Fig. 2 shows the packing diagram of the unit cell. The intermolecular contacts are illustrated by the thin lines. The N(3) atom is connected to the $O_t(A)$ (2·77 Å) and $O_t(B)$ (2·82 Å) atoms which belong to the two anions related to each other by the screw axis along **a**. This is the major reason why the highly symmetric $[H_2PTi_2W_{10}O_{40}]^{5-}$ anion is not completely disordered in this crystal unlike the other substituted Keggin anions. The elongated shape along the *a* axis of the crystal is due to the same reason. This is the first X-ray structure analysis which has succeeded in identifying the substituted sites of an α-Keggin anion and observing the structural deviations caused by the metal substitution.

References

BARRETT, A. S. (1972). *Diss. Abstr. B*, **33**, 1475.
BROWN, I. D. & ALTERMATT, D. (1985). *Acta Cryst.* B41, 244–247.

DOMAILLE, P. J. & KNOTH, W. H. (1983). *Inorg. Chem.* **22**, 818–822.
FUCHS, J., THIELE, A. & PALM, R. (1981). *Z. Naturforsch. Teil B*, **36**, 544–550.
GILMORE, G. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
JEANNIN, Y., LAUNAY, J. P. & SEDJADI, M. A. S. (1980). *Inorg. Chem.* **19**, 2933–2935.
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
MATSUMOTO, K. Y. & SASAKI, Y. (1976). *Bull. Chem. Soc. Jpn*, **49**, 156–158.
MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Analysis Package.* MSC, 3200A Research Forest Drive, The Woodlands, TX77381, USA.
NISHIKAWA, K., KOBAYASHI, A. & SASAKI, Y. (1975). *Bull. Chem. Soc. Jpn*, **48**, 3152–3155.
POPE, M. T. (1983). *Heteropoly and Isopoly Oxometalates*, p. 105. New York: Springer-Verlag.
ROBERT, F., TÉZÉ, A., HERVÉ, G. & JEANNIN, Y. (1980). *Acta Cryst.* B36, 11–15.

Structure of LaCuO3 by Powder Neutron Diffraction

BY D. B. CURRIE AND M. T. WELLER

Department of Chemistry, The University, Southampton, SO9 5NH, England

Abstract. Lanthanum copper oxide, $LaCuO_3$, $M_r =$ 250·46, hexagonal, $P6_3$, $a = 5·50195$ (1), $c =$ 13·2124 (4) Å, $V = 346·4$ Å^3, $Z = 6$, $D_x =$ 7·20 g cm^{-3} at room temperature; $a = 5·49219$ (1), $c = 13·1545$ (2) Å, $V = 346$ Å^3 at 5 K, $R_p = 6·2\%$. The structure of the title compound, synthesized at 5×10^9 Pa, was refined using time-of-flight powder neutron diffraction methods. The structure is perovskite based with octahedral copper(III), Cu—O 1·9511 (3) Å, and a strongly distorted 12-coordinated lanthanum, La—O 2·483 (2)–3·019 (2) Å.

Introduction. Ternary oxides containing copper(III) in association with alkali metals are well known and are readily prepared at around 673 K in oxygen. Some evidence exists for ternary oxides of copper with alkaline earths, particularly barium in the compounds $BaCuO_{2+x}$ and Ba_2CuO_{3+x}, though no pure copper(3 +) compound with these elements is known. $LaCuO_3$ was first described by Demazeau, Parent, Pouchard & Hagenmuller (1972) who synthesized it rapidly under very high oxygen pressures; the material is isomorphous with $LaNiO_3$, having rhombohedrally distorted perovskite structure. Webb *et al.* (1989) have studied this compound more

recently and describe an irreversible transformation to a tetragonal phase above about 673 K.

As a result of the high pressures required for the synthesis of $LaCuO_3$, only milligram quantities are generally available. Such quantities are sufficient for powder X-ray work and allowed Demazeau *et al.* to define a structure by comparison with $LaNiO_3$; a more accurate structure refinement, particularly of the oxygen position, occupancy and temperature factors could be obtained from neutron diffraction data. However, this technique normally requires multigram quantities. In this article we describe the struc-

Table 1. *Experimental data*

Instrument	POLARIS, ISIS Rutherford– Appleton Laboratory
Sample container	Vanadium can 5 mm diameter
Time-of-flight range	4000–18000 μs (0·7 < 3·2 Å)
Number of points	1303
Number of reflections	150
Absorbtion correction	None
Geometric constriction	None
Number of cycles in final refinement	5
Number of structural parameters	10
Number of profile parameters	15
Maximum shift/e.s.d. for final cycle	0·0009

Table 2. *Atomic parameters at* 298 K *with e.s.d.'s in parentheses*

	Site symmetry	x	y	z	n	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
La	6(a)	0	0	0.25	1.0	0.15 (8)	0.15	0.36 (13)	0.07		
Cu	6(b)	0	0	0	1.0	0.12 (8)	0.11	0.32 (12)	0.06		
O	18(e)	0.4513 (4)	0	0	0.964 (16)	0.60 (8)	0.16 (9)	0.45 (9)	0.08	−0.57 (9)	−0.28

tural refinement of $LaCuO_3$ using neutron data collected on the high-flux diffractometer POLARIS (Hull & Mayers, 1989). The strength of this instrument in obtaining refinable neutron diffraction data over reasonable timescales on small samples is shown.

Experimental.

Synthesis. $LaCuO_3$ was prepared following the method described by Webb *et al.* (1989). La_2CuO_4, CuO and $KClO_3$ were mixed thoroughly in equimolar proportions and sealed in platinum tubing of approximate dimensions 3 mm diameter and 8 mm length. This tube was then mounted in a tetrahedral pyrophyllite block inside a graphite liner and a boron nitride sheath; the block was then mounted in an opposed anvil tetrahedral device. The reactant mixture was heated at 100 K min^{-1} to 1773 K, held for 5 min and then quenched. The products were washed with water to remove potassium chloride and the samples from four such runs combined to afford 400 mg ($\approx$0.05 cm^3) $LaCuO_3$. Powder X-ray diffraction data were obtained from the product using a Siemens D5000 diffractometer fitted with a primary-beam monochromator. The material was found to be of excellent crystallinity and the data, except for a few peaks assigned to residual copper oxide, was completely indexed on the unit cell for $LaCuO_3$ given by Demazeau *et al.* (1972). Powder neutron diffraction data were collected using the POLARIS diffractometer at the Rutherford–Appleton Laboratory; relevant experimental data are summarized in Table 1. Further shorter runs were carried out at 5 K in a helium cryostat and at 620 K in a furnace.

The room-temperature neutron diffractometer data was of excellent quality after a collection time of 20 h. The highest resolution data from the C bank of detectors, $130 < 2\theta < 158°$, were analyzed. The refinement was undertaken following the model of Demazeau *et al.* (1972) and using a time-of-flight version of the Rietveld program running as part of the CCSL library at the RAL. Refinement was carried out over the time-of-flight range 4000–16000 μs, which corresponds approximately to the d spacing values between 0.7 and 3.2 Å. Four portions of the profile which contained very weak reflections from the copper oxide impurity were excluded from the refinement. Neutron scattering lengths were taken from Koester & Yelon (1982) as La 0.827, Cu 0.7718 and O 0.5905 × 10^{-12} cm.

Table 3. *Calculated interatomic distances* (Å) *and angles* (°)

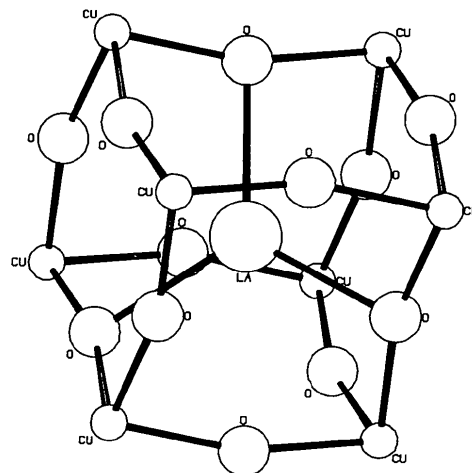| La—O	2.483 (2) × 3	O—Cu—O	91.28 (2)
	2.7283 (2) × 6	O'—Cu—O	88.72 (2)
	3.019 (2) × 3		
Cu—O	1.9511 (3) × 6		

Fig. 1. The distorted perovskite unit cell of $LaCuO_3$. Copper—oxygen bonds and the shortest lanthanum–oxygen interactions are shown.

The background was fitted using a tenth-order Chebyshev polynomial and pseudo-Voigtian peak shape was chosen. Initial stages of the refinement included scale factor, background parameters and cell constants and rapidly converged. Later stages introduced the oxygen position, anisotropic temperature factors and peak shape parameters. Finally the oxygen site occupancy was allowed to vary from unity. Final parameters for the room-temperature data set are summarized in Table 2;* interatomic distances and angles are in Table 3. Final R values obtained were $R_p = 6.2$, $R_{wp} = 5.3\%$ ($w_i = \sigma^{-2}$), with $R_{expected} = 2.2\%$, giving a χ^2 value of 5.8.

Refinement of a data set collected at 5 K was carried out on the same basis. Little variation was found in the parameters obtained; cell constants

* Crystallographic data, time-of-flight neutron powder diffraction details and full lists of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53572 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

contracted to 5·4922 (1) and 13·1546 (4) Å and the oxygen site x parameter shifted slightly to 0·4499 (8). The site occupancy for oxygen was within the e.s.d. of the room-temperature value.

Discussion. $LaCuO_3$ is isomorphous with $LaNiO_3$ and a number of other ABO_3 materials which contain two trivalent ions with a radius ratio of about 1:2. None of the ternary oxides with two trivalent cations forms a perfect cubic perovskite structure which reflects the incompatibility of the small ionic radii of such trivalent species with the ideal perovskite structure A site. The rhombohedral distortion maintains an octahedral geometry around the copper 'B' type ion but strongly distorts the lanthanum environment forming three short, six medium and three long interactions from the perfect perovskite regular 12-fold coordination, Fig. 1. This can be rationalized in terms of bond valence calculations (Brown & Altermatt, 1985) which for the $LaCuO_3$ structure obtained give an oxidation state for lanthanum of 2·94 whilst a perfect perovskite structure based on a Cu—O cube of dimension 3·902 Å would give a much lower value of 2·45. The derived bond valence for copper using this method is 3·3; this rather high value may reflect the constrained

nature of this structure (Brown, 1989). However, it is worth noting that the bond valence parameters for Cu^{III} are poorly defined as a result of the scarcity of materials containing this ion. The refined oxygen site occupancy is close to 1·0, though both room-temperature and 5 K refinements yield a value close to 0·96 (2); this may indicate some loss of oxygen from the material.

References

BROWN, I. D. (1989). *J. Solid State Chem.* **82**, 122–130.
BROWN, I. D. & ALTERMATT, D. (1985). *Acta Cryst.* B41, 244–247.
DEMAZEAU, G., PARENT, C., POUCHARD, M. & HAGENMULLER, P. (1972). *Mater. Res. Bull.* 7, 913–920.
HULL, S. & MAYERS, J. (1989). User Guide to the POLARIS powder diffractometer at ISIS. RAL Report 89–118. Rutherford–Appleton Laboratory, Didcot, England.
KOESTER, L. & YELON, W. B. (1982). Netherlands Energy Research Foundation, The Netherlands.
WEBB, A. W., SKELTON, E. F., QUDRI, S. B., CARPENTER, E. R., OSOFSKY, M. S., SOULEN, R. J. & LETOVRNEAU, Y. (1989). *Phys. Lett. A*, 37(4,5), 205–206.

Structure Cristalline de $Cs_2TiO(P_2O_7)$

PAR J. PROTAS, B. MENAERT, G. MARNIER ET B. BOULANGER

Laboratoire de Minéralogie, Cristallographie et Physique Infrarouge, URA CNRS n° 809, Université de Nancy I, BP 239, 54506 Vandoeuvre les Nancy CEDEX, France

Abstract. Dicaesium titanium diphosphate(4 −) oxide, $Cs_2Ti(P_{0.93}As_{0.07})_2O_8$, $M_r = 503·65$, orthorhombic, $P2_12_12_1$, $a = 7·275$ (2), $b = 9·452$ (1), $c = 13·569$ (2) Å, $V = 933·0$ Å^3, $Z = 4$, $D_m = 3·65$ (4), $D_x = 3·585$ g cm^{-3}, $\lambda(Ag\ K\alpha) = 0·56087$ Å, $\mu = 466·4$ cm^{-1}, $F(000) = 904$, $T = 293$ K, $R = 0·026$ ($wR = 0·023$) for 2324 unique reflections [$I > 3\sigma(I)$] and 121 refined parameters. The Ti atom exhibits an unusual five-coordination geometry corresponding to a square-base pyramid, with one very short apical Ti—O distance of 1·644 (4) Å. The four O atoms of the square base belong to the P_2O_7 groups. The short Ti—O distance which corresponds to the last O atom is normal to the plane of the sheets, which are held together by Cs—O bonds. The mean planes of the sheets are parallel to the crystallographic plane (100)

and are strongly corrugated along the b axis. The Cs atoms are located in the large channels parallel to the c axis. The crystal structure is isotypic with that of $Rb_2VO(P_2O_7)$.

Introduction. Cette étude entre dans le cadre d'un programme de recherches consacré à l'élaboration, à la croissance et à la caractérisation de matériaux lasers passifs appartenant à la famille de $KTiOPO_4$, en vue de leurs applications en optique non linéaire. De nombreux travaux sont actuellement consacrés à cette famille de matériaux et un excellent article de synthèse a été publié tout récemment sur ce sujet (Stucky, Phillips & Gier, 1989). Le travail présenté ci après concerne une nouvelle phase, de formule $Cs_2TiO(P_2O_7)$, obtenue par cristallisation de bains