

Transformation of the Defective Layered Structure into the Three-Dimensional Perovskite Structure under High Pressure

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A number of oxides with perovskite structures have been investigated to allow the understanding of ferroelectricity, magnetism, superconductivity, insulator-to-metallic transition behavior, and fluorescence property.^{1–4} Furthermore, many series of layered oxides with perovskite-related structures^{5–8} have been also extensively studied due to their intergrowth behavior, two-dimensional magnetism, high ionic conductivity, easy ion-exchange behavior, catalytic activity, and luminescence behavior.^{9–13} These layered structures consist of two-dimensional perovskite slabs which are separated by layers of different structure such as rock salt-type. Recently, it was reported that a “slicing” of the three-dimensional perovskite into a layered structure is induced in the presence of a large cation.¹⁴ For instance, oxides of the general composition $ALaSrNb_2M^{II}O_9$ and $ACa_2Nb_2M^{III}O_9$ adopt a three-dimensional perovskite structure when $A = Na$ or K but a layered structure when $A = Cs$. In this case, the two-dimensional structure has necessarily oxygen-deficient layers. If the vacancies are ordered around the central octahedra of

triple-perovskite slabs, such a structure would be a two-dimensional analogue of the brownmillerite structure.^{15,16}

It is well-known¹⁷ that the close-packed AO_3 layers tend to change their stacking sequence from cubic to one of several hexagonal sequences when the A cation of the ABO_3 perovskite is too large. Because cubic stacking is stabilized by hydrostatic pressure, it is possible to convert the hexagonal structures to the perovskite structure under pressure and high temperature.¹⁸ These particular hexagonal structures appear to be stabilized by the cation displacements, concomitant with alternating the stacking sequence. Extending this phenomenon, it was expected that we could prohibit slicing from a perovskite to a lower dimensional structure by applying high pressure. The two-dimensional stacking of $ALaSrNb_2M^{II}O_9$ ($A =$ large alkali metal such as Rb and Cs) with vacancies in the layer then could be transformed into the cubic stacking with no vacancy. Accordingly, we explored the possibility of the transformation from a layered to a three-dimensional structure by preparing $RbLaSrNb_2MO_9$ ($M = Mg, Cu, Zn$) under ambient pressure and high pressure (5 GPa). With $M = Mg$ and Zn , high pressure was required to form a single phase and neither layered-type nor three-dimensional structure was induced under normal conditions. To our surprise, the oxide $RbLaSrNb_2CuO_9$ had the defective layered structure under normal conditions but the three-dimensional structure under high pressure. Reported here is the first successful result of the strategy: the defective layered oxide can be converted to the perovskite structure under high pressure. During well-known transformation of graphite into the diamond structure under high pressure,¹⁹ the hybridization of carbon is changed from sp^2 to sp^3 . On the contrary, the transformation of $RbLaSrNb_2CuO_9$ is accompanied with an elimination of vacancies. Moreover, the oxides prepared under high pressure in this work would be novel members to be added to the growing list of perovskite-related phases.

Rb_2CO_3 , La_2O_3 , $SrCO_3$, Nb_2O_5 , and MO were used as starting materials for the syntheses. To prepare $RbLaSrNb_2MO_9$ ($M = Mg, Cu, Zn$) oxides, two different routes were used. In one procedure, the mixture of appropriate starting materials was fired at 900 °C in air for 10 h. The residue was reacted again at 1100 °C in air for 36 h with two intermittent grindings. An excess (~20 mol %) of Rb_2CO_3 was added to compensate for the loss due to volatilization at high temperature. The products were washed with distilled water and dried in air at 120 °C. The Na and K analogues were also prepared for comparison. $RbLaSrNb_2CuO_9$ was subsequently treated under high pressure (5 GPa) at 1050 °C for 30 min. In the other procedure, the calcination of a stoichiometric mixture²⁰ of starting

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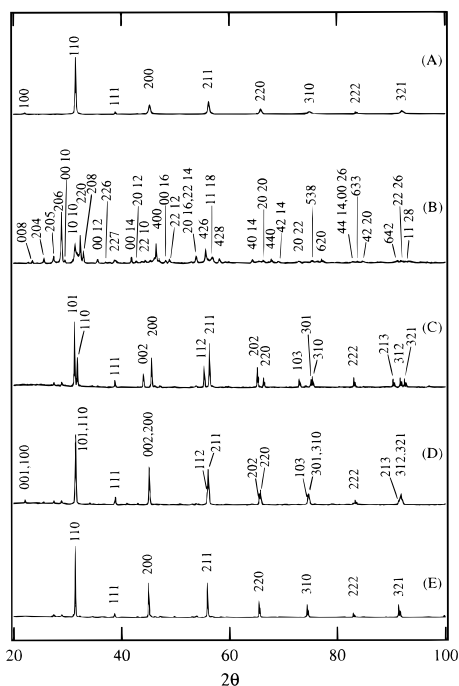


Figure 1. The powder X-ray diffraction patterns of (A) L-KLaSrNb₂CuO₉, (B) L-RbLaSrNb₂CuO₉, (C) H-RbLaSrNb₂CuO₉, (D) H-RbLaSrNb₂MgO₉, and (E) H-RbLaSrNb₂ZnO₉. L and H denote the low- and high-pressure form, respectively.

materials at 900 °C was followed by direct reaction under high pressure (5 GPa) at 1050 °C for 30 min. The high-pressure experiment was carried out with a link-type cubic anvil apparatus. A gold capsule containing ~60 mg of powdered sample was encapsulated into a graphite microfurnace which is enveloped by pyrophyllite. NaCl pellets and tube were used as the protecting layers. Molybdenum plates were used as an interface between the graphite and the electrode for current source. After reaction, the sample cell was cooled under pressure at the rate of ~35 °C/min, and ~50 mg of product was recovered.

The final products were characterized by powder X-ray diffraction (XRD) using a rotating anode installed (18 kW) diffractometer, energy-dispersive X-ray emission (EDX) analysis, and electron spin resonance (ESR) spectroscopy. To obtain XRD data of pressure-treated products, a small amount of sample powder was dispersed on a glass plate with absolute ethanol. Lattice parameters were derived from least-squares refinement of the powder XRD data.

The preparation of RbLaSrNb₂MO₉ (M = Mg and Zn) was not successful under ambient pressure because an impurity phase, RbLaNb₂O₇,²¹ could not be avoided. On the contrary, the low-pressure form (L) of RbLaSrNb₂CuO₉ was easily obtained by heating under normal conditions. As shown in Figure 1B, relatively strong (00*l*) reflections observed in the low-angle region indicated the formation of a layered structure. This XRD pattern is similar to those¹⁴ of CsLaSrNb₂MO₉, with oxygen vacancies in the perovskite slabs. Therefore, the

Table 1. Lattice Parameters for RbLaSrNb₂M^{II}O₉ (M = Mg, Cu, Zn) Prepared under Normal Pressure and 5 GPa of Hydrostatic Pressure

composition ^a	lattice parameters (Å)	
	<i>a</i>	<i>c</i>
L-KLaSrNb ₂ CuO ₉	4.008(2)	
L-RbLaSrNb ₂ CuO ₉	7.815(2)	30.21(1)
H-RbLaSrNb ₂ CuO ₉	3.980(1)	4.108(5)
H-RbLaSrNb ₂ MgO ₉	4.01(1)	4.04(2)
H-RbLaSrNb ₂ ZnO ₉	4.030(1)	

^a L and H denote the oxides prepared under low and high pressure, respectively.

structure of L-RbLaSrNb₂CuO₉ was characterized by a tetragonal unit cell of *c* ~ 30 Å. The XRD pattern of KLaSrNb₂CuO₉ prepared for comparison with the ESR spectra of ALaSrNb₂CuO₉ (A = Na and Rb) was indexed on a cubic unit cell of the three-dimensional perovskite similar to those of the sodium analogues.¹⁴ Refined lattice parameters are given in Table 1.

Using high pressure, the composition RbLaSrNb₂MO₉ (M = Mg and Zn) was successfully prepared. All reflections were indexed on the unit cell of the three-dimensional structure except the reflections from the minor impurities (<3%).²² The RbLaSrNb₂ZnO₉ crystallizes in a simple cubic perovskite structure. The Nb and Zn ions may be accordingly arranged in a disordered manner. For A(B_{2/3}B'_{1/3})O₃-type perovskite (A = Sr, Ba; B and B' = smaller cation), a cubic structure is generally favored when the B and B' ions are disordered, while the hexagonal structure is formed when they are ordered.²³ The XRD pattern of RbLaSrNb₂MgO₉ could be also indexed on a simple unit cell. However, shoulders observed in the (211), (220), (310), and (321) reflections indicated that there should be a slight tetragonal distortion from the cubic structure (Table 1). More importantly, the high-pressure form (H) of RbLaSrNb₂CuO₉ could be obtained by direct reaction under high pressure as well as by a transformation from L-RbLaSrNb₂CuO₉. It is clearly shown in Figure 1B,C that the structure of RbLaSrNb₂CuO₉ was completely changed by pressure. Furthermore, the XRD pattern of H-RbLaSrNb₂CuO₉ showed no (00*l*) reflections attributed to the layered structure. Indeed, all reflections could be interpreted with a three-dimensional unit cell. Such a change would be illustrated as following Scheme 1;

In contrast to the Mg or Zn analogues, a strong tetragonal distortion is induced in H-RbLaSrNb₂CuO₉.

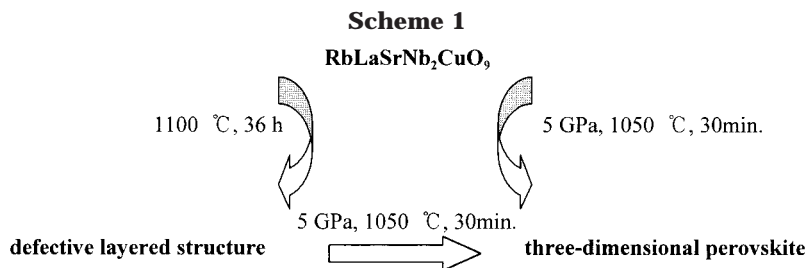
In the ESR spectra at room temperature for NaLaSrNb₂CuO₉ and KLaSrNb₂CuO₉ with cubic structure, an isotropic ($\Delta H \sim 35$ mT) signal centered at *g* = 2.18 was observed. On the contrary, a slightly anisotropic signal was observed for L- and H-RbLaSrNb₂CuO₉, but no clearly resolved *g*_⊥ and *g*_∥ values could be obtained. The estimated average \bar{g} value from a broad ($\Delta H \sim 41$ mT) anisotropic spectrum was ~2.16 for both forms. These ESR spectra are in agreement with the crystal

(20) Because a loss due to volatilization of rubidium is avoided under high pressure, a stoichiometric mixture of starting materials is required.

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(22) Compared with the XRD patterns of the samples prepared under normal conditions, such reflections are likely attributed to a remaining layered phase. The higher pressure condition may be therefore required for the stabilization of a three-dimensional phase. Unfortunately, our high-pressure apparatus was limited to the maximum pressure of 5 GPa.

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symmetries determined by the X-ray diffraction. Such a quasi-isotropic signal may be associated with the dynamic Jahn–Teller effect of the Cu²⁺ ion. The temperature-dependent ESR spectra will be further studied.

Finally, CsLaSrNb₂MO₉ (M = Mg, Cu, Zn) were also examined under 5 GPa at 1050–1100 °C. Unfortunately, a disproportionation into two different cubic forms was always observed, even with the longer reaction times (1–1.5 h), one of which corresponds to Sr(Nb_{2/3}M_{1/3})O₃²³ and the other perhaps corresponding to (CsLa)(Nb_{4/3}M_{2/3})O₆. Higher pressure and temperature may be needed to obtain a single-phased three-dimensional structure of (CsLaSr)(Nb₂M)O₉. As far as we know, the composition (CsLa)(Nb_{4/3}M_{2/3})O₆ is an unknown phase. The isolation of this composition under

high pressure and the investigation of its ferroelectric properties are in progress.

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Supporting Information Available: Listings of *d* spacings and relative intensities for all compounds prepared in this work (3 pages). Ordering information is given on any current masthead page.

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