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BRIEF COMMUNICATION

Growth and Structural Refinement of Orthorhombic $SrCuO_2$ Crystals

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Orthorhombic $SrCuO_2$ single crystals are grown between 1050–950°C under ambient pressure using CuO self-flux method. $SrCuO_2$: $M_r = 183.16$, orthorhombic, *Cmcm* (No. 63), $a = 3.577(1)$ Å, $b = 16.342(1)$ Å, $c = 3.9182(7)$ Å, $Z = 4$, $D_x = 5.311$ g/cm^3, $\mu(MoK\alpha) = 321.79$ cm^{-1}, $F(000) = 332.00$. The anisotropic temperature factors converge to the values of $R = 0.0289$ and $wR = 0.0286$ for 532 independent reflections. The crystal structure has two kinds of cation-polyhedral double layers of SrO_7 and CuO_4 that alternately connect parallel to the *b* axis direction, and the stacking along the *c* axis is closely related to the NaCl-like TlI-type structure. The NaCl-related structure is formed by cell-twinning parallel to the $\langle 110 \rangle_{NaCl}$ direction. The periodic units (N) are 5 and the lengths (D) are 14.23 Å for the cation arrangements and 14.24 Å for the anion arrangements, respectively. The formula is determined to be $Sr_{0.964}Cu^{2+}{}_{0.950}O_{1.91}$ from X ray refinements and bond-valence calculations.

1. INTRODUCTION

Recently, it was discovered that strontium cuprate, $SrCuO_2$, is one of the remarkable compounds related to the high-temperature cuprate superconducting materials. $SrCuO_2$ with infinite two-dimensional CuO_2-layer structure synthesized under high pressure (1) or by sputtering techniques (2) has a perovskite-like tetragonal structure and is the simplest compound showing superconducting transition above the liquid-nitrogen temperature up to 100 K (3).

The structure of orthorhombic $SrCuO_2$ crystals grown under ambient pressure was solved by data from single-crystal X ray photographs (4) and was determined to be the isotype of $SrCu_{0.75}Ni_{0.25}O_2$ (5). The present paper describes the growth of orthorhombic $SrCuO_2$ single crystals by the CuO-flux method. The results of the structure refinement using the obtained crystals are also reported in order to elucidate the accurate atomic positions as well as the site occupancies, which are closely related to the physical properties such as superconductivity.

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2. EXPERIMENTAL AND REFINEMENT

(1) *Single Crystal Growth*

Single crystals of orthorhombic $SrCuO_2$ were grown by the self-flux method using CuO in the following ways. Appropriate amounts of $SrCO_3$ (3 N) and CuO (4 N), supplied from High Purity Chemetals Laboratory Co., were well mixed in stoichiometric proportions of $SrCuO_2$ and were calcinated twice at 1000°C for 48 hr in air. The final specimens were prepared by thoroughly mixing with excess CuO for the flux material in the final ratio 80.8 mol% $SrCuO_2$ and 19.2 mol% CuO. They were placed in an Al_2O_3 crucible and were heated at 1050°C for 3 hr in air. It was then cooled to 950°C at a rate of 2°C/hr, and finally cooled down to room temperature at a rate of about 200°C/hr. The needle-like crystals having maximum size of 0.2 × 0.2 × 2 mm with metallic luster were grown in a cave of solidified flux, as shown in Fig. 1. Several crystals were examined by EDAX technique (JEOL JSM-T220) and were found to have uniform cation composition of Sr : Cu ≈ 1 : 1. No superconductivity was observed in SQUID measurements at 4.2 K.

(2) *X Ray Experimental*

The precession photographs indicated the space group *Cmcm*. The ground crystal (0.1 × 0.1 × 0.3 mm) was set along the axis direction parallel to the Ψ axis of an RIGAKU AFC5S diffractometer using pyrolitic-graphite monochromatized Mo$K\alpha$ radiation, and the unit cell was

0022-4596/94 $6.00

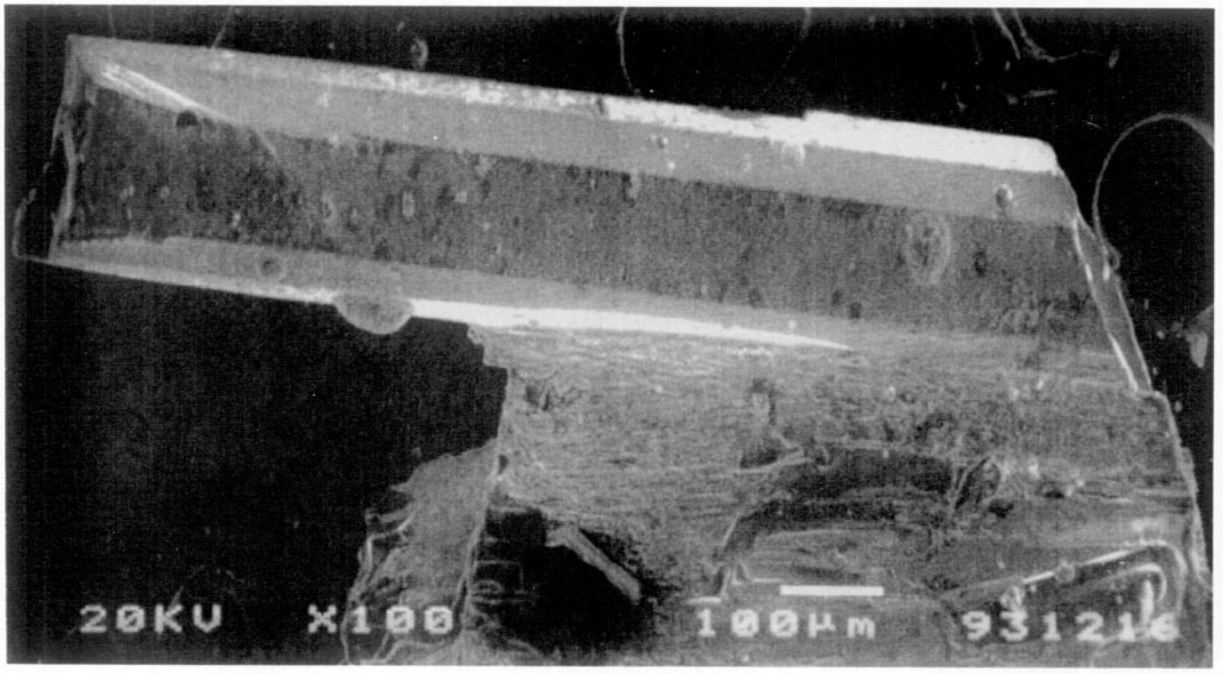

FIG. 1. SEM photograph of as-grown needle-like orthorhombic $SrCuO_2$.

obtained by the least-squares procedure of the setting angles of 25 reflections, well centered in the range of $42° < 2\theta < 53°$ using MoKα_1 (0.71073 Å). Details of the diffraction intensity study are summarized in Table 1.

The structure was solved by the direct method [SAPI91] (6) and refined on the structure factor F by full-matrix least-squares methods with a weighting scheme of $1/\sigma^2|F_0|$. From this result, all atoms are located on the 4c (0, y, $\frac{1}{2}$) site of *Cmcm*. Before the refinement of anisotropic temperature factors, the F_0 values were corrected for absorption effect with the program [DIFABS] (7) in the mode that utilizes θ-dependent systematic deviations $|F_0| - |F_c|$. The site occupancies of Sr and Cu were refined to be 0.964(11) and 0.950(11), respectively, and the formula for this compound is represented by $Sr_{0.964}Cu_{0.950}O_2$. The neutral atomic form factors and values for dispersion corrections for all atoms were provided by *International Tables for X-ray Crystallography*, vol. IV (1974). The final R and wR values for 532 reflections were 2.89 and 2.86%, respectively. Further details of the refinements are referred to Table 1. The resulting atomic parameters are listed in Table 2.[1] All of the structural refinements were executed using the TEXRAY program system [teXsan] (8).

[1] The table for the final structure amplitudes is deposited on 5 pages in NAPS Document 05139 for 7 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 for up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for each additional 10 pages of material, plus $1.50 for postage of any microfiche orders.

3. RESULTS AND DISCUSSION

(1) *General Features*

The structure thus refined is fundamentally the same as that in the previous report (4). The present results, however, provide a more accurate structure of $SrCuO_2$, as shown in Fig. 2. Selected atomic distances and angles are listed in Tables 3 and 4.

The SrO_7 polyhedra construct the one-dimensional infinite double-layer slab that zigzags parallel to the c axis direction, and has the finite layer parallel to the a axis. The CuO_4 square plates construct the one-dimensional infinite double-layer slab that zigzags parallel to the c axis direction. Both slabs are alternately connected parallel to the b axis direction (Fig. 3).

(2) *The Cell-Twinning Structure in Orthorhombic $SrCuO_2$*

As mentioned above, the orthorhombic $SrCuO_2$ structure has two kinds of polyhedra, which form a NaCl-related layer structure on the (100) plane (Fig. 3). That is, the stacking features parallel to the b axis are explained by two kinds of distorted NaCl-like structures. These are characterized as follows:

(A) The Cu–Cu layers are made of the distorted NaCl-type structure, and

(B) the Cu–Sr and Sr–Sr layers have the TlI-type structure.

TABLE 1
Experimental Conditions for the Refinement of Orthorhombic $SrCuO_2$

Crystal data	
Unit cell dimension (Å)	a = 3.577(1), b = 16.342(1), c = 3.9182(7)
Z	4
Space group	*Cmcm* (No. 63)
Intensity data collection	
Scan technique	$\omega - 2\theta$
Scan width (°)	1.26 + 0.25 tan θ
Scan speed (°/min)	6
Maximum number of repetition	10
Maximum (sin θ)/λ (Å^{-1}), 2θ (°)	1.0779, 100
Range of index	$-7 \le h \le 7$, $-35 \le k \le 35$, $0 \le l \le 8$
Number of measured reflections	1874
Number of unique reflections	733 (R_{int} = 0.079)
Intensity monitorius	
Reference reflections	$0\bar{8}0$, $\bar{1}70$, $0\bar{4}1$
Interval	Every 150 reflections
Intensity variation (%)	−0.24
Intensity data reduction	
Lp correction	Yes
Absorption correction method	DIFABS
Absorption coefficient (cm^{-1})	μ = 321.79
Minimum/Maximum transmission	0.8805/1.0573
Structure refinement	
Number of used reflections	532 [$I_0 > 3.00\ \sigma$ (I_0)]
Final R/wR values	0.0289/0.0286
Final scale factor	0.183(1)
Maximum final shift/e.s.d.	0.000
Goodness of fit	1.77
Maximum/Minimum density in the final D-Fourier map (e/Å^3)	0.93/−1.02
Secondary extinction	g = 3.07(1) × 10^{-6}

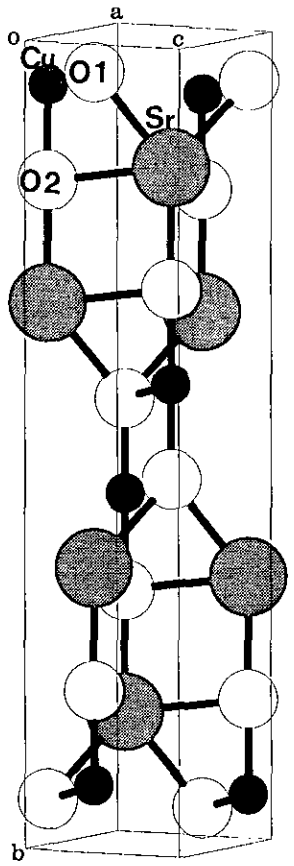

FIG. 2. The crystal structure of orthorhombic $SrCuO_2$ projected down to the (112) plane.

Furthermore, these NaCl-like structures were also explained as a twinning relation on the unit-cell level (11). The cell-twinning of this structure is formed only by the cation or anion arrangement parallel to the $\langle 110 \rangle_{NaCl}$ direction. The periodic units (N) are 5 atoms for both of the cation and anion arrangements, and the periodic lengths (D) are 14.23 Å for the cation arrangements and 14.24 Å for the anion, respectively. From this result and the different radii between strontium and copper, the copper square plate was distorted from the ideal TlI-type structure.

(3) *Oxygen and Copper Valence Calculations by the Bond-Valence Method*

The results of the occupancy refinement for cation sites suggest that a part of divalent copper is changed to a trivalent state. Thus, we have tried to determine the oxygen and copper valences using the bond-valence method (12).

We first estimated the oxygen occupancies to each oxy-

TABLE 2
Final Structure Parameters for Orthorhombic $SrCuO_2$

	y	B_{eq} (Å^2)	U_{11}	U_{22}	U_{33}	Occ. (X-ray)	Occ. (Bond-Valence method)
Sr	0.33096(2)	0.522(5)	0.0043(1)	0.0091(2)	0.0064(1)	0.482(8)Sr	Fixed 0.482Sr
Cu	0.06109(3)	0.476(7)	0.0066(2)	0.0077(2)	0.0037(2)	0.475(8)Cu	Fixed 0.475Cu
O1	0.9442(2)	0.76(4)	0.012(1)	0.010(1)	0.0062(9)	Fixed 0.5	0.50
O2	0.1792(2)	0.71(4)	0.011(1)	0.009(1)	0.0066(9)	Fixed 0.5	0.46

Note. All atoms are located on 4c site of *Cmcm*. Values in parentheses are estimated standard deviations. The thermal parameters refer to the expression, $T = \exp[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*)]$, where $U_{12} = U_{23} = U_{31} = 0$. Isotropic temperature factors (B_{eq}) are calculated from the anisotropic thermal parameters, U_{11}, U_{22}, and U_{33}.

TABLE 3
Final Atomic Distances (Å) for Orthorhombic $SrCuO_2$

(1) SrO_7 polyhedron	
Sr–O2[a]	2.480(3)
–O1[b,c]	2.574(3) × 2
–O2[d,e,f,g]	2.6579(6) × 4
Average	2.609(2)
Sr–Cu[d,e,f,g]	3.1859(6) × 4
(2) CuO_4 square plate	
Cu–O1[h]	1.910(3)
–O2[a]	1.930(3)
–O1[i,j]	1.9610(4) × 2
Average	1.941(2)
Cu–Cu[k,l]	2.7973(6) × 2

Note. E.s.d.'s are in parentheses. Symmetry codes are as follows: (a) X, Y, Z; (b) $X + \frac{1}{2}$, $Y + \frac{3}{2}$, Z; (c) $X + \frac{3}{2}$, $Y + \frac{3}{2}$, Z; (d) $-X + \frac{1}{2}$, $-Y + \frac{1}{2}$, Z; (e) $-X + \frac{1}{2}$, $-Y + \frac{1}{2}$, $Z - 1$; (f) $-X + \frac{3}{2}$, $-Y + \frac{1}{2}$, $Z - 1$; (g) $-X + \frac{3}{2}$, $-Y + \frac{1}{2}$, Z; (h) X, $Y + 1$, Z; (i) $-X$, $-Y - 1$, $-Z - 1$; (j) $-X$, $-Y - 1$, $-Z$; (k) $-X$, $-Y$, $-Z - 1$; (l) $-X$, $-Y$, $-Z$.

TABLE 4
Final Bond Angles (°) for Orthorhombic $SrCuO_2$

(1) SrO_7 polyhedron		
O1[b]–Sr–	O1[c]	88.04(7)
O1[c]	O2[d,e,f,g]	64.99(7) × 4
O2[a]	O2[d,e,f,g]	86.42(7) × 4
O2[e]	O2[d]	94.965(7)
O2[f]	O2[g]	94.965(7)
O2[e]	O2[f]	84.587(6)
O2[d]	O2[g]	84.587(6)
(2) CuO_4 square plate		
O1[h]–Cu–	O1[i,j]	87.5(1) × 2
O2[a]	O1[i,j]	92.5(1) × 2

Note. E.s.d.'s are in parentheses. Symmetry codes are as follows: (a) X, Y, Z; (b) $X + \frac{1}{2}$, $Y + \frac{3}{2}$, Z; (c) $X + \frac{3}{2}$, $Y + \frac{3}{2}$, Z; (d) $-X + \frac{1}{2}$, $-Y + \frac{1}{2}$, Z; (e) $X + \frac{1}{2}$, $-Y + \frac{1}{2}$, $Z - 1$; (f) $-X + \frac{3}{2}$, $-Y + \frac{1}{2}$, $Z - 1$; (g) $-X + \frac{3}{2}$, $-Y + \frac{1}{2}$, Z; (h) X, $+ 1$, Z; (i) $-X$, $-Y - 1$, $-Z - 1$; (j) $-X$, $-Y - 1$, $-Z$.

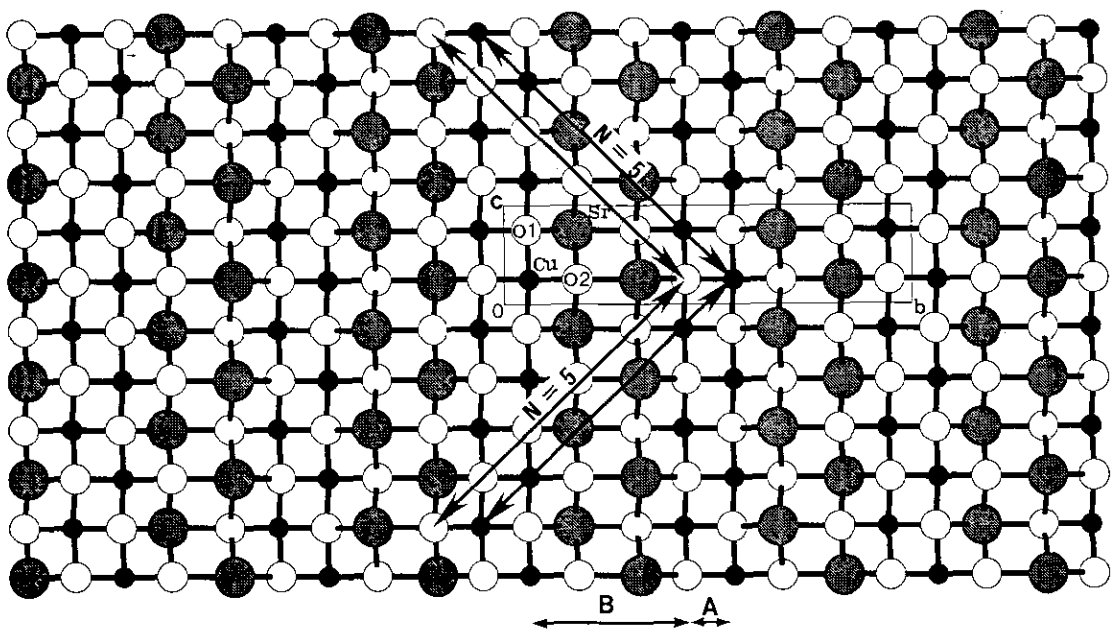

FIG. 3. The atomic arrangement of Sr (hatched large circle), Cu (solid circle), and O (open circle) at the (100) plane in orthorhombic $SrCuO_2$. Cell-twinning structures are oriented parallel to the $(110)_{NaCl}$ direction. The periodic units (N) are 5, and the periodic lengths (D) are 14.23 Å for the cation arrangements and 14.24 Å for the anion arrangements, respectively.

gen site using the cation occupancy values from X ray refinement. In this result, the O1 site is occupied by 1.00 oxygen and the O2 by 0.91 oxygen; the resulting formula is $Sr_{0.964}Cu_{0.950}O_{1.91}$ (Table 2). Subsequently, we calculated the copper valence using the strontium and oxygen occupancy values obtained above. The result shows that a part of the copper atom is monovalent (normalized $Cu^{2+}/Cu^{+} = 0.992/0.008$). However, this Cu^{+} value is too small. Accordingly, the formula is finally estimated to be $Sr_{0.964}Cu^{2+}_{0.950}O_{1.914}$, suggesting that the flux-grown $SrCuO_2$ crystals would be slightly doped with electrons, when they are semiconductive.

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