

LETTER TO THE EDITOR

X-Ray Single Crystal Structure Analysis of the Three-Leg-Ladder Compound $(\text{Sr}, \text{Ca})_4\text{Cu}_6\text{O}_{10}$

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Communicated by J. M. Honig November 17, 1997; accepted November 19, 1997

Crystals with the general formula $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ belong to the “ladder” compounds, a new series of high-pressure materials. They are expected to have interesting magnetic properties and are possible candidates for HT_c superconductors. For the first time single crystals of $(\text{Sr}, \text{Ca})_4\text{Cu}_6\text{O}_{10}$ have been grown using a high-Ar-gas-pressure method. A crystal was measured on an X-ray four circle single crystal diffractometer and the structure was refined to $R = 0.056$ with F data and $wR = 0.094$ with F^2 data. $(\text{Sr}, \text{Ca})_4\text{Cu}_6\text{O}_{10}$ crystallizes with space group No. 65 $Cmmm$ ($Z = 1$) and has lattice parameters $a = 3.9299(5)$ Å, $b = 19.392(3)$ Å, $c = 3.4358(5)$ Å. The Ca content at the Sr site was refined to 4.3(8)%. The crystal structure consists of layers with coupled chains formed by both edge- and corner-sharing CuO_4 units (“ladders”) separated by layers of Sr/Ca atoms.

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INTRODUCTION

In the system Sr–Ca–Cu–O there exists a large variety of structure types depending on the p – T conditions. A common feature of the structures is the square planar CuO_4 units, which are combined in three different ways:

1. Pure corner-sharing connections are realized in Sr_2CuO_3 , forming one-dimensional CuO_2 chains (1), or in high-pressure SrCuO_2 , forming infinite layer CuO_2 planes like in all HT_c cuprate superconductors (2). These materials may be superconducting upon doping (3, 4).

2. Pure edge-sharing CuO_4 units lead to CuO_2 ribbons (double chains) in ambient pressure SrCuO_2 (5) or to one-dimensional single chains in high-oxygen-pressure compounds $\text{Sr}_{0.73}\text{CuO}_2$ (6, 7) or $\text{Ca}_{0.85}\text{CuO}_2$ (8). These materials are not superconducting but show an interesting magnetic behavior (7).

3. Combined edge- and corner-sharing CuO_4 squares are found in $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (9, 10) or the “ladder” compounds $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ (11).

Very recently, $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ has found to be superconducting upon doping (12) and under pressure (13). This is the first cuprate superconductor which does not contain pure corner-sharing CuO_4 units. Instead, the structure is stacked alternately of Cu–O layers forming either infinite edge-sharing chains or combined edge- and corner-sharing “ladders.”

It is now important to know in which structural unit superconductivity occurs—in the infinite chain or in the ladder layers. We succeeded in growing single crystals containing only one of these structural features: $\text{Sr}_{0.73}\text{CuO}_2$ with infinite CuO_2 chains (6, 7), and $(\text{Sr}, \text{Ca})_4\text{Cu}_6\text{O}_{10}$ with a Cu_3O_5 three-leg-ladder sublattice which is discussed here. This material was first synthesized by Hiroi *et al.* (10) at a pressure $p = 6$ GPa. Kazakov *et al.* (14) refined the crystal structure with the Rietveld method with powder neutron diffraction data. Ladder compounds are in particular interesting because theoretical predictions promise possibly superconductivity for materials with an even number of legs (15, 16).

Here, we present the X-ray structure refinement of the first single crystal of this interesting phase.

EXPERIMENTAL

Synthesis, Crystal Growth, and Characterization

$(\text{Sr}, \text{Ca})_4\text{Cu}_6\text{O}_{10}$ single crystals were grown with the high-argon-gas-pressure technique (17), using a gas compressor and a pressure intensifier. The starting materials SrCuO_2 and Ca_2CuO_3 have been prepared from high-purity ($\geq 99.99\%$) SrCO_3 , CaCO_3 , and CuO by annealing at 950–970°C for 100 h. SrCuO_2 , Ca_2CuO_3 , and CuO were mixed in the cationic ratio Sr:Ca:Cu = 0.9:0.1:1.1. This material was calcinated in air at 940°C for 15 h; afterward it was melted in an alumina crucible at an Ar partial gas pressure $p = 18.2$ kbar at 1300–1350°C, followed by a slow cooling to 1240–1290°C in a three-zone Kanthal furnace.

Black crystals grew in a plate-like shape, with (001) as the main face.

The crystal was not superconducting, and a magnetic measurement did not show a diamagnetic transition. We could exclude the incorporation of aluminum from the crucible in the crystals by an EDX analysis.

Structure Analysis

Crystals were examined with an X-ray precession camera (Mo radiation) in order to check crystal quality and to find lattice parameters, systematic extinctions, and possible superstructures. This method confirmed lattice parameters and the C-centered orthorhombic Bravais lattice observed by Hiroi *et al.* (10). We could not find any superstructure or additional systematic extinctions, except those due to C-centering. A suitable single crystal was selected and mounted on an X-ray four circle Siemens P4 diffractometer. For

TABLE 1
Data Collection and Refinement Parameters for (Sr, Ca)₄Cu₆O₁₀

Formula	Sr _{3.83} Ca _{0.17} Cu ₆ O ₁₀
Formula weight	883.64 g/mol
Crystal size	0.13 × 0.23 × 0.02 mm ³
Color	Black
Diffractometer	Siemens P4
Monochromator	Graphite
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)
Temperature	293 K
<i>a</i>	3.9299(5) \AA
<i>b</i>	19.392(3) \AA
<i>c</i>	3.4358(5) \AA
<i>V</i>	261.84(6) \AA^3
<i>Z</i>	1
Space group	<i>Cmmm</i> (No. 65)
Density ρ_x	5.604 g/cm ³
μ (MoK α)	31.4 mm ⁻¹
Scan mode	ω - 2θ
2θ range	2–80°
<i>h, k, l</i>	$-7 \leq h \leq 7$; $-34 \leq k \leq 34$; $-6 \leq l \leq 6$
No. of measured reflections	3337
No. of unique reflections	511
R_{int} (F^2)	0.061
No. of refined parameters	25
Refinement method	Full matrix least squares on $ F^2 $
F_{000}	402.9
$R1^a$ (all data), $R1^a$ ($F_0 > 4\sigma$)	0.062, 0.036
$wR2^b$ (all data)	0.094
Goodness of fit, S^c (all data)	1.115
$\Delta\rho_{\text{max}}$ at <i>x, y, z</i>	2.52 electrons/ \AA^3 at 0, 0.411, 0.326
Weighting factor ^d <i>a</i>	0.0422
Extinction factor ^e <i>y</i>	0.004(1)

$$^a R1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$$

$$^b wR2 = [\sum (w(F_0^2 - F_c^2)^2) / \sum (w(F_0^2)^2)]^{1/2}.$$

$$^c S = [\sum (w(F_0^2 - F_c^2)^2) / (N_{\text{ref}} - N_{\text{par}})]^{1/2}.$$

$$^d w = 1/[\sigma^2 F_0^2 + (a(1/3 F_0^2 + 2/3 F_c^2))^2].$$

$$^e F_c = F_c k [1 + 0.001 y F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}; k: \text{overall scale factor.}$$

TABLE 2
Structural Parameters of (Sr, Ca)₄Cu₆O₁₀

Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{11}	U_{22}	U_{33}
Sr/Ca ^a	4 <i>j</i>	0	0.39841(3)	1/2	0.0049(2)	0.0093(3)	0.0109(3)
Cu(1)	2 <i>a</i>	0	0	0	0.0030(3)	0.0061(4)	0.0112(4)
Cu(2)	4 <i>i</i>	0	0.19961(4)	0	0.0024(3)	0.0061(3)	0.0152(4)
O(1)	2 <i>b</i>	1/2	0	0	0.004(2)	0.009(3)	0.013(3)
O(2)	4 <i>i</i>	0	0.1003(3)	0	0.005(2)	0.008(2)	0.019(2)
O(3)	4 <i>i</i>	0	0.2997(3)	0	0.001(2)	0.008(2)	0.024(2)

^aCa content 4.3(8)%.

Note. Temperature factor $T = \exp(-2\pi^2[h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + \dots + 2hka^* b^* U_{12}]) [\text{\AA}^2]$ ($U_{12} = U_{23} = U_{13} = 0$).

determination of the lattice parameters and the orientation matrix 60 reflections with maximum $2\theta = 45^\circ$ have been centered. Reflection profiles were measured with graphite-monochromated MoK α radiation from the whole Ewald sphere. Three check reflections have been measured after 100 collected data which varied by $\pm 1\%$. Intensity data were corrected for Lorentz and polarization effects. Analytical absorption corrections were applied to the data by calculating the beampath of each reflection through the crystal defined by $\{100\}$ faces and a $(20-1)$ face. Intensities were averaged according to Laue group *mmm* and full matrix least squares refinement of structural parameters was performed with $|F^2|$ data. All structural calculations have been done with the SHELXTL-5 program (18). Details of data collection and structure refinement are given in Table 1.

The starting model for the refinement was constructed from data given by Hiroi *et al.* (11) with space group *Cmmm*. The refinement used all reflections and converged at $wR2 = 0.094$ with a Ca content of 4.3(8)%. The same refinement was repeated with a data set reduced to structure factors $|F|$ ($R_i = 0.029$); the corresponding refinement with SHELXTL-PC (19) converged at $R = 0.056$ ($R_w = 0.049$) with the same parameters and the same Ca content.

TABLE 3
Selected Bondlengths and Angles in (Sr, Ca)₄Cu₆O₁₀

Atoms	Distance	Atoms	Angles
Sr/Ca–O(1)	2.6138(5) $\text{\AA} \times 2$		
Sr/Ca–O(2)	2.6101(3) $\text{\AA} \times 4$		
Sr/Ca–O(3)	2.601(4) $\text{\AA} \times 2$		
Cu(1)–O(1)	1.9649(3) $\text{\AA} \times 2$		
Cu(1)–O(2)	1.946(5) $\text{\AA} \times 2$		
Cu(2)–O(2)	1.925(5) $\text{\AA} \times 1$	O(2)–Cu(2)–O(3)	91.5(3)°
Cu(2)–O(3)	1.902(5) $\text{\AA} \times 1$	O(3)–Cu(2)–O(3)	88.5(2)°
Cu(2)–O(3)	1.9656(3) $\text{\AA} \times 2$	O(3)–Cu(2)–O(3)	176.97(3)°

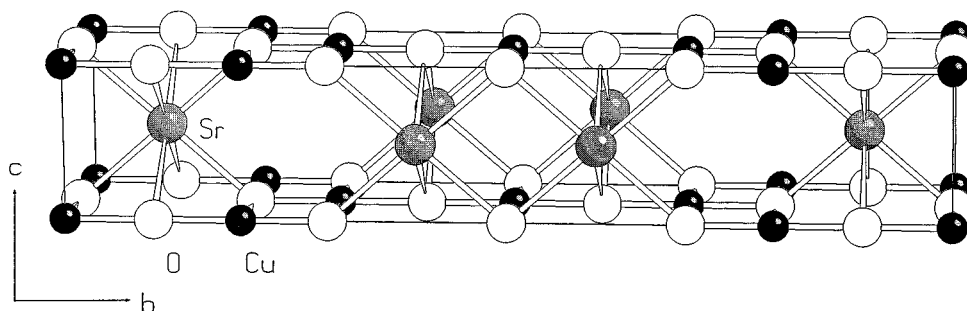


FIG. 1. Perspective view of the $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ crystal structure.

Observed systematic extinctions permit also the noncentrosymmetrical space groups $Cmm2$ (No. 35), $C222$ (No. 21), and $Amm2$ (No. 38) for $(\text{Sr}, \text{Ca})_4\text{Cu}_6\text{O}_{10}$. In space group $C222$ the same special positions are occupied as in $Cmmm$; $Cmm2$ allows shifts of the z/c parameters which are constrained to 0.0 or 0.5 in $Cmmm$, and in $Amm2$ all Cu and O atoms are located at the twofold site $(2a) 0, 0, z$. However, corresponding structure refinements did not improve R , and the variations of parameters have been within the error limits.

RESULTS AND DISCUSSION

Refined structural parameters and selected bondlengths are given in Tables 2 and 3, and a perspective view of the $(\text{Sr}, \text{Ca})_4\text{Cu}_6\text{O}_{10}$ crystal structure is shown in Fig. 1. The structure consists of Cu_3O_5 planes separated by layers of

Sr/Ca atoms, which are stacked in the c -direction. The Cu–O planes are constructed from square planar CuO_4 units which are linked by edge- and corner-sharing. This layer is called the “ladder” plane and is shown in more detail in Fig. 2: corner-sharing chains of CuO_4 squares form the legs of the ladder, running in the a -direction. Variation of the number of these chains from 2 to ∞ results in structures of 2-, 3-, n -leg-ladder until the infinite layer type. These ladders are connected by edge-sharing and form Cu–O double chains like in $\text{YBa}_2\text{Cu}_4\text{O}_8$ (20). This material belongs to a homologous series of the type $(\text{Sr}, \text{Ca})_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ with $n = 3, 5, 7, \dots, \infty$, respectively. The $n = 3, 5$, and ∞ members have been synthesized until now (2, 11, 14), but not always as single phase. From another point of view, these structures may be considered as the result of a shearing process in the infinite layer (IL) compound: removing one line of oxygen atoms and shifting the

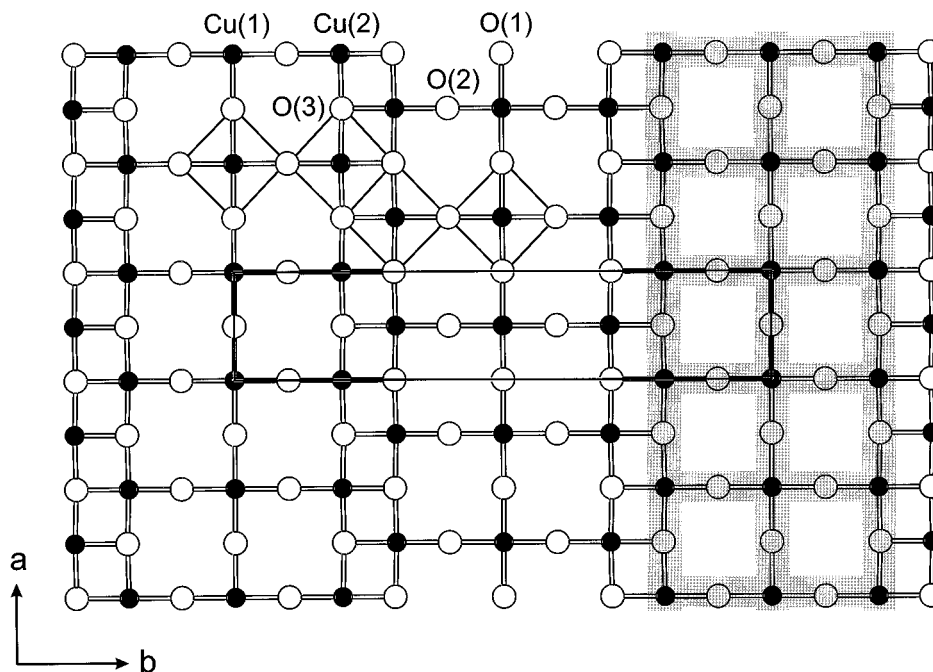


FIG. 2. The Cu_2O_3 plane in $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ constructed from corner- and mixed corner- and edge-sharing CuO_4 units. The “ladder” is shown in grey.

rest by $\frac{1}{2}[110]$ leads to a Cu–O double chain. The average Cu–Cu spacing is now decreased and therefore, the density of the cuprate layer is increased with increasing number of Cu–O double chains. The densest Cu–O layer of the $n = 3$ phase (2-leg-ladder) explains the highest pressure $p = 60$ kbar necessary for synthesis (14) in contrast to the IL end member with $n = \infty$, which needs ≤ 20 kbar (21). In general, the highest pressures for synthesis are expected for compounds with the highest density. However, the overall density within the $(\text{Sr}, \text{Ca})_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$ series is increasing from $n = 3$ to ∞ . This apparent contradiction is easily explained by the fact that the relative content of Sr heavy atoms is decreasing from IL compound (Sr/Cu = 1) to 2-leg-ladder $\text{Sr}_2\text{Cu}_4\text{O}_6$ (Sr/Cu = 0.5).

Generally, the bondlengths follow the expected trends: the ionic radius of calcium ($r = 1.12 \text{ \AA}$) is smaller than that of strontium ($r = 1.26 \text{ \AA}$); therefore, the lattice parameters in $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ are decreased upon Ca doping, as are the bond distances. Surprisingly, the a - and c -lattice parameters are close to those of undoped IL SrCuO_2 . Cu(1)–O bondlengths in the corner-sharing units are larger than Cu(2)–O which form the double chain. However, they are not large enough to allow n -type superconductivity, which requires distances of Cu–O $> 1.96 \text{ \AA}$ (21). Cu(2)–O(2) is smaller and Cu(2)–O(3) is larger than the corresponding distances in undoped $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ (14). The distortion of the Cu(2)O₄ squares is less in the presence of Ca: binding angles O–Cu(2)–O are by 1° closer to 90° than in $\text{Sr}_4\text{Cu}_6\text{O}_{10}$. The Sr/Ca–O distances are also more uniform (2.60–2.61 \AA) in Ca-doped material than in $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ with Sr–O distances varying from 2.61 to 2.64 \AA . In conclusion, the introduction of Ca in $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ seems to reduce distortions and stress in the crystal structure. As the observed Cu–O bondlengths are quite close 1.96 \AA it will be interesting to try to induce n -type superconductivity by doping with appropriate heavy atoms.

ACKNOWLEDGMENTS

P. Wägli kindly performed EDX analyses of our crystals. We acknowledge financial support by the Swiss National Foundation.

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