New-Type Ordering Behavior in the Layered Perovskite Compound $RbLa_2Ti_2NbO_{10}$

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Layered perovskite compound $RbLa_2Ti_2NbO_{10}$ has been successfully characterized by the Rietveld analysis of powder X-ray diffraction pattern and lattice energy calculation. The $RbLa_2Ti_2NbO_{10}$ represents a unique example of layered perovskite in which equal numbers of Ti^{4+} and Nb^{5+} cations were statistically distributed in the outer octahedra, and only Ti^{4+} cations occupied the middle octahedra.

In 1981, Dion et al. synthesized a new family of the layered oxides, $MCa_2Nb_3O_{10}$ (M = alkali metal).[1] These compounds consist of perovskite-structured $Ca_2Nb_3O_{10}$ layers, which are separated by M cations along one of the perovskite cubic directions. Subsequently, a number of compounds, $K[Ca_2Na_{n-3}Nb_nO_{3n+1}]$, $NaLaNb_2O_7$, $K_{1-x}La_xCa_{2-x}Nb_3O_{10}$, $KCa_{2-x}La_xTi_xNb_{3-x}O_{10}$, and $RbLaSrNb_2CuO_9$, have been synthesized and named after the Dion-Jacobson series.[2-6] Their protonated phases are known to exhibit acid catalytic and photo-catalytic activities for the evolution of H_2 gas from a methanol solution.[7] Therefore, it is very important to understand the factors for controlling the acidity of solid oxides since the rational design of acid catalysts for specific purposes is possible. Based on the bond character of octahedra, it has been reported that the acidity of $HCaLaTiNb_2O_{10}$ is stronger than that of $HLa_2Ti_2NbO_{10}$.[5] Such a difference comes from that the protons attached to NbO_6 are assumed to be more acidic than those attached to TiO_6, as evidenced by the acidity order of $HNb_3O_8{\cdot}H_2O > HTiNbO_5 > H_2Ti_4O_9$.

In this work, we were able to demonstrate that equal numbers of Ti^{4+} and Nb^{5+} cations are statistically distributed in the outer octahedra with only Ti^{4+} occupying the middle octahedra in $RbLa_2Ti_2NbO_{10}$.

An excess amount of Rb_2CO_3 (25 mol%) was added in the starting mixtures, Rb_2CO_3, La_2O_3, TiO_2, and Nb_2O_5, to compensate for the loss of the rubidium component. The mixtures were ball-milled in ethanol and then calcined at 1050 °C for 24 h in alumina crucibles. The products consisted of a layered perovskite compound with an unwanted $La_2Ti_2O_7$ (JCPDS No. 28-0517). Therefore, the product obtained at 1050 °C was again mixed with the 25 wt% of Rb_2CO_3 and reheated at 1150 °C. The obtained powder was washed in hot distilled water. Energy-dispersive X-ray emission analysis showed that the percentages of Rb, La, Ti, and Nb atoms in $RbLa_2Ti_2NbO_{10}$ were 11.3, 37.2, 13.9, and 14.3 wt%, respectively, while corresponding calculated percentages are 12.0 39.0, 13.5, and 13.1, respectively. Powder X-ray diffraction (XRD) data were recorded at room temperature on a Philips X'pert MPD using Bragg-Brentano geometry with Cu Kα radiation. Step scans were performed over the angular range $10 < 2\theta/° < 110$ with the step size of 0.02° and the counting time of 10 s. The compounds were refined by the Rietveld method using the Fullprof program.[8]

All peaks of X-ray diffraction pattern of $RbLa_2Ti_2NbO_{10}$ were indexed on a tetragonal cell with a = 3.8351(2) and c = 15.2273(7) Å. There was no reflection conditions for this indexing, leading to the space group *P4/mmm*. Figure 1 shows the observed, calculated, and difference XRD profiles of the selected 2θ ranges. At first, the compound was refined by using the B cation arrangement proposed by Gopalakrishnan et al.[5] Then it gave the agreement factors of $R_p = 22.0$, $R_{wp} = 28.2$, and $R_I = 12.6\%$ (Figure 1(a)). In fact, Ti^{4+} and Nb^{5+} cations can be distributed over two crystallographic sites; 1a (0,0,0) and 2g (0,0,~0.29) in *P4/mmm*. This indicates that there exist three kinds of the model of B cation arrangement, depending on the distribution of Ti^{4+} and Nb^{5+} cations, as shown in Figure 2. The refinement with the model 2 gave a rather improved results of the agreement factors of $R_p = 15.5$, $R_{wp} = 19.0$, and RI = 7.18% (Figure 1(b)), but they were still high to accept. The refinement was carried out by introducing a new B-site cation arrangement model, where TiO_6 octahedra are flanked by the outer $(Ti_{1/2}Nb_{1/2})O_6$ octahedra (Figure 2(c)). The agreement factors were significantly improved to $R_p = 12.1$, $R_{wp} = 15.0$, and $R_I = 4.08\%$ (Figure 1(c)). The occupation factors of Ti^{4+} and Nb^{5+} cations were finally refined, but no significant deviation was found. The refined atomic positions and isotropic thermal parameters are listed in Table 1.

It is noteworthy that the new-type ordering sequence of $(Nb_{1/2}Ti_{1/2})O_6$-TiO_6-$(Nb_{1/2}Ti_{1/2})O_6$ was found even though the

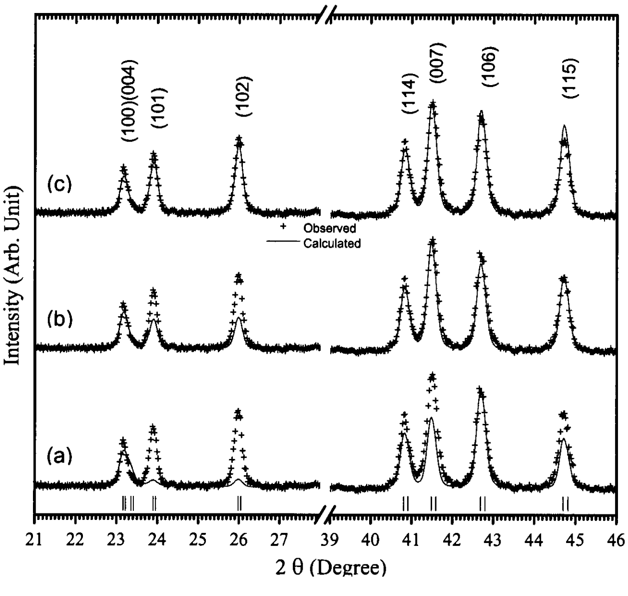

Figure 1. Observed and calculated powder XRD profiles of the selected 2θ ranges for $RbLa_2Ti_2NbO_{10}$, according to (a) model 1, (b) model 2, and (c) model 3. Bragg positions are marked.

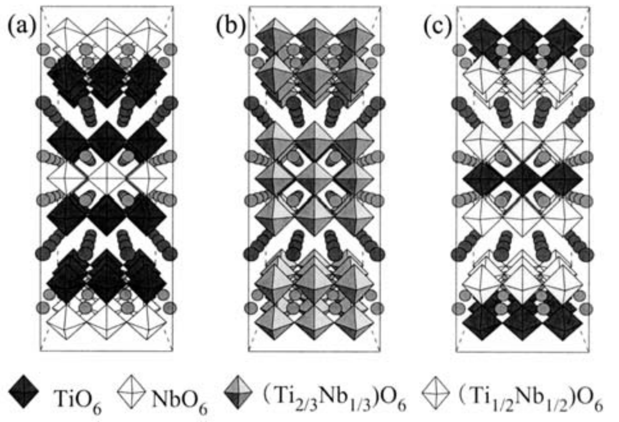

Figure 2. Three models for B cation arrangement. (a) model 1, TiO_6-NbO_6-TiO_6, (b) model 2, $(Ti_{2/3}Nb_{1/3})O_6$-$(Ti_{2/3}Nb_{1/3})O_6$-$(Ti_{2/3}Nb_{1/3})O_6$, and (c) model 3, $(Ti_{1/2}Nb_{1/2})O_6$-TiO_6-$(Ti_{1/2}Nb_{1/2})O_6$.

Table 1 Crystallographic data of $RbLa_2Ti_2NbO_{10}$

Atom	Site	g	x	y	z	B_{iso}/ Å ^{2}
Rb	1d	1	0.5	0.5	0.5	2.5(1)
La	2h	1	0.5	0.5	0.1426(1)	0.60(5)
Ti(1)	1a	1	0	0	0	0.22(7)
Ti(2)	2g	0.5	0	0	0.2885(2)	0.22(7)
Nb(2)	2g	0.5	0	0	0.2885(2)	0.22(7)
O(1)	2f	1	0	0.5	0	1.7(1)
O(2)	2g	1	0	0	0.1236(8)	1.7(1)
O(3)	4i	1	0	0.5	0.2547(6)	1.7(1)
O(4)	2g	1	0	0	0.4033(9)	1.7(1)

differences in size and charge of B cations are not significant. To explain why such an ordering appeared in a layered perovskite, let's imagine $RbLa_2Ti_2NbO_{10}$ as the composite of RbO rock salt and $La_2Ti_2NbO_9$ perovskite layers. Then, it can be simply depicted as a chain of $[RbO]^{-1}$-$[La_{1/2}(Ti_{1-x}Nb_x)O_3]^{z-0.5}$-$[La(Ti_{2x}Nb_{1-2x})O_3]^{-2z+2}$-$[La_{1/2}(Ti_{1-x}Nb_x)O_3]^{z-0.5}$-$[RbO]^{-1}$, depending on the distribution of B cations. It gives the ideal charge distribution of [-1]-[0]-[+1]-[0]-[-1] when x = 0.5. It can be, therefore, demonstrated that the insertion of $[RbO]^{-1}$ layer with negative charge into 3-dimensional perovskite structure contributes to the new-type ordering along (00*l*) direction by electrostatic stabilization. To confirm the distribution of B-site cations, the lattice energy was calculated using the program MADEL (Macintosh version) attached in FAT-RIETAN. It is particularly interesting to note that the calculated lattice energies are –290, –480, and –505 kJ/mol for x = 0, 0.67, and 1, respectively, resulting in the most stable sequence of $(Nb_{1/2}Ti_{1/2})O_6$-TiO_6-$(Nb_{1/2}Ti_{1/2})O_6$. The ordering behavior in the layered perovskites should be viewed consideration of the electrostatic effect of the interlayer, in addition to the size and charge differences. It is, therefore, necessary to readdress the distribution of B cations in layered perovskite compounds with mixed B cations.

From the concept of the building block, the distortion of the Ti/Nb(2)-O bonds, coming from the different bond lengths of 2.499(8) Å for Ti/Nb(2)-O(2) and 1.728(9) Å for Ti/Nb(2)-O(4), is explained by a formal charge separation in $[La_{1/2}(Ti_{1-x}Nb_x)O_3]$ blocks. That is, the formal charge of [-1]-[0]-[+1]-[0]-[-1] at x = 0.5 is considered as [-1]-[δ^+---δ^-]-[+1]-[δ^----δ^+]-[-1], resulting in displacement of Ti/Nb(2) cation from the center of the octahedra. This concept can be applied to the other layered perovskites. Toda et al. have reported that the distortion of Ta-O bonds in $Li_xLaTa_2O_7$ (x=1 or 2) becomes less significant with the lithium intercalation.[9] In the same way, the distributions of formal charge are viewed as $[LiO]^{-1}$-$[La_{1/2}TaO_3]^{0.5}$-$[La_{1/2}TaO_3]^{0.5}$-$[LiO]^{-1}$ for $LiLaTa_2O_7$ and $[Li_2O]^0$-$[La_{1/2}TaO_3]^0$-$[La_{1/2}TaO_3]^0$-$[Li_2O]^0$ for $Li_2LaTa_2O_7$. That is, the charge separation between the $[Li_xO]$ and perovskite layers decreases with lithium intercalation, and the Ta-O bond is less distorted.

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