

BRIEF COMMUNICATION

$\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$, a New Layered Cuprate with Hematophanite Structure

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A new layered cuprate $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ has been successfully synthesized and identified by X-ray diffraction analysis. The compound crystallizes in the hematophanite structure with the space group $P4/mmm$. The lattice parameters of $a = 3.8921(1)$ Å and $c = 15.3835(4)$ Å were obtained by fitting the observed XRD pattern using the Rietveld refinement method. The structure of $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ is built up by $[\text{Pb}_2\text{Cl}]$ layer, CuO_5 pyramidal layers, and SrTaO_3 perovskite layer alternatively along the c direction. Although complete CuO_5 pyramidal planes exist in the present compounds, the as-prepared samples are insulating. © 1997 Academic Press

1. INTRODUCTION

More than 50 new cuprate superconductors have been discovered since the first report on high- T_c superconductivity in the LaBaCuO system a decade ago (1). All these cuprates possess layered structures and contain copper-oxygen planes. From a crystal chemistry point of view, the structure of the layered cuprates can be thought as composed of Cu-O planes and other block layers (2). We have further classified the block layers into *connecting layer* (which connects the Cu-O planes at the apical sites) and *separating layer* (which separates the Cu-O planes at the basal sites) (3). For example, in $\text{LaBa}_2\text{Cu}_2\text{TaO}_8$ (4) and $\text{TaSr}_2(\text{Ln}, \text{Ce})_2\text{Cu}_2\text{O}_{10}$ (5), the TaO_6 octahedral layer can be viewed as the connecting layer, while the La^{3+} and $(\text{Ln}, \text{Ce})_2\text{O}_2$ layers are acting as the separating layers. Similarly, the $[\text{PbSr}]\text{Cl}$ (CsCl -type) layer in $\text{Pb}_3\text{Sr}_3\text{Cu}_3\text{O}_8\text{Cl}$ (6) can be classified as a separating layer as well. We note that such a CsCl -type Pb_2Cl layer also exists in a mineral ferrate, $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$, known as hematophanite (7, 8). By combining the Pb_2Cl layer with CuO_5 planes and the connecting layer of TaO_6 , we succeeded in preparing a new structure type of layered cuprates: $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$. The preparation and preliminary structure study will be reported here.

2. EXPERIMENTAL

Samples of the title compound $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ were prepared by solid-state reaction from PbO (99%), PbCl_2 (98%), $\text{Sr}(\text{NO}_3)_2$ (99.5%), Ta_2O_5 (99.95%), and CuO (99%). The mixtures of the starting materials with stoichiometric ratios for $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ were thoroughly ground and preheated several times at 500, 550, 600, 650°C in air for 12 h each with intermittent grindings. The resulting powders were reground, pelletized, and calcined in air at 700°C for 24 h and then allowed to cool in the furnace. The powder diffraction data for Rietveld analysis were collected in the range of 21–135° (2θ) at a step of 0.03° (2θ) and a counting time of 3 s on a Rigaku Dmax/rB diffractometer equipped with a high intensity rotating anode source ($\text{CuK}\alpha$ radiation) and curved graphite monochromator.

3. RESULTS AND DISCUSSION

From the XRD patterns of the $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ samples at different preparing stages, we found that the title compound begins to form at about 550°C and coexists with CuO , $\text{Sr}_3\text{CuTa}_2\text{O}_y$, and an unknown impurity phase. Above 700°C, the XRD peaks due to impurity phases grow stronger again. It is found that more grinding and sintering cycles reduced the amounts of impurity phases. However, probably because of high stability of $\text{Sr}_3\text{CuTa}_2\text{O}_y$, the impurities remain after over 10 sintering cycles and over one-week sintering time. Sintering the samples in flowing nitrogen and higher temperature were also unsuccessful to improve the phase purity.

The lattice parameters obtained from fitting the XRD pattern (Fig. 1) of purest $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ sample obtained at present are $a = 3.8921(1)$ Å, $c = 15.3835(4)$ Å, and the systematic absences of diffraction lead to a choice of a primitive tetragonal cell, which both are consistent with those of hematophanite ($a = 3.9097$ Å, $c = 15.2873$ Å, $P4/mmm$) (7). Structure refinement was performed by the

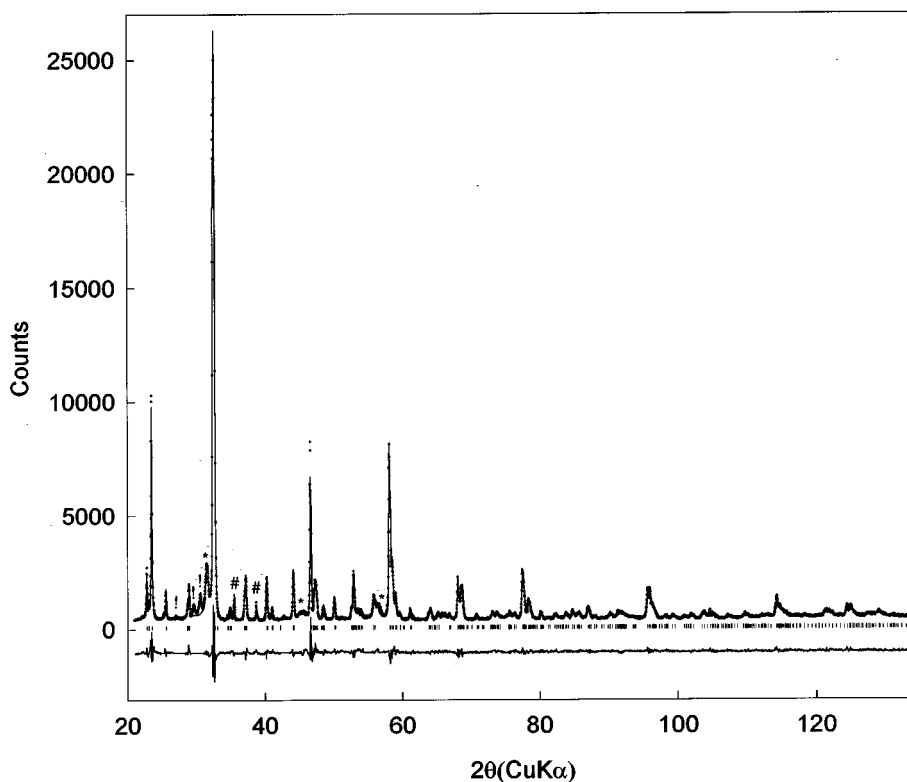


FIG. 1. Observed (dotted) and calculated (solid line) X-ray diffraction patterns of $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ (the peaks due to the impurity phases of CuO , $\text{Sr}_3\text{CuTa}_2\text{O}_3$, and that unknown are labeled with #, *, and ! respectively).

Rietveld method using the DBWS-9411 package (9), and atomic positions from the hematophanite structure (7) (Fig. 2a) were taken as the starting points. The impurity phases of CuO and a perovskite-related phase $\text{Sr}_3\text{CuTa}_2\text{O}_y$ (or $(\text{Sr}, \text{Pb})(\text{CuTa})\text{O}_3$) were included in the refinement. The unknown impurity peaks at $2\theta = 27.06^\circ$, 29.67° , 30.6° , 42.8° , and 56.6° were excluded. The pseudo-Voigt function was taken to describe the individual peak profile. A total of 48 parameters, including 4 polynomial background and 20 structural parameters for the main phase and 24 parameters for other phases and for the global parameters of zero point, scale factor, preferred orientation, and peak shape were simultaneously refined. The refinement converged quickly to relatively low agreement indices except that the temperature factors of O_2 and O_3 are quite large and that of O_1 went to a meaningless negative value. Not only was the agreement improved but also the temperature factors of O_2 and O_3 went to reasonable values after allowing the O_2 and O_3 atoms to occupy split sites (8t, 4o). The displacement of O_3 were also observed in the $\text{TaSr}_2(\text{Nd}, \text{Ce})_2\text{Cu}_2\text{O}_{10}$ (10) and resulted in a rotation of TaO_6 octahedron (Fig. 2b) around c axis. Such a distortion gives a longer Ta–O in-plane bond which may help to release the bond length mismatch between the Ta–O and Cu–O layers. The temper-

ature factor of O_1 was fixed at 0.3 in the subsequent refinement (actually the selection of 0, 0.3, or -0.5 of B_{O_1} did not alter the agreement). The disordering occupations of Pb/Sr and Ta/Cu were also considered. We found that only about 14% Sr entered the $[\text{Pb}_2\text{Cl}]$ layer, the Sr site in the SrTaO_3 layer is solely occupied by the Sr atom, and similarly Ta and Cu atoms are also fully ordered. Following agreement indices, $R_{\text{wp}} = 6.70\%$, $S = 1.90$, and $R_{\text{B}} = 4.95\%$ were obtained after the final refinement. The refinement also shows that the main phase is about 85 wt% pure in the 10-cycle sintered sample.

The refined atomic positions of $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ are listed in Table 1. Table 2 lists the selected interatomic distances between the metal and oxygen atoms calculated from the refined atomic parameters. The structure of $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ (Fig. 2a) can be thought of as an element-substituted product of hematophanite, $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$, with Ta substitutes for the octahedral Fe1 site, and Cu replaces the pyramidal Fe2 site. To our knowledge it is the only derivative of that mineral which was claimed to be difficult to dope with other elements (7). Alternatively and more importantly, the title compound is also related to the high-Tc cuprate family $\text{TaSr}_2(\text{Ln}, \text{Ce})_2\text{Cu}_2\text{O}_{10}$, by replacing the fluorite Ln_2O_2 layer with a Pb_2Cl layer. Together

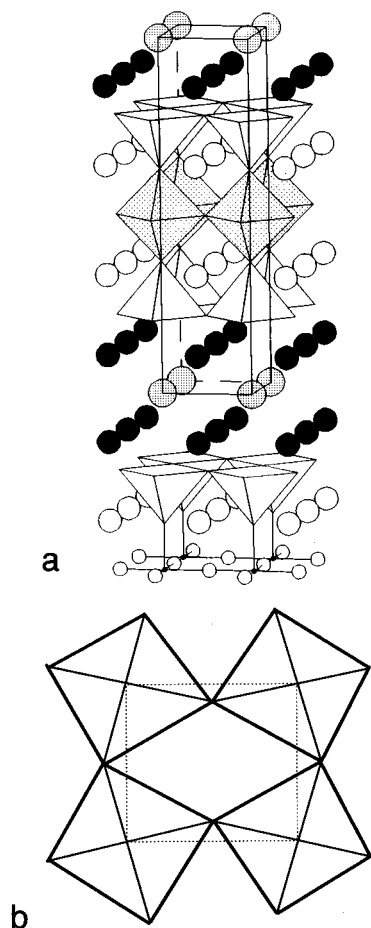


FIG. 2. Structure model of $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$. (a) Ideal structure of hematophanite, (b) the Ta-O layer distortion.

with the compound $\text{Pb}_3\text{Sr}_3\text{Cu}_3\text{O}_8\text{Cl}$ (6), it may mean that the CsCl-type Pb_2Cl or even Pb_2X layer may serve as an active new structural unit in the layered superconducting cuprate family.

TABLE 1
Refined Structural Parameters for $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ (Space Group $P4/mmm$ and Cell Parameters $a = 3.8921(1)$ Å, $c = 15.3835(4)$ Å, $R_{\text{wp}} = 6.70\%$, $R_{\text{B}} = 4.95\%$)

Atom	Site	x	y	z	n	B (Å ²)
Pb/Sr	2h	0.5	0.5	0.1225(1)	0.86 (1)/0.14 (1)	1.18(5)
Sr	2h	0.5	0.5	0.3464(2)	1	0.64(7)
Ta	1b	0	0	0.5	1	0.30(6)
Cu	2g	0	0	0.2292(3)	1	0.41(9)
O(1)	2e	0	0	0.3715(1)	1	0.3 ^a
O(2)	8t	0.03(1)	0.5	0.2187(6)	0.25	1.8(5)
O(3)	4o	0.12(1)	0.5	0.5	0.5	0.4(5)
Cl	1a	0	0	0	1	4.6(5)

^a Fixed.

TABLE 2
Selected Bond Lengths of $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$

Bond	r (Å)	Bond	r (Å)
Ta-O ₁	1.976	Ta-O ₃	2.002
Cu-O ₁	2.189	Cu-O ₂	1.956
Pb-O ₂	2.445	Pb-Cl	3.336
Sr-O ₁	2.784	Sr-O ₂	2.684, 2.849
Sr-O ₃	2.788		

Because of the presence of complete two-dimensional CuO_5 planes in the structure of the title compound as in common cuprate superconductors, it is hoped that $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ could be a new superconductor when properly doped. However, electrical measurements showed that the as-prepared samples are insulating with room temperature resistance in the MΩ range.

4. CONCLUSION

A new layered cuprate $\text{Pb}_2\text{Sr}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ was successfully prepared and characterized. It crystallizes in the hematophanite structure and is built up by $[\text{Pb}_2\text{Cl}]$ layers, CuO_5 planes, and perovskite SrTaO_3 layers alternatively along the c axis. Although the compound shares common structure units with the high- T_c superconductors, the as-prepared samples are highly resistive.

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