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Slicing the Perovskite Structure into Layers: Synthesis of Novel Three-Dimensional and Layered Perovskite Oxides, $ALaSrNb_2M^{II}O_9$ (A = Na, Cs)[†]

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The oxides possessing perovskite ($CaTiO_3$)-related structures are indeed legion.[1] Besides the stoichiometric (ABO_3) perovskites and their ordered variants (e.g., $A_2BB'O_6$, $A_3BB'_2O_9$), quite a few defective perovskites (e.g., ABO_{3-x}) forming a variety of perovskite superstructures are known.[2] Furthermore, a number of layered oxides, such as the Ruddlesden−Popper phases[3] and the Aurivillius phases,[4] which could be regarded as derivatives of the perovskite structure, are also known. These materials contain two-dimensional (2-D) perovskite slabs of composition $[A_{n-1}B_nO_{3n+1}]$ as one of the units building the layered structure. The $A_{n-1}B_nO_{3n+1}$ units may be thought of as derived by slicing, as it were, the three-dimensional (3-D) perovskite structure along one of the three cubic directions.[5]

Considering the large number of perovskite-related oxides known at present,[1] one would feel that all the possible combinations of elements that would give perovskite-related oxides have already been exhausted. Fortunately, this is not so, because time and again, novel members are being added to the growing list of perovskite-related phases. A typical example is the discovery of superconducting $YBa_2Cu_3O_7$, which possesses a unique vacancy-ordered perovskite structure.[6]

As a part of our continuing efforts to synthesize novel layered oxides exhibiting interlayer chemistry,[7] we investigated the formation of perovskite-related phases for the compositions $ALaSrNb_2M^{II}O_9$ (A = alkali metal and M = Co, Ni, Cu, or Zn). To our surprise, the compositions adopted a cubic (3-D) perovskite structure when A = Na and a layered (2-D) perovskite structure, related to $CsCa_2Nb_3O_{10}$,[8] when A = Cs. This result, which is reported in this communication, reveals the interesting possibility of tailoring perovskite (ABO_3) oxides into 2-D or 3-D structures by the appropriate choice of A-site cations. Furthermore, the strategy can be extended to synthesize layered perovskite oxides of variable thickness by choosing appropriate chemical compositions. We believe that the present discovery assumes greater significance in light of the current interest in artificially tailoring oxide materials into thin layers of nanometer scale.[9]

Table 1. Characterization of $ALaSrNb_2M^{II}O_9$ Perovskite Oxides

		lattice parameters (Å)			
composition	color	*a*	*c*	structure	μ_{eff} $(\mu_B)^a$
$NaLaSrNb_2CoO_9$	brown	3.967(5)		3-D perovskite	4.00
$NaLaSrNb_2NiO_9$	gray	3.966(3)		3-D perovskite	2.96
$NaLaSrNb_2CuO_9$	brown	3.978(5)		3-D perovskite	1.70
$NaLaSrNb_2ZnO_9$	white	3.988(4)		3-D perovskite	
$CsLaSrNb_2CuO_9$	gray	7.846(5)	30.49(2)	2-D perovskite	1.68
$CsLaSrNb_2ZnO_9$	white	7.837(8)	30.66(3)	2-D perovskite	

[a] Calculated from Curie−Weiss plots of inverse molar magnetic susceptibility, χ_M^{-1}, versus temperature, *T*.

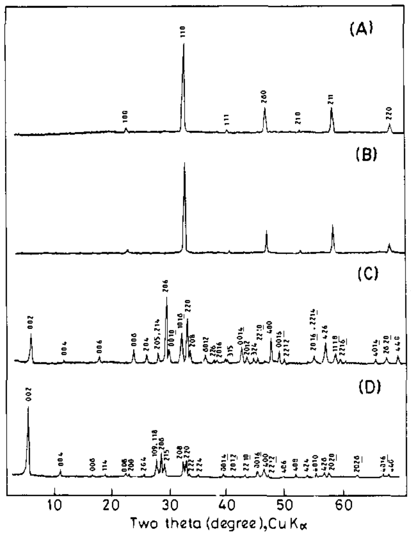

Figure 1. X-ray powder diffraction patterns (Cu Kα) of (A) $NaLaSrNb_2CoO_9$, (B) $NaLaSrNb_2CuO_9$, (C) $CsLaSrNb_2CuO_9$, and (D) $HLaSrNb_2CuO_9{\cdot}1.5H_2O$.

We have prepared $ALaSrNb_2MO_9$ (A = Na, Cs) oxides for M = Ni, Cu, or Zn by reacting stoichiometric mixtures of A_2CO_3, La_2O_3, $SrCO_3$, Nb_2O_5, and MO at 1100−1150 °C in air for 2 days with one grinding in between.[8a,10] We have carried out the synthesis of the corresponding Co(II) oxides in a flowing N_2 atmosphere using $CoC_2O_4{\cdot}2H_2O$ as the source for Co(II). The sodium contents of the solid products, determined by flame photometry, are consistent with the formula $NaLaSrNb_2MO_9$. Chemical (iodometric) titrations and magnetic susceptibility measurements (Table 1) of the cobalt-, nickel-, and copper-containing oxides reveal that the M atoms in $ALaSrNb_2MO_9$ are present in the M^{II} state, as expected.

X-ray powder diffraction (XRD) patterns (Figure 1) reveal that, while the sodium-containing members, $NaLaSrNb_2MO_9$, are all isostructural, crystallizing in a simple cubic ($a \sim 3.97$ Å) perovskite structure, the cesium analogs adopt a more complicated structure. The presence of a low-angle reflection at $d \sim 15.3$ Å and the general similarity of the patterns to that[8a] of $CsCa_2Nb_3O_{10}$ suggest that $ALaSrNb_2MO_9$ phases for A = Cs most likely adopt a layered structure related to $CsCa_2Nb_3O_{10}$. We could accordingly index the XRD patterns of A = Cs phases on tetragonal cells ($a \sim 7.82$ Å, $c \sim 30.6$ Å) similar to that of $CsCa_2Nb_3O_{10}$.[11] In Table 1, we give the lattice parameters of

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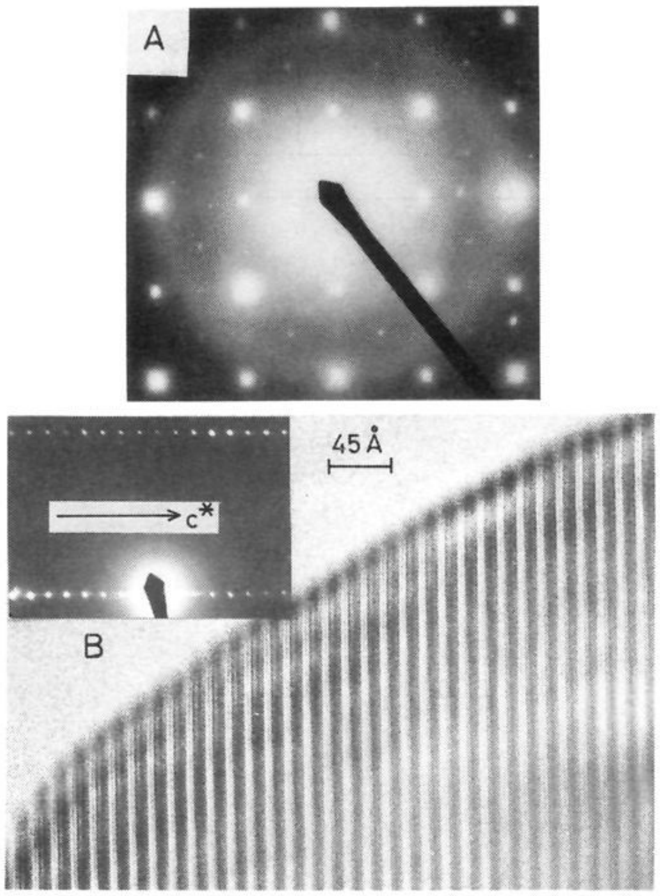

Figure 2. (A) Electron diffraction pattern of $NaLaSrNb_2CuO_9$ showing 3-D perovskite structure. (B) Lattice image of $CsLaSrNb_2CuO_9$ showing ~15 Å repeat along the *c*-axis. The inset shows the corresponding electron diffraction pattern.

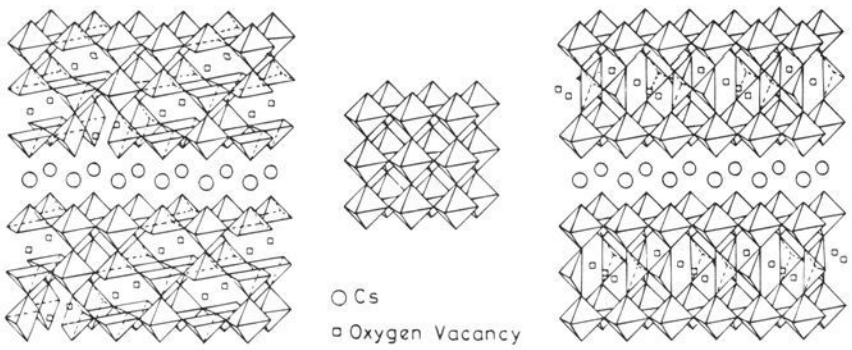

Figure 3. Schematic representation of the possible structures of $NaLaSrNb_2M^{II}O_9$ (3-D perovskite) (center), $CsLaSrNb_2M^{II}O_9$ (M = Cu, Zn) (disordered 2-D perovskite structure) (left), and $CsLaSrNb_2M^{II}O_9$ (M = Zn) (ordered 2-D perovskite structure) (right).

all the members of $ALaSrNb_2MO_9$ together with other details of characterization.

The formation of a 3-D perovskite structure for the sodium compounds and a 2-D perovskite structure for the cesium compounds of the $ALaSrNb_2MO_9$ series is further confirmed by electron diffraction and ion-exchange studies. While $NaLaSrNb_2CuO_9$ shows electron diffraction patterns characteristic of a 3-D perovskite structure (Figure 2A), the diffraction pattern and the corresponding lattice image of $CsLaSrNb_2CuO_9$ (Figure 2B) clearly reveal the layered structure with a ~15 Å repeat along the *c* direction. The cesium compounds readily exchange the alkali ions with protons in 2 N HCl,[12] giving the corresponding protonated derivatives, $HLaSrNb_2MO_9$, the behavior being very similar to that of the layered perovskite,[13] $CsCa_2Nb_3O_{10}$. A similar exchange does not occur with the 3-D perovskites, $NaLaSrNb_2MO_9$.

In Figure 3, we show schematically the possible structures of $ALaSrNb_2MO_9$. It is straightforward to visualize a 3-D perovskite structure for $NaLaSrNb_2MO_9$, (Figure 3), the Nb and M atoms occupying the octahedral sites at random and the Na, La, and Sr atoms, the dodecahedral sites of the cubic perovskite structure. Indeed, these phases could be regarded as derivatives of the perovskite oxides,[14] $Sr_3Nb_2MO_9$, where two Sr(II) atoms have been substituted by Na(I) + La(III) to give $NaLaSrNb_2MO_9$. While several of the $Sr_3Nb_2MO_9$ (M = Ni, Zn, Mg) oxides[1c,14] exhibit hexagonal superstructures due to ordering of M atoms, we do not see evidence for such an ordering in the XRD patterns of $NaLaSrNb_2MO_9$ reported here (Figure 1).

The layered structure of $ALaSrNb_2MO_9$ for A = Cs would most likely consist of perovskite-like slabs of composition $[LaSrNb_2MO_9]$ interleaved by the large Cs cations, similar to the $CsCa_2Nb_3O_{10}$ structure. As compared to the perovskite slabs of $CsCa_2Nb_3O_{10}$, the perovskite slabs, $[LaSrNb_2MO_9]$, of $ALaSrNb_2MO_9$ (A = Cs) are necessarily oxygen-deficient, one out of 10 oxygens in every slab missing. The oxygen vacancies, which are likely distributed around M^{II} rather than Nb^{V}, could be ordered or disordered. While a disordered structure containing a statistical distribution of Nb/M atoms as well as oxygen vacancies in the perovskite slabs $[LaSrNb_2MO_9]$ (Figure 3) is perhaps most likely for the as-prepared samples, it is possible to visualize the formation of ordered structures (Figure 3) consisting of octahedral $NbO_{6/2}$–tetrahedral/square planar $MO_{4/2}$–octahedral $NbO_{6/2}$ sequences on annealing of $CsLaSrNb_2MO_9$. We have recently reported the formation of such an ordered structure[15] for a similar composition, $CsCa_2Nb_2AlO_9$.

Finally, the adoption of a 3-D perovskite structure by the sodium compounds and a 2-D perovskite structure by the cesium compounds of the series $ALaSrNb_2MO_9$ could be understood in terms of Goldschmidt's tolerance factor,[16] $t = (r_A + r_O)/(2)^{1/2}(r_B + r_O)$, where r_A, r_B, and r_O are the ionic radii of A, B, and O^{2-} ions, respectively. The tolerance factors[17] for $NaLaSrNb_2MO_9$ (0.954–0.968) lie in the range, $0.8 < t < 1.0$, expected for a 3-D perovskite structure. On the other hand, the tolerance factors for $CsLaSrNb_2MO_9$ are >1.0, suggesting that a 3-D perovskite structure may not be stable for these compositions. Several alternative structures are possible for ABO_3 compositions when $t > 1.0$.[1a] For example, $BaNiO_3$, $BaMnO_3$, and $BaTiO_3$, for all of which $t > 1.0$, adopt different polytypic structures, where the BO_6 octahedra share faces and corners. $CsLaSrNb_2MO_9$ do not, however, adopt such structures, presumably because of the presence of multiple valent cations (Nb^{V} and M^{II}) at the B site. Accordingly, these compositions choose a different mode of accommodating large tolerance factors, viz., slicing the 3-D perovskite structure into a 2-D structure.

We have recently reported[15] the formation of a 3-D perovskite structure for the composition $KCa_2Nb_2FeO_9$ and a 2-D perovskite structure (related to $CsCa_2Nb_3O_{10}$) for the composition $CsCa_2Nb_2FeO_9$. While we did not realize the implication of the result at that time, the present work together with our previous work[15] clearly reveals that oxides of the general composition $ALaSrNb_2M^{II}O_9$ and $ACa_2Nb_2M^{III}O_9$ adopt a 3-D perovskite structure when A = Na or K and a 2-D perovskite structure when A = Cs, suggesting that the 3-D perovskite structure could be "sliced" into a layered structure in the presence of a large A cation like cesium.

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Supplementary Material Available: Table of X-ray powder diffraction data for $CsLaSrNb_2CuO_9$ (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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