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Structure of $La_2Cu_2O_5$ by High-Resolution Synchrotron X-ray Powder Diffraction

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Abstract. Dicopper(II) dilanthanum pentaoxide, $La_2Cu_2O_5$, $M_r = 484.90$, orthorhombic, *Pbam*. At $T = 300$ K: $a = 5.5490\,(1)$, $b = 10.4774\,(2)$, $c = 3.8796\,(1)$ Å, $V = 225.557\,(8)$ Å^3, $Z = 2$, $D_x = 7.139$ g cm^{-3}, $\lambda = 1.2000$ Å. Final $R_I = 6.20$, $R_p = 14.6$ and $R_{wp} = 20.61\%$, 124 independent reflections observed. The structure has been refined from high-resolution synchrotron X-ray powder diffraction data using the Rietveld method. It is of the oxygen-defect perovskite type and is composed entirely of corner-shared CuO_5 square pyramids, which share oxygen vacancies forming vacancy tunnels along the *c* axis. The La atoms reside at a perovskite-like *A*-site and are tenfold coordinated by oxygen.

Introduction. $La_2Cu_2O_5$ is the end member of the oxygen-defect perovskite series $LaCuO_{3-\delta}$ (Bringley, Scott, La Placa, Boehme, Shaw, McElfresh, Trail & Cox, 1990). This series of compounds is closely related to the well known high-temperature superconducting cuprates (Bednorz & Müller, 1986) and, therefore, may serve as a unique model system for characterizing the electronic and magnetic properties of the superconducting and related cuprates. Although superconductivity has not been observed in this system, its oxygen stoichiometry range, $0.0 \le \delta \le 0.5$, is the widest yet found in a cuprate, allowing the formal oxidation state of copper to be varied from +2 to +3 within the same basic perovskite framework. Depending on composition, three distinct oxygen-defect perovskites are observed in this system. A tetragonal perovskite with a homogeneity range $0 \le \delta \le 0.2$, a monoclinic perovskite with a homogeneity range of $0.2 \lesssim \delta \lesssim 0.4$, and an orthorhombic phase, whose structure is discussed herein, existing over the interval $0.43 \lesssim \delta \lesssim 0.5$. The tetragonal phase at $\delta = 0$ undergoes a transformation to rhombohedral symmetry at high pressure (Darracq, Largeteau, Demazeau, Scott & Bringley, 1992). As a result of their relationship to the high-temperature superconducting cuprates, a knowledge of their structures and crystal–chemical properties is of general importance.

Experimental. A polycrystalline sample of $La_2Cu_2O_5$ was prepared by reducing the tetragonal form of the perovskite, $LaCuO_3$ (Bringley, Scott, La Placa, Mehran, McGuire & McElfresh, 1993), in a dry argon atmosphere. A Pt crucible containing $LaCuO_{2.95}$ (3.0 g, 0.012 mol) was heated at a rate of 100 K h^{-1} to 725 K, held at this temperature for 12 h, and cooled at a rate of 100 K h^{-1} to 373 K, all under a dry argon flow. Compositions were established by thermogravimetric analyses and by iodometric titration (Nazzal, Lee, Engler, Jacowitc, Tokura & Torrance, 1988) with an accuracy in δ of ± 0.02. The two techniques were in excellent agreement. X-ray powder diffraction confirmed the integrity of the product with no observable impurities within the detection limit of our diffractometer ($\ge 3\%$).

High-resolution synchrotron X-ray powder diffraction data were collected at beamline X7*A* of the Brookhaven National Synchrotron Light Source with a channel cut Si(111) monochromator and a flat Ge(220) analyser at a wavelength of 1.2000 Å. Samples were packed in rectangular flat plate holders and step scans performed at 0.005° intervals over the angular range of $2\theta = 10$–$70°$. The polycrystalline sample was approximately $2.0 \times 2.0 \times 0.5$ cm in a shallow-well sample holder and was measured in the symmetrical reflection geometry. The samples were rocked at each point to obtain a proper powder average over the crystallites. Each measured profile intensity was normalized with respect to the incident-beam monitor count and scaled to counts per second per 100 mA ring current. 124 independent Bragg intensities observed in the region studied were used in the refinement; very weak intensities attributed to trace impurities of La_2CuO_4 and CuO were not excluded from the refinement. Structural refinements were performed using a modified version of the Rietveld program (Rietveld, 1969; Hewat, 1973),

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with a pseudo-Voigt peak-shape function, which approximates the convolution of Gaussian and Lorentzian functions. The atomic scattering factors used were the neutral-atom scattering factors for La, Cu and O from *International Tables for X-ray Crystallography* (1974, Vol IV). 24 parameters were refined including cell parameters, atomic and isotropic thermal parameters, overall scale factor, peak-shape functions, half-width parameters and a zero-point error. Atomic coordinates for the isomorphous $CaMnO_{2.5}$ (Poeppelmeier, Lebnowicz, Scanlon, Longo & Yelon, 1982) were used as a starting point for the refinement. The observed and difference powder-diffraction profiles are shown in Fig. 1. A satisfactory refinement of the data was achieved, with convergence to the final agreement factors $R_I = 6.20$, $R_p = 14.57$ and $R_{wp} = 20.61\%$. The statistically expected R factor, R_{exp}, was 14.91%, leading to a goodness-of-fit, $S^2_{wp} = (R_{wp}/R_{\text{exp}})^2 = 1.91$. The R values and goodness-of-fit are defined in Attfield, Cheetham, Cox & Sleight (1988).

Table 1. *Positional and thermal parameters of* $La_2Cu_2O_5$ *with e.s.d.'s in parentheses*

	Position	x	y	z	B (Å^2)
Cu	4(*g*)	0.2917 (4)	0.1064 (2)	0.0	−0.64 (5)
La	4(*h*)	0.3107 (2)	0.3601 (1)	0.5	−0.37 (2)
O(1)	4(*h*)	0.295 (2)	0.1019 (9)	0.5	1.4 (2)
O(2)	4(*g*)	0.578 (2)	0.2112 (9)	0.0	0.1 (2)
O(3)	2(*a*)	0.0	0.0	0.0	1.2 (4)

Table 2. *Bond distances* (Å) *and angles* (°) *in* $La_2Cu_2O_5$

Cu—O(2)	1.920 (11) 1 ×	La—O(3)	2.648 2 ×
Cu—O(1)	1.941 2 ×	La—O(1)	2.717 (9) 1 ×
Cu—O(3)	1.962 (2) 1 ×	La—O(1)	2.718 (11) 1 ×
Cu—O(2)	2.260 (10) 1 ×	La—O(1)	2.890 (11) 1 ×
La—O(2)	2.455 (6) 2 ×	La—O(2)	2.892 (7) 2 ×
La—O(1)	2.591 (9) 1 ×		
O(2)—Cu—O(2)	87.2 (3) 1 ×	O(3)—Cu—O(2)	92.5 (3) 1 ×
O(1)—Cu—O(3)	89.6 (3) 2 ×	O(1)—Cu—O(1)	176.5 (3) 1 ×
O(2)—Cu—O(1)	90.4 (3) 2 ×	O(2)—Cu—O(3)	179.7 (3) 1 ×
O(1)—Cu—O(2)	91.7 (3) 2 ×		

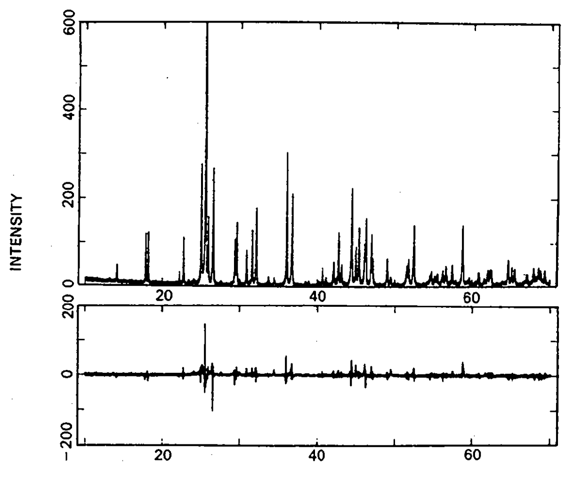

Fig. 1. The observed (above) and difference powder-diffraction profiles for $La_2Cu_2O_5$ at room temperature. Note that the difference profile is shown on a contracted scale.

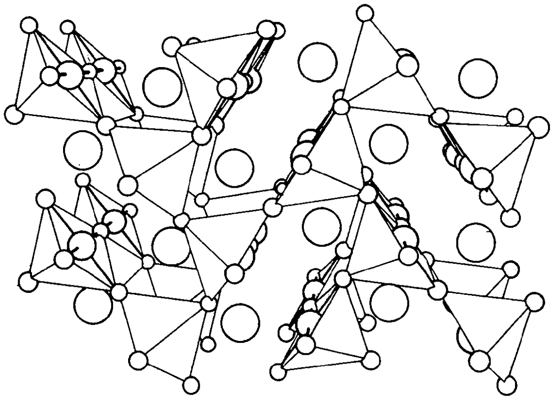

Fig. 2. A polyhedral representation of the structure of $La_2Cu_2O_5$ viewed approximately 15° off the *c* axis. Two perovskite slabs are shown. La atoms are represented by large open circles, Cu by shaded circles and O by small open circles.

Discussion. Final positional and isotropic thermal parameters are given in Table 1* with selected bond distances and angles in Table 2. A polyhedral representation of the structure of $La_2Cu_2O_5$ is given in Fig. 2. This phase is derived from its parent tetragonally distorted perovskite, $LaCuO_{3-\delta}$, through an ordering of oxygen vacancies in the (00*l*) planes. This ordering is complete at $\delta = 0.5$, and creates a unit cell which is related to the original perovskite subcell by $a \simeq (2a_p)^{1/2}$, $b \simeq 2(2a_p)^{1/2}$ and $c \simeq c_p$. The structure is isomorphous with $Ca_2Mn_2O_5$ (Poeppelmeier *et al.*, 1982) and consists of corner-shared CuO_5 square pyramids, which are typical for Cu^{II} compounds. The CuO_5 polyhedra exhibit a Jahn–Teller distortion with four shorter Cu—O bonds of approximately 1.94 Å and one long bond of 2.26 Å. The Cu—O—Cu bond angles are also slightly distorted from their ideal value of 180°. The La atoms reside in a perovskite-like *A*-site, but due to oxygen defects are only tenfold coordinated by oxygen. Unlike the cuprate superconductors, which possess highly anisotropic structures, the CuO_5 polyhedra of $La_2Cu_2O_5$ display a three-dimensional connectivity. The unique oxygen ordering creates one-dimensional channels of vacancies which run parallel to the *c* axis.

During the preparation of this manuscript a paper appeared (Cava, Siegrist, Hessen, Krajewski, Peck, Batlogg, Takagi, Waszczak, Schneemeyer &

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* The numbered intensity of each measured point on the profile has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71025 (264 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1018]

Zandbergen, 1991) describing a new homologous series $La_{4+4n}Cu_{8+2n}O_{14+8n}$. The $n = 2$ member of this series is $La_2Cu_2O_5$. As described by Cava *et al.*, this phase is structurally unrelated to $La_2Cu_2O_5$ described herein, and contains copper in four- and sixfold coordination. Close examination of the X-ray powder patterns of the two phases revealed no obvious similarities. Thus, as with $LaCuO_3$, $La_2Cu_2O_5$ adopts more than one structural type.

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Structure of Hexakis(3-methylpyridinium) Decavanadate Bis(3-methylpyridinium perchlorate) Dihydrate

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Abstract. $[V_{10}O_{28}(C_6H_7NH)_6].2(C_6H_7NH).2(ClO_4).2H_2O$, $M_r = 1945.4$, monoclinic, $P2_1/c$, $a = 12.580\ (2)$, $b = 26.262\ (5)$, $c = 11.340\ (4)$ Å, $\beta = 108.11\ (2)°$, $V = 3561\ (2)$ Å^3, $Z = 2$, $D_m = 1.8\ (1)$ (by flotation in $CHBr_3$–CCl_4), $D_x = 1.81$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.38$ mm^{-1}, $F(000) = 1960$, $T = 298$ K, $R = 0.025$ for 1789 observed reflections. The formula unit consists of the decavanadate anion, two perchlorate anions, eight 3-methylpyridinium cations and two water molecules and is centrosymmetric. The polyanion is similar to other known decavanadates. The perchlorate ions are disordered.

Introduction. The structures of several decavanadates have been described previously: $K_2Zn_2(V_{10}O_{28}).16H_2O$ (Evans, 1966), $Ca_3(V_{10}O_{28}).17H_2O$ (Swallow, Ahmed & Barnes, 1966), $Nd_2V_{10}O_{28}.28H_2O$ (Saf'yanov & Belov, 1976), $Y_2V_{10}O_{28}.24H_2O$ (Saf'yanov, Kuz'min & Belov, 1978*a*), $La_2V_{10}O_{28}.20H_2O$ (Saf'yanov, Kuz'min & Belov, 1978*b*), $Na_6V_{10}O_{28}.18H_2O$ (Durif, Averbuch-Pouchot & Guitel, 1980), $(H_9C_7NH)_4H_2V_{10}O_{28}$ (Debaerdemaeker, Arrieta & Amigó, 1982), $(H_3NCH_2CH_2NH_3)_3V_{10}O_{28}.6H_2O$ (Shao, Wang, Zhang & Tang, 1983), $Er_2V_{10}O_{28}.25H_2O$ (Rivero, Rigotti, Punte & Navaza, 1984), $(C_7H_{13}N_2)_4H_2V_{10}O_{28}.6H_2O$ (Shao, Wang, Zhang & Tang, 1984), $(C_{10}H_{14}N_5O_4)_4H_2V_{10}$-

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