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Neutron diffraction study on protonated and hydrated layered perovskite

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Abstract

A layered perovskite compound with Na^+, D_3O^+ ions (H_3O^+) and D_2O molecules (H_2O) in the interlayer, $D_xNa_{1-x}LaTiO_4 \cdot yD_2O$, has been prepared by an ion-exchange/intercalation reaction with dilute DCl solution, using an $n = 1$ Ruddlesden–Popper phase, $NaLaTiO_4$. Its structure has been analyzed in order to clarify the interlayer structure by Rietveld method, using powder neutron diffraction data. The structure analysis revealed that the layered structure changed from the space group $P4/nmm$–$I4/mmm$ after the ion-exchange/intercalation reaction, and it induced the transformation of perovskite layers from staggered to an eclipsed configuration. The D_2O molecules and D_3O^+ ions loaded in the interlayer statistically occupied the sites around a body center position of rectangular space surrounded by eight apical O atoms of TiO_6 octahedra in upper and lower layers.

Keywords: Layered perovskite; Ruddlesden–Popper phase; Ion exchange; Intercalation; Hydration; Crystal structure; Neutron diffraction

1. Introduction

Soft-chemical processing allows the preparation of unique compounds not accessible by the conventional synthetic methods such as solid-state reaction, liquid phase reaction methods, etc. [1–6]. Recently, we have reported the synthesis of new hydrated and protonated layered perovskite compound, $H_xNa_{1-x}LaTiO_4 \cdot yH_2O$ [7], by ion-exchange/intercalation reactions of layered perovskite compound, $NaLaTiO_4$, which is categorized as a Ruddlesden–Popper family with a general formula of $A'_2[A_{n-1}B_nO_{3n+1}]$ (A and A' = alkali, alkaline or rare earth, B = transition metal) [8]. Furthermore, we have found that the situation of H_3O^+ ion and/or H_2O molecule in the interlayer of hydrated protonated forms derived from $RbLa_2Ti_2TaO_{10}$ governed the n-alkylamine intercalation into the interlayer, which leads the formation of organic–inorganic complex materials [9]. However, the structural information such as positions of the intercalated water molecules (H_2O) and hydronium ions (H_3O^+ ions) in the interlayer of those compounds have not been revealed in the previous reports, because the O and H atoms give weak atomic scattering cross sections for X-ray diffraction, compared with the La and Ti atoms. In addition, the precise interlayer structure of hydrated layered perovskites has been hardly revealed yet, though it is well known that some of the hydrated layered perovskites show excellent physical and chemical properties, such as high photocatalytic activity for the decomposition of water [10] and the proton conduction through the hydrogen network produced by intercalating water molecules in the interlayer [11].

In such a background, neutron diffraction is a useful means for precisely determining the positions of light elements such as protons and oxygen in compounds containing heavy elements. The crystal structure analysis of deuterated layered perovskite compounds by Rietveld method, using powder neutron diffraction data, brings information on the interlayer structure, which could help

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scientists explain physical and chemical properties of these compounds. Thus, we have performed the structure refinement of $D_xNa_{1-x}LaTiO_4 \cdot yD_2O$ ($H_xNa_{1-x}LaTiO_4 \cdot yH_2O$) by Rietveld method using powder neutron diffraction data to determine the accurate interlayer structure. In this paper, we present the crystal structure of $D_xNa_{1-x}LaTiO_4 \cdot yD_2O$ and compare with the parent $NaLaTiO_4$ [12–14] and deuterated $DLaTiO_4$ ($HLaTiO_4$) [15,16].

2. Experimental

The starting compound, $NaLaTiO_4$, was prepared by the conventional solid-state reaction [7,12–14]. Prior to the preparation, La_2O_3 was predehydrated at 900 °C for 9 h, because La_2O_3 agent contains a small amount of $La(OH)_3$. Stoichiometric amounts of TiO_2 and La_2O_3 and 50% excess of Na_2CO_3 were mixed, and heated at 900 °C for 30 min after preheating at 700 °C for 2 h in the air. The product was washed to remove excess Na_2O with distilled water and dried at 160 °C. The ion-exchange/intercalation of deuterium and heavy water molecule into the sample was carried out in deuterium chloride, DCl, solution of 10^{-5} M (mol dm^{-3}), which was adjusted by deuterium oxide, D_2O, at room temperature for 72 h in N_2 atmosphere. The product was washed with D_2O and dried at room temperature in N_2 atmosphere. The product was identified by powder X-ray diffraction (XRD), using a Rigaku RINT2100/PC diffractometer with monochromated Cu $K\alpha$ radiation.

Neutron diffraction data of deuterated specimens were measured on a time-of-flight (TOF) neutron diffractometer at room temperature, using *Vega* at the pulsed spallation neutron facility KENS, High Energy Accelerator Research Organization in Japan. The specimens of ca. 5 g were sealed in a vanadium tube in Ar atmosphere, and set on the diffractometer. The observed data as a function of time were converted into those as a function of d values, referring to intensity data observed in a separate measurement of Si powder as a standard sample. The collected diffraction data were analyzed by Rietveld method, using the program RIETAN-TN for TOF neutron diffraction [17,18].

3. Results and discussion

The powder XRD pattern of the compound prepared by the ion-exchange/intercalation reaction of $NaLaTiO_4$ was identical to that of $H_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59H_2O$ in the previous study, and showed no peaks due to impurities [7]. Thus, the resulting materials were employed in the measurement for the neutron diffraction.

As the measured neutron diffraction data had diffraction peaks of vanadium arising from the sample holder, the refinement was performed as a mixture of two phases. Starting structural models of $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$ were constructed as follows. The composition of $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$ was approximated as $D_{0.3}Na_{0.7}LaTiO_4 \cdot 0.6D_2O$, and the constraints were applied to the site occupancy factors for all atoms, in the first step of the refinements. As the XRD indicated that $H_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59H_2O$ was isostructural with $NaEuTiO_4 \cdot 0.5H_2O$ in the previous report [7], the crystal structure of $D_{0.3}Na_{0.7}LaTiO_4 \cdot 0.6D_2O$ was refined in the space group I4/*mmm* on applying isotropic temperature factors to all atoms. The atomic positional data of the Na atom in the interlayer and Eu, Ti and O atoms in the perovskite layer for $NaEuTiO_4 \cdot 0.5H_2O$, reported by Toda et al. [19], were used as initial parameters. Furthermore, two interlayer structural models were constructed; one is a model that 0.3 mol of D_3O^+ ions and D_2O molecules exist in the interlayer, and the other is a model that 0.3 mol of D^+ ions and 0.6 mol of D_2O molecules exist in the interlayer. The former is based on the results of the previous report [7], and the latter is based on the compositional ratios in the specimen.

The refinement was first performed without setting the D atom to determine the position of O atoms in D_2O molecules and/or D_3O^+ ions for both the models. Setting the O atoms at several positions in the interlayer, both the models were refined. Consequently, the best agreement between the observed and calculated diffraction patterns was obtained, when both of the O atoms in D_2O molecules and D_3O^+ ions in the former model were simultaneously located in 8*j* site. Then, the parameters of the D atoms were added around the determined O atom sites, referring to the bond distances and bond angles in H_2O molecule and H_3O^+ ion [20]. Furthermore, the site occupancy factors (g) of D atoms (D1 and D2) of D_3O^+ ion and D_2O molecule were employed as parameters and those of Na atom and O atom (O*w*) of D_2O molecule were reset, i.e., g (Na) = 1–g (D1) and g (Ow) = 2∗g (D2), respectively. After several cycles of the least-square refinement, the structural parameters converged into the reasonable values as listed in Table 1, when two D atoms in D_2O molecules and D_3O^+ ions and the other D atom in D_3O^+ ions were set at 32*o* and 4*e* sites, respectively. The chemical composition estimated from the results of neutron diffraction was compatible with that previously reported, i.e., $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$. The observed and calculated diffraction patterns were in good agreement with each other as illustrated in Fig. 1.

The refined structural illustration of $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$ is shown in Fig. 2, together with those of $NaLaTiO_4$ [12] and $DLaTiO_4$ [15,16]. In the previous study [7], the crystal structure of $H_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59H_2O$ has been expected as follows. The structure of $H_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59H_2O$ consists of (a) TiO_6 octahedral layers, (b) interlayers and (c) LaO_9 polyhedral layers ordered with a sequence of –(a)–(b)–(a)–(c)–(a)- along the *c*-axis similar to those of $NaLaTiO_4$ and $DLaTiO_4$. The perovskite layers shift toward the ⟨110⟩ direction through the ion-exchange/intercalation reaction. That is, the stacking of perovskite layers change from a staggered to an

Table 1
Structural parameters and final R values for $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$[a]

Atom	Site	g	x	y	z	U_{iso}[b] (Å^2)
D1	4*e*	0.355(10)	0	0	0.4772(9)	0.035(5)
D2	32*o*	0.155(5)	0.250(5)	0.242(6)	0.4705(5)	0.064(4)
Na	4*e*	0.645	0	0	0.4018(5)	0.044(4)
La	4*e*	1.0	0	0	0.3020(1)	0.016(1)
Ti	4*e*	1.0	0	0	0.1231(4)	0.007(2)
O1	4*e*	1.0	0	0	0.0577(3)	0.012(2)
O2	8*g*	1.0	0	1/2	0.1379(2)	0.014(1)
O3	4*e*	1.0	0	0	0.2171(3)	0.011(2)
Ow	8*j*	0.310	0.249(4)	1/2	0	0.041(4)

[a] Tetragonal, *I4/mmm*, $a = 3.7549(1)$ Å, $c = 28.024(1)$ Å, $R_{wp} = 2.56\%$, $R_p = 2.01\%$, $R_B = 5.23\%$. $R_{wp} = [\Sigma w_i(y_{io} - y_{ic})^2/\Sigma w_i(y_{io})^2]^{1/2}$, $R_p = \Sigma|y_{io} - y_{ic}|/\Sigma y_{io}$, $R_B = \Sigma|I_{io} - I_{ic}|/\Sigma I_{io}$.

[b] $B_{iso} = 8\pi^2 U_{iso}$.

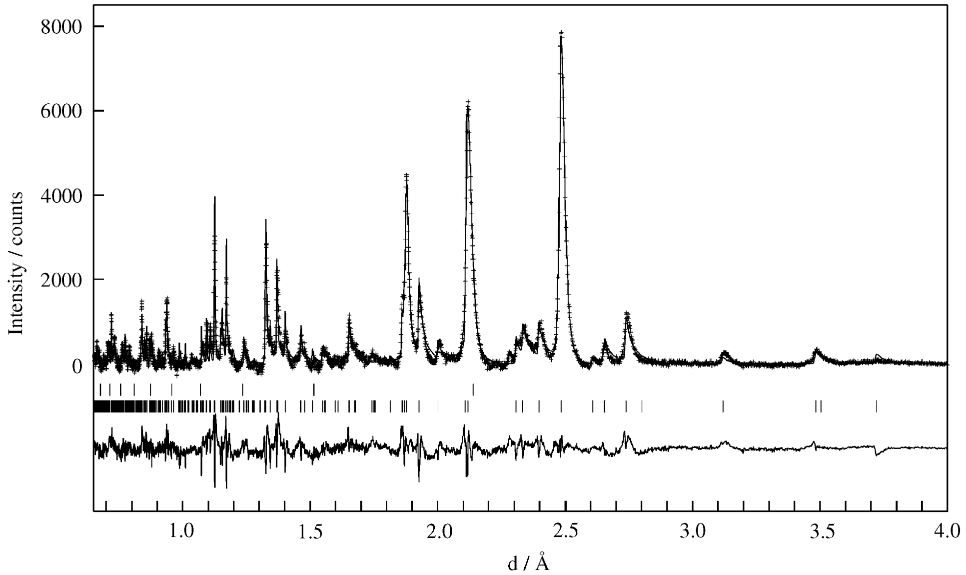

Fig. 1. Observed (plus signs), calculated (solid line), and difference (solid line on the bottom) patterns for TOF neutron powder diffraction of $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$. Vertical marks represent positions calculated for Bragg reflections (upper, vanadium holder and lower, $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$).

eclipsed configuration. Furthermore, it has been suggested that ca. 0.3 mol of H_2O molecules and H_3O^+ ions and 0.66 mol of Na^+ ions existed in the interlayer of $H_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59H_2O$. The results obtained by the present study confirmed the expectation in the previous study, and made clear the interlayer structure with D_2O (H_2O) molecules and D_3O^+ (H_3O^+) ions.

Fig. 3 shows the enlarged illustration of the interlayer where the D_2O molecules, D_3O^+ ions and Na^+ ions are located. The D_2O molecules and D_3O^+ ions in the interlayer statistically occupied the sites around a body center position of rectangular space surrounded by eight apical O atoms of TiO_6 octahedra in upper and lower layers. The estimated D–O bond lengths and D–O–D bond angles of D_2O molecule and/or D_3O^+ ion in the interlayer, as seen in Fig. 3(a), were approximately close to those of H_2O molecule and/or H_3O^+ ion reported in the literature [20]. Fig. 3(b) shows the local circumstance of Na^+ ion bonding to O atoms of TiO_6 octahedra, D_2O molecules and/or D_3O^+ ions. The estimated Na–O*w* and Na–O1 bond lengths were slightly longer than the sum (ca. 2.64 Å) of ionic radii of Na^+ and O^{2-} ions [21], while the estimated Na–O2 bond lengths were shorter than it. This result could be brought by the interaction between D_3O^+ and Na^+ ions in the interlayer.

Selected interatomic distances and bond angles of $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$ are compared with $NaLaTiO_4$ and $DLaTiO_4$ in Table 2, and Fig. 4 shows the comparison among TiO_6 octahedra in $NaLaTiO_4$, $DLaTiO_4$ and $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$. No significant difference was observed in Ti–O equatorial bond lengths among these materials, whereas some differences were observed in Ti–O apical bond lengths and O–Ti–O equatorial bond angles. As a result, the ratio of O1–O2 distance/O1–O3 distance in $NaLaTiO_4$ became larger than 1.0, while that in $DLaTiO_4$ became smaller than 1.0. That

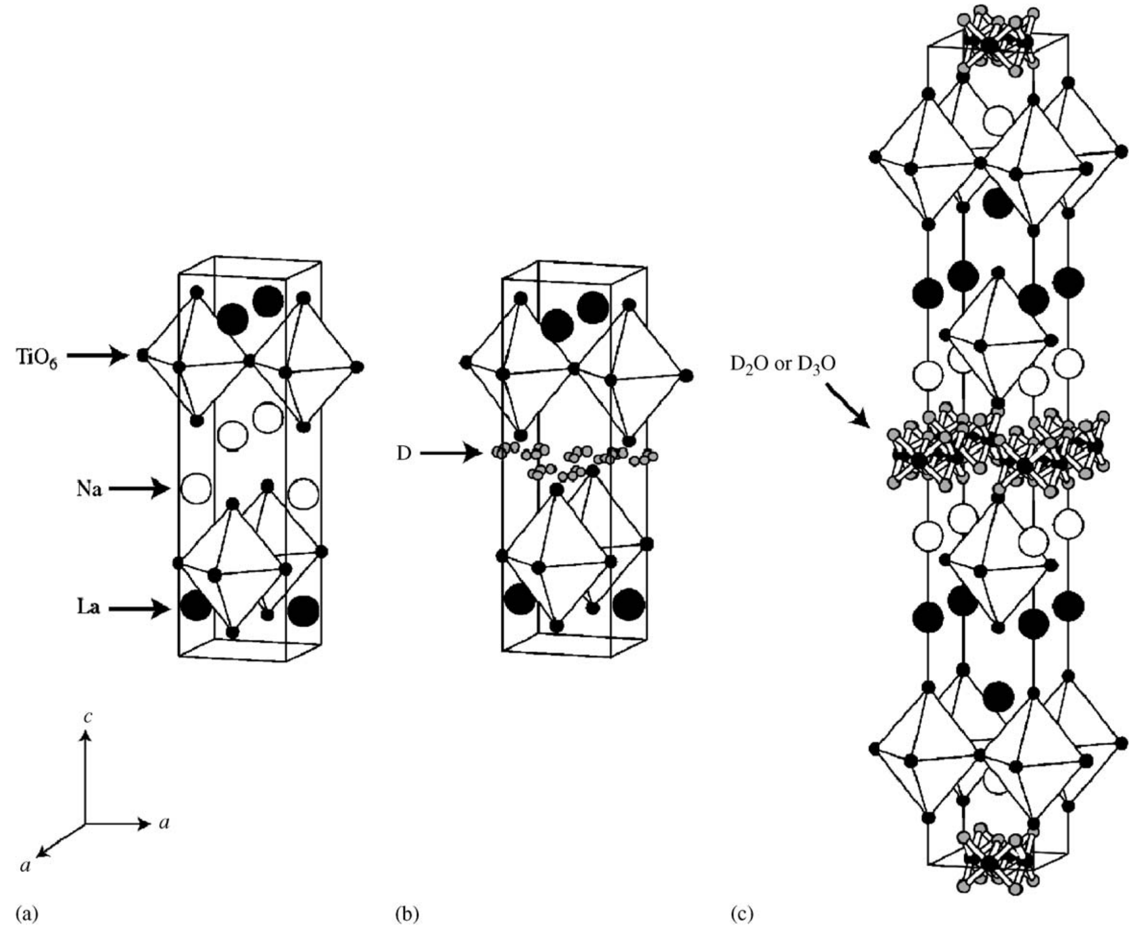

Fig. 2. Schematic illustrations of the crystal structures of (a) $NaLaTiO_4$ [12], (b) $DLaTiO_4$ [15,16] and (c) $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$.

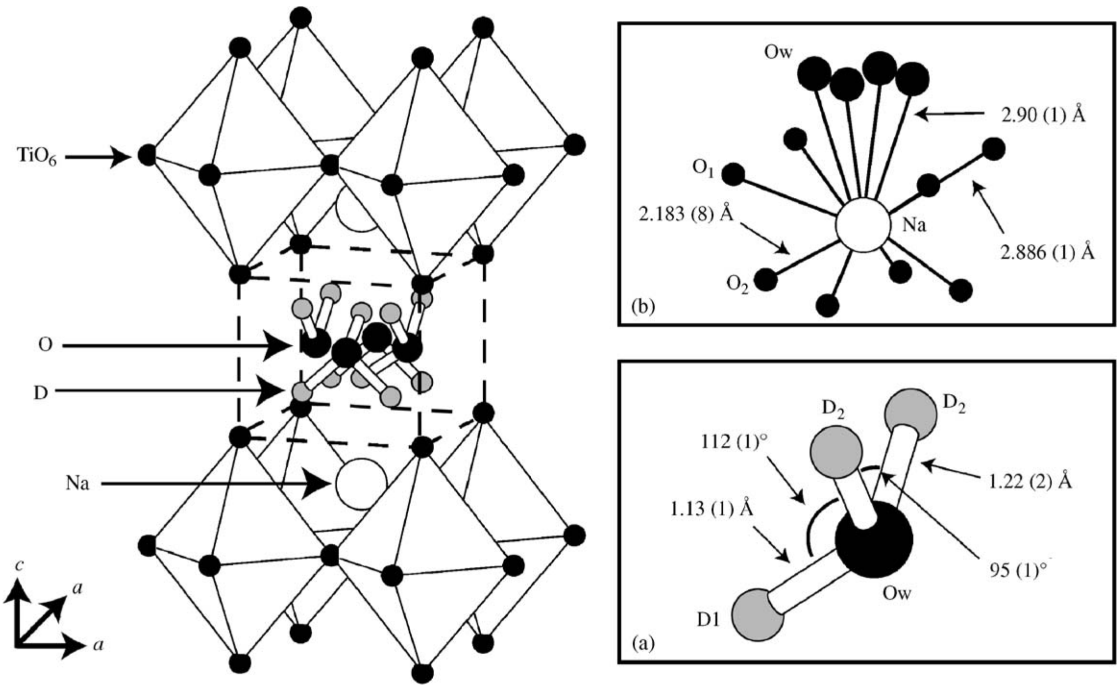

Fig. 3. Schematic illustrations of the locations of D_2O molecules, D_3O^+ ions and Na^+ ions in the interlayer. All sites for D (D1 and D2) atoms were not illustrated in the figure to help understand the formation of D_2O molecule and D_3O^+ ion. The local circumstance of (a) D_2O molecule and D_3O^+ ion and (b) Na^+ ion are shown in inserted boxes. D_2O molecules in (a) consists of two D2 atoms and one O*w* atom.

Table 2
Selected interatomic distances (Å) and bond angles (deg) of $NaLaTiO_4$, $DLaTiO_4$ and $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$

$NaLaTiO_4^{\text{i}}$[a]		$DLaTiO_4^{\text{ii}}$[a]		$D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$	
Interatomic distances					
Ti–O1(× 4)	1.935	Ti–O1(× 4)	1.934(1)	Ti–O2(× 4)	1.922(3)
Ti–O2(× 1)	2.65	Ti–O2(× 1)	2.731(4)	Ti–O3(× 1)	2.63(1)
Ti–O3(× 1)	1.70	Ti–O3(× 1)	1.769(5)	Ti–O1(× 1)	1.83(1)
O1–O2	2.81	O1–O2	2.885(2)	O2–O3	2.927(8)
O1–O3	2.74	O1–O3	2.955(3)	O2–O1	2.908(8)
Bond angles					
O1–Ti–O1$^{\text{i}}$[b]	154.7	O1–Ti–O1$^{\text{i}}$[b]	148.4(2)	O2–Ti–O2$^{\text{ii}}$[b]	155.1(8)

[a] References: (i) [12]. (ii) [15,16].
[b] Symmetry codes: (i) x, $1+y$, z, (ii) x, $-1+y$, z.

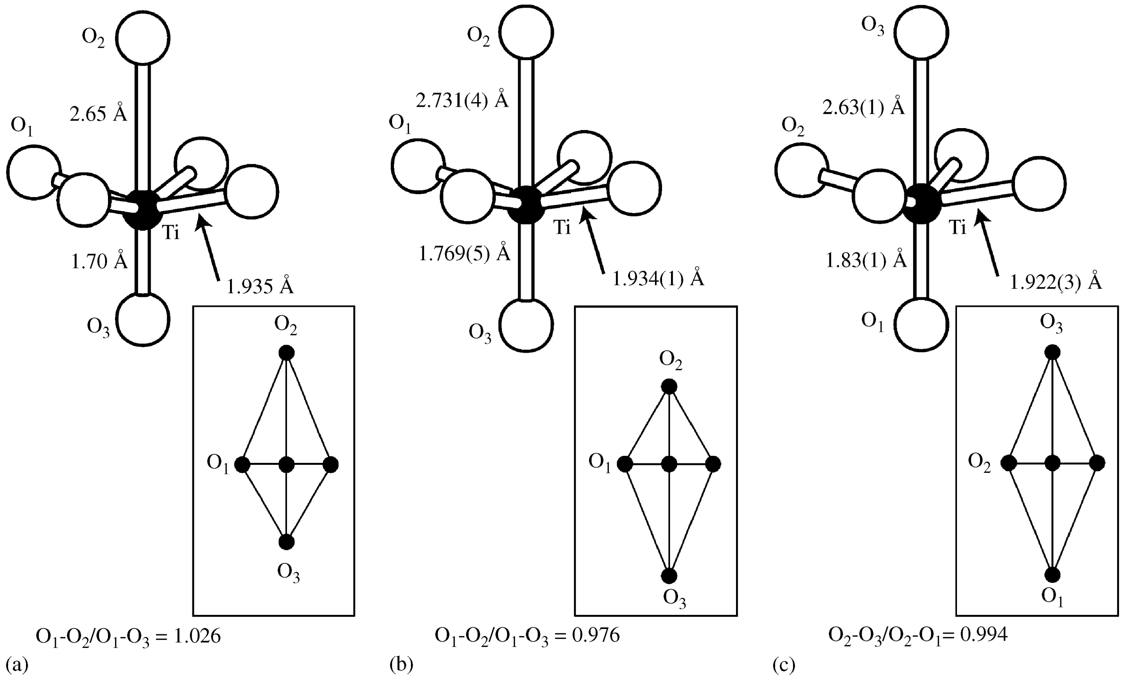

Fig. 4. Schematic illustrations of TiO_6 octahedra in (a) $NaLaTiO_4$ [12], (b) $DLaTiO_4$ [15,16] and (c) $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$. The images of the TiO_6 octahedral distortion are shown in inserted boxes.

is, both the TiO_6 octahedra are disproportionately distorted in one direction of the interlayer or the LaO_9 polyhedral layer. On the other hand, the ratio of O2–O3 distance/O2–O1 distance in $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$, which corresponds to that of O1–O2 distance/O1–O3 distance in $NaLaTiO_4$ and $DLaTiO_4$, was close to 1.0. This indicates that there is no difference in the degree of distortion toward both the interlayer and the LaO_9 polyhedral layer sides in TiO_6 octahedra of $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$. Consequently, it was revealed that the intercalation of D_2O molecules into the interlayer and the ion exchange of Na^+ with D_3O^+ ions modified not only the interlayer structure but also the TiO_6 octahedral layer structure. Furthermore, the modification of the TiO_6 octahedral layer structure depended on a species of cation and/or molecule located in the interlayer.

4. Conclusions

Neutron diffraction study has concluded the crystal structure of $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$ ($H_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59H_2O$) prepared by the ion-exchange/intercalation reaction of $NaLaTiO_4$ as follows. $D_{0.34}Na_{0.66}LaTiO_4 \cdot 0.59D_2O$ crystallized in the space group *I4/mmm*, while $NaLaTiO_4$ crystallized in the space group *P4/nmm*. This structural change resulted from the transformation of the perovskite layers from staggered to an eclipsed configuration through the ion-exchange/intercalation reactions. The D_2O molecules and D_3O^+ ions in the interlayer statistically occupied the sites around a body center position of rectangular space surrounded by eight apical O atoms of TiO_6 octahedra in upper and lower layers, and interacted with the Na^+ ions, which were also located in the interlayer. In addition to the modification of the interlayer structure accompanied by the shift of perovskite layers, the ion-exchange/intercalation reaction also modified TiO_6 octahedral layer structure.

Acknowledgments

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