Assembly of Metal−Anion Arrays within a Perovskite Host. Low-Temperature Synthesis of New Layered Copper−Oxyhalides, (CuX)LaNb₂O₇, X = Cl, Br

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Abstract: A low-temperature topotactic route is used to assemble metal−anion arrays within a perovskite host. Ion exchange between $RbLaNb_2O_7$ and CuX_2 (X = Cl, Br) results in a new set of layered copper−oxyhalide perovskites, $(CuX)LaNb_2O_7$. Rietveld structural analysis of X-ray powder diffraction data confirms the formation of a two-dimensional copper−halide network in the double-layered perovskite interlayer. This new structure type contains unusual CuO_2X_4 octahedra that corner-share with NbO_6 octahedra from the perovskite slab and edge-share with each other along all four equatorial edges. Magnetic susceptibility measurements show that both products exhibit antiferromagnetic transitions below 40 K. Additionally, these materials are found to be low-temperature phases, decomposing completely by 700 °C. The synthetic approach described in this work is significant in that it demonstrates how host structures can be used as templates in the directed low-temperature assembly of extended metal−anion arrays.

Introduction

As part of our continuing efforts to develop new low-temperature ($\leq$500 °C) synthetic strategies for the manipulation of nonmolecular compounds,[1] we have sought to construct covalently bound metal−anion arrays within receptive host materials. Our goal is to use the hosts as templates for the rational assembly of specific structural motifs. Of particular interest here are two-dimensional transition-metal systems in that such layered compounds can demonstrate a range of interesting properties including high-temperature superconductivity and colossal magnetoresistance (CMR).[2] There are only a few general examples of topochemical manipulation of layered compounds that result in covalent cross-linkages between host layers; bifunctional organic anions have been "grafted" to select layered compounds while pillaring reactions have been reported in several systems.[3,4] We seek, however, to establish covalent bonding not only between host layers but also continuously within the assembled layer itself. To our knowledge there are no reports of low-temperature topotactic routes being utilized to construct extended inorganic arrays in receptive host materials. Herein we describe the synthesis and characterization of a new set of perovskite-related layered copper−oxyhalides, $(CuX)LaNb_2O_7$ (X = Cl and Br), where a copper−halide network was assembled within a double-layered perovskite host.

Experimental Section

Synthesis. The *n* = 2 Dion−Jacobson phase, $RbLaNb_2O_7$, was prepared by a method similar to that of Gopalakrishnan et al.[5] from La_2O_3 (Alfa, 99.99%), Nb_2O_5 (Alfa, 99.9985%), and Rb_2CO_3 (Alfa, 99%). The La_2O_3 was heated at 1050 °C for 24 h prior to use to remove any water or carbonates. Stoichiometric amounts of La_2O_3 and Nb_2O_5 along with a 25% molar excess of Rb_2CO_3 were ground together, heated for 12 h at 850 °C, ground again, and then heated an additional 24 h at 1050 °C. The product was washed thoroughly with distilled water and then dried at 120 °C overnight. The unit cell parameters (*a* = 3.896 (9) Å, *c* = 11.027(2) Å) were in good agreement with literature values (*a* = 3.885(2) Å, *c* = 10.989(3) Å).[5]

$(CuCl)LaNb_2O_7$ and $(CuBr)LaNb_2O_7$ were prepared by a single-step ion-exchange reaction. Initially, $CuCl_2$ (Alfa, 99%) and $CuBr_2$ (J. T. Baker, 99%) were dried overnight at 140 °C. $RbLaNb_2O_7$ was then combined with a 2-fold molar excess of the anhydrous copper halide in sealed, evacuated ($<10^{-3}$ Torr) Pyrex tubes and heated for 7 days at 325 °C. X-ray powder diffraction of the unwashed products showed the presence of rubidium halide byproduct. Samples were washed with copious amounts of water to remove excess copper halide and the rubidium byproduct; the products were green and dark reddish-brown for the chloride and bromide compounds, respectively. The exchange of other related double-layered perovskites, $ALaNb_2O_7$ (A = H, Li, Na, K, NH₄), was also screened.

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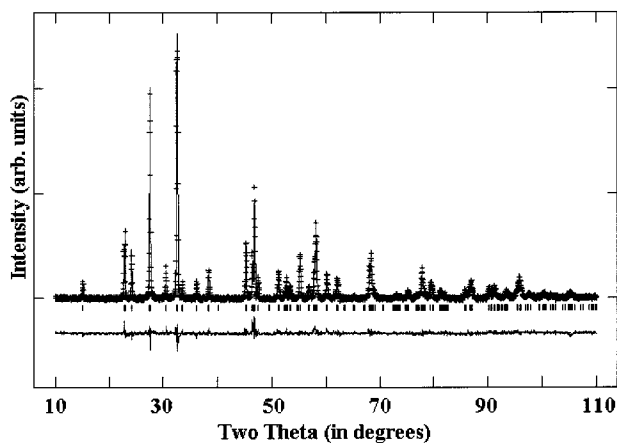
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Figure 1. Experimental, calculated, and difference X-ray powder patterns for the Rietveld refinement of (CuCl)LaNb$_2$O$_7$.

Characterization. The products would not dissolve in a variety of acids and bases, even with the use of a microwave digestion bomb. Compositional analysis was therefore based on energy dispersive spectroscopy (EDS) of sets of individual crystallites. Analyses were carried out on a JEOL JSM 5410 scanning electron microscope (SEM) equipped with an EDAX DX PRIME microanalytical system. The parent compound, RbLaNb$_2$O$_7$, CuCl (Aldrich, 99.999%), and CuBr (Aldrich, 98%) were used as standards. The chloride product was found to have copper, chlorine, lanthanum, and niobium in the ratios of 1.03(4):0.99(2):1.01(5):2.00, respectively. For the bromide product, the copper, bromine, lanthanum, and niobium were in ratios of 1.04(5):1.2(1):1.03(4):2.00, respectively. Rubidium was not detected in either of the products.

X-ray diffraction data from a Philips X'pert-MPD system (Cu Kα radiation, $\lambda = 1.5418$ Å) equipped with a graphite monochromator were collected in step-scanning mode between 10 and 110° 2θ with a 0.02° step width and 10 s count time. Magnetic susceptibility measurements were made on a Quantum Design MPMS-5S SQUID susceptometer between 2 and 300 K at 1000 G (field cooled). The decomposition of (CuCl)LaNb$_2$O$_7$ was examined by a combination of thermogravimetric analysis (TGA) and by heating a series of (CuCl)LaNb$_2$O$_7$ samples at various temperatures overnight in sealed, evacuated Pyrex or fused-silica tubes. TGA were performed on a TA Instruments Thermal Analyst 2000 system over the temperature range 25−800 °C with a ramp of 10 deg/min under flowing nitrogen. Decomposition products were determined by X-ray powder diffraction.

Rietveld refinements were carried out with the GSAS programs.[6] Profile refinements utilized the psuedo-Voigt function. The background was refined with six variables using a linear interpolation function. The host has been well characterized by others,[5,7] so the site occupancies for the niobium, lanthanum, and oxygen were all fixed at 100% and only the copper and halogen occupancies were varied in the refinement. The R-factor (R_p) and the weighted R-factor (R_{wp}) are defined as $R_p = \sum|I_o - I_c|/\sum I_c$ and $R_{wp} = [\sum w(I_o - I_c)^2/\sum(wI_o^2)]^{1/2}$, where I_o and I_c are the observed and calculated intensities, respectively.

Results and Discussion

Synthesis. (CuX)LaNb$_2$O$_7$ (X = Cl, Br) form from an ion exchange reaction between RbLaNb$_2$O$_7$ and the copper(II) halides, CuX$_2$.[8]

$$RbLaNb_2O_7 + CuX_2 \rightarrow$$
$$(CuX)LaNb_2O_7 + RbX \quad (X = Cl, Br)$$

Typically exchange reactions in these perovskite systems only involve cations. In RbLaNb$_2$O$_7$, however, we see the co-exchange of both copper and halide ions. Though this behavior is not common, some examples have been reported. Researchers examining the exchange of zeolites for the preparation of cracking catalysts noted co-exchange from aqueous copper−chloride solutions.[9] Others studying the absorption of copper(II) on cation-exchange resins observed a similar effect.[10] In both these cases, reactions presumably involved the species [CuCl-(H$_2$O)$_3$]$^+$. In contrast, a very recent report on the synthesis of CuLa$_2$Ti$_3$O$_{10}$ from the solid-state reaction of CuCl$_2$ and the Ruddlesden−Popper triple-layered perovskite, Na$_2$La$_2$Ti$_3$O$_{10}$, showed no anion incorporation.[11] Here, however, it is expected that the greater layer charge of the host, twice that of RbLaNb$_2$O$_7$, is important: to maintain a charge balance, Na$_2$-La$_2$Ti$_3$O$_{10}$ would have to exchange two "CuCl$^+$" units, for which there may not be enough room in the interlayer. In a similar result on the direct reaction of KLaNb$_2$O$_7$ and CuSO$_4$, Cu$_{0.48}$-LaNb$_2$O$_7$ formed with only a small amount of sulfur detected in the product.[12] The larger size, as well as the higher charge of the sulfate ion, likely suppresses its exchange. Our initial studies on the exchange of CuX$_2$ (X = Cl, Br) with the series ALaNb$_2$O$_7$ (A = H, Li, Na, K, Rb, NH$_4$) also indicate that the size of the anion may be important. The smaller chloride ion (1.69 Å)[13] readily co-exchanges into all members of this series, while the bromide ion (1.82 Å) only reacts with the compounds having the largest interlayer spacings, RbLaNb$_2$O$_7$ and NH$_4$-LaNb$_2$O$_7$. Further studies on RbLaNb$_2$O$_7$ and the other layered perovskites are needed to develop a full understanding as to when the co-exchange of cations and anions will occur.

Structure. On exchange, the layers of the perovskite host were found to significantly expand (ca. 0.70 Å) in c relative to the parent for both the chloride and the bromide (Table 1).

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

compd	unit cell (Å)	cell vol (Å^3)	lit. cell (Å)
RbLaNb$_2$O$_7$	$a = 3.896(9)$ $c = 11.027(2)$	167.4	$a = 3.885(2)^5$ $c = 10.989(3)$
(CuCl)LaNb$_2$O$_7$	$a = 3.8792(1)$ $c = 11.7282(3)$	176.49	this work
(CuBr)LaNb$_2$O$_7$	$a = 3.8995(1)$ $c = 11.7060(3)$	178.00	this work

Various structural models were considered that could account for the expansion as well as accommodate the copper and halide ions in the interlayer. The most reasonable one had copper cations surrounded by four coplanar halide ions and bridging between apical oxygens of the perovskite slabs. Rietveld refinements on this model gave the best profile fits. The observed, calculated, and difference plots for the Rietveld refinement of (CuCl)LaNb$_2$O$_7$ based on this model are shown in Figure 1. Table 2 presents the structural parameters for (CuCl)LaNb$_2$O$_7$ and (CuBr)LaNb$_2$O$_7$. The thermal parameters for both the chlorine (0.133 Å^2) and bromine (0.087 Å^2) atoms

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(8) These reactions are carried out below the decomposition/melting points of the copper halides and of the rubidium−halide byproducts. It is possible that a eutectic may form between the copper and rubidium halides to assist in the diffusion process, otherwise these reactions likely proceed by solid-state diffusion of the ions.

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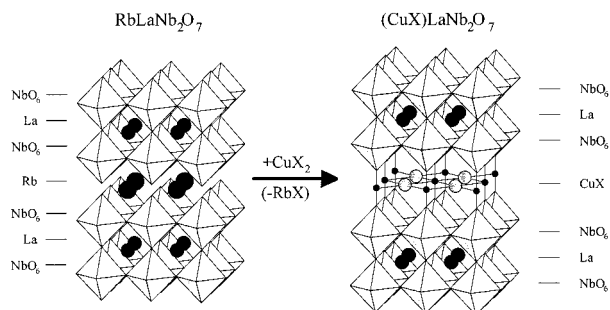
Figure 2. The structure of $(CuX)LaNb_2O_7$ relative to that of the parent, $RbLaNb_2O_7$. The large dark spheres in the interlayer of $RbLaNb_2O_7$ are rubidiums while the small dark and the larger light-colored spheres of $(CuX)LaNb_2O_7$ are the copper and halide ions, respectively.

Table 2. Crystallographic Data for $(CuX)LaNb_2O_7$ (X = Cl, Br)

sample	atom	site	x	y	z	g	$U_{iso}(\text{Å}^2)$
$(CuCl)LaNb_2O_7{}^a$	Cu	1d	0.5	0.5	0.5	1.00(1)	0.011(1)
	Cl	1b	0	0	0.5	1.01(1)	0.133(6)
	La	1a	0	0	0	1	0.0017(6)
	Nb	2h	0.5	0.5	0.1908(1)	1	0.0022(6)
	O1	4i	0	0.5	0.1595(6)	1	0.005(2)
	O2	2h	0.5	0.5	0.342(1)	1	0.036(6)
	O3	1c	0.5	0.5	0	1	0.020(6)
$(CuBr)LaNb_2O_7{}^b$	Cu	1d	0.5	0.5	0.5	1.009(9)	0.024(2)
	Br	1b	0	0	0.5	1.02(1)	0.087(3)
	La	1a	0	0	0	1	0.011(7)
	Nb	2h	0.5	0.5	0.1904(2)	1	0.0070(7)
	O1	4i	0	0.5	0.1583(8)	1	0.001(3)
	O2	2h	0.5	0.5	0.338(1)	1	0.024(7)
	O3	1c	0.5	0.5	0	1	0.021(9)

^{a} $P4/m$, $Z = 1$, $R_p = 6.92\%$, $R_{wp} = 8.90\%$. ^{b} $P4/m$, $Z = 1$, $R_p = 6.39\%$, $R_{wp} = 8.31\%$.

Table 3. Selected Bond Distances (Å) for $(CuX)LaNb_2O_7$

compd	Cu−O2	Cu−X^a	Nb−O1	Nb−O2	Nb−O3
$(CuCl)LaNb_2O_7$	1.97(1)	2.7430(1)	1.974(1)	1.66(1)	2.238(2)
$(CuBr)LaNb_2O_7$	1.99(1)	2.7573(1)	1.990(1)	1.63(1)	2.230(2)

^{a} See text.

were found to be large. Such large values are often attributed to either nonstoichiometry or disorder. Analytical data were in reasonable agreement with the copper−halide stoichiometries determined from the refinement, so it was expected that the halogens were disordered off the ideal 0, 0, $^1/_2$ position. Anisotropic refinement of the halogen atoms was consistent with this in that both the chlorine and bromine thermal ellipsoids were found to be oblate, extending significantly in the $a−b$ plane.[14] It is known that copper(II), as a Jahn−Teller ion, tends to have both short and long bonding interactions. If the halogens are responding to the bonding preferences of copper, they would disorder selectively in the $a−b$ plane. Initial efforts to model disorder in the bromide compound showed that bromine is slightly displaced off the 0, 0, $^1/_2$ site.[15] It is expected that similar behavior occurs in the chloride compound, though the larger thermal parameter would indicate that chlorine moves much further off the ideal position. Efforts to obtain synchrotron and neutron data on these systems are currently underway; though

Figure 3. (a) Magnetic susceptibility (χ) versus temperature for $(CuCl)LaNb_2O_7$ relative to the parent compound $RbLaNb_2O_7$. (b) Inverse susceptibility ($1/\chi$) versus temperature. The solid line indicates a fit to the Curie−Weiss law above 50 K.

we have clearly established the existence of copper halide arrays within the host materials, refinements on higher quality data would allow us to better address some of these structural details.

An idealized structure of $(CuX)LaNb_2O_7$ is shown in Figure 2 relative to the parent, $RbLaNb_2O_7$. As would be expected for a topotactic reaction, the host layer itself is essentially unchanged. In the interlayer of the product, distorted CuO_2X_4 octahedra are found to corner-share with the NbO_6 octahedra of the perovskite slabs while edge-sharing with other CuO_2X_4 octahedra in the $a−b$ plane. This arrangement is similar to what is seen for mercury in NH_4HgCl_3.[16] Copper−anion bond distances (Table 3) are consistent with known copper compounds,[17,18] though in light of the apparent disorder of the halides, the Cu−X distances are best viewed as rough averages.

Other examples of perovskite-related layered copper oxyhalides are known. Müller-Buschbaum[18] and others[19] have studied a number of compounds and recently there have been reports

(14) Anisotropic refinement of the chloride and bromide atoms produced U_{11}, U_{22}, and U_{33} values of 0.166, 0.166, and 0.063, and 0.101, 0.101, and 0.048, respectively.

(15) In modeling disorder in the bromide compound, the bromine was refined on an x, x, $^1/_2$ site in the $P4/mmm$ space group. This resulted in a slight movement off the 0, 0, $^1/_2$ position to $x = 0.061(2)$. Also, the bromine thermal parameter dropped to 0.033(4), the site occupancy on this 4-fold site refined to the expected value of 0.25 (0.249(2)), and the R-factors decreased to 6.01% and 7.93% for R_p and R_{wp}, respectively.
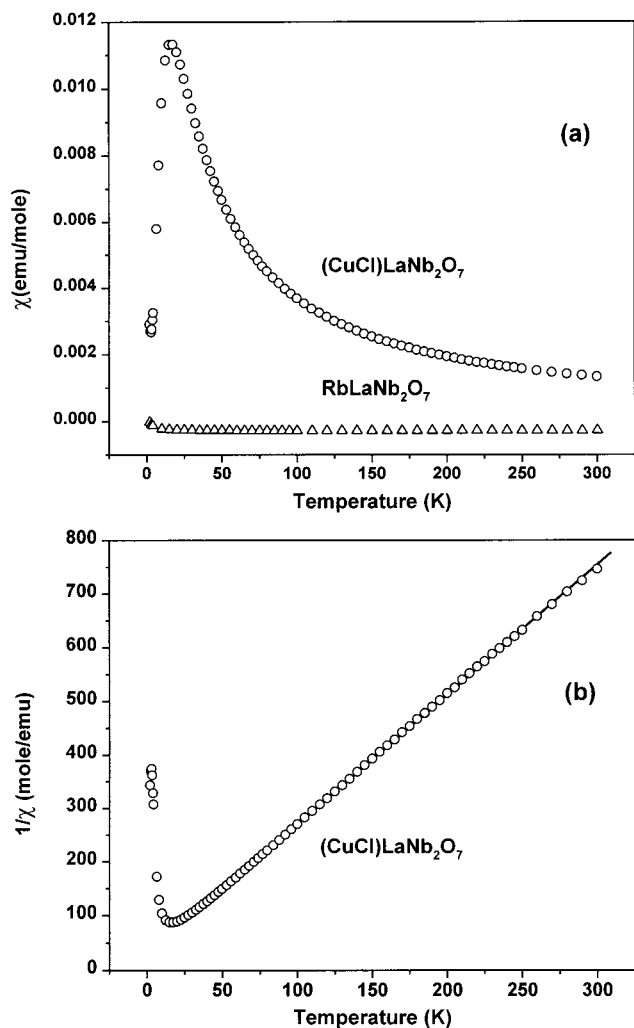
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of copper−oxyhalide superconductors.[20,21] Though most of these materials have been prepared at temperatures in excess of 800 °C, some have used low-temperature methods in fluorine intercalation.[21] None of these copper oxyhalides, however, are isostructural with those reported in this study.

Magnetism. Figure 3a shows a plot of magnetization versus temperature for $(CuCl)LaNb_2O_7$ relative to the diamagnetic parent. The high-temperature data ($T > 50$ K) of the chloride compound (Figure 3b) demonstrate Curie−Weiss behavior ($C = 0.404$ emu·K/mol, $\theta = -5.06$ K) with an effective magnetic moment (μ_{eff}) of 1.86 μ_B. Analogous behavior is observed in the bromide ($C = 0.424$ emu·K/mol, $\theta = -11.99$, $\mu_{eff} = 1.79$ μ_B). The μ_{eff} values are consistent with the presence of Cu^{2+} where moments are typically found in the range 1.75 to 2.10.[22] The low-temperature magnetic response of these materials gives further support for the establishment of copper−halide arrays within the perovskite layers. The compounds show antiferromagnetic (AFM) transitions at 16 and 37 K for the chloride and bromide, respectively. Coupling necessitates the presence of the halide in that it is required to mediate the magnetic exchange process.[23] Similar AFM transitions are seen in several other copper−halide compounds.[24] It should be noted that a small amount of paramagnetism was observed below the transition temperature in each sample. Though this may be due

to a minor impurity introduced in the exchange step, it is also possible that there are some copper ions in the interlayer that were not accompanied by halides on exchange. These species could be magnetically isolated from adjacent coppers, resulting in a paramagnetic response.

Thermal Analysis. Thermal analysis experiments showed that $(CuCl)LaNb_2O_7$ starts to decompose with loss of $CuCl_2$ by 450 °C and Cu_2OCl_2 by 550 °C. Complete collapse of the host structure then occurs by 700 °C. This indicates that these compounds are low-temperature phases and are likely not accessible by direct reaction since the parent compound must be synthesized at temperatures well above 700 °C.

Conclusions

The assembly of metal−anion networks within receptive hosts could prove to be an important advance in low-temperature syntheses as applied to nonmolecular systems. The ability to prepare hosts at high temperatures, where interatomic spacings and topologies can be varied, and then to use them as templates in the low-temperature construction of metal−anion arrays, offers a significant route to new rationally designed materials. We have already found that similar chemistry with the copper halides can be performed in various $n = 2$ and 3 members of the Dion−Jacobson series.[25] Should other effective ion-exchange reagents also be identified, such as metal halides, chalcogenides, pnictides, etc., then this unique approach to materials synthesis could be further exploited, possibly leading to whole new classes of low-temperature or even metastable compounds.

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