710 *Inorg. Chem.* **2001,** *40,* 710−714

Construction of Copper Halide Networks within Layered Perovskites. Syntheses and Characterization of New Low-Temperature Copper Oxyhalides

Thomas A. Kodenkandath,[†,‡] Amar S. Kumbhar,[†,‡] Weilie L. Zhou,[‡] and John B. Wiley*,[†,‡]

Department of Chemistry and Advanced Materials Research Institute, University of New Orleans,
New Orleans, Louisiana 70148-2820

Received July 21, 2000

The construction of two-dimensional (2D) copper halide networks within a variety of perovskite hosts by a low-temperature topochemical method is demonstrated. Ion exchange between some layered perovskite oxides of the type $A'[A_{n-1}(M,M')_nO_{3n+1}]$ (A' = alkali metal, H, NH_4; A = alkaline earth, rare earth, or Bi; M,M' = Nb, Ta, Ti; $n = 2, 3$) with CuX_2 (X = Cl, Br) results in the oxyhalides $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$. Rietveld refinements from X-ray powder diffraction data show that the structures of these new copper oxyhalides contain edge-sharing CuO_2X_4 octahedra sandwiched between the $M/M'O_6$ octahedra of the perovskite slabs. The compounds are low-temperature phases that decompose well below 700 °C. The copper oxyhalides exhibit antiferromagnetic ordering resulting from the magnetic exchange interactions within the planar Cu−X networks.

Introduction

Recently topotactic approaches toward the synthesis of rationally designed novel materials have attracted considerable interest among solid-state chemists.[1] In this regard, layered perovskites of the Ruddlesden−Popper (RP), $A'_2[A_{n-1}(M,M')_nO_{3n+1}]$,[2] and Dion−Jacobson (DJ) series, $A'[A_{n-1}(M,M')_nO_{3n+1}]$ (A' = alkali metal, H, NH_4, A = alkaline earth, rare earth, or Bi, M/M' = Nb, Ti, etc.),[3] are very attractive in that they are amenable to a rich variety of soft chemistry techniques such as ion exchange and intercalation. The structures of these compounds consist of perovskite slabs, *n* layers thick, that are separated by ion-exchangeable interlayer A' cations.[4] Several new low-temperature and metastable compounds not accessible by traditional synthetic routes have been prepared from the above two series.[5]

As a part of our continuing efforts to develop low-temperature synthetic methods to rationally design new materials with novel structure and properties, we have explored the possibility of constructing covalently bound metal−anion networks within the interlayers of the DJ type compounds while retaining the basic perovskite lattice. Our aim is to use DJ phases as templates for the assembly of an additional transition metal−anion network so that the resulting compounds will have two distinct but interconnected metal−anion sublattices. In this direction, recently we reported the synthesis and characterization of compounds of the type $(CuX)LaNb_2O_7$ (X = Cl, Br).[6] We have extended our synthetic strategy to demonstrate the versatility of this approach to a wide number of DJ host materials, and here, we report the synthesis, structure, and properties of a new family of perovskite-related layered copper oxyhalides of the type $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$.

Experimental Section

Synthesis. Parent compounds belonging to the Dion−Jacobson (DJ) series of layered perovskites, $A'[A_{n-1}(M,M')_nO_{3n+1}]$ (A' = alkali metal, H, NH_4, A = alkaline earth, rare earth, or Bi, M/M' = Nb, Ta, Ti) with $n = 2, 3$, were synthesized by standard high-temperature solid-state or low-temperature ion exchange reaction methods according to the literature. The compounds $A'LaNb_2O_7$ (A' = K, Rb),[7] $RbNdNb_2O_7$,[8] $RbLaTa_2O_7$,[9] $RbLaBi_2O_7$,[10] $RbCa_2Nb_3O_{10}$,[11] and $RbLa_2Ti_2NbO_{10}$ [12] were prepared from K_2CO_3 (Alfa, 99.8%), Rb_2CO_3 (Alfa, 99%), La_2O_3 (Alfa, 99.99%, preheated at 1000 °C for 12 h), Nd_2O_3 (Aldrich, 99.99%),

---

[†] Department of Chemistry.

[‡] Advanced Materials Research Institute.

(1) (a) Gopalakrishnan, J. *Chem. Mater.* **1995**, *7*, 1265. (b) *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Elsevier Science: Oxford, U.K., 1996; Vol. 7. (c) Jacobson, A. J. In *Solid State Chemistry Compounds*; Cheetham, A. K., Day, P., Eds.; Clarendon Press: Oxford, U.K., 1991; pp 182−233 and references therein.

(2) Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1957**, *10*, 538. Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1958**, *11*, 54.

(3) (a) Dion, M.; Ganne, M.; Tournoux, M. *Mater. Res. Bull.* **1981**, *16*, 1429. (b) Dion, M.; Ganne, M.; Tournoux, M.; Ravez, J. *Rev. Chim. Min.* **1984**, *21*, 92. (c) Jacobson, A. J.; Johnson, J. W.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 3729.

(4) (a) Sato, M.; Abo, J.; Jin, T.; Ohta, M. *J. Alloys Compd.* **1993**, *192*, 81. (b) Toda, K.; Sato, M. *J. Mater. Chem.* **1996**, *6*, 1067. (c) Fuuoka, H.; Isami, T.; Yamanaka, S. *J. Solid State Chem.* **2000**, *151*, 40. (d) Hong, Y. S.; Kim, S.-J.; Choy, J.-H. *J. Mater. Chem.* **2000**, *10*, 1209.

(5) (a) Schaak, R. E.; Mallouk, T. E. *J. Am. Chem. Soc.* **2000**, *122*, 2798. (b) Fukuoka, H.; Isami, T.; Yamanaka, S. *Chem. Lett.* **1997**, 703. (c) Gómez-Romero, P.; Palacin, M. R.; Casañ, N.; Fuestes, A. *Solid State Ionics* **1993**, *63−65*, 424. (d) Thangadurai, V.; Subbanna, G. N.; Gopalakrishnan, J. *Chem. Commun.* **1998**, 1299. (e) McIntyre, R. A.; Falster, A. U.; Li, S.; Simmons, W. B.; O'Connor, C. J.; Wiley, J. B. *J. Am. Chem. Soc.* **1998**, *120*, 217. (f) Lalena, J. N.; Cushing, B. L.; Falster, A. U.; Simmons, W. B.; Seip, C. T.; Carpenter, E. E.; O'Connor, C. J.; Wiley, J. B. *Inorg. Chem.* **1998**, *37*, 4484. (g) Cushing, B. L.; Wiley, J. B. *J. Solid State Chem.* **1998**, *141*, 385. (h) Cushing, B. L.; Wiley, J. B. *Mater. Res. Bull.* **1999**, *34*, 271. (i) Schaak, R. E.; Mallouk, T. E. *Chem. Mater.* **2000**, *12*, 2513. (j) Gopalakrishnan, J.; Sivakumar, T.; Ramesha, K.; Thangadurai, V.; Subbanna, G. N. *J. Am. Chem. Soc.* **2000**, *122*, 6237.

(6) Kodenkandath, T. A.; Lalena, J. N.; Zhou, W. L.; Carpenter, E. E.; Sangregorio, C.; Falster, A. U.; Simmons, W. B.; O'Connor, C. J.; Wiley, J. B. *J. Am. Chem. Soc.* **1999**, *121*, 10743.

(7) Gopalakrishnan, J.; Bhat, V.; Raveau, B. *Mater. Res. Bull.* **1987**, *22*, 413.

(8) Dion, M.; Ganne, M.; Tournoux, M. *Rev. Chim. Miner.* **1986**, *23*, 61.

(9) Toda, K.; Sato, M. *J. Mater. Chem.* **1996**, *6*, 1067.

(10) Subramanian, M. A.; Gopalakrishnan, J.; Sleight, A. W. *Mater. Res. Bull.* **1988**, *23*, 837.

(11) Dion, M.; Ganne, M.; Tournoux, M. *Mater. Res. Bull.* **1981**, *16*, 1429.

(12) Gopalakrishnan, J.; Uma, S.; Bhat, V. *Chem. Mater.* **1993**, *5*, 132.

10.1021/ic0008215 CCC: $20.00

Bi_2O_3 (Alfa, 99%), $CaCO_3$ (Alfa, 99.95%), Nb_2O_5 (Alfa, 99.9985%), Ta_2O_5 (Alfa, 99.993%), and TiO_2 (Aldrich, 99.99%). Starting mixtures with appropriate stoichiometries and a 20−25% molar excess of A_2CO_3 (to compensate for the loss of the oxide due to volatilization) were ground together and heated in alumina boats initially at 850−900 °C for 12 h followed by a treatment at 1050−1100 °C for 24−48 h with one intermittent grinding. The products were then washed thoroughly with distilled water to remove the excess alkali carbonates/oxides and dried overnight at 120 °C. $HLaNb_2O_7$ was prepared by the ion exchange of $KLaNb_2O_7$ with 6 M HNO_3 at 60 °C for 24 h.[7] $LiLaNb_2O_7$, $NaLaNb_2O_7$, and $NH_4LaNb_2O_7$ were synthesized by ion exchange of $RbLaNb_2O_7$ with the corresponding nitrates at 350 °C for 3 days.[7] The unit cell parameters of the $A'[A_{n-1}(M,M')_nO_{3n+1}]$ host materials were in good agreement with the values reported in the literature.[7−12]

The syntheses of $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ ($X = Cl, Br$) type phases were achieved by a single-step low-temperature ion exchange reaction between the parent DJ phases with cupric halides $CuCl_2$ (Alfa, 99%) and $CuBr_2$ (T. J. Baker, 99%). The parent materials were mixed thoroughly with a 2-fold molar excess of the cupric halide (dried overnight at 120 °C), sealed in evacuated ($<10^{-3}$ Torr) Pyrex tubes, and heated at 325−350 °C for 7−12 days. The samples were then washed with copious amounts of cold and hot distilled water to remove the excess cupric halides and $A'X$ byproduct. Attempts were also made to synthesize copper fluoride containing phases under similar conditions using CuF_2 (Aldrich, 98%).

Characterization. The products were found to be insoluble in a variety of acids, including aqua regia. Hence, chemical analyses were based on energy dispersive spectroscopy (EDS) of sets of individual grains. These were carried out on a JEOL (model JSM-5410) scanning electron microscope (SEM) equipped with an EDAX (DX-PRIME) microanalytical system. Parent compounds, CuCl (Aldrich, 99.999%), and CuBr (Aldrich, 98%) were used as standards.

Powder X-ray diffraction data were collected between 5° and 95° 2θ (step = 0.2° with a 2 s count time) on an automated Philips X'Pert-MPD diffractometer equipped with a graphite monochromator using Cu Kα ($\lambda = 1.5418$ Å) radiation. X-ray data for the Rietveld structural refinements were collected between 10° and 110° 2θ with a 0.02° step width and 10 s count time. The refinements were carried out with the GSAS set of programs[13] using a pseudo-Voigt profile function. The background was refined using a linear interpolation function with six variables. The initial structural models were based on the host structures, which are well documented in the literature.[4a,b] The site occupancies of copper and halogen were refined keeping those of other cations and oxygen fixed at 100%. The R factor (R_p), the weighted R factor (R_{wp}), and χ^2 are defined as the following: profile, $R_p = \sum[y_{io} - y_{ic}]/\sum y_{io}$; weighted profile, $R_{wp} = [\sum w_i(y_{io} - y_{ic})^2/\sum w_i(y_{io})^2]^{1/2}$; and goodness of fit (GOF), $\chi^2 = [R_{wp}/R_{exp}]^2$. $R_{exp} = [(N - P)/\sum w_i y_{io}^2]^{1/2}$, y_{io} and y_{ic} are the observed and calculated intensities, w_i is the weighting factor, N is the total number of y_{io} data when the background is refined, and P is the number of adjusted parameters.

The stability of the products was examined by thermogravimetric analysis using a TA Instruments Thermal Analyst-2000 system over the temperature range 25−800 °C with a ramp of 10 °C/min in flowing N_2 atmosphere. Magnetic susceptibility measurements were made on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5S) between 2 and 300 K in a field of 1000 G (field-cooled).

Results and Discussion

Synthesis. The formation of $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ was found to follow the general reaction

$$A'[A_{n-1}(M,M')_nO_{3n+1}] + CuX_2 \rightarrow (CuX)[A_{n-1}(M,M')_nO_{3n+1}] + A'X$$

The X-ray diffraction of the unwashed reaction mixture showed the presence of the $A'X$ byproduct. The chloride products were green, while bromide phases were dark reddish-brown. Chemical analysis of thoroughly washed products exhibited a nearly 1:1 ratio of Cu to X (no or very little A' was detected) and the ratio of A to M to M′ remained the same as in the case of the starting host. Table 1 summarizes the various phases synthesized in the present study along with their oxide hosts. It should be noted that single-phase $(CuCl)BiNb_2O_7$ could not be prepared; samples were always accompanied by unreacted starting materials (even after 3 weeks) and BiOCl.

Table 1. Unit Cell Parameters for the DJ Parent Compounds and the Exchange Products

compd	A′	a (Å)	c (Å)	vol (Å^3)
$A'LaNb_2O_7$[a]	Rb	3.896(9)	11.027(2)	167.4
	CuCl	3.8792(1)	11.7282(1)	176.49
	CuBr	3.8995(1)	11.7060(3)	178.00
$A'LaTa_2O_7$	Rb	3.8807(6)	11.0852(1)	166.94
	CuCl	3.8839(4)	11.7472(9)	177.20
	CuBr	3.8965(1)	11.7125(6)	177.83
$A'NdNb_2O_7$	Rb	3.8728(4)	10.9318(1)	163.96
	CuCl	3.8498(2)	11.6597(4)	172.81
$A'Ca_2Nb_3O_{10}$	Rb[b]	3.8662(5)	14.9424(6)	223.35
	CuCl	3.8496(2)	15.6593(7)	232.06
$A'La_2Ti_2NbO_{10}$	Rb	3.8383(9)	15.2189(9)	224.21
	CuCl	3.8356(9)	15.9010(4)	233.93
	CuBr	3.8469(8)	15.8971(2)	235.26

[a] Reference 6. [b] In ref 11, the compound was indexed on the supercell, 7.725(2), 14.909(2) Å.

The syntheses of the $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ compounds were achieved at 325 °C. This temperature is well below the melting/decomposition points of the hosts, cupric halides, and $A'X$ byproducts. Hence, it is possible that the reaction proceeded through the formation of a eutectic between the copper halide and alkali metal halide byproducts to aid the diffusion process. The reactions were generally complete within 1 week for X = Cl, whereas longer reaction times were necessary for X = Br depending on the host. Our efforts to improve the reaction kinetics at higher temperatures resulted in the formation of undesired byproducts. For example, in the case of $CuCl_2$ and $RbLaNb_2O_7$, reactions carried out at 350 °C resulted in $LaCuO_2$ as an impurity. It is also important to perform the syntheses under a controlled atmosphere (evacuated, sealed tubes). CuO formation was observed in samples prepared in open air at 325 °C.

While copper chloride phases formed easily with all the host DJ phases, copper bromide phases were produced only from select members of the series $NH_4LaNb_2O_7$, $RbLaNb_2O_7$, $RbLaTa_2O_7$, and $RbLa_2Ti_2NbO_{10}$. Table 2 compares the reactivity of the chloride series with that of the bromide. Also included are the relative layer orientations and the layer spacings derived from unit cell parameters. The difference in reactivity likely correlates with the smaller size of the chloride ion (1.67 Å) relative to that of bromide ion (1.82 Å);[14] bromide exchange typically takes place with those host materials with larger layer spacings. One exception here is $RbBiNb_2O_7$, where the more highly polarizable bismuth (vs lanthanum) may influence the exchange chemistry of this host. Attempts to synthesize copper fluoride containing phases were not successful because reaction with CuF_2 resulted in the degradation of the host and formation of CuO. Our efforts to prepare $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ phases by high-temperature solid-state reactions were also ineffective, indicating that more conventional methods are not suitable for the synthesis of these phases. This is in accordance with the TGA results (see below) that indicate that $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ are low-temperature phases.

---

(13) Larson, A.; Von Dreele, R. B. *GSAS: Generalized Structure Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 1994.

(14) Radii are from: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Table 2. Comparison of Exchange Behavior of Copper Chloride vs Copper Bromide in DJ Perovskites[a]

compd	chloride	bromide	layer orientation[b]	layer spacing (Å)
$RbLaNb_2O_7$	y	y	E	10.989[7]
$HLaNb_2O_7$	y	n	E	10.459[7]
$LiLaNb_2O_7$	y	n	S	10.16[7]
$NaLaNb_2O_7$	y	n	S	10.45[7]
$KLaNb_2O_7$	y	n	P	10.77[7]
$NH_4LaNb_2O_7$	y	y	E	10.95[7]
$RbNdNb_2O_7$	y	n	E	10.733[8]
$RbLaTa_2O_7$	y	y	E	11.1053[9]
$RbBiNb_2O_7$	y[c]	n	E	11.22[10]
$RbCa_2Nb_3O_{10}$	y	n	E	14.909[11]
$RbLa_2Ti_2NbO_{10}$	y	y	E	15.24[12]

[a] y = yes; n = no. [b] E = layers are eclipsed; S = layers are staggered; P = layers are partially eclipsed. [c] Reaction incomplete even after 3 weeks.

Cation exchange reactions are well-known compared to those involving anions. Though they are relatively rare, reactions involving the coexchange of both cations and anions have also been reported; examples include zeolites and cation-exchange resins.[15] The reaction of CuX_2 and $RbLaNb_2O_7$ represents the first example of such behavior in perovskites.[6] In the present investigation, we have been able to extend this low-temperature synthetic strategy to convert a variety of perovskite hosts into new copper oxyhalides through simultaneous ion exchange of copper and halide ions. Ion exchange using $CuCl_2$ in another perovskite-related material, $Na_2La_2Ti_3O_{10}$ (a triple layer RP type perovskite), resulted in $CuLa_2Ti_3O_{10}$ with no anion incorporation.[16] Here, because of the greater interlayer charge of the host, twice that of the Dion−Jacobson type perovskites, two $CuCl^+$ units would have to exchange to maintain charge balance. There is likely not enough room in the RP interlayer to accommodate both units. With this in mind, the lower interlayer cation density in DJ phases compared to RP phases appears to be instrumental in the successful coexchange phenomenon in these perovskites.

Thermal Stability. Thermal analysis experiments show that the $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ compounds are low-temperature phases. They start decomposing around 450 °C with the loss of $CuCl_2$ before decomposing completely above 700 °C. Experiments carried out in inert (flowing N_2) and oxidizing atmosphere (static air) indicate that the decomposition leads to stable phases of the A−M/M′−O systems. In the case of $(CuCl)LaNb_2O_7$ for example, we find $LaNbO_4$ and $CuNb_2O_6$ as the decomposition products. Our complementary experiments to study the thermal stability of $(CuCl)LaNb_2O_7$ under dynamic vacuum show that the decomposition proceeds through the formation of an intermediate phase having the composition $Cu_{0.5}LaNb_2O_7$. Details of the isolation, structure, and properties of $Cu_{0.5}LaNb_2O_7$ will be described elsewhere.[17] Similar decomposition pathways are expected for the other $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ phases.

Structure. The most striking observation from X-ray analysis is the significant expansion seen in the *c* lattice parameter of the host materials upon exchange (Table 1). As shown in our earlier work,[6] this expansion is due to the insertion of Cu cations that bridge between the apical oxygens of the perovskite blocks; each copper ion is also surrounded by four coplanar halide ions. The structures of $(CuX)[A_{n-1}(M,M')_nO_{3n+1}]$ phases then have an eclipsed configuration of the $M,M'O_6$ octahedra between the adjacent perovskite layers irrespective of their arrangement in the starting host. For example it is well-known that depending on the size of the A′ cation, the structures of $A'LaNb_2O_7$ (A′ = Li, Na, K, Rb, NH_4) phases adopt a staggered (Li, Na), partially staggered (K), or fully eclipsed (Rb, NH_4) configuration of the perovskite layers. However, the products from exchange reactions with these hosts all have an eclipsed configuration. Such a structural reorganization is necessary to accommodate Cu in the bridging position described above. Rietveld refinements were based on this structural model. Profile fits for the two compounds $(CuCl)LaTa_2O_7$ and $(CuCl)Ca_2Nb_3O_{10}$ are presented in Figure 1. Structural parameters and selected bond distances for these compounds are listed in Table 3. Somewhat large isotropic thermal parameters suggest some amount of disorder for halogens around the ideal $0,0,{}^1/_2$ position. This behavior is common to all the phases reported in the present study. In the case of $(CuX)LaNb_2O_7$ (X = Cl, Br), anisotropic thermal parameter refinements established that the thermal ellipsoids of halogens are oblate, suggesting they are disordered selectively in the *ab* plane.[6] This observation supports the fact that Cu(II), being a Jahn−Teller ion, tends to prefer distorted octahedral coordination resulting from the short and long bonding interactions. Efforts to understand the nature of the disorder of halogens in these compounds are currently underway through structural refinements from neutron diffraction experiments.

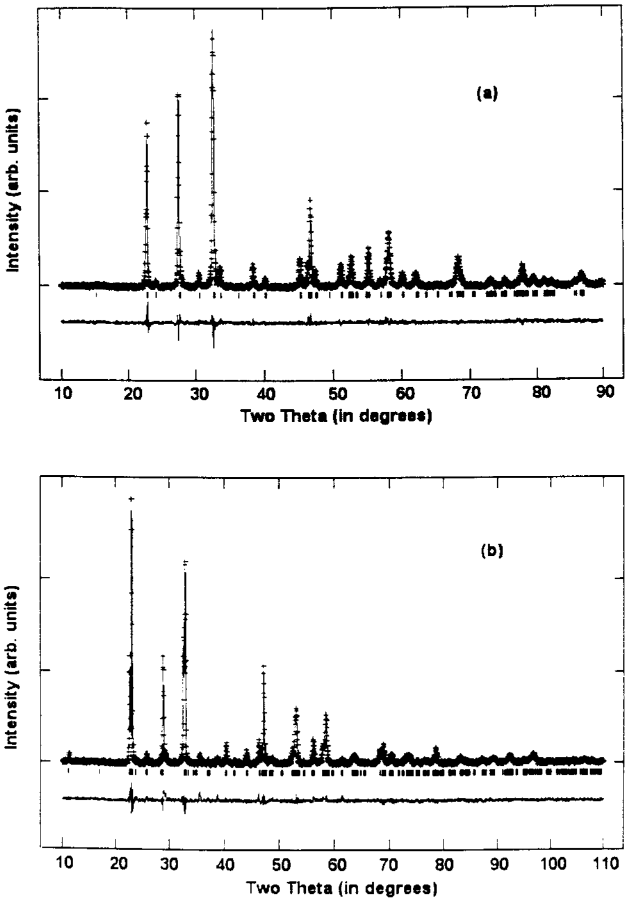

Figure 1. Rietveld refinement plots for (a) $(CuCl)LaTa_2O_7$ and (b) $(CuCl)Ca_2Nb_3O_{10}$.

The topotactic nature of the conversion of the oxide hosts to the copper oxyhalide is represented in Figure 2. As can be seen, the perovskite host layer is retained in the product and the interlayer contains an edge-sharing CuO_2X_4 octahedral network in the *ab* plane. These CuO_2X_4 octahedra have a compressed

---

(15) (a) Tsutsumi, K.; Fuji, S.; Takahashi, H. *J. Catal.* **1972**, *24*, 146. (b) Nardin, M.; Talbot-Besnard, S. *C. R. Acad. Sci. Paris* **1969**, *269*, 1608.

(16) Hyeon, K.-A.; Byeon, S.-H. *Chem. Mater.* **1999**, *11*, 352.

(17) Kodenkandath, T. A.; Wiley, J. B. Manuscript in preparation.

Table 3. Crystallographic Data and Selected Bond Distances for $(CuCl)LaTa_2O_7$ and $(CuCl)Ca_2Nb_3O_{10}$

$(CuCl)LaTa_2O_7$
Space Group: $P4/mmm$, $R_p = 5.66\%$, $R_{wp} = 7.18\%$, $\chi^2 = 1.66$

atom	site	x	y	z	g^a	U_{iso} (Å^2)
Cu	1d	0.5	0.5	0.5	0.98(1)	0.014(1)
Cl	1b	0	0	0.5	1.03(4)	0.143(3)
La	1a	0	0	0	1	0.089(4)
Ta	2h	0.5	0.5	0.1913(1)	1	0.097(1)
O1	4i	0	0.5	0.1574(9)	1	0.0132(9)
O2	2h	0.5	0.5	0.332(2)	1	0.0086(2)
O3	1c	0.5	0.5	0	1	0.0092(8)

Bond Distances (Å)

Cu−Cl = 2.7464(1)
Cu−O2 = 1.98(2)
Ta−O1 = 1.980(2)
Ta−O2 = 1.643(2)
Ta−O3 = 2.245(2)

$(CuCl)Ca_2Nb_3O_{10}$
Space Group: $P4/mmm$, $R_p = 8.69\%$, $R_{wp} = 6.49\%$, $\chi^2 = 2.46$

atom	site	x	y	z	g^a	U_{iso} (Å^2)
Cu	1b	0	0	0.5	0.960(1)	0.022(6)
Cl	1d	0.5	0.5	0.5	1.03(2)	0.165(7)
Ca	2h	0.5	0.5	0.1424(4)	1	0.0067(5)
Nb1	1a	0	0	0	1	0.0126(6)
Nb2	2g	0	0	0.2695(2)	1	0.0093(1)
O1	2f	0	0.5	0	1	0.0214(3)
O2	2g	0	0	0.124(1)	1	0.0237(1)
O3	4i	0	0.5	0.242(1)	1	0.01879(3)
O4	2g	0	0	0.3727(5)	1	0.0231(5)

Bond Distances (Å)

Cu−Cl = 2.7221(1)
Cu−O4 = 1.993(1)
Nb1−O1 = 1.9248(1)
Nb1−O2 = 1.94(2)
Nb2−O2 = 2.28(2)
Nb2−O3 = 1.971(3)
Nb2−O4 = 1.616(3)

[a] g is the site occupancy.

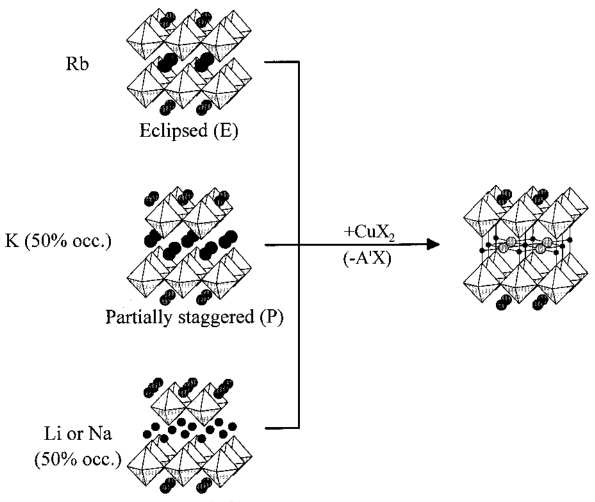

Figure 2. Schematic of topotactic transformation to the copper oxyhalide series through eclipsed (E), partially staggered (P), and staggered (S) layer configurations.

geometry, and they corner-share with M/M′O_6 octahedra of the perovskite layer. Figure 3 represents the local environment of the copper, tantalum, and niobium in $(CuCl)LaTa_2O_7$ and $(CuCl)Ca_2Nb_3O_{10}$. This arrangement for copper is similar to what is observed for mercury in NH_4HgCl_3 and thallium in $Tl(La_2Sr_2)Ni_2O_9$.[18,19] The Cu−X and Cu−O bond distances (Table 3) are consistent with known copper oxyhalides.[20] In light of the apparent disorder of the halides, Cu−Cl distances are best described as rough averages.

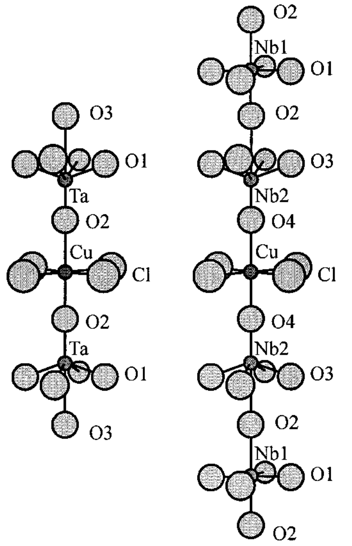

Figure 3. Idealized representation of local coordination in $(CuCl)LaTa_2O_7$ and $(CuCl)Ca_2Nb_3O_{10}$.

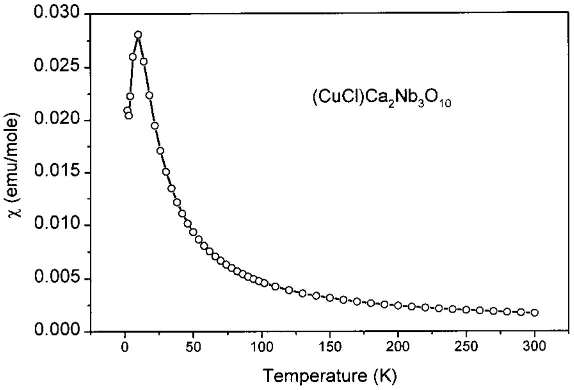

Figure 4. Plot of magnetic susceptibility vs temperature for $(CuCl)Ca_2Nb_3O_{10}$.

Perovskite-related copper oxyhalides are well-known in the literature and have recently received considerable attention as a novel family of copper-based superconductors.[21] Most of these materials are synthesized at high temperatures, although some have used low-temperature synthetic techniques. None of these copper oxyhalides, however, have the structural characteristics of those reported in this study.

Magnetism. Magnetic measurements were carried out on the copper oxychlorides $(CuCl)TaNb_2O_7$, $(CuCl)Ca_2Nb_3O_{10}$, and $(CuCl)La_2Ti_2NbO_{10}$. Similar to $(CuCl)LaNb_2O_7$,[6] samples show antiferromagnetic transitions around 10 K. Figure 4 shows a susceptibility vs temperature plot for $(CuCl)Ca_2Nb_3O_{10}$. The low-temperature antiferromagnetic ordering observed in these phases further supports the establishment of copper halide networks within the perovskite interlayers because such an ordering would require magnetic exchange interactions through the coplanar halide ions. Similar AFM transitions are well-

---

(18) Harmsen, E. J. *Z. Kristallogr.* **1938**, *100*, 208.
(19) Knee, C. S.; Weller, M. T. *J. Solid State Chem.* **2000**, *150*, 1.
(20) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: New York, 1986; pp 1135−1141.
(21) (a) Al-Mamouri, M.; Edwards, P. P.; Greaves, C.; Slaski, M. *Nature* **1994**, *369*, 382. (b) Hiroi, H.; Kobayashi, N.; Takano, M. *Nature* **1994**, *371*, 139. (c) Jin, C.-Q.; Wu, X.-J.; Laffez, P.; Tatsuki, T.; Tamura, T.; Adachi, S.; Yamauchi, H.; Koshizuka, N.; Tanaka, S. *Nature* **1995**, *375*, 301.

known in other copper halides and oxyhalides.[22] It should be noted that both the tantalate and the niobate exhibit a small paramagnetic tail below T_N; this may be due to the presence of a small amount of a paramagnetic impurity or from copper ions within the perovskite that are magnetically isolated because of a local absence of bridging chloride ions.

Conclusion

The present study demonstrates that 2D copper halide networks can be assembled within a variety of DJ type perovskites to produce a new class of copper oxyhalides with novel structural features. We have been able to show that host materials synthesized at high temperatures can act as templates for the low-temperature construction of Cu−X networks. If similar chemistry can be extended for the assembly of other transition metal anion networks, the synthetic approach described here will be an important advance in the rational design and syntheses of novel materials. The success of such an approach, dependent on the identification of effective ion-exchange reagents, should lead to new classes of low-temperature or metastable compounds.

Acknowledgment. The authors gratefully acknowledge support from the NSF (DMR-9983591) and the DOD (DARPA MDA972-97-1-0003).

IC0008215

---

(22) König, E. In *Magnetic Properties of Transition-Metal Compounds*; Landolt-Börnstein 2; Springer-Verlag: New York, 1966; pp 321−322. Escoffier, P.; Cauthier, J. *Compt. Rend.* **1961**, *252*, 271.