

## LETTER TO THE EDITOR

### New Cu(III) Oxychlorides in the Ba–Cu–*M*–O–Cl (*M* = Li, Na) System

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**New Cu(III) oxychlorides with the stoichiometry Ba<sub>4</sub>(Cu, *M*)O<sub>4</sub>Cl<sub>4</sub> (*M* = Li, Na) have been identified in the title system under ambient synthetic conditions and are found to possess the layered K<sub>2</sub>NiF<sub>4</sub>-type structure.** © 1997 Academic Press

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The extensive work of Müller-Buschbaum and co-workers has shown the existence of four oxychlorides in the Ba–Cu–O–Cl system: Ba<sub>2</sub>CuO<sub>2</sub>Cl, Ba<sub>2</sub>Cu<sub>3</sub>O<sub>4</sub>Cl<sub>2</sub>, Ba<sub>3</sub>Cu<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>, and Ba<sub>9</sub>Cu<sub>7</sub>O<sub>15</sub>Cl<sub>2</sub> (1). Only Ba<sub>2</sub>Cu<sub>3</sub>O<sub>4</sub>Cl<sub>2</sub> has a structure containing layers that form from edge-sharing CuO<sub>4</sub> square units with elongated CuO<sub>4</sub>Cl<sub>2</sub> octahedra. The recent discovery of high *T<sub>c</sub>* superconductivity in copper oxyhalides has generated renewed interest in perovskite-derived Cu oxyhalides (2–5). Recently, Ba<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> with a layered K<sub>2</sub>NiF<sub>4</sub>-type structure has been reported to form under high pressure synthesis conditions (6). We have reported the stabilization of this phase under ambient conditions by the partial (~20 at.%) substitution of octahedral Cu-sites by larger isovalent ions such as Ca or Cd (7). This was found to satisfy the essential crystallographic requirements (optimum tolerance factor and elongation of the Cu–O bonds beyond 2 Å) for the formation of layered structures involving Ba and Cu. The undoped Cu oxyhalides known so far are found to contain only either Cu(I) or Cu(II); there are no reports on the stabilization of an oxyhalide matrix containing only Cu(III) (1, 8). It is believed that such a situation is energetically unfavorable due to the presence of highly oxidized Cu(III) at the center of a coordination environment containing reducing halide ions, leading to a disproportionation of Cu(III)/Cl(–1) to Cu(II)/Cl<sub>2</sub> (the energy of the 3*d* level of Cu(III) is below that of chlorine 3*p*). The observation of superconductivity in

oxyhalides suggests that at least partial oxidation of Cu(II) to Cu(III) is a prerequisite for the occurrence of hole-doped superconductivity. However, it should be noted that hole doping in superconducting oxyhalides was achieved primarily under high oxygen pressure synthetic conditions (3–5). In an attempt to stabilize Cu(III) containing oxychloride under ambient pressure conditions, we have investigated the Ba–Cu–*M*–O–Cl (*M* = Li, Na) system and identified compounds of the type Ba<sub>4</sub>Cu*M*O<sub>4</sub>Cl<sub>4</sub>. The new phases represent the first examples of oxyhalides which contain only Cu(III) in an oxychloride octahedral coordination. In this communication, the synthesis and preliminary structural, electrical, and magnetic data of the new phases are reported.

Compounds with the stoichiometry Ba<sub>2</sub>(Cu<sub>1–*x*</sub>*M<sub>x</sub>*)O<sub>2</sub>Cl<sub>2</sub> (*M* = Li or Na and 0.0 < *x* < 0.5) were prepared from high purity (better than 99.99%) starting reagents by high temperature solid state reactions. No carbonate containing starting salts were used, in order to avoid the formation of perovskite-type oxycarbonates which have been found to be highly stable in the cationic system under investigation (9). The reactions were carried out in a flowing, CO<sub>2</sub> free, oxygen atmosphere at relatively low temperatures, in the range 700–800°C with intermittent grindings; the samples were furnace-cooled to room temperature after heat treatment for 24 hr. The phase formation was monitored by X-ray diffraction (XRD) using Ni-filtered Cu*K*α radiation. The lattice parameters were calculated using a least squares fitting method. The oxygen contents were established by standard iodometric procedures. The temperature dependence of magnetic susceptibility was measured with a SQUID magnetometer in an applied field of 5000 G in the range 4–300 K.

In agreement with previous reports, Ba<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> does not form under atmospheric pressure conditions. However, evidence for the formation of K<sub>2</sub>NiF<sub>4</sub>-type phases is seen when Li or Na is substituted for Cu in Ba<sub>2</sub>Cu<sub>1–*x*</sub>*M<sub>x</sub>*O<sub>2</sub>Cl<sub>2</sub>.

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Nearly single-phase samples are obtained only for one composition corresponding to  $x = 0.5$ , i.e.,  $\text{Ba}_4\text{CuMO}_4\text{Cl}_4$ . This is in contrast to the Cu(III) containing oxide solid solution series of the type  $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ , where the parent  $\text{La}_2\text{CuO}_4$  phase exists (10, 11). At  $x = 0.0$ , the major phase is  $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ ; however, as  $x$  increases from 0.0 to 0.5, the  $\text{Ba}_2\text{CuMO}_4\text{Cl}_4$  phase grows, while the relative amount of  $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  phase diminishes. This indicates that the  $\text{Ba}_4\text{CuMO}_4\text{Cl}_4$  phases are new stoichiometric line-phases. The oxygen content determined ( $3.87 \pm 0.05$ ) was close to the anticipated ideal value (4.00), based on the stoichiometry indicating that the Cu ions in these compounds are nearly in a formal valence state of  $3+$ . The XRD patterns exhibit a strong similarity to the well known phases of the type  $A_2\text{CuO}_2\text{Cl}_2$  ( $A = \text{Ca}, \text{Sr}; X = \text{Cl}, \text{Br}$ ) and were indexed in analogy to these phases (Fig. 1). The tetragonal cell parameters are presented in Table 1. The significantly smaller  $c$  parameter observed for  $\text{Ba}_4\text{CuMO}_4\text{Cl}_4$ , compared to those of similar phases containing Cu(II), provides further support for the presence of Cu(III) in the new phases from ionic radii considerations. The smaller  $a$  parameter observed in the case of the high pressure synthesized  $\text{Ba}_2\text{CuO}_2\text{Cl}_2$  could be due to the 10% chlorine deficiency noted in that sample (6). Variation of the  $a$  parameter of the new phases also shows dependence on the ionic radii of the  $M$  ion. The absence of any satellite reflections corresponding to a larger super cell (e.g.,  $a^* = \sqrt{2}a$  and  $c^* = c$ ) indicates that the Cu and  $M$  ions do not order in the lattice, as in  $\text{La}_2\text{CuO}_{0.5}\text{Li}_{0.5}\text{O}_4$ . This is unexpected, since the electrostatic potential usually induces an ordering of ions for sufficient differences in the size and/or charges of cations, such as Cu(III) and Li/Na(I), occupying crystallographically equivalent sites (10, 11). However, we believe that such an ordering can be achieved in these compounds by modifying the synthetic conditions, for example varying the annealing conditions, and/or the cooling rates. In fact, we have demonstrated the dependence of ordering on annealing conditions in  $\text{Ba}_4(\text{Cu}, \text{Na})\text{O}_4(\text{CO}_3)_2$  (12). The new phases,  $\text{Ba}_4\text{CuMO}_4\text{Cl}_4$  are isostructural with the well-known  $\text{K}_2\text{NiF}_4$ -type structure (tetragonal,  $I4/mmm$ ,  $Z = 2$ ), in which Ba is in the 9-coordinated site and the 6-coordinated site is statistically distributed between Cu(III) and Li(I), with the apical positions of the octahedra occupied by Cl ions. Preliminary structure refinements by the Rietveld method also support this model. The temperature dependent magnetic susceptibility shows diamagnetic behavior similar to that observed for  $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$  (11), supporting the presence of Cu(III). A sharp transition observed in the susceptibility of  $\text{Ba}_4\text{CuNaO}_4\text{Cl}_4$  around 250 K is currently being analyzed. The new phases are deep red and highly insulating, which is likely due to the random occupancy of the Cu(III) and  $M$ (I) ions at the planar octahedral sites, interrupting the effective overlap between the Cu  $3d$  and O  $2p$ . We also have grown good quality single crystals

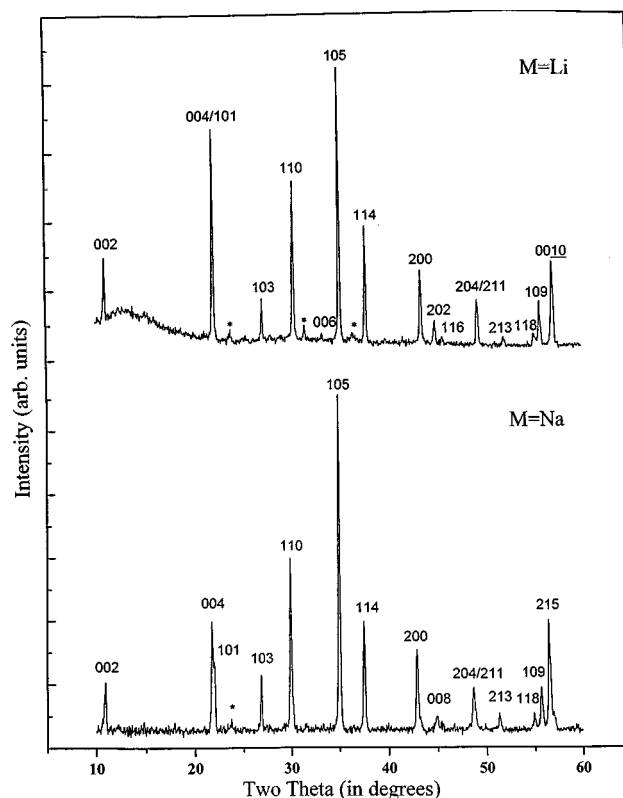


FIG. 1. Powder X-ray diffraction patterns of the  $\text{Ba}_2\text{CuMO}_2\text{Cl}_2$  phases;  $M = \text{Li}$  (top) and  $M = \text{Na}$  (bottom). Unidentified impurity reflections are marked (\*).

of the new phases and a detailed structural analysis by single crystal, powder X-ray, and neutron diffraction refinements is now in progress.

In conclusion, evidence for the formation of Cu(III) containing layered oxychlorides under ambient pressure conditions is reported. The new phases,  $\text{Ba}_4\text{CuMO}_4\text{Cl}_4$  ( $M = \text{Li}, \text{Na}$ ), represent the first examples of oxyhalides containing only Cu(III) and are isostructural with the recently discovered high  $T_c$  oxyhalide family with  $\text{K}_2\text{NiF}_4$ -type structure.

TABLE 1  
The Lattice Parameters of  $\text{Ba}_2\text{CuO}_2\text{Cl}_2$  and Related Phases

Compound	$a$ (Å)	$c$ (Å)	Reference
$\text{Ba}_2\text{CuO}_2\text{Cl}_2$	4.1026(3)	16.442(1)	6
$\text{Ba}_2(\text{Cu}_{0.8}\text{Ca}_{0.2})\text{O}_2\text{Cl}_2$	4.1779(1)	16.2303(2)	7
$\text{Ba}_2(\text{Cu}_{0.8}\text{Cd}_{0.2})\text{O}_2\text{Cl}_2$	4.1721(1)	16.2298(1)	7
$\text{Ba}_4\text{CuLiO}_4\text{Cl}_4$	4.1558(1)	16.1248(2)	Present work
$\text{Ba}_4\text{CuNaO}_4\text{Cl}_4$	4.2183(2)	16.1567(2)	Present work

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## REFERENCES

1. Hk. Müller-Buschbaum, *Angew. Chem. (Int. Ed. Engl.)*, **30**, 723 (1991).
2. M. Al-Mamouri, P. P. Edwards, C. Greaves, and M. Slaski, *Nature* **369**, 382 (1994).
3. Z. Hiroi, N. Kobayashi, and M. Takano, *Nature* **371**, 139 (1994).
4. C.-Q. Jing, X.-J. Wu, P. Laffez, T. Tatsuki, T. Tamura, S. Adachi, H. Yamauchi, N. Koshizuka, and S. Tanaka, *Nature* **375**, 301 (1995).
5. Y. Zenitani, K. Inari, S. Saboda, M. Uehara, J. Akimitsu, N. Kubota, and M. Ayabe, *Physica C* **248**, 167 (1995).
6. T. Tatsuki, A. T. Yamamoto, T. Tamura, Y. Moriawaki, X.-J. Wu, S. Adachi, and K. Tanabe, *Physica C* **265**, 323 (1996).
7. T. Kodenkandath, G. Calestani, and F. C. Maticotta, *J. Mater. Chem.* **6**(9), 1575 (1996).
8. K. V. Ramanujachary, M. Greaney, R. L. Fuller, and M. Greenblatt, *J. Solid State Chem.* **93**, 263 (1991); R. L. Fuller and M. Greenblatt, *J. Solid State Chem.* **92**, 386 (1991).
9. G. Calestani, P. Ganguli, F. C. Maticotta, P. Nozar, A. Migliori, K. A. Thomas, and A. Tomasi, *Physica C* **247**, 359 (1995); P. D. Vernooy and A. M. Stacy, *J. Solid State Chem.* **98**, 270 (1991).
10. J. P. Attfield and G. Ferey, *J. Solid State Chem.* **80**, 112 (1989).
11. J. L. Sarrao, D. P. Young, Z. Fisk, E. G. Moshopoulou, J. D. Thompson, B. C. Chakoumakos, and S. E. Nagler, *Phys. Rev. B* **54**(17), 12,014 (1996).
12. F. C. Maticotta, P. Nozar, K. A. Thomas, G. Calestani, and A. Migliori, *Mater. Res. Bull.* **30**(7), 821 (1995).