A New Chlorooxocuprate, $Ca_3Cu_2O_4Cl_2$, with an Oxygen Defect Intergrowth

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A new chlorooxocuprate, $Ca_3Cu_2O_4Cl_2$, is prepared and the crystal structure is determined by Rietveld analysis of X-ray powder diffraction data. This compound crystallizes in tetragonal symmetry with a space group of $I4/mmm$ and with lattice parameters of $a = 3.863$ Å and $c = 21.364$ Å. The crystal structure is similar to that of $Sr_2Ti_3O_7$ except for oxygen vacancies located between two-dimensional Cu–O planes, and for chloride anions occupying apical sites of doubled copper octahedra. Interatomic distances of the compounds are comparable to those of $Ca_2CuO_2Cl_2$ with a K_2NiF_4 structure. © 1990 Academic Press, Inc.

Recently, the crystal structures and electric properties of layered oxocuprates have been researched intensively because of their potential to become superconductors. A well known layered oxocuprate, $La_{2-x}Ba_xCuO_4$, was first discovered to be a high-T_c superconductor (1). It has a K_2NiF_4 structure with two-dimensional Cu–O planes. Another oxocuprate, $La_2SrCu_2O_{6+y}$ (2), is also known to have a double-perovskite structure, similar to that of $Sr_2Ti_3O_7$. In this oxocuprate, oxygen vacancies are located between two-dimensional Cu–O planes, and it has a metallic conductivity when oxidized to $y = 0.2$ (2), but ex-

hibits no superconductive properties down to 5 K (3, 4). These two types of oxocuprates compose the Ruddlesden-Popper series, $AO(ABO_3)_n$, with $n = 1$ and $n = 2$ (5).

Layered oxocuprates are also seen in halooxocuprates, $M_2CuO_2X_2$ (M = Ca or Sr, and X = Cl or Br) (6), with a K_2NiF_4 structure. Although these halooxocuprates have two-dimensional Cu–O planes, as commonly observed in high-T_c superconductors, two halogen anions, instead of oxygen anions, coordinate to a copper atom in *trans*-positions (6). No halooxocuprates with a double-perovskite structure are yet known. During our research on electric properties of $Ca_2CuO_2Cl_2$, a new double-

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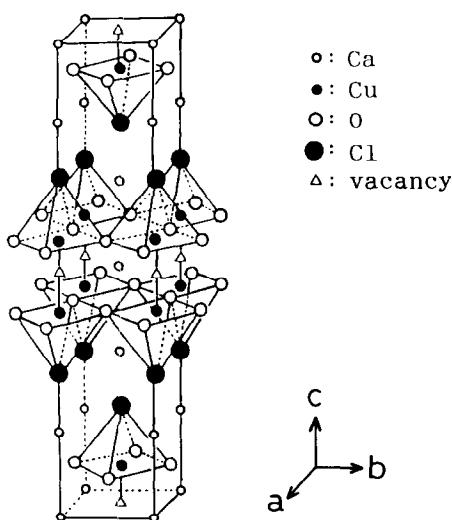FIG. 1. Idealized crystal structure of $Ca_3Cu_2O_4Cl_2$.

perovskite compound, $Ca_3Cu_2O_4Cl_2$ (Fig. 1), was unexpectedly found. This is the first discovery of halooxometallates with a double-perovskite structure. The new compound, together with $M_2CuO_2X_2$, is thought to be a member of the modified Ruddlesden-Popper series, $AX(ABO_2X)(ABO_2)_{n-1}$. We report here the preparation and the structural investigation of the new compound.

This compound was first observed in an X-ray diffraction (XRD) pattern as an impurity phase of a chloride-deficient sample, $Ca_2CuO_{2+x/2}Cl_{2-x}$. The almost single phase could be obtained with no detectable $Ca_2CuO_2Cl_2$, after optimizing the starting composition to $Ca:Cu:Cl = 3:2:2$. The new compound was prepared according to the following procedure. Appropriate amounts of $CaCO_3$, $CaCl_2$, and CuO were mixed according to a nominal composition of $Ca_3Cu_2O_4Cl_2$. The mixture was ground in agate mortar in a dry box, and calcined at 800°C for 10 hr in flowing O_2. The products were pulverized, pressed into pellets, and then sintered at 800°C for 10 hr. The crystal structure was investigated by powder X-ray diffraction. The data were taken at room temperature on a Philips 1050/1710 XRD system equipped with a curved graphite monocrometer in the scattered beam path. The intensity data were collected with $CuK\alpha$ radiation at a 0.02° step width for 10 sec over a 2θ range from 5 to 90°. A diffraction peak appearing at $2\theta = 8.3°$ (d-spacing $= 10.6$ Å) suggests the existence of long-range ordering in this compound. The XRD pattern obtained in 2θ regions from 20 to 90° is shown in Fig. 2. All diffraction peaks, except for a few originating from impurities, could be successfully indexed to a tetragonal unit cell with $a = 3.863$ Å and $c = 21.364$ Å.

The specific gravity, measured pycnometrically with toluene at 25°C, was 4.09. This value is comparable to the calculated value of 3.98, obtained using a chemical formula of $Ca_3Cu_2O_4Cl_2$ with the above-mentioned lattice constants. The difference between the observed and calculated values may be caused by the impurities and/or hygroscopic nature of this compound.

The lattice dimension of the a axis is very close to that of the parent compound, $Ca_2CuO_2Cl_2$ (3.866 Å) (6), suggesting that the
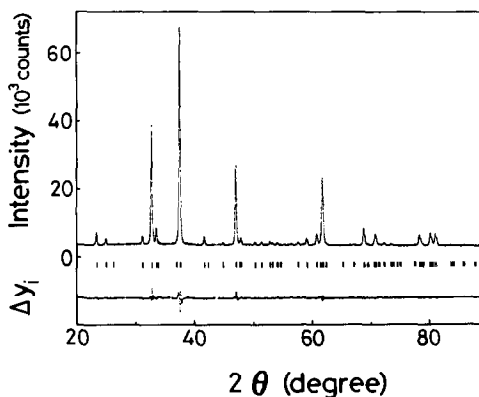

FIG. 2. Rietveld refinement patterns for $Ca_3Cu_2O_4Cl_2$. The solid lines are calculated intensities, crosses overlying them are observed intensities, and Δy_i is the difference between observed and calculated intensities. The short vertical lines mark the positions of calculated peaks.

a–b plane of the new compound is con-
structed from two-dimensional Cu–O
planes. On the other hand, the lattice di-
mension of the *c* axis is 1.4 times longer
than that of $Ca_2CuO_2Cl_2$. This value is com-
parable to the 1.47 obtained as a ratio of the
c-axis lattice dimension of $La_{1.9}Ca_{1.1}Cu_2O_6$
(19.420 Å) (7) to that of La_2CuO_4 (13.17 Å)
(8). These similarities as well as the reflec-
tion condition with $h + k + l = 2n$ strongly
suggest a structural model of $Ca_3Cu_2O_4Cl_2$
(Fig. 1), which is a double-perovskite struc-
ture closely related to that of $La_2SrCu_2O_6$,
where three Ca^{2+} cations occupy La^{3+} and
Sr^{2+} sites and two Cl^- anions are located on
apical sites of doubled Cu octahedra.

On the basis of the above structural
model, the crystal structure of the present
compound was refined by Rietveld analysis
of X-ray powder diffraction data with the
RIETAN program (9). Atomic scattering
factors used were those of Ca^{2+}, Cu^{2+}, O^{2-},
and Cl^- ions, and anomalous dispersion
was corrected. Intensity data in 2θ regions
from 20.0 to 90.0° were used for the refine-
ment, except for regions of 28.1–28.4°,
35.9–36.2°, and 43.5–44.0°, which contain
very weak peaks due to impurities. Pre-
ferred orientation was not corrected.

Final crystal-structural parameters are
listed in Table I. Quite low *R* factors were
obtained: $R_{wp} = 3.2\%$, $R_p = 2.4\%$, and R_F
= 2.7%. Figure 2 illustrates the profile fit

TABLE I

CRYSTAL-STRUCTURAL PARAMETERS OF $Ca_3Cu_2O_4Cl_2$

Atom	Site	x	y	z	B (Å²)	g
Ca(1)	2a	0.0	0.0	0.0	0.3	1.0
Ca(2)	4e	0.0	0.0	0.1478	0.6	1.0
Cu	4e	0.0	0.0	0.4265	0.8	1.0
O(1)	8g	0.0	0.5	0.0734	0.9	1.0
O(2)	2b	0.0	0.0	0.5	—	0.0
Cl	4e	0.0	0.0	0.2980	0.4	1.0

Note. *B* is the isotropic thermal parameter, and
g the occupation factor. $a = 3.863$ Å; $c = 21.364$ Å;
I4/mmm.

TABLE II

SELECTED INTERATOMIC DISTANCES IN $Ca_3Cu_2O_4Cl_2$,
$Ca_2CuO_2Cl_2$, AND $La_{1.9}Ca_{1.1}Cu_2O_6$ (IN Å)

	$Ca_3Cu_2O_4Cl_2$	$Ca_2CuO_2Cl_2^a$	$La_{1.9}Ca_{1.1}Cu_2O_6^b$
Cu–O$_{eq}^c$	1.932	1.93	1.912
Cu–Cl/O$_{ax}^c$	2.746	2.73	2.305
Cu–Ca(1)	3.151	—	—
Cu–Ca(2)	3.160	3.15	—
Cl–Ca(2)$_{ax}^c$	3.207	3.19	—
Cl–Ca(2)$_{eq}^c$	2.967	2.98	—
Cl–Cl	3.415	3.39	—
Cu–Cu^d	3.142	—	3.306
O–O^d	3.138	—	3.191

^{a} From Ref. (6).
^{b} From Ref. (7).
^{c} ax: axial (*c*) direction. eq: equatorial (*a–b*) direction.
^{d} Distance through a $z = \frac{1}{2}$ plane.

and difference patterns for $Ca_3Cu_2O_4Cl_2$,
showing that the agreement between the
calculated and observed intensities is very
satisfactory.

The occupation factor of Cl^- was refined
to 1, which means that no chloride anions
are replaced by oxygen anions or vacan-
cies. It was first assumed that an oxygen
atom is located at the 2b site. However,
refinement of the occupation factor of this
site shows that it is vacant.

Table II summarizes selected interatomic
distances of $Ca_3Cu_2O_4Cl_2$ together with
those of $Ca_2CuO_2Cl_2$ (6) and $La_{1.9}Ca_{1.1}$
Cu_2O_6 (7). The corresponding values of
these chlorooxocuprates are very close. In
double-perovskite compounds, the differ-
ence between Cu–Cu and O–O distances
through a $z = \frac{1}{2}$ plane indicates a puckering
of the Cu–O plane. The value in Ca_3Cu_2
O_4Cl_2 is small (0.004 Å) compared to that in
$La_{1.9}Ca_{1.1}Cu_2O_6$ (0.115 Å), showing that the
Cu–O plane in the former compound is al-
most flat.

The vacancy at the 2b site in $Ca_3Cu_2O_4Cl_2$
presumably results from a relatively short
Cu–Cu distance (3.142 Å) through the $z = \frac{1}{2}$
plane. The corresponding value in $La_{1.9}$
$Ca_{1.1}Cu_2O_6$ is 3.306 Å and this compound
also has a vacancy at the 2b site (7). On the

other hand, $La_2SrCu_2O_{6+y}$ ($y = 0.0$), having a longer Cu–Cu distance of 3.63 Å (10), can accommodate excess oxygen anions into the 2b site until $y = 0.2$ (2).

The new compound, $Ca_3Cu_2O_4Cl_2$, can be regarded as a member of the modified Ruddlesden-Popper series, $AX(ABO_2X)$ $(ABO_2)_{n-1}$, where $n = 2$. The intergrowth of the oxygen-deficient layer, (ABO_2), may produce other long-range-ordered new compounds if possible. The research on electric properties of this series of compounds is now in progress. The strontium analog could not be obtained, but products that partially substituted strontium for calcium were obtained.

Acknowledgment

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