

Formation of Metal–Anion Arrays within Layered Perovskite Hosts. Preparation of a Series of New Metastable Transition-Metal Oxyhalides, (MCl)LaNb₂O₇ (M = Cr, Mn, Fe, Co)

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Received January 9, 2002

A new series of transition-metal oxyhalides (MCl)LaNb₂O₇ (M = Cr, Mn, Fe, Co) have been prepared by a simple topochemical route. Layered perovskite hosts (ALaNb₂O₇, A = Li, Na, K or Rb) were reacted with the corresponding anhydrous metal halides under mild reaction conditions (<400 °C). The compounds were examined by X-ray powder diffraction; the series appears to be isostructural with (CuCl)LaNb₂O₇, and the layer spacings, with the exception of M = Co, follow the trend expected from transition-metal cationic radii. Thermal analysis with differential scanning calorimetry (DSC) shows the materials to be metastable where all four compounds decompose exothermically above 690 °C.

Introduction

Topotactic reactions—ion exchange, intercalation, and deintercalation—offer effective routes for the preparation of new compounds under mild conditions (often <500 °C). The use of such methods is especially appealing due to their ability to direct the placement and connectivities of cations and/or anions in the final product. Exploitation of a variety of hosts has resulted in a diverse range of materials with interesting structures and properties.¹ Some recent examples include the formation of new layered oxides by the extraction of bismuth oxide layers from Aurivillius-type phases,² the insertion of vanadium oxide species,³ and the use of a sequence of topotactic steps to prepare structured perovskites.⁴

Currently we are studying the use of topotactic methods for the construction of metal–halide arrays within perovskite hosts.^{5,6} In our initial studies on the formation of metal–anion arrays within layered hosts, we focused on copper halide systems. More recently we reported our first success with iron halides. Because a number of layered compounds exhibit technologically significant properties,⁷ the ability to expand this synthetic approach to other metal–anion combinations is desirable in that it would allow access to a variety of low-temperature, possibly metastable phases unobtainable by standard ceramic methods. Herein we report on a new series of transition-metal oxyhalide layered perovskites prepared by ion exchange. These results are noteworthy in that they demonstrate both that this simple synthetic approach can be readily used to construct compounds with metal–

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anion arrays of a variety of transition metals and that such methods lead to new metastable compounds.

Experimental Section

Synthesis. Transition-metal anion arrays were assembled within Dion–Jacobson double-layered perovskite hosts (ALaNb_2O_7 , A = alkali metal) by reaction with the anhydrous metal chloride (MCl_2). The perovskite hosts were prepared by methods similar to those previously reported;^{5,8} $\text{RbLaNb}_2\text{O}_7$ was synthesized from Rb_2CO_3 (Alfa, 99%), La_2O_3 (Alfa, 99.99%, preheated at 1050 °C for 16 h before use), and Nb_2O_5 (Alfa, 99.9985%). Stoichiometric amounts of the starting materials with 25% molar excess of Rb_2CO_3 were combined and heated at 850–900 °C for 24 h. The mixture was then reground and heated at 1050 °C for an additional 24–48 h before being thoroughly washed in distilled water. $\text{LiLaNb}_2\text{O}_7$ and $\text{NaLaNb}_2\text{O}_7$ were prepared by ion exchange from $\text{RbLaNb}_2\text{O}_7$; $\text{RbLaNb}_2\text{O}_7$ and a 10-fold molar excess of LiNO_3 (Alfa Aesar, 99.98%) were heated in air at 300 °C for 24 h to produce $\text{LiLaNb}_2\text{O}_7$. After a thorough water wash, the sample was dried for 12 h at 150 °C. For $\text{NaLaNb}_2\text{O}_7$, $\text{RbLaNb}_2\text{O}_7$ was treated three separate times with excess NaNO_3 (EM Science, 99.98%) at 400 °C for 3 days, washed, and dried overnight at 400 °C.

Transition-metal halide arrays were inserted into the perovskite hosts by heating intimate mixtures of the host and the anhydrous metal halide under mild conditions for several days. The particular host (ALaNb_2O_7 , A = Li, Na, K, or Rb) and the details of the preparation varied with the transition metal. In general, the perovskite and the metal halide mixtures were combined in a 1:2 molar ratio with thorough grinding, pressed into pellets, and sealed in evacuated Pyrex tubes ($<10^{-4}$ Torr, tube volume ca. 10 mL). $(\text{FeCl})\text{LaNb}_2\text{O}_7$ was synthesized from $\text{RbLaNb}_2\text{O}_7$ and anhydrous FeCl_2 (Alfa, 99.5%) at 350 °C for 14 days; it can also be readily prepared from ALaNb_2O_7 (A = Li, Na, K) under comparable conditions, but in less time (2–5 days). Single-phase $(\text{CrCl})\text{LaNb}_2\text{O}_7$, $(\text{MnCl})\text{LaNb}_2\text{O}_7$, and $(\text{CoCl})\text{LaNb}_2\text{O}_7$ could not be prepared from $\text{RbLaNb}_2\text{O}_7$, but could be prepared from $\text{LiLaNb}_2\text{O}_7$ or $\text{NaLaNb}_2\text{O}_7$. The Cr compound was synthesized from anhydrous CrCl_2 (Alfa, 99.9%) at 400 °C over 6 days, the Mn compound from anhydrous MnCl_2 (Alfa, 99.99%) at 390 °C over 7 days, and the Co compound from anhydrous CoCl_2 (Alfa, 99.7%) at 350 °C over a 9-day period. The reaction products, $(\text{MCl})\text{LaNb}_2\text{O}_7$ (M = Mn, Fe, Co), were washed thoroughly with water to remove the excess metal halide and the alkali-metal halide byproduct. The $(\text{CrCl})\text{LaNb}_2\text{O}_7$ product was washed in absolute ethanol. The final products were dark green, beige, light brown, and violet in color for the Cr, Mn, Fe, and Co compounds, respectively. While this report focuses on these four compounds, it is important to note that additional results show that this synthetic approach can be extended to vanadium as well;⁹ samples, however, contain small levels of impurities. Efforts to prepare a single-phase product are still under way.

Characterization. Products could not be dissolved, even in strong acids. Elemental analysis therefore relied on energy dispersive spectroscopy (EDS). Chemical compositions were determined by EDS on a JEOL (model JSM-5410) scanning electron microscope (SEM) equipped with an EDAX (DX-PRIME) microanalytical system. Compositions M:Cl:La:Nb were all found to be approximately 1:1:1:2. X-ray powder diffraction data were obtained

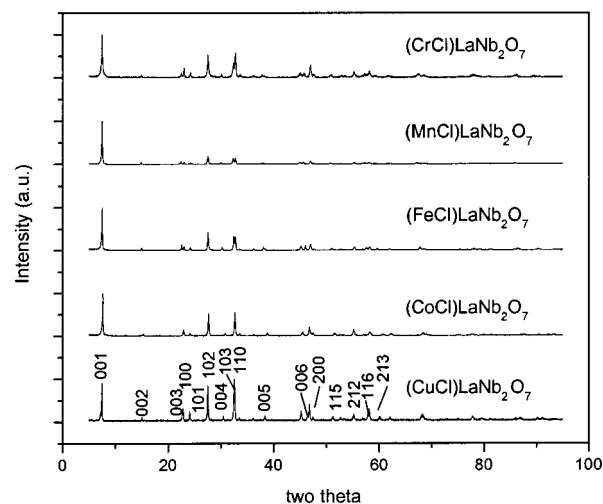


Figure 1. X-ray powder diffraction patterns for $(\text{MCl})\text{LaNb}_2\text{O}_7$ (M = Cr, Mn, Fe, Co, Cu). The Miller indices are indicated for selected reflections.

Table 1. Tetragonal Unit Cell Parameters for $(\text{MCl})\text{LaNb}_2\text{O}_7$

| M | <i>a</i> (Å) | <i>c</i> (Å) | vol (Å ³) | layer spacing (Å) ^a |
|-----------------|--------------|--------------|-----------------------|--------------------------------|
| Cr | 3.872(8) | 11.834(2) | 177.4 | 10.16 ^b |
| Mn | 3.871(3) | 11.92(7) | 178.6 | 10.45 ^c |
| Fe ^d | 3.8736(9) | 11.835(3) | 177.6 | 10.989 ^e |
| Co | 3.888(1) | 11.614(7) | 175.6 | 10.16 ^b |
| Cu ^f | 3.8792(1) | 11.7282(1) | 176.5 | 10.989 ^e |

^a Initial layer spacing of perovskite host. Data from ref 8. ^b $\text{LiLaNb}_2\text{O}_7$. ^c $\text{NaLaNb}_2\text{O}_7$. ^d Reference 6. ^e $\text{RbLaNb}_2\text{O}_7$. ^f Reference 5.

on a Philips X'Pert-MPD diffractometer equipped with a graphite monochromator and Cu K α ($\lambda = 1.5418$ Å) radiation. Unit cells were refined by a least-squares method with the program POLSQ.¹⁰ Differential scanning calorimetry (DSC) was carried out in flowing argon on a Netzsch 404S thermal analysis system; samples were heated at a rate of 10 °C/min in alumina pans.

Results

Synthesis. The series $(\text{MCl})\text{LaNb}_2\text{O}_7$ (M = Cr, Mn, Fe, Co) are all readily prepared by topotactic reaction from layered perovskite hosts. Single-phase products of the iron compound could be made from ALaNb_2O_7 (A = Li, Na, K, Rb). The other compounds were best prepared from $\text{LiLaNb}_2\text{O}_7$ and $\text{NaLaNb}_2\text{O}_7$; when the perovskite hosts with larger alkali-metal cations were used, incomplete reaction occurred, even after 2–3 weeks, and/or insoluble impurities were obtained. A further, likely related advantage of the lithium and sodium hosts was seen in the significantly reduced reaction times: in some instances single-phase products could be obtained in a few days.

Diffraction Studies. Figure 1 presents X-ray powder diffraction patterns for $(\text{MCl})\text{LaNb}_2\text{O}_7$ (M = Cr, Mn, Fe, Co). All the compounds can be indexed on tetragonal unit cells (Table 1). Unit cells obtained from this data show that the spacing between the perovskite layers expanded significantly on reaction relative to the starting materials. For comparison, the powder pattern of the known $(\text{CuCl})\text{LaNb}_2\text{O}_7$ is also shown in Figure 1. Except for slight

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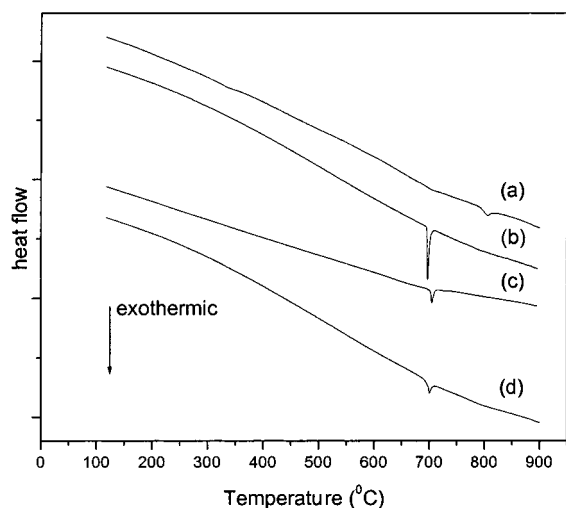


Figure 2. Differential scanning calorimetry for $(MCl)LaNb_2O_7$ ($M = Cr, Mn, Fe, Co$): (a) Cr, (b) Mn, (c) Fe, and (d) Co.

differences in peak positions due to small variations in cell parameters, the patterns are all quite similar, indicating that the set of compounds is isostructural.

Thermal Analysis. The thermal stability of $(MCl)LaNb_2O_7$ ($M = Cr, Mn, Fe, Co$) was investigated by DSC (Figure 2). The Mn, Fe, and Co compounds all decomposed exothermically around 700 °C. The Cr compound appeared to be slightly more stable, not showing an obvious transition until over 800 °C. A particularly interesting feature of the thermograms is the fact that all the decompositions are exothermic, indicating that all of the compounds are metastable. X-ray powder diffraction of the decomposition products typically showed the presence of MNb_2O_6 and $LaNbO_4$; no evidence for the metal halide was observed. The host $LiLaNb_2O_7$ was also investigated and was found to show a similar exotherm at 700 °C.

Discussion

Initial studies on the formation of transition-metal halide layers within perovskite hosts focused on copper chloride and copper bromide.^{5,6} There we were able to readily construct M–Cl layers, predominately Cu–Cl, within a series of Dion–Jacobson (DJ) type perovskite hosts, $A[A'_{n-1}(M,M')_nO_{3n+1}]$ ($A =$ alkali metal, H, NH_4 ; $A' =$ alkaline earth, rare earth, Bi; $M, M' = Nb, Ta, Ti$; $n = 2, 3$). Our first efforts to extend this reaction strategy to other transition metals were unsuccessful in that either no evidence for the target compounds was observed or single phases could not be obtained. Further studies showed that a variety of factors were important; all materials needed to be anhydrous, reaction temperatures were particular to the metal chloride under investigation, and the reactions were typically much more effective when the DJ host used contained the smaller alkali-metal cations. These reactions are thought to go by a simple ion exchange mechanism, where the interlayer alkali-metal cations of the perovskite host are replaced by both the transition-metal and chloride ions. Two important aspects of this type of reaction are (1) the diffusion of metal halide to the edge of the perovskite crystal and (2) the actual

exchange step, involving the simultaneous diffusion of metal and halide ions into the crystal and alkali-metal cations out of the crystal. The diffusion of metal halide will be helped by the relatively low melting points of the metal halides; the MCl_2 ($M = Cr, Mn, Fe, \text{ and } Co$) series melt at 820, 652, 676, and 724 °C, respectively.¹¹ Though all the reactions are carried out below these melting points, the diffusion rate of the ions is still expected to be significant. Adding to this could be the formation of a eutectic between the alkali-metal byproduct and the transition-metal halide: eutectics are common for most transition-metal–halide alkali-metal–halide systems.¹² A further consideration for the transport of metal halide species to the reaction interface is the formation of gas phase species where some metal halides are known to have a significant vapor pressure of $MCl_2(g)$.¹¹ Alkali-metal cation mobility, pertinent to actual exchange, has been studied for some of the $ALa Nb_2O_7$.¹³ The smaller cations, Li and Na, were found to have similar mobilities, while that of the K compound was lower. It is expected that the $RbLa Nb_2O_7$ will show an even lower cation mobility; similar trends have been observed in other layered alkali-metal-containing compounds.¹⁴ The decrease in reaction time and improved reactivity seen for $LiLa Nb_2O_7$ and $NaLa Nb_2O_7$ versus the potassium and rubidium analogues is likely related to this difference in alkali cation mobility.

The series $(MCl)LaNb_2O_7$ ($M = Cr, Mn, Fe, Co, Cu$) are isostructural. It is known from structural studies on $(CuCl)LaNb_2O_7$ that the increase observed in c is due to the formation of extended metal–halide arrays between the perovskite layers.⁵ The divalent metal cations (M) bridge between apical oxygens of the perovskite layers while surrounded by four chloride ions: the distorted octahedra edge-share with each other and corner-share with the octahedra of the perovskite layers. Figure 3 shows an idealized structure for the series. The slight variations in unit cell values for the Cr, Mn, Fe, and Cu compounds correlate well with variations in cationic radii, 0.94, 0.97, 0.92, and 0.87 Å, respectively.¹⁵ In contrast, the cobalt compound does not follow this same trend (Co^{2+} radius 0.885 Å).¹⁵ This likely indicates that the cobalt ion is deviating significantly off the ideal octahedral site, possibly distorting toward tetrahedral coordination, an environment common for $d^7 Co^{2+}$.¹⁶

The significance of topotactically based syntheses is that, because of the mild reaction conditions employed, such methods should be effective in the preparation of low-

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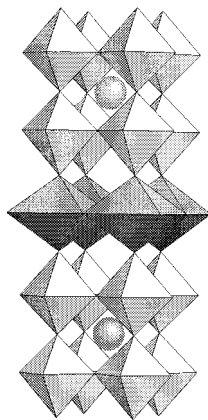


Figure 3. Idealized structural representation of the (MCl)LaNb₂O₇ structure type with corner-sharing NbO₆ octahedra (light gray) and corner- and edge-sharing MO₂Cl₄ octahedra (dark gray). The spheres represent lanthanum ions.

temperature, possibly metastable compounds, allowing preparation of compounds not accessible by traditional solid state synthetic routes. Johnson and co-workers¹⁷ have shown with their work on the preparation of thin films through the reaction of multilayer precursors that kinetic, metastable products are readily accessible. Topotactic reactions on layered hosts run parallel to such thin film studies except that the starting materials, often prepared at elevated temperatures (>900 °C), are inherently stable at these temperatures. It is the alteration of the contents of the host interlayer through synthetic manipulation that affects the stability of the layers and, correspondingly, the overall compound. Sato et al.¹⁸ have shown that if potassium ion is simply replaced (ion exchanged) with sodium in KLaNb₂O₇, the resulting metastable compound decomposes exothermically above 800 °C; this not only helps to illustrate the importance of topotactic routes to new materials inaccessible by direct reaction but also highlights the role of interlayer species in effectively stabilizing such layered systems: NaLaNb₂O₇ is not accessible by direct methods, and correspondingly, LaNb₂O₇⁻ layers require the presence of large alkali-metal cations, K, Rb, and Cs, for stabilization.

For the series (MCl)LaNb₂O₇ (M = Cr, Mn, Fe, Co), all of them show exotherms on decomposition. This signature is indicative of metastability. X-ray analysis shows that one of the decomposition byproducts is always LaNbO₄ (fergusonite structure). It is expected that the heat released in this reaction comes from the formation of LaNbO₄ on decom-

position of the LaNb₂O₇⁻ layer; the coordination of lanthanum and niobium drop from 12 and 6 to 8 and 4, respectively. In contrast, (CuCl)LaNb₂O₇ does not show the same exothermic signature on decomposition, though LaNbO₄ is observed after heating to 900 °C in argon. This difference likely relates to the fact that below 500 °C the copper compound starts to decompose with significant loss of CuCl₂⁶ and that the resulting phase, Cu_{0.5}LaNb₂O₇, has a different decomposition pathway that does not show an exotherm, possibly one that is second order.

Other metastable layered perovskites prepared by topotactic ion exchange methods are also known: NaLaNb₂O₇¹⁸ and its Ca²⁺ ion exchange product¹⁹ and Na_{1-x}Ca_{x/2}LaTiO₄.²⁰ These compounds are stable to high temperatures, decomposing exothermically at or above 800 °C. The series (MCl)LaNb₂O₇ (M = Mn, Fe, Co) and LiLaNb₂O₇ show exotherms around 700 °C, and (CrCl)LaNb₂O₇ exhibits one at ca. 820 °C. It is not clear at this point why there are differences in the decomposition temperatures for these compounds. Further studies are needed to illuminate the role that the alkali metal and metal halide play in stabilizing adjacent perovskite layers.

Conclusions

Ion exchange methods have been exploited to synthesize a series of metastable transition-metal oxyhalides. These results demonstrate that simple topotactic reactions can be applied to the construction of metal-anion arrays for a number of transition metals. The effectiveness of this approach emphasizes the utility of topotactic methods for the synthesis of new unusual materials. It is expected that the continued development of such synthetic strategies will eventually result in a general set of methodologies for the conscious design and preparation of intricate structural arrangements. This would be especially significant to the development of so-called “rational” materials for applications in various technologies including electronics, magnetics, and ceramics.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (DMR-9983591) and the Department of Defense (DARPA MDA972-97-1-0003).

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