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A Neutron Powder Diffraction Study of the Phase $Sr_5Pb_3CuO_{12}$

T. G. N. BABU AND C. GREAVES[1]

Superconductivity Research Group, School of Chemistry, University of Birmingham, Birmingham B15 2TT, England

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The phase of composition $Sr_5Pb_3CuO_{12}$ has been examined using time-of-flight neutron powder diffraction techniques. Structure refinement, which was based on the hexagonal space group $P\bar{6}2m$ (a = 10.1089(6) Å; c = 3.5585(2) Å), supported previously reported X-ray diffraction results for the positions and coordination of the Sr and Pb atoms. However, $P\bar{6}2m$ does not accurately represent the local symmetry of the Cu atoms and their coordinating O atoms, and a high degree of disorder was indicated. Based on the average unit cell, the Cu atoms appear to be 4-coordinate with a stereochemistry which may be described as a flattened tetrahedron.

Introduction

Syntheses of mixed metal oxides containing strontium, lead, and copper, for example the superconductor $(Bi/Pb)_2Sr_2Ca_2Cu_3O_{10}$ (*1, 2*) and related materials, often result in the formation of an insulating impurity or intermediate phase. This material, which has the approximate composition $Sr_5Pb_3CuO_{12}$ (*3*), was shown by X-ray single crystal diffraction to be hexagonal with chains of edge-shared PbO_6 octahedra (*3*). Its structure differs from that of Sr_2PbO_4, which is orthorhombic (*4*), in the relative orientations of the octahedra in adjacent chains. In this respect, it is structurally more closely related to Ca_2IrO_4 (*5*). Structure refinement implied the composition $Sr_{4.79}Pb_{3.21}Cu_{0.66}O_{11.12}$, and the proposed structure (space group $P\bar{6}2m$) has a high degree of disorder associated with the Cu atoms, since the two sites proposed for the Cu atoms and the coordinating O1 atoms are all partially occupied, as shown in Table I.

Although many of the structural features revealed by the X-ray study are clearly correct, some aspects appear unreliable. The Cu1 and Cu2 sites are each bonded to three O1 atoms at distances (1.77 Å and 2.20 Å, respectively) which appear too short or too long for Cu–O bonds, irrespective of the Cu oxidation state. It was proposed that a fourth O atom, at 1.71 Å, completes a tetrahedron around each Cu site and is situated either on a Cu1 site (to complete the Cu2 coordination) or a Cu2 site (to bond to Cu1). However, such a structure involving the partial occupancy of Cu1 and Cu2 sites by both Cu and O seems energetically unlikely due to electrostatic considerations. The presence of an O atom at either Cu1 or Cu2 would also result in unacceptably short O–O distances (1.77 Å and 2.20 Å) to O1 positions, which would effectively preclude the

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[1] To whom correspondence should be addressed.

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TABLE I

STRUCTURAL PARAMETERS REPORTED FOR $Sr_{4.79}Pb_{3.21}Cu_{0.66}O_{11.12}$ (*3*)

Atom	Position	*x*	*y*	*z*	Unit cell occupancy
Pb1	3*f*	0.3368(1)	0	0	3
Sr1	2*d*	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	2
Sr2	3*g*	0.7005(5)	0	$\frac{1}{2}$	2.79(4)
Pb2	3*g*	0.7005(5)	0	$\frac{1}{2}$	0.21(4)
Cu1	2*e*	0	0	0.371(8)	0.39(4)
Cu2	2*e*	0	0	0.112(9)	0.27(3)
O1	3*g*	0.170(4)	0	$\frac{1}{2}$	2.1(3)
O2	3*g*	0.4604(20)	0	$\frac{1}{2}$	3
O3	6*j*	0.2412(16)	0.4446(21)	0	6

Note. a = 10.072(3) Å, c = 3.542(3) Å; $P\bar{6}2m$.

occupation of three O1 sites for every Cu atom present in the structure. Although partial occupancy of O1 was suggested, the dual requirements of three O1 oxygen atoms for each Cu (to provide 4-coordination) and also three O1 vacancies for each Cu are mutually exclusive. Given that the dominant scattering of Pb atoms in such an X-ray diffraction examination necessarily results in somewhat imprecise information concerning the oxygen sublattice, a time-of-flight neutron powder diffraction study has been performed in order to clarify the above discrepancies and to establish the coordination details for Cu in this phase.

Experimental

Samples were prepared from intimate mixtures of high purity $SrCO_3$, PbO and CuO by heating at 800°C for two periods of 16 hr in air, with a thorough grinding between the heat treatments. X-ray powder diffraction traces (Philips PW 1050/70 using Cu*Kα* radiation) were consistent with a single phase product for Sr : Pb : Cu cation ratios of 5 : 3 : 1 and 3 : 2 : 1. Density measurements were performed using a displaced liquid (CCl_4) technique and a specific gravity bottle of nominal volume 10 cm^3. The immersed samples were evacuated to minimize the effects of occluded air.

Ambient temperature time-of-flight neutron diffraction data were collected from samples with Sr : Pb : Cu ratios of 3 : 2 : 1 and 5 : 3 : 1 (ca. 5 g in a vanadium container) using the diffractometer POLARIS at ISIS, Rutherford Appleton Laboratory. Structure refinement (for $0.57 < d < 1.82$ Å) was based on the Rietveld method using the Rutherford Appleton program TF15LS based on the Cambridge Crystallography Subroutine Library (*6, 7*). Neutron scattering lengths used were 0.702 (Sr), 0.9401 (Pb), 0.7718 (Cu), and 0.5805 (O), all $\times 10^{-12}$ cm.

Results and Discussion

The fact that the samples with overall compositions $Sr_5Pb_3CuO_x$ and $Sr_3Pb_2CuO_x$ both appeared to have negligible crystalline impurities suggested that the hexagonal phase under investigation is subject to some degree of cation substitution. This is supported by the refined cell parameters for the above compositions, which were slightly different: a = 10.1315(7), c = 3.5604(2) Å and a = 10.1089(6), c = 3.5585(2) Å, respectively (figures in parentheses are estimated standard deviations). In the previous X-ray diffraction study (*3*), it was also found that some Pb atoms were located on Sr sites, see Table I. The neutron diffraction refinements gave very similar results for both compositions, but since the data set for $Sr_3Pb_2CuO_x$ produced better agreement between observed and calculated profiles due to the absence of significant impurity peaks, the primary discussion of the structure will relate to this material. The determined density, 6.88(5) g cm^{-3}, is consistent with a unit cell containing three Pb atoms since the probable unit cell contents of $Sr_5Pb_3CuO_{12}$ and $Sr_{4.5}Pb_3Cu_{1.5}O_{12}$ give D_x values of 6.94 and 6.87 g cm^{-3}.

The structural parameters and space group given in Table I (*3*) were adopted as an initial structural model for refinement, except that Pb substitution on the Sr2 sites was not considered at this stage, and the Cu atoms and their coordinating O1 atoms were excluded. A difference Fourier synthesis was performed using observed intensities for overlapping peaks calculated from a deconvolution in accordance with the ratio of calculated peak intensities. Although such a method is biased toward the structural model adopted, it can still provide a very useful indication of many structural deficiencies. The principal feature on the Fourier map was a large peak, at around (0,0,0.37), corresponding to the Cu1 position of Table I. At no stage, however, was a peak corresponding to Cu2 observed. Refinement after including Cu at this position indicated the site occupancy to be 0.5, the maximum allowed in this space group, since the equivalent positions at (0,0,0.37) and (0,0,0.63) are separated by less than 1 Å.

A difference synthesis at this stage now clearly revealed two oxygen positions coordinated to the Cu, one consistent with O1 in Table I and the other displaced off the mirror plane at $z = \frac{1}{2}$ to around $z = 0.35$. Refinement of the unit cell occupancies of these two sites indicated a total of one atom of each type per unit cell. Given that angular 2-coordinate Cu is unlikely (the O–Cu–O angle would be around 120°), extra coordinated O atoms were sought by obtaining a new difference map. This suggested the possibility of nuclear scattering at approximately (0.95,0,0.9) and equivalent positions. This location being nearly midway between two possible Cu sites, (0,0,0.37) and (0,0,−0.37), suggested the likelihood that this atom acts as a link between two corner-shared CuO_4 polyhedra. In accordance with this model, which corresponds to a unit cell composition of $Sr_5Pb_3CuO_{12}$, very good agreement was obtained between observed and calculated diffraction profiles, see Fig. 1. In the final refinement, all unit cell occupancies were fixed, since relaxation of this constraint resulted in no significant shifts. Since a high isotropic temperature factor was obtained for Cu, anisotropic vibrations were allowed for this atom. The results of the refinement are presented in Table II, and metal–oxygen distances in Table III. A slightly simplified representation of the structure is shown in Fig. 2.

The high temperature factors observed for the Cu atoms suggest that the special position does not accurately reflect the true position, and this is reflected in imprecise values for the Cu–O distances, see Table III. The very short Cu–O4 distance is, however, worthy of note. An alternative model allowed the Cu atoms to move off this site, and an equally satisfactory refinement was obtained with Cu at (0.982(5),0,0.368(5)) and an isotropic temperature factor, 3.0(6) $Å^2$. If it is assumed that the Cu is shifted away from O4, then a more reasonable set of Cu–O distances is obtained, see Table III. Examination of O–O distances eliminates most possible arrangements for the occupation of the O atoms in the O1, O4, and O5 sites coordinating to Cu. For example, for an O5 atom at (0.952,0,0.879), a neighboring O1 atom must occupy (0.183,0,$\frac{1}{2}$) rather than the equivalent positions, (0,0.183,$\frac{1}{2}$) and (−0.183,−0.183,$\frac{1}{2}$), to avoid unacceptably short O–O distances of 2.14 Å. In this way, it is possible to determine the likely oxygen environment around the Cu sites and the way the Cu polyhedra are linked. The proposed linking of the CuO_4 polyhedra to form chains along [001] is shown in Fig. 3. In this model it should be noted that all O–O distances are reasonable (ca. 2.7 Å or greater) except for a very short O5–O4 distance of 2.40(4) Å. This may indicate that the description is only an approximation to the real structure in the vicinity of the Cu sites. This is to be expected since we are forced to deduce the local structure from the average unit cell obtained from a high symmetry space group, which is clearly not appropriate for the Cu polyhedra. However, short O–O distances do occur where bond-

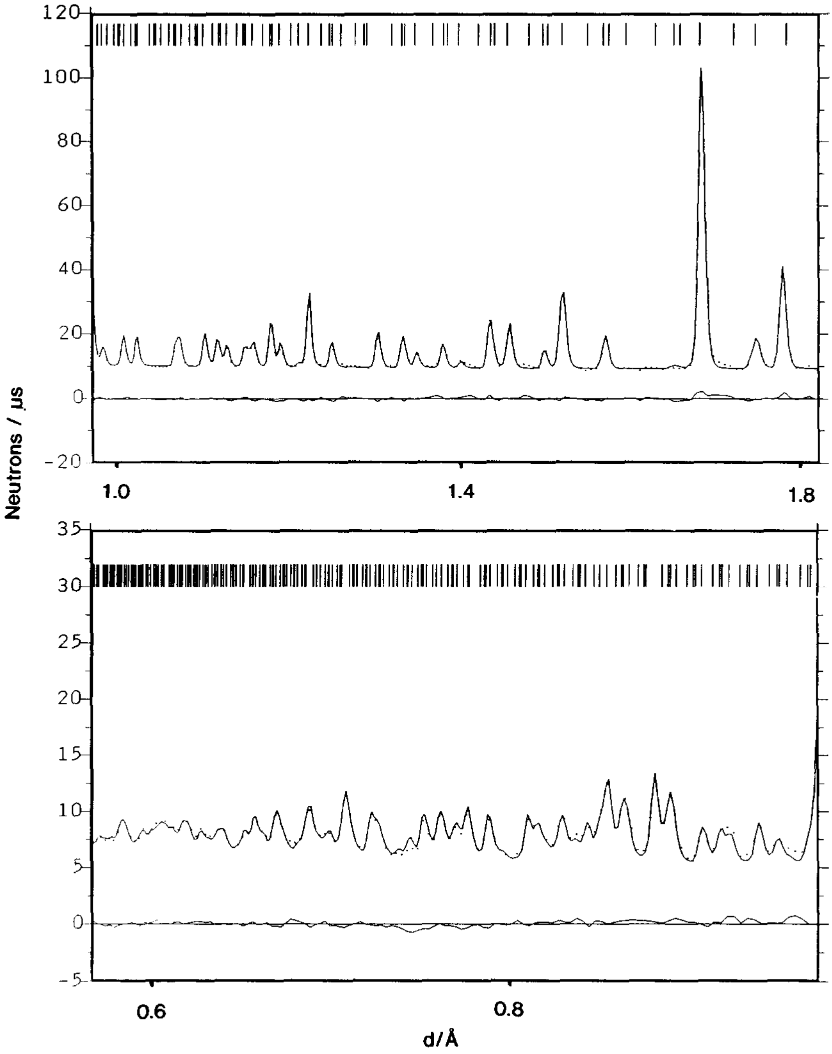

FIG. 1. Observed (dots), calculated (solid line), and difference neutron diffraction profiles for $Sr_5Pb_3CuO_{12}$. Reflection positions are marked at the top of the figure.

ing has a high degree of covalence, especially where the O atoms constitute a common edge between linked polyhedra. Indeed, in the structurally related material Ca_2IrO_4 (5), an O–O distance of 2.48(2) Å is reported linking two IrO_6 octahedra. In the present material, the short O4–O5 distance forms a common edge between the Cu and Sr2 polyhedra.

The proposed structure is seen to be very similar to that previously suggested (*3*), except for the distribution of the Cu atoms and their stereochemistry. It is interesting to note that the Cu2 site suggested by the X-ray diffraction study, see Table I, was only partially occupied, and is very close to the O5 position found in the present study ((0,0,0.888) compared with (0.952,0,0.879)).

TABLE II

STRUCTURAL PARAMETERS OF $Sr_5Pb_3CuO_{12}$ REFINED FROM NEUTRON DIFFRACTION DATA

Atom	Position	x	y	z	B/B_{eq} (Å^2)	Unit cell occupancy
Pb	3f	0.3375(3)	0	0	0.71(4)	3
Sr1	2d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	0.61(8)	2
Sr2	3g	0.7024(4)	0	$\frac{1}{2}$	0.80(5)	3
Cu	2e	0	0	0.368(4)	3.9(4)[a]	1
O1	3g	0.183(1)	0	$\frac{1}{2}$	0.7(2)	1
O2	3g	0.4619(5)	0	$\frac{1}{2}$	1.13(8)	3
O3	6j	0.2392(4)	0.4484(5)	0	1.08(4)	6
O4	6i	0.161(2)	0	0.341(5)	0.9(3)	1
O5	6i	0.952(2)	0	0.879(5)	1.2(3)	1

[a] Anisotropic thermal parameters (Å^2) defined by $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$: $B_{11} = B_{22} = 4.7(4)$, $B_{33} = 2.3(5)$, $B_{12} = 2.4(2)$, $B_{13} = B_{23} = 0$; $a = 10.1089(7)$, $c = 3.5585(2)$ Å, $P\bar{6}2m$; $R_{wp} = 4.17\%$; $R_{exp} = 2.87\%$; $R_I = 5.94\%$.

It is therefore likely that this site was previously mistakenly assigned to Cu with a unit cell occupancy of 0.27 rather than oxygen with an occupancy of 1.0. It is also relevant to note that the O1 site occupancy previously reported (0.71(9)) is consistent with the present study, in which this site has been split to give O1 and O4 positions. Taken together, their site occupancies would be equivalent to an O1 occupancy of $\frac{2}{3}$.

The Cu stereochemistry, see Fig. 3, is unusual and can be described as a tetrahedron, which has been flattened along a $\bar{4}$ axis. Such a flattening, which results in an increase in two of the tetrahedral angles (109°) and a decrease in four, is consistent with a Jahn–Teller distortion, but in this case the effect is very large. In $CuCr_2O_4$, the tetrahedral Cu^{2+} ions have four O atoms at 1.94 Å, with four O–Cu–O angles of 103° and two of 122° (*8*). In the present study, approximate O–Cu–O angles are 165°, 120°, 102°, 96°, 91°, and 86°, which are indicative of a more severe distortion toward the lim-

TABLE III

METAL–OXYGEN BOND DISTANCES (Å)

Pb–O3 2.096(2) [×2]	Sr2–O5 2.86(2) [×2]
–O1 2.37(2) [×2]	–O3 2.596(3) [×4]
–O4 2.16(2) [×2]	–O1 2.63(2) [×2]
–O2 2.179(4) [×2]	–O4 2.67(2) [×4]
	–O2 2.431(6)
Sr1–O3 2.615(3) [×6]	Cu–O1 1.9(2)[a] 1.83(4)[b]
–O2 2.943(3) [×3]	–O4 1.6(2)[a] 1.81(4)[b]
	–O5 1.8(2)[a] 1.77(4)[b]
	–O5 1.9(2)[a] 1.91(4)[b]

[a] For Cu at (0,0,0.368) with anisotropic thermal parameters.

[b] For Cu at (0.982,0,0.368) with isotropic thermal parameter (3.0(6) Å^2).

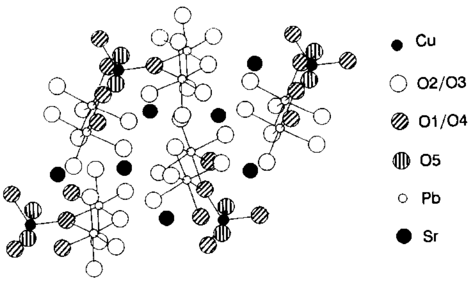

FIG. 2. The structure of $Sr_5Pb_3CuO_{12}$ viewed approximately along [001]. For simplicity, a common site for the O1 and O4 positions has been assumed, and of the three sites of this type bonded to a given Cu atom, one will be vacant. Similarly the O5 atoms are positioned in an "average" location at (0,0,0.879).

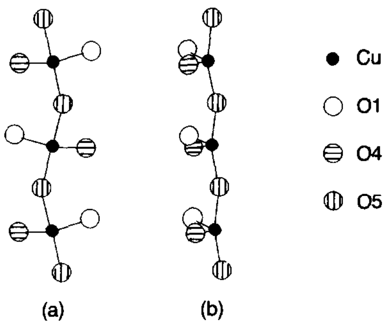

FIG. 3. The probable coordination around Cu demonstrating the formation of chains along [001]. The chains are viewed (a) along [100], and (b) along the perpendicular direction [120].

iting 4-coordinate planar stereochemistry with angles of around 90° and 180°. The Cu–O bond distances in $Sr_5Pb_3CuO_{12}$ are also significantly shorter than in $CuCr_2O_4$ and are similar to those of Cu^{3+} oxides such as $NaCuO_2$ and $KCuO_2$ (*9*), which have average distances of about 1.83 Å. It is therefore considered that the Cu sites are primarily occupied by Cu^{3+} ions, which are known to prefer planar 4-coordinate sites. By comparison with other well characterized materials, bond length criteria (*10*) can provide a guide to the probable oxidation state of a cation in a given site. The use of the parameter appropriate to Cu^{2+} in an oxide environment (*10*) with the determined Cu–O distances yields a Cu valence of 2.68, whereas adoption of the Cu^{3+} parameter (*11*) provides the more self-consistent valence of 3.08. The presence of Cu^{3+} ions in a material of composition $Sr_5Pb_3CuO_{12}$ requires partial reduction of Pb^{4+} to Pb^{2+}. The distorted stereochemistry around the Pb site appears compatible with this, as was previously proposed (*3*).

An interesting feature of the neutron study is the significant disagreement between the Sr : Pb : Cu ratio in the starting mixture (3 : 2 : 1), compared with that in the refined structure (5 : 3 : 1). Indeed, the neutron diffraction data indicated that the 3 : 2 : 1 sample was purer than the 5 : 3 : 1 sample. The main discrepancy concerns the Cu content, but chemical analysis (*12*) showed no loss of Cu, as expected. Although the presence of an essentially amorphous second phase could account for this observation, no evidence for this is apparent in the neutron diffraction background, which is quite level. The presence of cation disorder provides an alternative explanation, and the significantly different unit cell parameters determined for the (3 : 2 : 1) and (5 : 3 : 1) ratios support such a disordered model. Energy dispersive X-ray spectroscopy of the single crystal studied by X-ray diffraction (*3*) suggested a Sr : Pb : Cu ratio of 50 : 35 : 15, which is in close agreement with the 3 : 2 : 1 ratio employed in the bulk preparation here. The presence of Pb on Sr sites was suggested by the X-ray study (*3*), and the location of some Cu on either Pb or Sr sites could account for the discrepancy. For example if the nominal stoichiometry is represented $(Sr_5)[Pb_3]CuO_{12}$, the cation distributions $(Sr_{4.5}Cu_{0.5})[Pb_3]CuO_{12}$ and $(Sr_{4.5}Pb_{0.5})[Pb_{2.5}Cu_{0.5}]CuO_{12}$ both provide the required 3 : 2 : 1 ratio and would give a density of 6.87 g cm^{-3}. With respect to the neutron diffraction refinements, both formulations have been shown to result in no significant changes to the structural parameters or agreement indexes. This is particularly true for the former formula, where the similar scattering lengths for Sr and Cu would result in an average increase in the scattering at the Sr site by only 1%. Although the Sr sites are not appropriate for the accommodation of Cu ions, since the Sr–O distances are too long, it should be noted that more favored square pyramidal 5-coordinate positions are only ca. 0.6 Å from both the Sr1 and Sr2 sites. However, the occupation of these positions could not be confirmed by our study, and no indications of such disorder were apparent in the X-ray diffraction study (*3*). It is also pertinent to note that the thermal parameters for the Sr, Pb, and O atoms (Table II) are normal, whereas high values might be anticipated for significant Cu substitutions. At present, therefore, the apparent discrepancy between the bulk composition and that corresponding to the neutron diffraction refinement remains unresolved.

Acknowledgments

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