959) and a powder X-ray determination of the crystal structure indicated that it adopted the K₂NiF₄ structure with an unusual compressed geometry for the PbO₆ octahedron [$r(\text{Pb—O}_{eq}) = 2.14$, $r(\text{Pb—O}_{ax}) = 2.06$ Å] (Weiss & Faivre, 1959). In view of this and the possible analogies with the layered cuprate systems, such as La₂CuO₄, characterized by low symmetry distortions, a high-resolution powder neutron diffraction study of Ba₂PbO₄ at ambient and low temperatures was undertaken.

Experimental. Preparative techniques based on solid-state reactions of PbO or PbO₂ with BaCO₃ at high temperatures were found to be unsatisfactory, leading to the loss of PbO and phase separation. A low-temperature preparative route using the citrate sol-gel method (Rosseinsky, Prassides & Day, 1989) often led to the presence of BaPbO₃ as an impurity. High purity samples were prepared by an adaptation of the method of Vidyasagar, Gopalakrishnan & Rao (1985). Stoichiometric quantities of barium and lead nitrates are dissolved in the minimum quantity of distilled water. The nitrate solution is added dropwise into rapidly stirred ice-cold concentrated nitric acid, and a white precipitate forms immediately. The Ba₂Pb(NO₃)₆ precipitate is filtered, dried at 393 K overnight and decomposed at 1273 K in air in an alumina crucible for 12 h. The product is a red-orange solid and was characterized by powder X-ray diffraction.

Powder neutron data were then collected at both ambient temperature and 5 K at the 1 m position at the High-Resolution Powder Diffractometer

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Table 1. Neutron diffraction data collection and analysis

Diffractometer	HRPD, Rutherford Appleton Laboratory
Data range (μs)	30 000–130 000 collected; 30 000–103 000 at 5 K (184 contributing reflections) and 35 000–110 000 at 298 K (122 contributing reflections) analysed
Sample can	Flat plate aluminium can with thin vanadium windows
Scattering lengths (fm)	Ba 5.270; Pb 9.401; O 5.805
Refinement	Rietveld technique; program <i>TF12LS</i> (David, Ibberson & Wilson, 1988; Brown & Matthewmann, 1987)
Background	Five-term Chebychev polynomial
Function minimized	$\sum w_i [y_i(\text{obs.}) - y_i(\text{calc.})]^2$; $w_i = 1/\sigma_i^2$
Peak shape	Voigt convoluted with a double exponential decay (David, Akporiaye, Ibberson & Wilson, 1988)

Table 2. Coordinates and equivalent isotropic temperature factors for Ba₂PbO₄

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>T</i> (K)	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Ba	4(e)	5	0.0	0.0	0.3554 (1)
	298	0.0	0.0	0.3551 (1)	0.94 (5)
Pb	2(a)	5	0.0	0.0	0.12 (4)
	298	0.0	0.0	0.0	0.31 (5)
O(1)	4(e)	5	0.0	0.0	0.1619 (1)
	298	0.0	0.0	0.1618 (1)	1.39 (5)
O(2)	4(c)	5	0.0	0.5	0.0
	298	0.0	0.5	0.0	0.56 (5)
					0.96 (5)

(HRPD) at ISIS (Rutherford Appleton Laboratory). The data were normalized to the incident beam, binned in groups of four and refined using the *TF12LS* code (David, Ibberson & Wilson, 1988). Details of the data collection and structure refinement are given in Table 1. The five parameters used to describe the background were included as variables in the least-squares procedure. The exponential contributions to the peak-shape function were fixed by instrumental characteristics and only the parameters of the Voigt function were refined.

Discussion. The initial structural model used was that deduced from powder X-ray diffraction by Weiss & Faivre (1959). All the reflections in the room-temperature neutron diffraction pattern could be indexed on the *I4/mmm* K₂NiF₄ cell, and no peaks attributable to impurity phases were observed. The cell parameters and all coordinates and isotropic temperature factors were refined, the final values being given in Table 2. Refinement of anisotropic temperature factors at both oxygen sites did not produce a significant improvement over the isotropic description. The refinement gave $R_{wp} = 5.1$, R_{wp} (background subtracted) = 13.0 [$R_{exp} = 3.0$, R_{exp} (background subtracted) = 7.5, $N - P + C = 2200$] and a goodness-of-fit index $\chi^2 = (R_{wp}/R_{exp})^2 = 3.0$ [R factors as defined by Rietveld (1969), N = number of observations, P = number of parameters, C = number of constraints]. The low-temperature data, before binning in groups of four, were carefully examined for evidence of reduction of symmetry due to a tilting transition. The technique employed was to focus only the six inner rings of the detector bank of the HRPD diffractometer. This gives a resolution improvement from $\Delta d/d \sim 8 \times 10^{-4}$ (1 m position) to $\sim 5 \times 10^{-4}$ (equivalent to a 2 m sample position). No evidence of any peak splittings or relative broadenings was apparent even at this improved resolution. The refined room-temperature structure was then used as a starting model and refinement of the cell

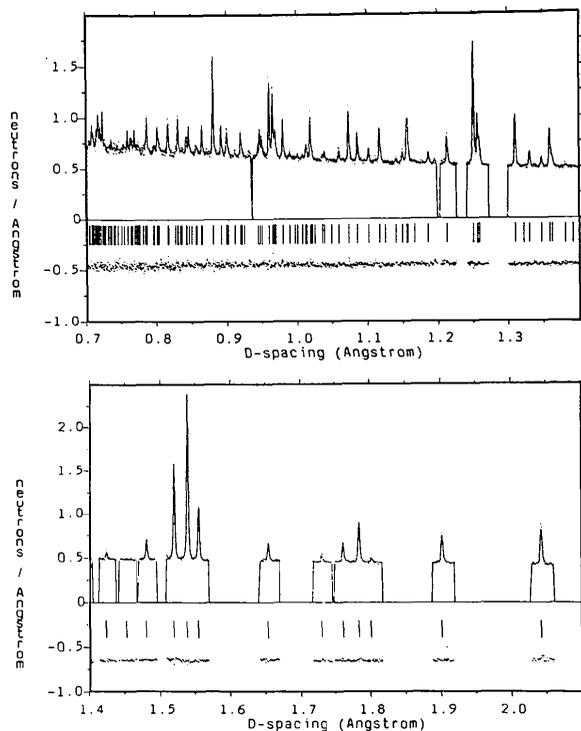


Fig. 1. The observed (dots), calculated (line) and difference profiles from the time-of-flight powder neutron diffraction study of Ba₂PbO₄ at 5 K. Reflection positions are marked by vertical lines.

parameters and all coordinates and isotropic temperature factors led to $R_{wp} = 2.6$, R_{wp} (background subtracted) = 14.0 [$R_{exp} = 2.1$, R_{exp} (background subtracted) = 11.4, $N - P + C = 2430$] and a goodness-of-fit index $\chi^2 = 1.5$. The observed, calculated and difference profiles, plotted on the same scale, are shown in Fig. 1.* The final values of the refined parameters are also given in Table 2.

* Lists of observed and calculated profile intensities for Ba₂PbO₄ at 298 and 5 K have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54324 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Selected bond lengths for Ba_2PbO_4 at room temperature and 5 K are presented in Table 3. The coordination geometry of lead is similar to the one in BaPbO_3 , though more regular in the layered compound. At room temperature, there are three pairs of $\text{Pb}-\text{O}$ bonds with lengths equal to 2.1444 (6), 2.152 (1) and 2.157 (1) Å in BaPbO_3 (Ritter, Ihringer, Maichle, Prandl, Hoser & Hewat, 1989). In Ba_2PbO_4 , we find two $\text{Pb}-\text{O}$ bonds equal to 2.145 (2) and four equal to 2.1512 Å. However, the PbO_6 octahedra in the layered compound (Fig. 2) are not tilted unlike those in the three-dimensional perovskite, BaPbO_3 (Ritter, Ihringer, Maichle, Prandl, Hoser & Hewat, 1989). This reflects the rigidity of the intervening rock salt (Ba_2O_2) layers in the 2D perovskite. Furthermore, the tolerance factor (Poix, 1980) for the K_2NiF_4 -type structure, defined by $t = R_{\text{Ba}-\text{O}}/2^{1/2}R_{\text{Pb}-\text{O}}$, where $R_{\text{Ba}-\text{O}}$ and $R_{\text{Pb}-\text{O}}$ are the sums of the ionic radii for Ba and Pb cations and the oxide ion in nine and sixfold coordination, respectively, is equal to 1.02. This shows the excellent matching of lead-oxygen and barium-oxygen bond lengths, resulting in a stress-free PbO_2 planar network. This is in contrast to the highly compressed CuO_2 layers in the 2D cuprates where severe mismatch between the copper layers and the lanthanide bilayers leads to the existence of tilting distortions of the CuO_2 layers (Rosseinsky, Prassides & Day, 1989).

It is also apparent from Table 3 that the PbO_6 octahedra possess a compressed geometry with the two axial bond distances shorter than the four equatorial ones. This compressed geometry was identified in the original powder X-ray study but the magnitude of the compression was overestimated ($r_{\text{ax}} - r_{\text{eq}} = 0.08$ compared to 0.006 Å in the present study). This result is very significant since band-structure calculations have recently shown that the shortened axial $\text{Pb}-\text{O}$ bond distance is instrumental in opening a band gap of 1.7 eV in Ba_2PbO_4 (Mattheiss, 1990). BaPbO_3 , on the other hand, is metallic (Mattheiss & Hamann, 1982) with the $\text{Pb}(6s)$ band lying ~ 2 eV below the $\text{O}(2p)$ manifold, whereas the existence of the gap in the layered Ba_2PbO_4 compound is attributed to antibonding $sp\sigma$ interactions between the $\text{Pb}(6s)$ and axial $\text{O}(2p_z)$ orbitals. The strength of this antibonding interaction is strongly related to the $\text{Pb}-\text{O}_{\text{ax}}$ bond lengths and consequently to the compressed or elongated geometry of the PbO_6 octahedra. The over-short axial $\text{Pb}-\text{O}$ distance in the earlier study has led to overemphasizing the importance of the interaction by the calculation. Indeed, preliminary extended Hückel band-structure calculations using the correct geometry lead to a significant reduction of the gap as the antibonding interaction weakens upon elongation (Green, Johnston & Prassides, 1991). Similar

Table 3. Selected interionic distances (Å) for Ba_2PbO_4

	5 K	298 K
Ba—O(1) × 1	2.561 (3)	2.563 (3)
—O(1) × 4	3.047 (1)	3.050 (1)
—O(2) × 4	2.876 (2)	2.885 (2)
Pb—O(1) × 2	2.141 (2)	2.145 (2)
—O(2) × 4	2.14825 (1)	2.15121 (1)
O(1)—O(2) × 4	3.033 (2)	3.038 (2)
O(2)—O(2) × 4	3.03808 (1)	3.04227 (1)

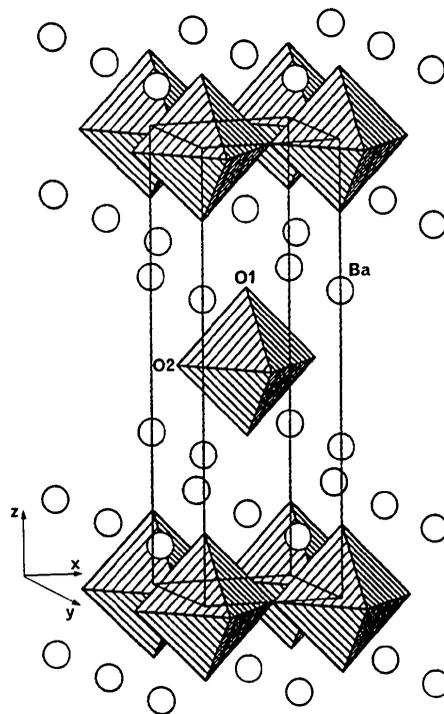


Fig. 2. The crystal structure of Ba_2PbO_4 . The shaded octahedra represent PbO_6 units [O(1) and O(2) label the axial and equatorial oxygen ions, respectively] and the open circles Ba^{2+} cations.

conclusions are also reached by LMT0 calculations whence a band gap of 0.6 eV is calculated for the correct geometry (Temmerman & Rosseinsky, 1991).

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Structure of Pentasilver(I) Dicopper(II) Mononitrate Tetraselenite(IV)

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Abstract. Ag₅Cu₂(NO₃)(SeO₃)₄, $M_r = 1236.26$, triclinic, $P\bar{1}$, $a = 5.148$ (2), $b = 7.050$ (2), $c = 10.540$ (3) Å, $\alpha = 73.09$ (1), $\beta = 89.08$ (1), $\gamma = 88.50$ (1)°, $V = 365.85$ Å³, $Z = 1$, $D_x = 5.61$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 18.6$ mm⁻¹, $F(000) = 556$, room temperature, $R(F) = 0.045$ for 3026 independent reflections with $F_o > 3\sigma(F_o)$ and 143 variables. Elongated tetragonal dipyramids Cu^{[4+2]O₆} and SeO₃ groups are corner connected to form layers in (010). Irregularly coordinated Ag atoms with Ag—O ≥ 2.202 Å join them to form a three-dimensional network. The orientation of the nitrate group is disordered with the N atom formally on $\bar{1}$.

Introduction. Syntheses within the system Ag₂O—CuO—SeO₂ and nitric solvents produced the new compound Ag₅Cu₂(NO₃)(SeO₃)₄. Copper(II)-nitrate-selenite(IV) salts are known from the two compounds PbCu₃(OH)(NO₃)(SeO₃)₃·½H₂O and Pb₂Cu₃O₂(NO₃)₂(SeO₃)₂ (Effenberger, 1986). In connection with systematic studies of the stereochemistry of Cu^{II} with O atoms the crystal structure of the title compound was determined.

Experimental. For synthesis 2 g of an equimolar mixture of Cu(OH)₂, SeO₂ and AgNO₃ were heated under hydrothermal conditions in a Teflon-lined autoclave (~6 ml capacity, $T = 503$ K, 80% degree of filling, reaction time 2 d). The ratio of primary products can be varied over a wide range yielding the same reaction products but in different amounts. The

title compound forms emerald green, multifaceted crystals, typically 0.1 to 0.5 mm in diameter, which were easily separated from the accompanying reaction products (Ag₂SeO₃ and CuSeO₃·2H₂O) by hand picking.

Single-crystal X-ray Weissenberg photographs showed a metrically triclinic cell. Data collection from a 0.16 × 0.23 × 0.39 mm single crystal, crystallographic forms {010}, {011}, {01 $\bar{1}$ }, {001}, {210}, {211} and {021}; Stoe-AED2 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from 75 reflections with $44.3 \leq 2\theta \leq 55.0^\circ$; $2\theta/\omega$ -scan mode, step width of 1.44° increased for α_1 - α_2 dispersion, 0.24° on each side for background correction, scan speed 1.2 to 3.6° per min; three standard reflections, intensity drop 14% during data collection; 7021 reflections in the range $4.0 \leq 2\theta \leq 70.0^\circ$ ($h: -8 \rightarrow 8$, $k: -11 \rightarrow 11$, $l: -17 \rightarrow 17$), 3221 reflections in unique data set [$R_{\text{int}}(F^2) = 0.060$], 3026 reflections with $F_o > 3\sigma(F_o)$ were used for structure refinement, absorption correction according to crystal shape (Gaussian integration: transmission factors from 0.021 to 0.162), corrections for Lorentz and polarization effects. Complex neutral atomic scattering functions (*International Tables for X-ray Crystallography*, 1974, Vol. IV). All calculations were performed with the program system STRUCSY on an ECLIPSE S140 (Data General). Some of the atomic coordinates of the Ag, Cu and Se atoms were located by direct methods, the others by subsequent Fourier and difference Fourier summations. The nitrate group shows an