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Redetermination of the Structure of $\text{La}_2\text{Cu}_2\text{O}_5$ by Neutron Powder Diffraction

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Abstract

Dicopper(II) dilanthanum pentaoxide, $\text{La}_2\text{Cu}_2\text{O}_5$, has been prepared using a high-pressure technique. Its structure at 296 and 10 K was analyzed by Rietveld refinements using neutron powder diffraction data. The structure of $\text{La}_2\text{Cu}_2\text{O}_5$ comprises CuO_5 square pyramids connected to each other in three dimensions by corner sharing and ten-coordinate La^{3+} ions occupying positions next to oxygen vacancies which form tunnels along the *c* axis.

Comment

Recent work on the antiferromagnetic spin-ladder compound $(\text{La}_{1-x}\text{Sr}_x)_2\text{Cu}_2\text{O}_5$ (Hiroi & Takano, 1995) has aroused much interest because no other spin-ladder compounds have been doped with holes. A marked insulator-to-metal transition was observed with increasing Sr content, *x*. The structural parameters of the initial member in this solid solution, $\text{La}_2\text{Cu}_2\text{O}_5$ (*x* = 0), have been refined using X-ray powder diffraction data (La Placa, Bringley, Scott & Cox, 1993; Hiroi & Takano, 1995), leaving some ambiguity in the structural details. In fact, refinements based on synchrotron X-ray powder diffraction data resulted in negative isotropic displacement parameters, *B*, for La and Cu, and in a very low *B* value of 0.1 Å² for O2 (La Placa, Bringley, Scott & Cox, 1993). Although abnormal displacement parameters are often observed in crystal data obtained from synchrotron powder diffraction data, these displacement parameters may reflect the low quality of the sample, which was prepared under ambient pressure. The structural parameters determined by Hiroi & Takano (1995) with a sample synthesized at high pressure are reasonable, but of low precision because a conventional X-ray powder diffractometer was used. The present investigation was undertaken to obtain more reliable struc-

tural parameters for $\text{La}_2\text{Cu}_2\text{O}_5$ by using high-resolution neutron powder diffraction and a well crystallized and single-phase sample.

We analyzed neutron diffraction data for $\text{La}_2\text{Cu}_2\text{O}_5$ at 296 and 10 K by the Rietveld method on the basis of space group *Pbam*, using as initial parameters those obtained previously (La Placa, Bringley, Scott & Cox, 1993; Hiroi & Takano, 1995). Finally, we confirmed full occupation of all the five sites and the absence of oxygen at the 2*c* position, (0, 1/2, 0), corresponding to the oxygen vacancies along the *c* axis (Fig. 1). This result supports the idea that the present sample is a stoichiometric compound with chemical composition $\text{La}_2\text{Cu}_2\text{O}_5$. Fig. 2 shows the observed, calculated, and difference patterns at 296 K. Tables 1 and 2 list structural parameters with their estimated standard deviations in parentheses (Young, 1993).

The results of our refinement for $\text{La}_2\text{Cu}_2\text{O}_5$ at 296 K are in good agreement with those reported previously (La Placa, Bringley, Scott & Cox, 1993; Hiroi & Takano, 1995). However, the precision of the structural parameters for the O atoms has been improved considerably, and our *B* values for the La, Cu, and O2 atoms are reasonable, in contrast with those reported in the synchrotron X-ray diffraction study (La Placa, Bringley, Scott & Cox, 1993). Neither structural changes nor magnetic scattering was observed on lowering the tempera-

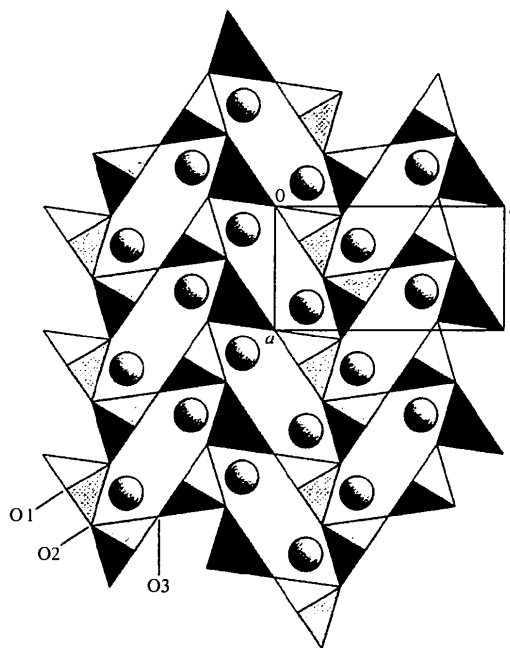


Fig. 1. Crystal structure of $\text{La}_2\text{Cu}_2\text{O}_5$ represented with CuO_5 square pyramids and La^{3+} ions.

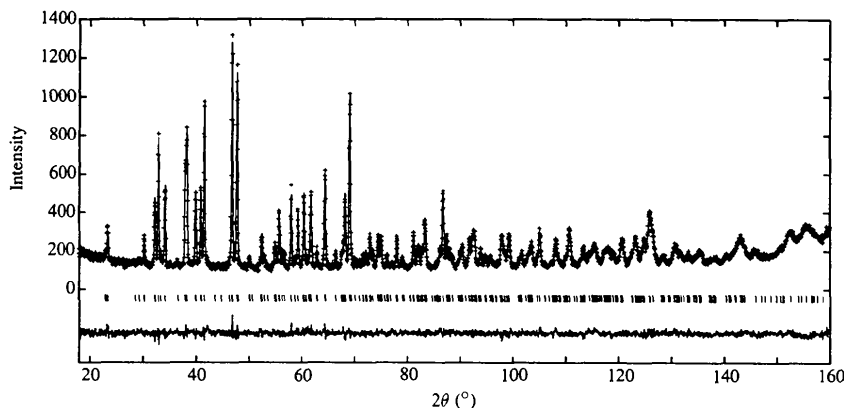


Fig. 2. Rietveld refinement pattern for La₂Cu₂O₅ at 296 K. Observed diffraction intensities are represented by plus (+) marks, and the calculated pattern by the solid line. The differences between the observed and calculated intensities are shown near the bottom of the figure. Short vertical marks below the observed and calculated patterns indicate the positions of the allowed Bragg reflections.

ture to 10 K. It is interesting to note that *B*(O1) appears to change only slightly upon cooling.

The orthorhombic form of La₂Cu₂O₅ is isomorphous with Ca₂Mn₂O₅ (Poepelmeier, Lebnowicz, Scanlon, Longo & Yelon, 1982). Its structure (Fig. 1) can be derived from that of the distorted perovskite-type oxide LaCuO₃, which crystallizes in rhombohedral (Demazeau, Parent, Pouchard & Hagenmuller, 1972) and tetragonal (Bringley *et al.*, 1990) modifications at 65 and 0.2–1 kbar, respectively. Systematically removing one-sixth of the O atoms in LaCuO₃ leads to La₂Cu₂O₅, with a corresponding decrease in the formal oxidation state of Cu from +3 in LaCuO₃ to +2 in La₂Cu₂O₅. The removal of oxygen also decreases the coordination numbers of the metal atoms in La₂Cu₂O₅, which are 10 for La and 5 for Cu in the orthorhombic form (the present compound) and 9 for La, and 4 and 6 for Cu in the monoclinic form (Cava *et al.*, 1991; Norrestam, Nygren & Bovin, 1991). In oxygen-deficient La₂Cu₂O₅, the O atoms are perfectly ordered so as to form one-dimensional channels of vacancies running parallel to the *c* axis (Fig. 1). Such unique oxygen ordering affords an orthorhombic unit cell with dimensions $a = \sqrt{2}a_p$, $b = 2\sqrt{2}a_p$ and $c = a_p$, where a_p is the typical lattice parameter of a perovskite-type compound.

Each Cu atom forms a CuO₅ square pyramid with Jahn–Teller distortion characteristic of the *d*⁹ electronic configuration for the Cu²⁺ ion. That is, the CuO₅ pyramid contains four short Cu—O bonds [1.9408 (1), 1.9408 (1), 1.908 (3), 1.965 (2) Å] and a long axial Cu—O bond [2.279 (3) Å]. Every O atom is bonded to two different Cu atoms; in other words, it is corner-shared by two square pyramids. The Cu—O1 and Cu—O3 bonds are all short, whereas O2 forms one short and one long Cu—O2 bond. Both the short Cu—O2 and Cu—O3 bonds are approximately perpendicular to the *c* axis. The short Cu—O1 bond is roughly parallel to the *c* axis, with the O1 atom shared by two CuO₅ square pyramids.

The temperature-dependent magnetic susceptibilities of La₂Cu₂O₅ are characteristic of a low-dimensional Heisenberg antiferromagnet with a magnitude of the spin gap comparable to that of SrCu₂O₃ (Hiroi & Takano, 1995). Thus, La₂Cu₂O₅ is a two-chain spin-ladder compound where there is strong pseudo one-dimensional antiferromagnetic interaction within each ladder but no appreciable magnetic interaction between the two neighboring ladders (Hiroi & Takano, 1995). The axial Cu—O2 bond is, however, rather short for an axial bond [2.279 (3) Å] and this bond should not be neglected when considering the structural features of La₂Cu₂O₅.

The La³⁺ ion is coordinated to ten oxide ions belonging to three different ladders, with an average La—O bond length of 2.689 Å. This value is close to the sum of the effective ionic radii (Shannon, 1976) for ten-coordinate La³⁺ and five-coordinate O²⁻ ions of 2.66 Å.

In conclusion, the structure of La₂Cu₂O₅ comprises CuO₅ square pyramids connected to each other in three dimensions by corner sharing and La³⁺ ions occupying positions next to the oxygen vacancies (Fig. 1). From a crystal chemistry point of view, La₂Cu₂O₅ should therefore be regarded as having a three-dimensional tunnel structure.

Experimental

A base material, La₂Cu₂O₅, was prepared according to the method reported by Cava *et al.* (1991). Powders of this compound were sealed in gold capsules and treated at 1173 K and 6 GPa for 30 min using a cubic-anvil-type high-pressure apparatus. No impurities were detected in the product by X-ray powder diffraction.

La₂Cu₂O₅ at 296 K

Crystal data

La₂Cu₂O₅
M_r = 484.90

Neutron radiation
 $\lambda = 1.5396 \text{ \AA}$

Orthorhombic
Pbam
 $a = 5.54640 (13) \text{ \AA}$
 $b = 10.4720 (3) \text{ \AA}$
 $c = 3.87959 (8) \text{ \AA}$
 $V = 225.334 (9) \text{ \AA}^3$
 $Z = 2$
 $D_x = 7.147 \text{ Mg m}^{-3}$

Cell parameters from 294 reflections
 $\theta = 9\text{--}80^\circ$
 $T = 296 \text{ K}$
 Powder sample
 Black

Refinement
 $R_p = 0.0444$
 $R_{wp} = 0.0560, R_c = 0.0221$
 $R_I = 0.0263$
 $R_F = 0.0143$

Coherent scattering lengths from *International Tables for Crystallography* (1992, Vol. C)
 3040 data points

Data collection

Neutron powder diffractometer at the NIST research reactor
 Monochromator: Cu(311)
 Horizontal divergences: incident beam (15'), monochromatic beam (20') and diffracted beam (7') collimators

Specimen mounting: vanadium can with a diameter of 6 mm
 Measured $2\theta_{\min} = 3, 2\theta_{\max} = 168^\circ$
 Step width: 0.05° in 2θ
 3300 measured data points

Table 2. Fractional atomic coordinates and isotropic displacement parameters (\AA^2) for $\text{La}_2\text{Cu}_2\text{O}_5$ at 10 K

	Wyckoff position	x	y	z	B_{iso}
La	4h	0.3119 (3)	0.3603 (2)	1/2	0.41 (4)
Cu	4g	0.2922 (4)	0.1060 (2)	0	0.23 (5)
O1	4h	0.2875 (5)	0.1015 (3)	1/2	0.98 (5)
O2	4g	0.0767 (4)	0.2901 (2)	0	0.35 (5)
O3	2a	0	0	0	0.65 (8)

Refinement

$R_p = 0.0434$
 $R_{wp} = 0.0542, R_c = 0.0208$
 $R_I = 0.0171$
 $R_F = 0.0092$

Coherent scattering lengths from *International Tables for Crystallography* (1992, Vol. C)
 3040 data points

Table 3. Selected geometric parameters ($\text{\AA}, ^\circ$) for $\text{La}_2\text{Cu}_2\text{O}_5$

	296 K	10 K
La—O1'	2.581 (3)	2.579 (4)
La—O1''	2.644 (3)	2.663 (4)
La—O1	2.714 (3)	2.709 (4)
La—O1'''	2.955 (3)	2.930 (3)
La—O2	2.454 (2)	2.446 (2)
La—O2''	2.454 (2)	2.446 (2)
La—O2'	2.902 (2)	2.893 (3)
La—O2''	2.902 (2)	2.893 (3)
La—O3'	2.6407 (11)	2.6388 (12)
La—O3''	2.6407 (11)	2.6388 (12)
Cu—O1	1.9408 (1)	1.9371 (1)
Cu—O1''	1.9408 (1)	1.9371 (1)
Cu—O2'	1.908 (3)	1.913 (3)
Cu—O2	2.279 (3)	2.263 (3)
Cu—O3	1.965 (2)	1.960 (2)
O1—Cu—O1''	176.2 (2)	176.8 (2)
O1—Cu—O2	90.13 (10)	90.79 (12)
O1''—Cu—O2	90.13 (10)	90.79 (12)
O1—Cu—O2'	91.88 (10)	91.42 (11)
O1''—Cu—O2'	91.88 (10)	91.42 (11)
O1—Cu—O3	88.12 (10)	88.58 (11)
O1''—Cu—O3	88.12 (10)	88.58 (11)
O2—Cu—O2'	87.23 (7)	87.21 (8)
O2—Cu—O3	92.42 (9)	92.60 (11)
O2'—Cu—O3	179.66 (13)	179.81 (15)

Table 1. Fractional atomic coordinates and isotropic displacement parameters (\AA^2) for $\text{La}_2\text{Cu}_2\text{O}_5$ at 296 K

	Wyckoff position	x	y	z	B_{iso}
La	4h	0.3117 (3)	0.3610 (2)	1/2	0.73 (4)
Cu	4g	0.2926 (3)	0.1058 (2)	0	0.62 (4)
O1	4h	0.2834 (5)	0.1022 (2)	1/2	1.14 (5)
O2	4g	0.0755 (4)	0.2906 (2)	0	0.75 (5)
O3	2a	0	0	0	1.02 (8)

$\text{La}_2\text{Cu}_2\text{O}_5$ at 10 K

Crystal data

$\text{La}_2\text{Cu}_2\text{O}_5$
 $M_r = 484.90$
 Orthorhombic
Pbam
 $a = 5.53528 (14) \text{ \AA}$
 $b = 10.4490 (3) \text{ \AA}$
 $c = 3.87265 (8) \text{ \AA}$
 $V = 223.987 (10) \text{ \AA}^3$
 $Z = 2$
 $D_x = 7.190 \text{ Mg m}^{-3}$

Neutron radiation
 $\lambda = 1.5396 \text{ \AA}$
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Data collection

Neutron powder diffractometer at the NIST research reactor
 Monochromator: Cu(311)
 Horizontal divergences: incident beam (15'), monochromatic beam (20') and diffracted beam (7') collimators

Specimen mounting: vanadium can with a diameter of 6 mm
 Measured $2\theta_{\min} = 3, 2\theta_{\max} = 168^\circ$
 Step width: 0.05° in 2θ
 3300 measured data points

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iv) $x, y, 1 + z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (vi) $x, y, z - 1$.

The two sets of intensity data were analyzed by the Rietveld method with *RIETAN94* (Izumi, 1993; Kim & Izumi, 1994). The profile shape was represented by the modified pseudo-Voigt function (Thompson, Cox & Hastings, 1987; Young, 1993), with profile asymmetry introduced by employing a multi-term Simpson's rule integration (Howard, 1982). The background function was a finite sum of Legendre polynomials orthogonal relative to integration over the interval $[-1, 1]$. In addition to profile, lattice, and structure parameters, the zero-point shift, eight background parameters, and the scale factor were refined without correcting for preferred orientation. Thermal vibrations were assumed to be isotropic. The interatomic distances and bond angles were calculated with *ORFFE* (Busing, Martin & Levy, 1964). Molecular graphics: *ATOMS* (Dowty, 1995).

Lists of observed and calculated intensity data have been deposited with the IUCr (Reference: OH1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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CsAg_{0.64}Mn_{1.18}Te₂

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Abstract

The structure of CsAg_{0.64}Mn_{1.18}Te₂ has been determined from single-crystal X-ray data. It exhibits the ThCr₂Si₂ structure type, comprising layers of Ag- and Mn-centered tetrahedra that are stacked perpendicular to [001]. The Ag⁺ and Mn²⁺ cations are disordered over the same site.

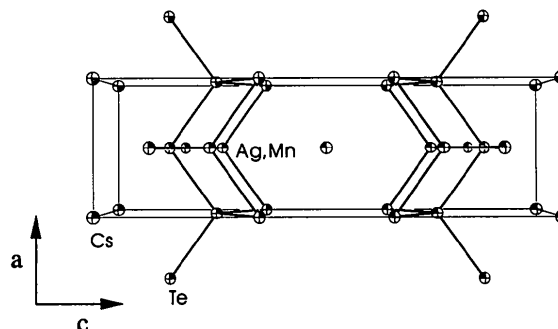


Fig. 1. View of the CsAg_{0.64}Mn_{1.18}Te₂ unit cell along *b* with 50% probability displacement ellipsoids.

Experimental

Cs₂Te₃, Ag (Aesar, 99.99%), Mn (Johnson Matthey, 99.9%), and Te (Aldrich, 99.8%) were combined in the molar ratio 1:1:2:1. Cs₂Te₃ was synthesized at 194 K from the stoichiometric reaction of Cs (Aldrich, 99.5%) and Te in liquid ammonia under an N₂ atmosphere. The reaction mixture was ground together, sealed under vacuum in a fused silica tube, heated to 1173 K for 8 days, then cooled to room temperature at 3 K h⁻¹. The red plates used for structure determination were manually extracted from the melt. Analysis of these crystals with an EDX-equipped Hitachi S-570 SEM showed the presence of Cs, Ag, Mn, and Te in the approximate ratio 1:0.5:1.5:2. We have also synthesized the potassium analogue of CsAg_{0.64}Mn_{1.18}Te₂ by a similar method, as confirmed by precession photographs.

Crystal data

CsAg_{0.64}Mn_{1.18}Te₂

M_r = 521.968

Tetragonal

I4/mmm

a = 4.520 (2) Å

c = 15.484 (8) Å

V = 316.3 (3) Å³

Z = 2

D_x = 5.469 Mg m⁻³

D_m not measured

Mo Kα₁ radiation

λ = 0.70930 Å

Cell parameters from 26 reflections

θ = 19.5–21.5°

μ = 18.88 mm⁻¹

T = 113 (2) K

Plate

0.431 × 0.319 × 0.078 mm

Red

Data collection

Picker diffractometer

θ–2θ scans

Absorption correction:

analytical

T_{min} = 0.037, *T_{max}* =

0.226

2621 measured reflections

245 independent reflections

R_{int} = 0.0600

Refinement

Refinement on *F*²

R(*F*) = 0.0308

wR(*F*²) = 0.1182

S = 2.392

245 reflections

θ_{max} = 34.97°

h = –7 → 7

k = –7 → 7

l = –24 → 24

6 standard reflections

monitored every 100

reflections

intensity decay: none

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0103 (24)