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Single-Crystal Structure Determination of High Pressure Prepared $Sr_{0.74}Ca_{0.26}CuO_2$

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$Sr_{0.74}Ca_{0.26}CuO_2$ single crystals have been grown from a melt at high pressure. The compound is isostructural with the "infinite layer" parent compound $Sr_{0.14}Ca_{0.86}CuO_2$, prepared at ambient pressure. It crystallizes in the tetragonal space group *P4/mmm* (No. 123) with the lattice parameters $a = 3.907$ Å and $c = 3.362$ Å. Magnetic measurements down to 4.2 K revealed no indications for superconductivity.

INTRODUCTION

The "infinite layer" structure $ACuO_2$, which results from the perovskite lattice by omitting two oxygen atoms in the *trans*-position of the octahedral Cu^{2+} coordination, was first described by Siegrist *et al.* (1) for $Sr_{0.14}Ca_{0.86}CuO_2$ and is composed of planar $[CuO_2]$ sheets separated by Ca(Sr) ions. At ambient pressure this structure can only be stabilized for a ratio Ca : Sr of about 6 : 1 to 10 : 1. Using high pressure techniques the stability range of this structure type was extended: $Ba_{0.33}Sr_{0.67}CuO_2 \leftrightarrow SrCuO_2 \leftrightarrow Sr_{0.33}Ca_{0.67}CuO_2$ (2). The high pressure synthesis of further $ACuO_2$ compounds with this structure led to the discovery of superconductivity in Sr–Nd–Cu–O ($T_c \approx 60$ K) (3), Ba–Sr–Cu–O ($T_c \approx 90$ K) (4), Sr–Cu–O ($T_c \approx 100$ K) (5), and Sr–Ca–Cu–O mixed crystals ($T_C \approx 110$ K) (6), respectively. The origin of superconductivity in most of these compounds is still uncertain (4–6). Concerning the structure of the compounds prepared under high pressure no single-crystal studies have been undertaken so far.

In this contribution we report about the high pressure preparation of small single-crystals with the composition $Sr_{0.74}Ca_{0.26}CuO_2$ and their structural characterization by X-ray diffraction.

EXPERIMENTAL

A solution of $SrCO_3$, CaO, and CuO (0.7Sr : 0.3Ca : Cu) in 3 *N* HNO_3 was evaporated to dryness on a hot sand bath ($T \approx 400$°C). The residue was ground and heated to 950°C in air in order to decompose the nitrates. After a second grinding procedure the resulting solid was pressed into pellets ($p \approx 80$ MPa) and sintered at 950°C in air for another 12 hr. The pellets were reacted under a pressure of 3 GPa in a sealed platinum capsule (∅ = 4 mm, h = 12 mm) using a piston cylinder apparatus (∅ = 12.6 mm) with a graphite heater and a CaF_2 pressure cell. The heat treatment was the following: (1) heating with 60°C/min to 1300°C; (2) keeping the temperature for 15 min; (3) cooling to 900°C with 1°C/min; (4) quenching to room temperature.

The obtained high pressure product consisted of two fractions. In the center of the sample (∅ ≈ 3 mm) was a black, solidified melt, which contained small, metallic crystals. This fraction was embedded into a reddish brown "crust." The former phase could be identified by X-ray powder diffraction (Huber Guinier camera, $\lambda = 1.5405$ Å) as high pressure $Sr_{1-x}Ca_xCuO_2$ ($x \approx 0.3$), whereas the latter showed a diffraction pattern, which could not be indexed. The AAS analysis showed that the by-product contained more than 10 wt% platinum, probably due to the reaction with the container material. A magnetic SQUID measurement of both phases revealed no indications for superconductivity down to 4.2 K.

For data collection a crystal of the dimension 0.04 × 0.05 × 0.10 mm was mounted on a Siemens P4 four circle diffractometer. The lattice parameters were refined by least-squares analysis of 26 reflections in the range of $26.5° < 2\Theta < 48.1°$. A total of 1633 reflections was collected with the ω-2Θ scan technique (scan width $\Delta\omega$ = 0.8°). The intensity of three standard reflections was measured every 100 reflections. Details of the data collection and the refinement are summarized in Table 1. The structure was solved and refined with the computer program SHELXTL PLUS (7). A refinement of the Sr to Ca ratio, the deficiency parameter δ, and the oxygen occupancy number yielded the composition $(Sr_{0.74}Ca_{0.26})_{1-\delta}CuO_2$ ($\delta = 0$). The final R values with anisotropic thermal parameters for each atom were $R = 0.029$ and $R_w = 0.026$. Extinction and absorption corrections were applied. The

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TABLE 1
Measuring Conditions and Crystal Data for $Sr_{0.74}Ca_{0.26}CuO_2$

Refined composition	$Sr_{0.74}Ca_{0.26}CuO_2$
Formula weight (g/mole)	170.80
Calculated density (g/cm³)	5.53
Crystal system	Tetragonal
Space group	*P4/mmm* (No. 123)
a(Å)	3.907(3)
c(Å)	3.362(4)
Vol. (Å³)	51.32
Z	1
Diffractometer	Siemens P4
Radiation	λ = 0.71073 Å (Mo*Kα*)
Monochromator	Graphite
Temperature	20°C
2Θ range	10.4 to 59.4°
Absorption coefficient (cm⁻¹)	299
Absorption correction	Numeric
Data collected	$-5 \le h(k) \le 5$, $-4 \le l \le 4$
Scan mode	ω-scan
Scan speed	Automatic
Total reflections	1633
Observed reflections ($I > \sigma(I)$)	1372
Unique reflections	63
Data/parameter ratio	5.7
R	0.029
R_w	0.026
S = GOF	3.0

atomic positions and isotropic thermal parameters are given in Table 2, and the anisotropic thermal parameters in Table 3. Additional Buerger precession camera exposures in the [010] direction yielded no evidence for a superstructure along the *a*- and/or *c*-axis.

RESULTS

$Sr_{0.74}Ca_{0.26}CuO_2$, prepared at high pressure, crystallizes in the tetragonal space group *P4/mmm* (No. 123) with

TABLE 2
Atomic Positions, Occupancy Numbers and Isotropic Thermal Parameters for $Sr_{0.74}Ca_{0.26}CuO_2$, Space Group *P4/mmm* (No. 123)

Atom	Position	*x*	*y*	*z*	Occ.	U_{eq} [10^{-2}Å²]
Sr	1*d*	½	½	½	0.74(1)	0.77(4)
Ca	1*d*	½	½	½	0.26(1)	0.77(4)
Cu	1*a*	0	0	0	1	0.76(4)
O	2*f*	0	½	0	2	1.04(20)

Z = 1. It is isostructural with the "infinite layer" parent compound $Sr_{0.14}Ca_{0.86}CuO_2$, prepared at ambient pressure (1). The Cu–O spacings (1.954 Å) in the square-planar CuO_4 units and the Sr–O distances (2.577 Å) in the SrO_8 cube, which is slightly elongated along the *c*-direction, are longer than those in $Sr_{0.14}Ca_{0.86}CuO_2$ (1.931 Å and 2.507 Å). The increase of the latter bond lengths is nearly that expected on the basis of the Shannon radii for Ca^{2+} (1.12 Å) and Sr^{2+} (1.26 Å) in eightfold coordination (8). The structure of $Sr_{0.74}Ca_{0.26}CuO_2$ is shown in Fig. 1. The anisotropic ellipsoids of thermal motion are of comparable size to those of $Sr_{0.14}Ca_{0.86}CuO_2$. They reflect the crystal structue of this layer compound with prolate Cu and O ellipsoids perpendicular to the [CuO_2] planes and spherical Sr(Ca) ellipsoids between the layers. Because of the rather large anisotropic thermal parameter U_{33} of oxygen (Table 3) a refinement in *P4m2* (No. 115) was attempted. Though in this space group the oxygen atoms are allowed to occupy positions with $z \neq 0$, the refinement did not produce a significant deviation from $z = 0$.

Concerning the physical properties of $ACuO_2$ com-

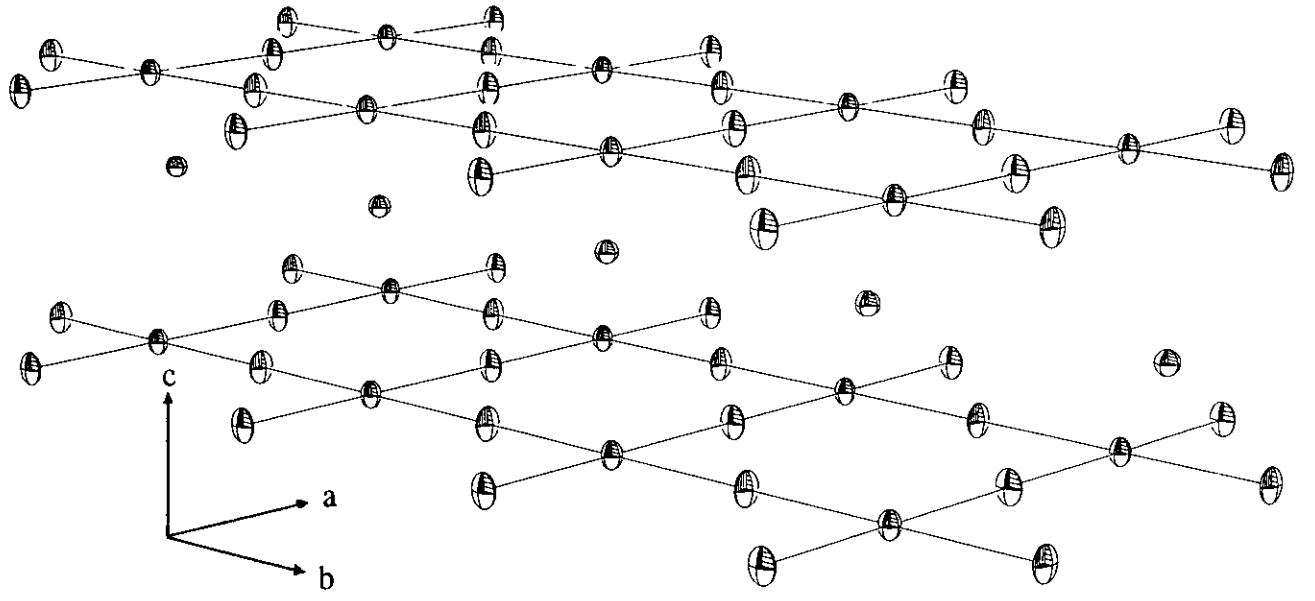

FIG. 1. View of the structure of $Sr_{0.74}Ca_{0.26}CuO_2$, detailing the anisotropic thermal ellipsoids at the 50% probability level. Only the Cu–O bonds are drawn.

TABLE 3
Anisotropic Thermal Parameters [10^{-2} Å^2] for $Sr_{0.74}Ca_{0.26}CuO_2$ ($\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots)]$, $U_{ij} = 0$ for $i \neq j$)

Atom	U_{11}	U_{22}	U_{33}
Sr(Ca)	0.77(6)	$=U_{11}$	0.77(7)
Cu	0.58(7)	$=U_{11}$	1.11(8)
O	1.12(39)	0.31(34)	1.70(30)

pounds with the infinite layer structure Azuma *et al.* (6) reported about superconductivity at 110 K in a compound with the nominal composition $[Sr_{0.7}Ca_{0.3}]_{0.9}CuO_{2-y}$ and the assumption $y = 0$. The given composition indicates a cation deficiency on the A position, suggesting a formal oxidation state of copper larger than two. The absence of superconducting properties of $Sr_{0.74}Ca_{0.26}CuO_2$ is probably due to the missing mixed valent behavior of this compound. Further single-crystal studies of superconducting $ACuO_2$-type compounds are in progress.

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