Inorg. Chem. **1997,** *36,* 4895−4896 **4895**

$Pb_2BaCuFeO_5X$ (X = Cl, Br): New Intergrowth Compounds Composed of CsCl Type and Bipyramidal Defective Perovskite Blocks

Rukang Li

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Received March 18, 1997

Introduction

Since the discovery of first high-T_c superconductor in the La−Ba−Cu−O system,[1] continuous efforts have been paid to search for new layered compounds containing Cu−O planes as potential high-T_c superconductors. More than 50 new structure types of layered cuprates have been reported so far. It is now well accepted that new layered compounds may be *designed* by different arrangements of some general building blocks.[2] We recently have found that the Pb_2Cl layer with a CsCl type structure can be accommodated in a compound, $Pb_2Ba_2Cu_2TaO_8Cl$, forming a new type of layered cuprate.[3] Such a Pb_2Cl layer interleaving the perovskite units was first observed in the structure of a mineral,[4] hematophanite, $Pb_4Fe_3O_8Cl$; however, according to Pannetier and Batail the mineral compound is unique and excludes any foreign cations from substituting the Pb or Fe sites.[5] Although a similar PbSrCl layer with CsCl type structure has also been found in lead-containing cuprates, $Pb_3Sr_3Cu_3O_8Cl$,[6] derived from the superconducting Pb-3212 ($Pb_2Sr_2YCu_3O_8$),[7] attempts to incorporate this PbSrCl layer into other layered cuprate compounds were also unsuccessful.[2a] To further explore the accommodation of Pb_2X layers into other structure systems related to high-T_c cuprates, we have succeeded in preparing two new compounds, namely $Pb_2BaCuFeO_5X$ (X = Cl, Br), composed of a bipyramidal defective perovskite block and a Pb_2X layer. The structure of the title compounds is equivalent to the hematophanite structure by removing the central $PbFeO_3$ layer.

Experimental Section

Samples were prepared by solid-state reaction from PbO (purity, 98%), $PbCl_2$ (99%), $Ba(NO_3)_2$ (99.5%), Fe_2O_3 (99.5%), $CuBr_2$ (>98.5%), and CuO (99%). The well-ground mixtures of the starting materials were placed in covered alumina crucibles and preheated at 550 and 600 °C in air for 12 h each with intermittent grinding. The resulting powders were reground, pressed into disks, and calcined in air at 680 °C (for the chloride compound) and 650 °C(for bromide) for 24 h and then quickly cooled to room temperature. The last cycle was repeated several times in order to obtain homogeneous samples.

The powder X-ray diffraction (XRD) patterns were collected on a Rigaku Dmax/r_B diffractometer equipped with a high-intensity rotating anode source (Cu Kα radiation) and curved graphite monochromator. Step-scans with a step-width of 0.03° (2θ) and step counting time of 3 s were applied in the collections of the XRD patterns. Structural parameters of the compound were refined by using the Rietveld method with the DBWS-9411 package.[8] In total, 26 parameters including structural, polynomial background, surface roughness, and other global parameters were simultaneously refined, and the Pearson VII function was taken to simulate the individual XRD peak profile.

Table 1. Refined Structural Parameters for Pb2BaCuFeO5Cl[a]

atom	site	*x*	*y*	*z*	*B* (Å^2)
Pb	*2h*	0.5	0.5	0.1654(1)	1.1(1)
Ba	*1d*	0.5	0.5	0.5	1.1(1)
Cu/Fe	*2g*	0	0	0.3183(2)	0.6(2)
O_1	*1b*	0	0	0.5	2.6(5)
O_2	*4i*	0.5	0	0.2931(6)	0.7(3)
Cl	*1a*	0	0	0	1.7(3)

[a] Space group *P*4/*mmm*, with $a = 3.9340(1)$ Å, $c = 11.3415(3)$ Å, $Z = 1$, $R_{wp} = 9.43\%$, $R_B = 3.84\%$, $S = 1.93$. $R_{wp} = (\sum w_i(y_{oi} - y_{ci})^2/\sum w_i(y_{oi})^2)^{1/2}$; $R_B = \sum|I_o - I_c|/\sum I_o$, $S = R_{wp}/R_{exp}$.

Table 2. Selected Bond Lengths of $Pb_2BaCuFeO_5Cl$

bond	length (Å)	bond	length (Å)
Cu/Fe−O_1	2.061(2)	Cu/Fe−O_2	1.988(1)
Ba−O_1	2.7818(1)	Ba−O_2	3.062(5)
Pb−O_2	2.443(4)	Pb−Cl	3.355(1)

The temperature-dependent gram magnetic susceptibility was measured in an automated extracting sample magnetometer with an applied magnetic field of 5 T in the range of 5−300 K.

Results and Discussion

The starting structure model for the Rietveld refinement was derived from that of $YBaCuFeO_5$ by replacing the single Y layer with the CsCl type Pb_2X double layers.[9] The primitive unit cell with cell parameters of $a = 3.9340(1)$ Å, $c = 11.3415(3)$ Å for $Pb_2BaCuFeO_5Cl$ and $a = 3.9474(1)$ Å, $c = 11.5571(3)$ Å for $Pb_2BaCuFeO_5Br$ were established after indexing their XRD patterns. The refined atomic positions and isotropic temperature factors (Table 1) of $Pb_2BaCuFeO_5Cl$ were obtained by fitting the XRD pattern in the 2θ range of 20−132° (Figure 1). Diffraction peaks due to traces of CuO and an unknown phase were excluded in the refinement. The preferred orientation was clearly seen in the XRD pattern during the early refinement stage and was then modeled by the one-parameter March−Dollase function as provided in the DBWS package.[8] The structure was first refined in the centrosymmetric space group *P*4/*mmm* and the refinement quickly converged to $R_{wp} = 9.43\%$ and goodness of fit $S = R_{wp}/R_{exp} = 1.93$. Subsequent refinements with lowering the symmetry to the polar space group *P*4*mm* or ordering of Cu, Fe ions in separated planes did not improve the agreement indices. Although setting the O_1 atom to split sites (refined to 0.17 Å above or below the symmetric *1b* position) reduces the isotropic temperature factor of O_1 from 2.6 to 1.5 Å^2, the agreement indices remain constant. Both facts led us to constrain the average structure to the most symmetric one with the space group *P*4/*mmm*.

The structure of $Pb_2BaCuFeO_5X$ can be viewed as being built up by oxygen-defective perovskite units $Pb_2BaCuFeO_5$ and a square net of a Cl layer along the *c* direction in a sequence Cl−Pb−Cu/FeO_5−Ba−Cu/FeO_5−Pb−Cl. The chlorine atom is coordinated by eight lead atoms in a slightly flatten cube environment, and bromine is coordinated in a more regular cube; both are identical to their coordinations in the CsCl type

---

(1) Bednorz, J. G.; Müller, K. A. *Z. Phys. B: Condens. Matter* **1986**, *64*, 189.

(2) (a) Tokura, Y.; Arima, T. *Jpn. J. Appl. Phys.* **1990**, *29*, 2388. (b) Li, R. K. *Appl. Phys. Commun.* **1992**, *11*, 295. (c) Tao, Y. K.; Sun, Y. Y.; Hor, P. H.; Chu, C. W. *J. Solid State Chem.* **1993**, *105*, 171.

(3) Li, R. K. *J. Solid State Chem.* **1997**, *130*, 154; *Physica* C **1997**, *277*, 252.

(4) Rouse, R. C. *Mineral. Mag.* **1973**, *39*, 49.

(5) Pannetier, J.; Batail, P. *J. Solid State Chem.* **1981**, *39*, 15.

(6) Cava, R. J.; Bordet, P.; Capponi, J. J.; Chaillout, C.; Chenavas, J.; Fournier, T.; Hewat, E. A.; Hodeau, J. L.; Levy, J. P.; Marezio, M.; Batlogg, B.; Rupp, L. W., Jr. *Physica* C **1990**, *167*, 67.

(7) Cava, R. J.; Batlog, B.; Krajewski, J.; Rupp, L. W., Jr.; Schneemeyer, L. F.; Siegrist, T.; van Dover, R. B.; Marsh, P.; Peck, W. F., Jr.; Gallagher, P. K.; Glarum, S. H.; Marshall, J. H.; Farrow, R. C.; Waszczak, J. V.; Hull, R.; Trevor, P. *Nature* **1988**, *326*, 221.

(8) Young, R. A.; Sakthivel, A.; Moss, T. S.; Paiva-Santos, C. O. *J. Appl. Crystallogr.* **1995**, *28*, 366.

(9) Er-Rakho, L.; Michel, C.; Lacorre, P.; Raveau, B. *J. Solid State Chem.* **1988**, *73*, 531.

S0020-1669(97)00314-5 CCC: $14.00

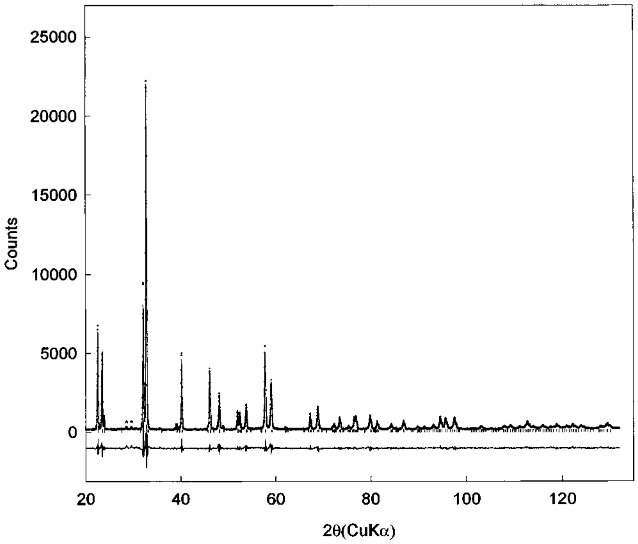

Figure 1. Observed (dotted) and calculated (solid line) X-ray diffraction pattern of $Pb_2BaCuFeO_5Cl$. (Stars indicate the diffraction peaks due to an unknown impurity which were excluded in the refinement.)

structure. The Cu/Fe ion is coordinated to five oxygen atoms in a pyramid with nearly equal apical and equatorial Cu/Fe−O bond lengths, and the Cu/Fe ions sit at about 0.25−0.28 Å above the base in the pyramid. The halogen atoms are too far from the Cu/Fe ions, 3.61−3.69 Å, to be bonded to them. Another structural feature of the present compounds is the large Cu/Fe−Cu/Fe separation through the weakly bonded Pb_2X layer, which is also the reason for the easy (001) cleavage and appearance of the (001) preferred orientation in the XRD peaks. The structure of $Pb_2BaCuFeO_5X$ may alternatively be considered as resulting from the removal of the central perovskite unit in the mineral hematophanite structure;[8] thus the bipyramidal layer is formed via direct joining of the apical oxygen atoms of the remaining two pyramidal Cu/FeO_5 planes. Similar to hematophanite, the present compounds also are highly resistive with room-temperature resistance over the 10^6 Ω range.

The magnetic susceptibility of $Pb_2BaCuFeO_5Cl$ is small and nearly independent with temperature change (Figure 2). A broad maximum at around 120 K may be originated from the antiferromagnetic ordering of the spins on the Fe/Cu ions and is also consistent with the two-dimensional nature with large separations of the magnetic ions (Fe/Cu). The temperature dependence of magnetic susceptibility also resembles to those of related compounds $Y_2SrCuFeO_{6.5}$ and $YBaCuFeO_5$ containing the same mixed Cu/Fe bipyramidal layer.[10,11] A general trend of systematic increase of the ordering temperature, i.e. 120 K for $Pb_2BaCuFeO_5Cl$, 265 K for $Y_2SrCuFeO_{6.5}$,[10] and 441 K for $YBaCuFeO_5$,[11] was observed which is a consequence of the increase of 3-dimensionality with decreasing layer separations from the title compound to $YBaCuFeO_5$.

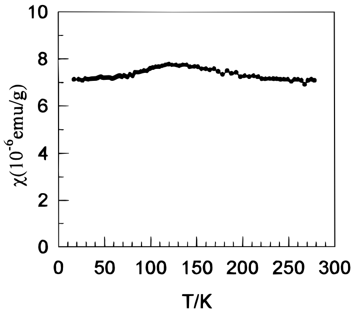

Figure 2. Temperature-dependent gram magnetic susceptibility of the $Pb_2BaCuFeO_5Cl$ sample.

Acknowledgment. The present work was supported by the Fok Yingdong Education Foundation and partially by an ICDD grant.

Supporting Information Available: Tables of the output of the Rietveld refinement, including *hkl*, 2*θ*, I_{cal}, I_{obs}, overall, and structural parameters (7 pages). Ordering information is given on any current masthead page.

IC970314W

---

(10) Kim, J. S.; Lee, J. Y.; Swinnea, J. S.; Steinfink, H.; Reiff, W. M.; Lightfoot, P.; Pei, S.; Jorgensen, J. D. *J. Solid State Chem.* **1991**, *90*, 331.

(11) Caignaert, V.; Mirebeau, J.; Bouree, F.; Nguyen, N.; Ducouret, A.; Greneche, J. M.; Raveau, B. *J. Solid State Chem.* **1995**, *114*, 24.