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The Crystal Structure of $CaSmCuO_3Cl$

K. V. RAMANUJACHARY, M. GREANEY, R. L. FULLER, AND
M. GREENBLATT*

*Department of Chemistry, Rutgers The State University of New Jersey,
New Brunswick, New Jersey 08903*

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Single crystals of $CaSmCuO_3Cl$ have been grown by high temperature reactions with Sm_2O_3, CuO, and excess $CaCl_2$. Its structure was determined by single crystal X-ray diffraction. $CaSmCuO_3Cl$ crystallizes with a tetragonal T^* structure (space group *P4/nmm* No. 129) with $a = 3.894(3)$ Å and $c = 13.416(8)$ Å. The structure can be described as an intergrowth of T and T' forms of the rare-earth copper oxides. The observed interatomic distances are comparable to those observed for $Ca_2CuO_4Cl_2$ and $Ca_3Cu_2O_4Cl_2$. © 1991 Academic Press, Inc.

Introduction

Following the discovery of superconductivity in substituted Ln_2CuO_4 (Ln = La, Pr, Nd, Sm, and Eu) type compounds (*1, 2*), there has been some effort directed toward the study of structurally related oxyhalides. Despite the structural similarities between the oxides and oxyhalides crystallizing with K_2NiF_4-related structures, it is well established that their transport properties are widely different. For example, in the isostructural pairs of $La_2CuO_4/Sr_2CuO_2Cl_2$ and $La_2SrCu_2O_6/Ca_3Cu_2O_4Cl_2$, the oxides show metal-to-superconducting transitions under appropriate conditions, while the oxyhalides are always insulating (*1, 3–6*). The observation of superconductivity in the Ln_2CuO_4 type oxides is believed to be associated with the presence of mixed-valent copper in the Cu–O planes, whereas the insulating state of the oxyhalides has been attributed to the antiferromagnetic ground state of the Cu^{2+} ions (*7, 8*). Attempts to modify the transport properties of the oxychlorides by modulating the copper valence so far have been unsuccessful, primarily due to their inertness toward chemical substitutions. To further understand the differences between the transport properties of the oxides and the oxyhalides, the determination of accurate structural parameters for the oxyhalides would be helpful in the evaluation of their electronic-band structures. To date, such data is available only on a few oxyhalides, thus rendering a comparative study of the electronic properties of oxides and oxyhalides difficult.

Recently, we have synthesized and characterized a new family of halo-oxo-cuprates of the type $MLnCuO_3Cl$ (M = Sr or Ca and Ln = Nd, Sm, Eu, or Gd) (*9*). An examination of the powder X-ray patterns revealed that these compounds crystallized with the so-called T^* structure, similar to the one reported for $Nd_{1.4}Ce_{0.2}Sr_{0.4}CuO_4$ (*10*). These

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* To whom correspondence should be addressed.

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compounds are the first examples of oxyhalides with the T^* structures. The structural determination of the T^* oxides has been limited to polycrystalline specimens using neutron or powder X-ray diffraction, most likely due to a lack of single crystals. We have succeeded in growing good quality single crystals of $CaSmCuO_3Cl$ suitable for X-ray diffraction and have determined its structure.

Crystal Growth

Crystals of $CaSmCuO_3Cl$ were grown by high temperature reactions with $CaCl_2$, Sm_2O_3, and CuO in the stoichiometric ratio 5 : 1 : 2. Intimately ground mixtures of the reactants were pelletized and placed in a gold foil and heated at 860°C for 5–6 days in a flowing oxygen atmosphere. The products were then quenched to room temperature. Plate like crystals ($0.2 \times 0.2 \times 0.04$ mm^3) were recovered by washing away the excess $CaCl_2$ with water. Preliminary identification of the crystals was carried out in a SCINTAG PAD V X-ray powder diffraction system. All the lines observed in the diffraction pattern were successfully indexed based on a cell proposed in the literature (*9, 11*).

Structure Determination

A thin plate like crystal ($0.2 \times 0.2 \times 0.02$ mm) was mounted on a glass fiber. The intensity data were collected on an Enraf–Nonius CAD4 automated four-circle diffractometer at ambient temperature. Parameters used in the data collection are summarized in Table I. Unit cell parameters and orientation matrices were obtained from 25 centered reflections. Axial photographs and the systematic absences ($h + k = 2n + 1$ for $hk0$ reflections) are consistent with the space group *P4/nmm* (No. 129). The refinement was carried out successfully in the centric setting of this space group. The structure was solved using the MOLEN structure determination package developed by Enraf–Nonius. The data were corrected for absorption by an empirical method, using high χ-angle ψ-scan data. Standard Lorentz polarization and anomalous dispersion corrections were applied. Initial refinement was attempted using the positional coordinates of the heavy atoms (Sm, Ca, and Cu) reported by Kwei *et al.* (*11*). The remaining atomic positions were determined by difference Fourier methods. A differential absorption correction was applied during the final stages of the refinement (MOLEN). All the atoms were refined anisotropically using full matrix least square routines. The final unweighted R-factor converged to 0.055. Lists of observed and calculated structure factors, and of anisotropic temperature factors, are available as supplementary material.[1]

Structure Description and Discussion

The atomic coordinates and the isotropic thermal parameters are presented in Table II. Important bond lengths are given in Table III. The unit cell of $CaSmCuO_3Cl$, as well the coordination environments of Ca, Sm, and Cu ions, are illustrated in Fig. 1. As can be seen, the rare-earth ion is located in a cube-like arrangement of oxide ions, whereas the Ca ion exists in a capped square antiprismatic coordination formed by four oxide and five chloride ions. The Cu ions are present in the basal plane of a square-

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[1] See NAPS document No. 04871 for 7 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 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 additional 10 pages of material, \$1.50 for postage of any microfiche orders.

TABLE I

COLLECTION PARAMETERS

Empirical formula	$CaSmCuO_3Cl$
Formula weight	337.42
Crystal color	Black
Crystal dimensions	0.2 × 0.2 × 0.02 mm
Lattice parameters	$a = 3.894(3)$ Å $c = 13.416(8)$ Å
Space group	*P4/nmm* (centric)
Z value	2
D_{calc}	5.5 g/cm^3
$\mu(MoK\alpha)$	215.5 cm^{-1}
Diffractometer	CAD 4
Radiation	Mo*K*α (λ = 0.71069 Å)
2θ (max)	80°
Total No. of reflections collected	3592
No. of independent reflections ($I > 3.00(\mathrm{sig}(I))$)	371
No. of variables	19
Agreement factors (R_{merge})	0.055
Residuals: R, R_w	0.055, 0.070
Largest peak in final difference map	4.1 e/Å^3

pyramidal coordination with the lone chloride ion occupying the apical position. The structure can also be viewed as a hybrid derived from joining half a unit cell of the $Ca_2CuO_4Cl_2$ (*T* phase) and Sm_2CuO_4 (*T′* phase). Although the coordination of copper is square pyramidal in the *T** structure (unlike octahedral or square-planar, as has been observed for *T* and *T′* structures, respectively (*3*)) the Cu–Cl distance is quite long. A comparison of the interatomic distances between those observed for $CaSmCuO_3Cl$ and those of related oxychlorides are presented in Table III. There appears to be a good correlation among these parameters, indicating that the bonding in the *T** oxychlorides is essentially similar to other *T* and

TABLE II

ATOMIC COORDINATES FOR $CaSmCuO_3Cl$

Atom	Site	*x*	*y*	*z*	*B*(Å^2)
Sm	2c	1/4	1/4	0.4100(1)	0.40(1)
Ca	2c	1/4	1/4	0.1609(4)	0.66(4)
Cu	2c	3/4	3/4	0.2770(2)	0.41(3)
Cl	2c	3/4	3/4	0.0740(5)	1.02(6)
O(1)	4f	1/4	3/4	0.275(1)	0.9(2)
O(2)	2b	1/4	3/4	1/2	0.4(2)

TABLE III

SELECTED INTERATOMIC DISTANCES FOR $CaSmCuO_3Cl$ AND OTHER OXYCHLORIDES

Bond	$CaSmCuO_3Cl$ (Å)	$Ca_2CuO_4Cl_2$[a] (Å)	$Ca_3Cu_2O_4Cl_2$[b] (Å)
Cu–O1	1.9472(2)	1.93	1.930
Cu–Cl	2.723(7)	2.73	2.716
Ca–O1	2.48(1)	2.49	2.466
Ca–Cl[c]	2.990(3)	2.98	2.967
Ca–Cl[d]	3.152(8)	3.19	3.207
Sm–O1	2.66(1)	—	—
Sm–O2	2.2910(7)	—	—

[a] Ref. (*3*)

[b] Ref. (*6*)

[c] Axial bonds.

[d] Equitorial bonds.

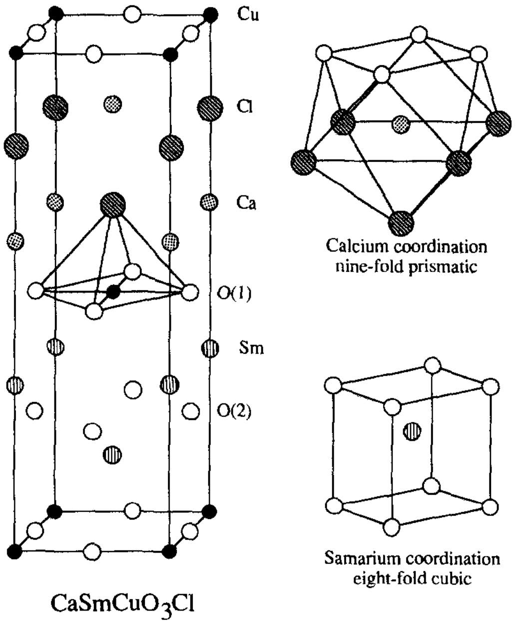

FIG. 1. Proposed unit cell of $CaSmCuO_3Cl$. The coordinations of Ca and Sm are illustrated separately.

T′ phases. The Sm–O(1) and Sm–O(2) bond distances observed in the present study (2.66 and 2.29 Å, respectively), however, showed small differences compared to the corresponding distances reported for $Sm_{1.0}La_{0.75}Sr_{0.25}CuO_{3.95}$ (2.59 and 2.35 Å) by Tokura *et al.* (*12*) from the Rietveld refinement of the powder X-ray diffraction pattern. Although the *T** oxychlorides show several resemblances in their structural parameters with both the *T* and the *T*′ phases, their transport properties (viz., insulating behavior) are closely related to their parent *T* phase oxychlorides. By contrast, the magnetic properties of these phases resemble those of the *T*′ oxides (*9*). This could be attributed to the nearly identical coordination of the magnetic rare earth ions in both the *T** and the *T*′ structures.

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