

Structure Determination of New Layered Perovskite Compound, $\text{NaLaTa}_2\text{O}_7$, Synthesized by Ion-Exchange Reaction

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イオン交換反応により合成した新しい層状ペロブスカイト化合物 $\text{NaLaTa}_2\text{O}_7$ の構造決定

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A new layered perovskite compound, $\text{NaLaTa}_2\text{O}_7$, was synthesized by ion-exchange reaction of the rubidium compound, $\text{RbLaTa}_2\text{O}_7$. The crystal structure of the compound was determined by the Rietveld analysis for powder X-ray diffraction pattern. The crystal structure is analogous to that of the corresponding niobate compound, $\text{NaLaNb}_2\text{O}_7$. This layered perovskite compound is a new member of the Dion-Jacobson series with $n=2$ for the general formula $\text{M}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ ($\text{M}=\text{alkali metals}$).

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1. Introduction

The discovery of new solid state compounds with unique structures and physical properties is related to the development in synthesis techniques such as soft chemical routes. Several examples are reported by Gopalakrishnan.¹⁾ Ion-exchange reactions in inorganic solids can be used to provide metastable phases. The ion-exchangeable layered perovskites have enough spaces to allow ion transport. The inter-layer positions of ion-exchangeable layered perovskites can be occupied by alkali ions. These compounds exhibit a variety of chemical properties such as ion-exchange and intercalation reactions. There are two series of ion-exchangeable layered perovskites; one is Ruddlesden-Popper series²⁾⁻⁵⁾ with the general formula $\text{M}_2[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ ($\text{M}=\text{alkali metal}$, $\text{B}=\text{Ti}$) and the other is Dion-Jacobson series^{6),7)} with $\text{M}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$ ($\text{M}=\text{alkali metal}$, $\text{B}=\text{Nb}$).

Recently, we prepared a new ion-exchangeable layered perovskite compound, $\text{RbLaTa}_2\text{O}_7$, and determined the crystal structure of its derivative, $\text{LiLaTa}_2\text{O}_7$.⁸⁾ These layered perovskite compounds are new members of the Dion-Jacobson series with $n=2$. In the course of the study for this compound, we have found that the rubidium ions in the $\text{RbLaTa}_2\text{O}_7$ are readily exchanged with sodium ions to give a new layered perovskite compound, $\text{NaLaTa}_2\text{O}_7$.

In this paper, we report the synthesis of new layered perovskite compound, $\text{NaLaTa}_2\text{O}_7$ and its hydrate. The crystal structures of both compounds were determined by the Rietveld analysis for powder X-ray diffraction patterns. We discuss the stacking feature of the perovskite layer on the basis of these structure refinement.

2. Experimental

The parent compound, $\text{RbLaTa}_2\text{O}_7$, was prepared by a conventional solid-state reaction. The starting material was a mixture of rubidium carbonate, lanthanum oxide and tantalum oxide. An excess amount of rubidium carbonate (50 mol%) was added to compensate for the loss due to the volatilization of rubidium component. The pellet was placed in an alumina crucible and then heated at 1373K for 4h in air. Ion exchanged compound, $\text{NaLaTa}_2\text{O}_7$, was prepared by the ion-exchange reaction from the parent compound.

The ion exchange of sodium compound was carried out by reacting the parent compounds with molten NaNO_3 at 673K for 24h. After the reaction, the precipitates of the products were collected, washed with distilled water and air-dried at room temperature. The completion of the ion-exchange reaction was confirmed by X-ray diffraction (XRD) pattern.

Powder XRD patterns were recorded on a Rigaku RAD-rA diffractometer equipped with a curved crystal graphite monochromator using $\text{Cu K}\alpha$ radiation at 298K. The data were collected by a step-scanning mode in the 2θ range of $5\text{--}100^\circ$ with a step width 0.02° and a step time 4s. Since the $\text{NaLaTa}_2\text{O}_7$ compound was strongly hygroscopic upon exposure to the atmosphere, the powder XRD pattern of anhydrous compound was obtained at 573K. Indexing of the powder XRD pattern obtained was examined with the aid of the computer program CELL.⁹⁾ Data analysis was carried out by the Rietveld method, using the RIETAN94 profile refinement program.¹⁰⁾ The reflection peak observed at low 2θ was found to deviate greatly from the calculated peak profile due to an asymmetric effect of peak shape. Therefore, the reflection peaks below $2\theta=20^\circ$ were eliminated from the Rietveld refinement. Thermogravimetric analysis (TGA) was done using an SSI EXSTAR6000 at a heating rate of 2K min^{-1} in air.

3. Results and discussion

3.1 Synthesis of $\text{NaLaTa}_2\text{O}_7$

First, we attempted the solid-state reaction to obtain a layered perovskite compound, $\text{NaLaTa}_2\text{O}_7$. The corresponding niobate compound, $\text{NaLaNb}_2\text{O}_7$, could not be synthesized by the solid-state reaction.¹¹⁾ Even the tantalum compound, $\text{NaLaTa}_2\text{O}_7$, also is not able to be obtained by the solid-state reaction at temperatures ranging from 1273 to 1473K. The main product is a perovskite phase, NaTaO_3 , and a large amount of a second phase, LaTaO_4 , was present. Chincholkar reported that the tolerance factors of the pyrochlore structure for many ternary oxide systems, alkali metal-rare earths-pentavalent ions, is close to the values required from the ideal pyrochlore structure.¹²⁾ Our result is quite different from that obtained by Chincholkar. The

layered perovskite structure is thermodynamically less stable than the three-dimensional linked perovskite structure on this ternary system. The layered perovskite compound $\text{NaLaTa}_2\text{O}_7$, which is probably metastable, could only be obtained by the ion-exchange reaction.

3.2 Characterization of hydration

The XRD pattern of $\text{NaLaTa}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ shows that diffraction peaks corresponding to the d -spacings along the stacking direction of the perovskite layer shift to the lower side of the diffraction angle during hydration (Fig. 1). This obviously indicates that the water molecules can be inserted into the interlayer space. Figure 2 shows TGA data for the dehydration of the layered perovskite compound, $\text{NaLaTa}_2\text{O}_7 \cdot x\text{H}_2\text{O}$. The dehydration process of the interlayer water can be roughly classified into two stages. It is difficult to isolate a single-phase in the first step. Therefore, we do not discuss structural characteristics of this compound in detail here. The total weight loss of $\text{NaLaTa}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ corresponds to 1.9 mol of water compared to the anhydride, giving an initial composition of $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$. The anhydride and partially hydrate forms can be easily rehydrate in a wet atmosphere. The hydration–dehydration process was found to be reversible.

3.3 Crystal structure of hydrous compound, $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$

The reflection peaks of $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$ was indexed with a tetragonal symmetry. The reflection condition found was $h+k+l=2n$ for hkl reflections, leading to possible space groups with I -type lattice ($I4$, $\bar{I}4$, $I4/m$, $I422$, $I4mm$, $\bar{I}4m2$, $\bar{I}42m$ and $I4/mmm$). The Rietveld refinement was carried out for all space groups given by the CELL results in the first refinement stage. An initial structural model was

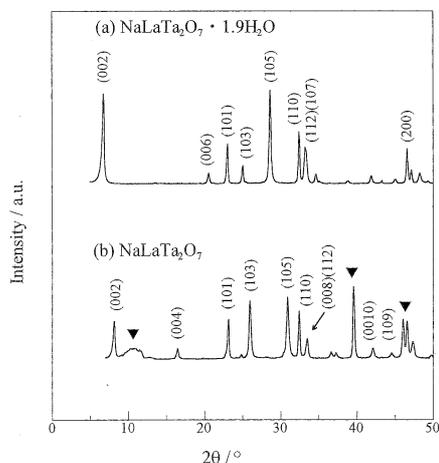


Fig. 1. Powder X-ray diffraction patterns for $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$ and $\text{NaLaTa}_2\text{O}_7$. The triangle (\blacktriangledown) represent the reflection of a sample holder and a furnace attachment.

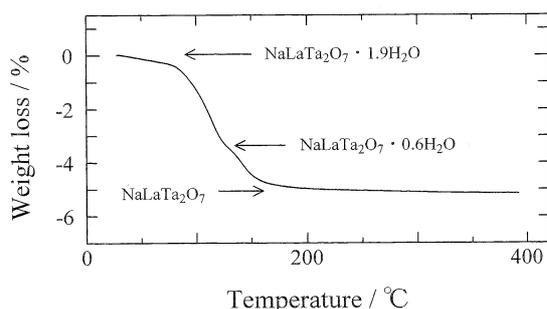


Fig. 2. TGA curve for $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$.

adopted on the basis of assumption that the main lattice constructs a double perovskite layer analogous to $\text{LiLaTa}_2\text{O}_7$ which has double perovskite layers with displacement of each layer. The perovskite layer only was first refined. A difference Fourier map was then generated from the observed and calculated structure factors. The most reliable solution with physically meaningful crystallographic parameters was finally achieved when adopting $I4/mmm$ space group for $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$.

The result of the pattern fitting is shown in Fig. 3. The structural model for $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$ is illustrated in Fig. 4. The crystallographic data finally refined by the Rietveld refinement are listed in Tables 1 and 2. Although the hydrous compound gave slightly poor crystallinity compared with the parent compound, the R -factors were reasonably converged to acceptable values. The sodium atom $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$ is surrounded by four oxygen atoms belonging to the water molecules. The distance between the oxygen atoms of water molecules is about 0.275 nm. This distance is close to that found in ice, 0.275 nm.¹³⁾ It is suggested that the hydrogen bonds is forming between the four water molecules.

3.4 Crystal structure of anhydrous compound, $\text{NaLaTa}_2\text{O}_7$

The indexing for anhydrous compound, $\text{NaLaTa}_2\text{O}_7$, was also examined. The reflection condition of XRD pattern found for $\text{NaLaTa}_2\text{O}_7$ was $h+k+l=2n$ for hkl reflections, giving eight possible space groups with I -type lattice. This condition is identical to that of hydrous compound. The result of pattern fitting for $\text{NaLaTa}_2\text{O}_7$ is shown in

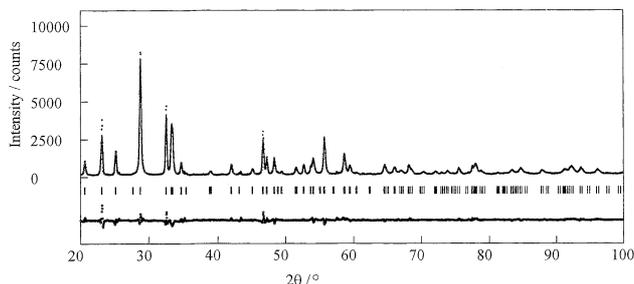


Fig. 3. X-ray powder pattern fitting for $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$. The calculated and observed patterns are shown on the top solid line and the dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The trace on the bottom is a plot of the difference between calculated and observed intensities.

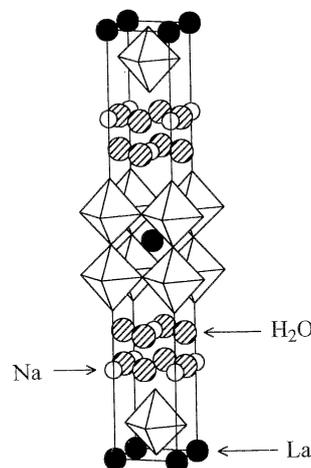


Fig. 4. Structural model of $\text{NaLaTa}_2\text{O}_7 \cdot 1.9\text{H}_2\text{O}$.

Table 1. Crystallographic Data of NaLaTa₂O₇·1.9H₂O

	Atom	Site ^{a)}	g ^{b)}	x	y	z	B / nm ²
NaLaTa ₂ O ₇ · 1.9H ₂ O	Na	4e	0.5	0.0	0.0	0.210(3)	0.03(2)
I4/mmm (No. 139)	La	2a	1.0	0.0	0.0	0.0	0.004(2)
a = 0.38950(2)nm	Ta	4e	1.0	0.0	0.0	0.4126(2)	0.001(2)
c = 2.5835(2)nm	O(1)	2b	1.0	0.0	0.0	0.5	0.001(9)
R _{wp} = 9.40 %	O(2)	8g	1.0	0.0	0.5	0.0747(2)	0.001(9)
R _p = 7.06 %	O(3)	4e	1.0	0.0	0.0	0.348(3)	0.001(9)
R _f = 4.09 %	Ow ^{c)}	8g	0.475	0.0	0.5	0.291(5)	0.04(3)
R _f = 2.13 %							

a) Multiplicity and Wyckoff notation.

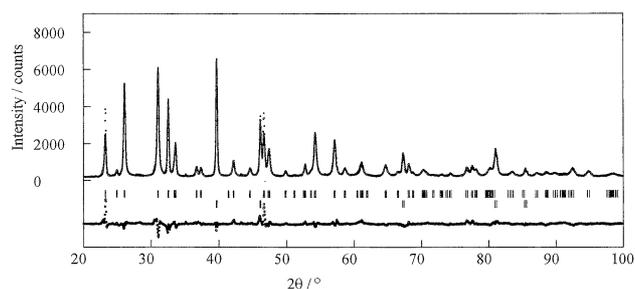
b) Occupancy.

c) Oxygen atom of water molecule.

Table 2. Selected Interatomic Distances for NaLaTa₂O₇·1.9H₂O

Bond	Distance (nm)	Bond	Distance (nm)
Ta - O(1)	0.2258(6)	Na - Ow	0.1948(3)
Ta - O(2)	0.1975(7)	O(3) - Ow	0.244(9)
Ta - O(3)	0.166(7)	Ow - Ow	0.27542(1)
La - O(1)	0.27542(1)		
La - O(2)	0.274(3)		

Fig. 5. The crystallographic data for NaLaTa₂O₇ are listed in Tables 3 and 4. Figure 6 shows the crystal structure of NaLaTa₂O₇, together with those for LiLaTa₂O₇, RbLaTa₂O₇ and KLaTa₂O₇, as a reference.^{8),14)} All structures are characterized as a nearly two-dimensional framework comprised of two corner-shared TaO₆ octahedra. The alkali ions in these layered compounds are located in the interlayer space between the perovskite slabs. The relative arrangement of the adjacent perovskite sheets is dependent on the size of ions existing in the interlayer. The perovskite layer in rubidium compound is stacked up without a displacement. The adjacent perovskite layers of the potassium compound are stacked with a displacement by 1/2 along the only one direction within the layer plane. The potassium

Fig. 5. X-ray powder pattern fitting for NaLaTa₂O₇. The additional rows of Bragg reflection marks corresponding to Pt holder.Table 3. Crystallographic Data of NaLaTa₂O₇

Sample	Atom	Site ^{a)}	g ^{b)}	x	y	z
NaLaTa ₂ O ₇	Na	4d	0.5	0.0	0.5	0.25
I4/mmm (No. 139)	La	2a	1.0	0.0	0.0	0.0
a = 0.38955(4) nm	Ta	4e	1.0	0.0	0.0	0.3944(4)
c = 2.1436(2) nm	O(1)	2b	1.0	0.0	0.0	0.5
R _{wp} = 10.29 %	O(2)	8g	1.0	0.0	0.5	0.084(3)
R _p = 7.79 %	O(3)	4e	1.0	0.0	0.0	0.311(4)
R _f = 5.10 %						
R _f = 2.52 %						
	Overall isotropic thermal parameter Q = 0.001(3) nm ²					

a) Multiplicity and Wyckoff notation.

b) Occupancy.

Table 4. Selected Interatomic Distances for NaLaTa₂O₇

Bond	Distance (nm)	Bond	Distance (nm)
Ta - O(1)	0.2263(9)	Na - Na	0.27546(3)
Ta - O(2)	0.200(1)	Na - O(3)	0.234(5)
Ta - O(3)	0.180(9)		
La - O(1)	0.27546(3)		
La - O(2)	0.265(4)		

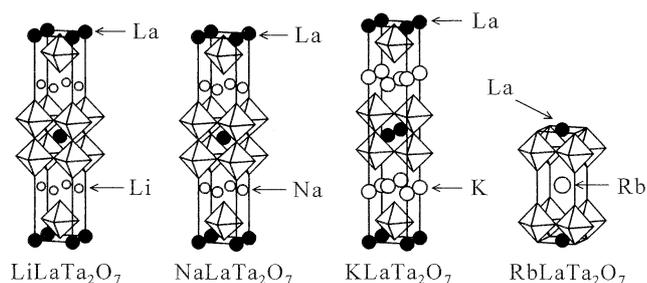


Fig. 6. Structural models of $MLaTa_2O_7$ ($M=Rb, K, Na, Li$).

ions are located in the interlayer space and are in a trigonal prismatic coordination. On the other hand, the adjacent perovskite sheets in sodium and lithium ion-exchanged compound are stacked with a displacement by $1/2$ along the diagonal direction within the layer plane. The sodium and lithium ions occupy the four-fold sites between the two perovskite layers. The tetrahedral coordination of Na-O found in $NaLaTa_2O_7$ is extremely rare in the normal oxides with layered structures. The coordination number of the sodium ions is usually larger than five. The tetrahedral coordination of sodium atoms are probably thermodynamically metastable. This seems to be one of the reasons for difficulty of direct synthesis.

This stacking feature is in contrast to that of titanate compound.^{4),5),15)} In titanate compounds, the relative arrangement of the adjacent perovskite sheets is independent of its ionic size while existing in the interlayer. The lower charge (4+) of the central ion in the titanate compound is compensated by two interlayer monovalent ions, i.e., a high positive charge density state is realized in the interlayer space. On the other hand, the high positive charge (5+) of the central ion in the tantalate compound can lead to a lower charge density state for the interlayer space. The coulomb interaction between the perovskite layer and the interlayer ion is relatively weak, reflecting a variety of stacking features of the adjacent perovskite layer blocks owing to the ionic size of the interlayer ions. The stacking sequences are dependent on the space volume formed between the perovskite layers. The structural features in these compounds are the same as those of the corresponding niobate compounds.¹¹⁾ It is very interesting that the structures of tantalate compounds and niobate compounds are same. Despite of the difference in electron configuration between the tantalum and niobium atoms, the crystal structures of the tantalate compounds are practically unchanged. The niobium and tantalum ions have the same electric charge and almost same ionic radius.¹⁶⁾ Structural data indicate that electric charge and ionic radius play an important role in structural properties of these materials.

Figure 7 shows the environment of tantalum atoms in $NaLaTa_2O_7$. The tantalum atom is fairly displaced from the center of the octahedron. The oxygen with a fairly shortened distance of Ta-O is located toward the interlayer. Such shortness of the Ta-O distance seems to cause less interaction between the rubidium and perovskite sheet. Therefore, it is possible in this situation to exchange the interlayer ions with other alkali ions. The Ta-O bonds in $NaLaTa_2O_7$ are classified into three types: i.e., a very short bond (0.180(9)nm) toward the interlayer, four normal

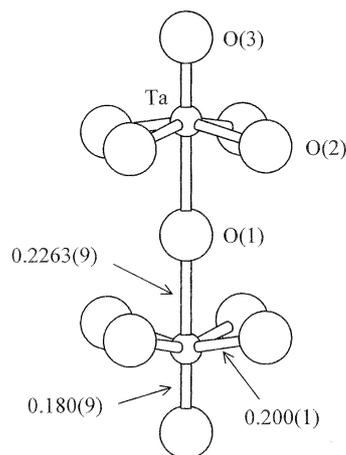


Fig. 7. Environment around tantalum atoms in $NaLaTa_2O_7$.

bonds (0.200(1)nm) linked within the perovskite layer and a long bond (0.2263(9)nm). These bond distances are similar to that of parent compound (0.169(5)nm, 0.1975(6)nm, 0.2285(4)nm). The ion-exchanged compound, $NaLaTa_2O_7$, retains the same bond character as that of the parent compound, $RbLaTa_2O_7$.⁸⁾ An important common structural feature for all the series of ion-exchangeable layered perovskite compounds is the presence of extremely short of metal-oxygen bonds in the direction of the interlayer alkali metals between the perovskite layers.^{4),5),8),11)}

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