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Synthesis and Structure of a New Layered Niobium Blue Bronze: $Rb_2LaNb_2O_7$

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The reduced layered niobate $Rb_2LaNb_2O_7$ was synthesized via the reaction of $RbLaNb_2O_7$ with rubidium vapor at temperatures between 200 and 250 °C. The structures of both materials have been determined by Rietveld analysis of time-of-flight powder neutron diffraction data. The cream-colored host compound $RbLaNb_2O_7$ (**I**) crystallizes in the space group *Imma* with cell constants $a = 5.4941(4)$ Å, $b = 21.9901(6)$ Å, $c = 5.4925(4)$ Å, and $Z = 4$. The blue-black reduced phase $Rb_2LaNb_2O_7$ (**II**) also adopts an orthorhombic structure (space group *Cmcm*) with $a = 22.30955(9)$ Å, $b = 5.69748(10)$ Å, $c = 5.69365(10)$ Å, and $Z = 4$. Both compounds adopt pseudotetragonal orthorhombic structures based on the Ruddlesden−Popper structure type. In **I**, double perovskite layers are separated by a single rubidium ion and adjacent blocks adopt an eclipsed conformation. The niobium adopts a strongly distorted octahedral coordination and is displaced from the center of the octahedron. In **II**, the layers are separated by a pair of rubidium ions and adjacent blocks have the staggered conformation usually associated with the Ruddlesden−Popper structure. Considerable expansion within the layers is observed as a result of partial reduction of Nb^V to Nb^{IV}, accompanied by a reduction in the distortion of the NbO_6 octahedra. The fractional expansion within the layers arising largely from electronic effects exceeds that perpendicular to the layers arising from steric effects.

Introduction

Several families of layered oxides based on the perovskite (ABO_3) structure have been described, including the Aurivillius[1] and Ruddlesden−Popper series.[2] Both of these series contain perovskite-based $A_{n-1}B_nO_{3n+1}$ units comprising corner-linked BO_6 octahedra. The thickness of these perovskite slabs is governed by the number (n) of BO_6 octahedra that are stacked along the [001] direction perpendicular to the layers. Ruddlesden−Popper phases have the general formula $A'_2[A_{n-1}B_nO_{3n+1}]$, examples of which include Sr_2TiO_4, $Sr_3Ti_2O_7$, and $Sr_4Ti_3O_{10}$. A closely related series was first reported by Dion *et al.* and has the general formula $A'[A_{n-1}B_nO_{3n+1}]$.[3] In most of these materials A′ represents an alkali metal cation and B = Nb, the stacking sequence being dictated by the size of the alkali metal.

Compounds in the series $A'[A_{n-1}B_nO_{3n+1}]$ with $n = 2-7$ have been described.[4] This group of compounds was recently dubbed the Dion−Jacobson series.[5] The alkali metal cations can readily be exchanged in acid solution to form protonated derivatives $H[A_{n-1}B_nO_{3n+1}]$ which exhibit strong Brønsted acidity.[6] These protonated species will form intercalation compounds with a range of organic bases.[4b,7] Recently Uma *et al.* described the preparation of the group of compounds $A_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ which bridge the two series.[5] In this case, the titanium to niobium ratio was used to control the alkali metal content. Attempts to optimize the properties of oxide superconductors highlight the importance of precise control over the oxidation state of the constituent atoms. Unfortunately, the conventional substitutional approach to the fine tuning of the oxidation state can often lead to unexpected structural rearrangements or entirely different products. For this reason the low-temperature reduction of existing oxides by alkali metal vapor,[8] or by solvated electron solutions,[9] is an attractive alternative strategy. Gómez-Romero *et al.* have reported the preparation of $H_{1+x}LaNb_2O_7$ by hydrogen reduction $HLaNb_2O_7$.[10] The rich intercalation chemistry of the Dion−Jacobson phases, combined with the existence of Ruddlesden−Popper phases of the form $A_2La_2Ti_3O_{10}$ (A = alkali metal),[11] suggested that new Ruddlesden−Popper materials could be synthesized from Dion−Jacobson starting materials via alkali metal intercalation. As part of a program designed to synthesize novel conducting compounds via alkali metal insertion reactions, we have prepared the Ruddlesden−Popper material $Rb_2LaNb_2O_7$ by reaction of the $n = 2$ member of the Dion−Jacobson series, $RbLaNb_2O_7$, with rubidium vapor. The structures of both materials have been determined by Rietveld analysis of powder neutron diffraction data.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1994.

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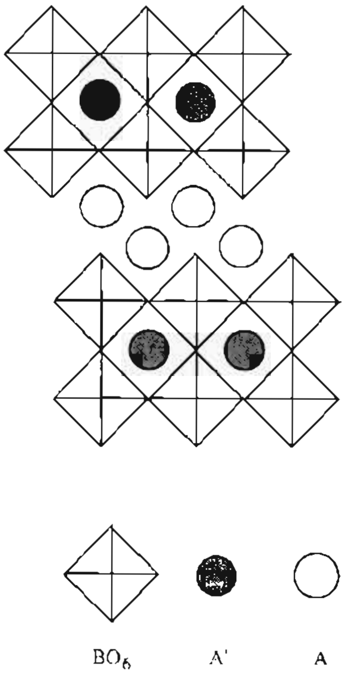

Figure 1. Schematic representation of the structure of $RbLaNb_2O_7$.

Experimental Section

Synthesis. The host compound $RbLaNb_2O_7$ was prepared using the method of Gopalakrishnan *et al.*[4b] A 25% excess of the Rb_2CO_3 starting material was used to allow for volatilization during the reaction. The powdered starting materials were given two firings of 20 h at 1110 °C, after which the sample was washed with distilled water and dried at 160 °C. The phase purity of the cream-colored parent phase was confirmed by powder X-ray diffraction. This parent phase was then allowed to react with a controlled amount of rubidium vapor at temperatures between 200 and 250 °C, in a sealed, evacuated quartz reaction tube, to yield the homogeneous blue-black solid $Rb_2LaNb_2O_7$.

Neutron Powder Diffraction. Neutron powder diffraction measurements were performed on the POLARIS high-intensity, medium-resolution diffractometer at the ISIS pulsed source of the Rutherford Appleton Laboratory. Data for the host phase was collected with the sample in a vanadium can, but since $Rb_2LaNb_2O_7$ was expected to be air sensitive, data for this compound were collected with the sample still in its quartz reaction vessel. In order to eliminate the amorphous silica background, data were also obtained from an empty sample tube. These data were then smoothed, appropriately scaled, and subtracted from the sample diffraction pattern to produce an essentially flat background.

The structures were refined by the Rietveld method using the program TF14LS based on the Cambridge Crystallographic Subroutine Library.[12] Neutron scattering lengths of 0.709, 0.824, 0.7054, and 0.5803 (all $\times 10^{-12}$ cm) were assigned to Rb, La, Nb, and O, respectively.[13] Gopalakrishnan *et al.* reported a primitive tetragonal structure for $RbLaNb_2O_7$ with $a = 3.885(2)$ Å and $c = 10.989(3)$ Å and suggested that the probable space group was either *P4/m* or *P4/mmm* (no systematic absences).[4b] A schematic representation of this structure is given in Figure 1. The large size of Rb^+ leads to eclipsing of perovskite blocks, unlike the staggered conformations adopted by $KLaNb_2O_7$ and $NaLaNb_2O_7$. Refinement in space group *P4/mmm* gave satisfactory results, but large temperature factors were observed for the oxygen atoms at the apexes of the NbO_6 octahedra and there were a number of additional peaks that could not be fitted. Use of a model-independent fit led to the identification of a $\sqrt{2} \times \sqrt{2} \times 2$ supercell. Determination of the systematic absences, and thus the space group, was complicated by substantial peak overlap even at long *d* spacings, arising from the fact that $4a \sim c$. A number of possible tetragonal space groups consistent with the structural model were tested, with *P4/nnc* giving the best results. However none of these tetragonal models gave a good fit to the superlattice reflections, and the thermal parameters remained large for the apical oxygen atoms. This suggested that the true symmetry was orthorhombic, although the resolution of POLARIS was insufficient to reveal clear visible evidence of orthorhombic splitting. Adoption of the orthorhombic space group *Imma* enabled excellent fitting of the superlattice reflections. There was no evidence for preferred orientation in either this phase or the Rb intercalated product. The refinement converged to $R_{wP} = 6.9\%$, $R_E = 5.2\%$, and $R_I = 5.4\%$, with profile fit shown in Figure 2. The atomic coordinates and isotropic thermal parameters are shown in Table 1.

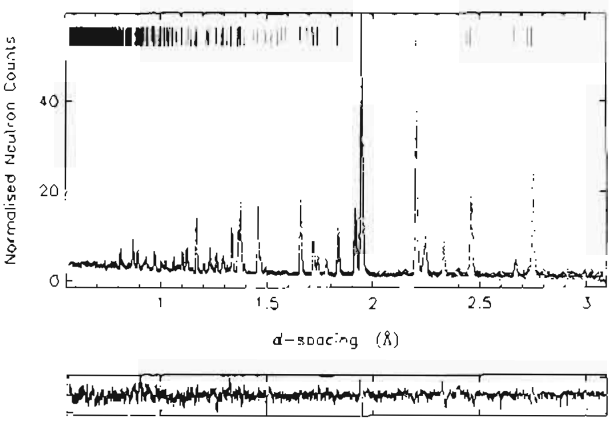

Figure 2. Profile fit for the refinement of the structure of $RbLaNb_2O_7$. The tick marks indicate the allowed reflections. The lower panel shows the difference/esd between calculated and observed profiles.

Table 1. Structural Parameters for $RbLaNb_2O_7$: Orthorhombic, Space group *Imma*; $a = 5.4941(4)$ Å, $b = 21.9901(6)$ Å, $c = 5.4925(4)$ Å[a]

atom	Wyckoff symbol	x/a	y/b	z/c	B_{iso}, Å^2
Nb	8h	0	0.35274(9)	0.4990(7)	0.30(3)
La	4e	0.5	0.25	0.4921(10)	0.24(4)
Rb	4a	0	0	0	1.98(7)
O1	4e	0	0.25	0.4469(12)	1.29(13)
O2	8h	0	0.4325(2)	0.5469(8)	1.06(6)
O3	8g	0.25	0.3435(2)	0.25	1.72(8)
O4	8g	0.75	0.3275(2)	0.75	0.76(5)

[a] $R_{wP} = 6.9\%$; $R_E = 5.2\%$; $R_I = 5.4\%$. $R_{wP} = [\sum_i w_i|y_i(\text{obs}) - y_i(\text{calc})|^2/\sum_i w_i y_i^2(\text{obs})]^{1/2}$; $R_E = [(N - P + C)/\sum_i w_i y_i^2(\text{obs})]^{1/2}$, where *N*, *P*, and *C* are the number of observations, parameters, and constraints, respectively; $R_I = [\sum|I_k(\text{obs}) - (1/c)I_k(\text{calc})|/\sum_k I_k(\text{obs})]$.

The initial structural model for $Rb_2LaNb_2O_7$ used in refinement assumed the ideal Ruddlesden–Popper structure, as adopted by $Sr_3Ti_2O_7$ (space group *I4/mmm*). A good fit to the data was obtained, but as with the host material, superlattice reflections were observed along with large temperature factors for the apical oxygen atoms. A model-independent fit confirmed the presence of a $\sqrt{2} \times \sqrt{2} \times 1$ supercell. As was found with the parent compound, a satisfactory fit to the additional reflections was not possible by assuming a tetragonal structure. An orthorhombic model based on that reported by Elcombe *et al.* for the Ruddlesden–Popper phase $Ca_3Ti_2O_7$ was tested.[14] In the case of $Ca_3Ti_2O_7$, the space group *Cmc*2$_1$, rather than the centrosymmetric *Cmcm*, was confirmed by convergent beam electron diffraction. The air sensitivity of $Rb_2LaNb_2O_7$ has precluded any electron diffraction measurements at present; thus, in the absence of any evidence for a lack of center of symmetry, the structure was refined in *Cmcm*. The refinement converged rapidly in this space group to $R_{wP} = 3.9\%$, $R_E = 1.2\%$, and $R_I = 3.0\%$, with atomic coordinates and isotropic thermal parameters given in Table 2 and the profile fit being shown in Figure 3.

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Table 2. Structural Parameters for $Rb_2LaNb_2O_7$: Orthorhombic, Space Group *Cmcm*; $a = 22.30955(9)$ Å, $b = 5.69748(10)$ Å, $c = 5.69365(10)$ Å[a]

atom	Wyckoff symbol	x/a	y/b	z/c	B_{iso}, Å	site occ
Nb	8g	0.09369(4)	0.2475(4)	0.75	0.185(12)	
La	4c	0	0.2603(5)	0.25	0.38(2)	
Rb	8g	0.19197(5)	0.7387(4)	0.75	0.68(3)	0.945(6)
O1	4c	0	0.7018(6)	0.25	1.17(6)	
O2	8g	0.17616(6)	0.7691(5)	0.25	0.78(2)	
O3	8e	0.08704(7)	0.5	0.5	0.60(2)	
O4	8e	0.07368(6)	0	0.5	0.36(2)	

[a] $R_{wp} = 3.9\%$; $R_E = 1.2\%$; $R_I = 3.0\%$.

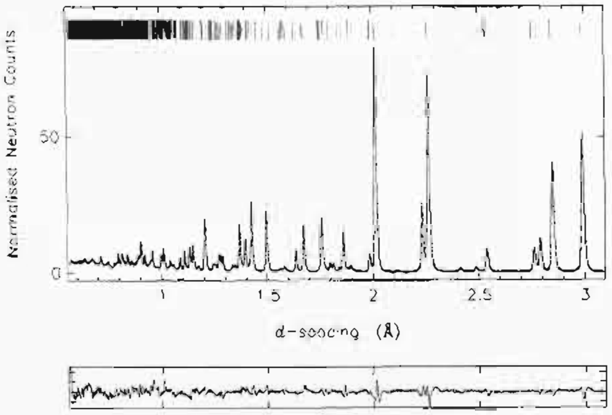

Figure 3. Profile fit for the refinement of the structure of $Rb_2LaNb_2O_7$.

Table 3. Selected Bond Lengths for $RbLaNb_2O_7$ and $Rb_2LaNb_2O_7$

$RbLaNb_2O_7$		$Rb_2LaNb_2O_7$	
Nb—O1	2.277(8) × 1	Nb—O1	2.111(4) × 1
Nb—O2	1.774(7) × 1	Nb—O2	1.842(4) × 1
Nb—O3	1.949(4) × 2	Nb—O3	2.029(3) × 2
Nb—O4	2.024(4) × 2	Nb—O4	2.053(3) × 2
La—O1	2.758(8) × 2	La—O1	3.185(5) × 1
	3.082(8) × 1		2.512(5) × 1
	2.411(8) × 1		2.855(5) × 2
La—O3	2.807(7) × 4	La—O3	2.768(3) × 4
La—O4	2.607(6) × 4	La—O4	2.632(3) × 4
Rb—O2	3.351(6) × 2	Rb—O2	2.874(4) × 1
	2.898(6) × 2		2.942(4) × 1
	3.133(6) × 4		2.914(4) × 1
			2.827(4) × 1
		Rb—O3	3.059(3) × 2
		Rb—O4	3.348(3) × 2

Results and Discussion

Synthesis. While the preparation of $Rb_2LaNb_2O_7$ proved remarkably straightforward, attempts to prepare intermediate compositions $Rb_{1+x}LaNb_2O_7$ ($0 < x < 1$) at this temperature yielded a mixture of the two end members. Annealing at higher temperatures around 500 °C was required to produce a single-phase product. Higher temperatures still (~600 °C) led to rubidium loss and decomposition of these materials of intermediate stoichiometry, the products being the end members once again. Thus, while a solid solution $Rb_{1+x}LaNb_2O_7$ exists for $0 \le x \le 1$, the two end members exhibit enhanced stability.

Structures of $Rb_2LaNb_2O_7$ and $Rb_2LaNb_2O_7$. Selected bond lengths for both $RbLaNb_2O_7$ and $Rb_2LaNb_2O_7$ are shown in Table 3. In the host compound, $RbLaNb_2O_7$, a strongly distorted coordination environment for niobium is revealed, involving a ferroelectric displacement from the center of its octahedron to give one short, one long, and four normal length bonds. Such a distortion of the NbO_6 octahedron has been reported for several oxy compounds of Nb^V; for example, $NbOPO_4$ has bond lengths nearly identical to those in $RbLaNb_2O_7$.[15] The structure of $RbLaNb_2O_7$ is shown in Figure 4.

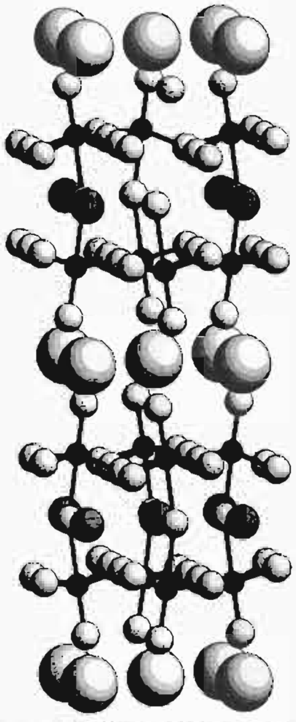

Figure 4. Structure of $RbLaNb_2O_7$. Nb—O bonds are shown. Large circles represent Rb, small black circles Nb, small pale circles O, and small darker circles La.

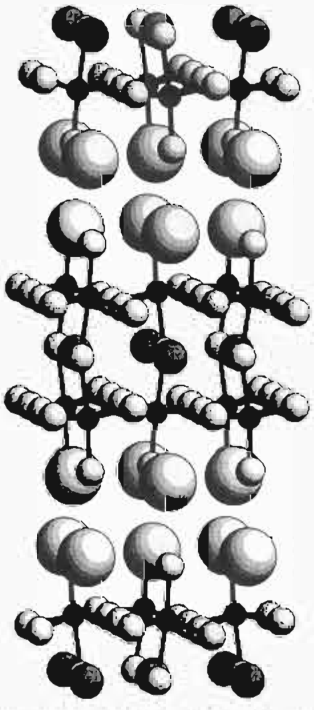

Figure 5. Structure of $Rb_2LaNb_2O_7$. Nb—O bonds are shown. Large circles represent Rb, small black circles Nb, small pale circles O, and small darker circles La.

For $Rb_2LaNb_2O_7$, lattice constants of $a = 22.30955(9)$ Å, $b = 5.69748(10)$ Å, and $c = 5.69365(10)$ Å indicate a marked expansion on Rb intercalation. This represents an expansion

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[15] Longo, J. M.; Kierkegaard, P. *Acta Chem. Scand.* **1966**, *20*, 72.

of 1.5% perpendicular to the layers and 3.7% within the layers, contrary to what might be expected from purely size considerations. The expansion within the layers presumably occurs as a result of partial reduction of Nb^{V} to Nb^{IV}. Examination of the Nb—O bond lengths (Table 3) shows a sizable contraction in the Nb—O1 distance and a smaller expansion in the Nb—O2 distance. This discrepancy may arise as a result of partial Nb^{IV} character since Nb^{IV} as a d^1 ion would be expected to show a Jahn–Teller compression. Refinement of the rubidium site occupancy yielded a value of 0.945(6). The structure is shown in Figure 5.

The concept of bond valence sums (BVS) devised by Brown has been widely applied to estimate valences in inorganic solids, most recently in the field of high-temperature superconductivity. BVS for niobium in $RbLaNb_2O_7$ and $Rb_2LaNb_2O_7$ have been calculated using the formula of Brown and Altermatt.[16] The BVS calculated for Nb in $RbLaNb_2O_7$ is 5.10, while that for $Rb_2LaNb_2O_7$ is 4.60, in excellent agreement with the theoretical valence of 4.56, assuming that rubidium incorporation leads to reduction of Nb^{V} to Nb^{IV}.

Conclusion

We have demonstrated that controlled reaction with alkali metal vapor represents a relatively straightforward yet powerful method to synthesize new solids. In particular, it provides a means of modifying the properties of insulating layered or microporous materials by doping them with electrons. Rubidium insertion into $RbLaNb_2O_7$ leads to the formation of the mixed-valence Ruddlesden–Popper compound $Rb_2LaNb_2O_7$ and results in a sizable expansion within the layers and a reduction in the ferroelectric distortion of the NbO_6 octahedra. Work is underway to investigate the electronic and magnetic properties of this and related materials.

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