

# Structure determination of $n = 1$ Ruddlesden–Popper compound $\text{HLaTiO}_4$ by powder neutron diffraction

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## Abstract

A protonated  $n = 1$  Ruddlesden–Popper compound,  $\text{HLaTiO}_4$  ( $\text{DLaTiO}_4$ ), has been prepared by an ion-exchange reaction of  $\text{Na}^+$  ions in  $\text{NaLaTiO}_4$  with  $\text{H}^+$  ( $\text{D}^+$ ) ions, and its structure has been analyzed in order to clarify the location of protons in the interlayer space, using powder neutron diffraction data. The crystal structure of  $\text{DLaTiO}_4$  belongs to the same space group,  $P4/nmm$ , as that of parent  $\text{NaLaTiO}_4$ , and the D atoms were found to statistically occupy eight equivalent sites around an apical O atom of a  $\text{TiO}_6$  octahedron in the interlayer, which are different from the Na atom sites in  $\text{NaLaTiO}_4$ . A comparison between  $\text{DLaTiO}_4$  and  $\text{NaLaTiO}_4$  indicated that the protonation brought the shrinkage of the interlayer space and the distortion of the  $\text{TiO}_6$  octahedron.

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## 1. Introduction

Layered perovskite compounds are typically known as Dion–Jacobson (D–J) family,<sup>1,2</sup>  $A' [A_{n-1}B_nO_{3n+1}]$  ( $A$  and  $A'$  = alkali, alkaline or rare earth;  $B$  = transition metal), and Ruddlesden–Popper (R–P) family,<sup>3,4</sup>  $A'_2 [A_{n-1}B_nO_{3n+1}]$ , where  $A'$  is an interlayer cation and  $[A_{n-1}B_nO_{3n+1}]$  is the perovskite-type layer. These compounds have been extensively investigated, because the interlayer cations can be exchanged by other monovalent or divalent cations, such as  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and so on.<sup>5,6</sup> Protonated forms have especially attracted considerable attention as Brønsted acids, which form intercalation compounds with a variety of organic bases.<sup>5,7</sup> It has also been reported that such intercalation compounds could be exfoliated into single layers.<sup>8</sup> Moreover, proton conduction has appeared,<sup>9</sup>

or photocatalytic property has been improved<sup>10</sup> by the protonation. These results suggest that the protons loaded in the interlayer induce interesting physical and chemical properties. However, circumstances of the protons loaded in the interlayer are yet to be revealed. If any information on the location of the loaded protons is available, it could help scientists develop models to explain physical and chemical properties of protonated layered perovskites.

In such a background, we have studied crystal structures of protonated layered perovskite compounds by Rietveld method, using high-resolution powder neutron diffraction data. Neutron diffraction is useful for precisely determining the positions of light elements such as protons and oxygen in compounds containing heavy elements. In this paper, we present the structure refinement of a deuterated  $n = 1$  Ruddlesden–Popper compound,  $\text{DLaTiO}_4$  ( $\text{HLaTiO}_4$ ), which was prepared by an ion-exchange reaction of  $\text{NaLaTiO}_4$ .

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## 2. Experimental

The starting compound, NaLaTiO<sub>4</sub>, was prepared by the conventional solid-state reaction.<sup>11–13</sup> Prior to the preparation, La<sub>2</sub>O<sub>3</sub> was predehydrated at 900 °C for 9 h, because La<sub>2</sub>O<sub>3</sub> agent contains a small amount of La(OH)<sub>3</sub>. Stoichiometric amounts of TiO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> and 50% excess of Na<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub>O with distilled water and dried at 160 °C. Deuterium exchange of the sample was carried out in deuterium chloride, DCl, solution of 0.1 M (mol dm<sup>-3</sup>), which was adjusted by deuterium oxide, D<sub>2</sub>O, at room temperature for 12 h in N<sub>2</sub> atmosphere. The product was washed with D<sub>2</sub>O and dried at room temperature in N<sub>2</sub> atmosphere. The product was identified by powder X-ray diffraction (XRD), using a Rigaku RINT2100/PC diffractometer with monochromated Cu K $\alpha$  radiation, and the ion-exchange ratio was determined by measuring pH value and Na<sup>+</sup> ion concentration in filtrate, using a TOA HM-5S pH meter and a Shimadzu AA6800 atomic absorption spectrometer, respectively.

The neutron diffraction data of deuterated specimens were measured on a time-of-flight (TOF) neutron diffractometer at room temperature, using *Srius* with high-resolution (ca.  $1.0 \times 10^{-3}$  in  $\Delta d/d$ ) at the pulsed spallation neutron facility KENS, High Energy Accelerator Research Organization in Japan. The specimens of ca. 5 g were loaded in a vanadium tube in Ar atmosphere, and set on the diffractometer. The data collection was made by an array of 320 position-sensitive detectors installed in a backward bank with the range  $150 \leq 2\theta$  (°)  $\leq 175$ . 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 in the range  $0.3 \leq d$  (Å)  $\leq 2.3$  were analyzed by Rietveld method, using the program RIETAN-TN for TOF neutron diffraction.<sup>14,15</sup>

## 3. Results and discussion

The XRD revealed that NaLaTiO<sub>4</sub> prepared was a single phase with the tetragonal space group  $P4/nmm$  with  $a = 3.77404(5)$  and  $c = 13.0146(2)$  Å, referring to the previous descriptions.<sup>11–13</sup> The pH value and Na<sup>+</sup> ion concentration of the DCl solution increased during the contact with NaLaTiO<sub>4</sub>, suggesting that D<sup>+</sup> ion loadings into NaLaTiO<sub>4</sub> proceeded by an ion-exchange reaction. The exchange ratio of Na<sup>+</sup>/D<sup>+</sup> was estimated to be about 1.0, and it was found that all Na<sup>+</sup> ions were perfectly exchanged with D<sup>+</sup> ions from the pH change and analytical results by the atomic absorption. Thus, the resulting materials were employed in the measurement for the neutron diffraction, after their XRD pattern was confirmed to be identical to that of HLaTiO<sub>4</sub>.<sup>16</sup>

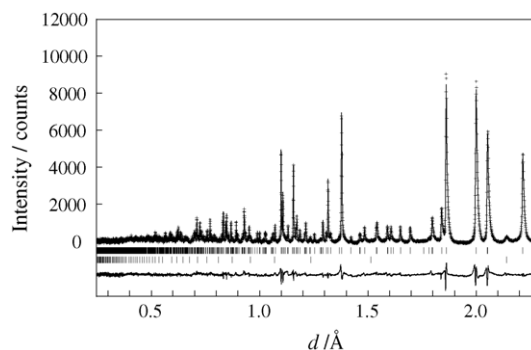


Fig. 1. Observed (plus signs), calculated (solid line), and difference (solid line on the bottom) patterns for TOF neutron powder diffraction of DLaTiO<sub>4</sub>. Vertical marks represent positions calculated for Bragg reflections (upper, DLaTiO<sub>4</sub> and lower, vanadium holder).

As the neutron diffraction data had diffraction peaks of vanadium arisen from the sample holder, the refinement was performed as a mixture of two phases. Starting structural models of DLaTiO<sub>4</sub> were constructed as follows: the constraint was applied to the site occupancy factor for all atoms, assuming that the composition ratios in the specimen were ideal values. As the XRD indicated that HLaTiO<sub>4</sub> was isostructural with parent NaLaTiO<sub>4</sub>, the atomic positional data of NaLaTiO<sub>4</sub>, reported by Toda et al.,<sup>11</sup> were used as initial parameters. The crystal structure of DLaTiO<sub>4</sub> was refined in the space group  $P4/nmm$  on applying isotropic temperature factors to all atoms. The refinement revealed that the structural model, where D atoms were located at the same sites, 2c, as Na atoms in NaLaTiO<sub>4</sub> was poor, because the isotropic temperature factor of the D atom became considerably large, compared with other atoms. Therefore, the structural model, where the D atom was set at the general position, 16k, was adopted in the refinement processes. After several cycles of the least-square refinement, the observed and calculated diffraction patterns were in good agreement with each other as illustrated in Fig. 1. The final structural parameters and  $R$  factors are listed in Table 1.

The refined structural illustration of DLaTiO<sub>4</sub> is shown in Fig. 2, together with that of NaLaTiO<sub>4</sub>. The structure of NaLaTiO<sub>4</sub> consists of (a) TiO<sub>6</sub> octahedral layers, (b) Na interlayers and (c) LaO<sub>9</sub> polyhedral layers ordered with a sequence of  $-(a)-(b)-(a)-(c)-(a)-$  along the  $c$ -axis.<sup>11</sup> The

Table 1  
Structural parameters and final  $R$  values for DLaTiO<sub>4</sub><sup>a</sup>

Atom	Site	$g$	$X$	$y$	$z$	$U_{iso}^b$ (Å <sup>2</sup> )
D	16k	1/8	0.114(1)	0.317(2)	0.4862(4)	0.037(1)
La	2c	1.0	0	1/2	0.8823(1)	0.0047(2)
Ti	2c	1.0	0	1/2	0.2991(2)	0.0093(7)
O1	4f	1.0	0	0	0.2563(1)	0.0064(3)
O2	2c	1.0	0	1/2	0.0772(2)	0.0077(4)
O3	2c	1.0	0	1/2	0.4429(2)	0.0234(6)

<sup>a</sup> Tetragonal,  $P4/nmm$ ,  $a = 3.7232(1)$  Å,  $c = 12.3088(2)$  Å,  $R_{wp} = 2.69\%$ ,  $R_p = 1.97\%$ ,  $R_{wp} = [\sum w_i (y_{io} - y_{ic})^2 / \sum w_i (y_{io})^2]^{1/2}$ ,  $R_p = \sum |y_{io} - y_{ic}| / \sum y_{io}$ .

<sup>b</sup>  $B_{iso} = 8\pi^2 U_{iso}$ .

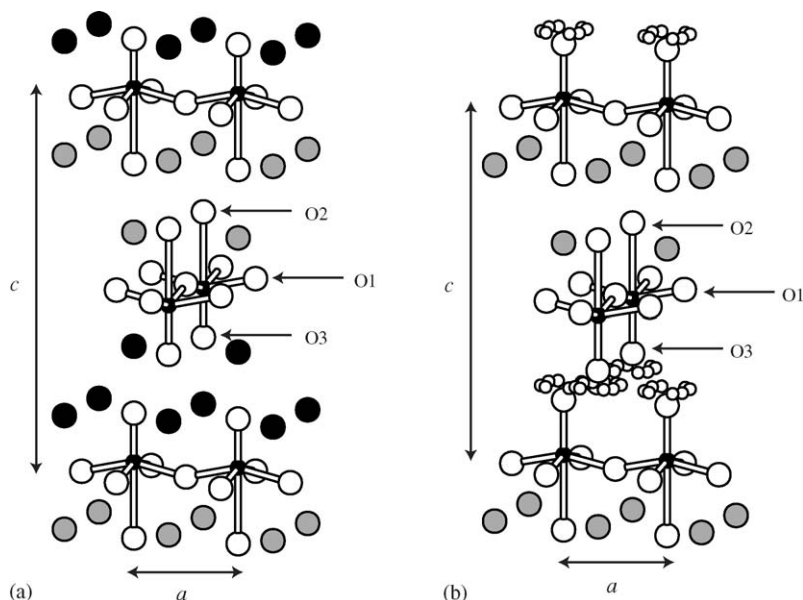


Fig. 2. Schematic illustrations of the structures of (a) NaLaTiO<sub>4</sub> and (b) DLaTiO<sub>4</sub>. Gray circle: La; large black circle: Na; small black circle: Ti; large open circle: O; and small open circle: D.

structure analysis revealed that the structure of DLaTiO<sub>4</sub> was basically similar to that of NaLaTiO<sub>4</sub> except the interlayer structure. The protons in the interlayer of DLaTiO<sub>4</sub> were located at the sites different from the Na atom sites in NaLaTiO<sub>4</sub>. As a result, the interlayer distance of DLaTiO<sub>4</sub> was shortened from ca. 4.57 to 3.7021(3) Å after the ion-exchange reaction. Fig. 3 shows enlarged illustrations of the interlayer where the protons were located. The loaded protons statistically occupied eight equivalent sites around an apical O atom, O<sub>3</sub>, of a TiO<sub>6</sub> octahedron, and the D–O<sub>3</sub> bond length was estimated to be 0.962(4) Å. The D–O<sub>3</sub> bond length was close to the covalent O–H bond length, e.g. the O–H bond length in ethanol is 0.971 Å.<sup>17</sup> It is noted that the D atoms are between two apical O<sub>3</sub> atoms facing each other in the interlayer, as seen in Fig. 3a. In addition to the formation of the

covalent D–O<sub>3</sub> bond, this suggests the formation of hydrogen bond to bridge the TiO<sub>6</sub> octahedral layers, and its bond length was estimated to be 2.054(4) Å.

Selected interatomic distances and bond angles of DLaTiO<sub>4</sub> are compared with the parent NaLaTiO<sub>4</sub> in Table 2, and Fig. 4 shows the comparison between TiO<sub>6</sub> octahedra in NaLaTiO<sub>4</sub> and DLaTiO<sub>4</sub>. The difference of the charge between Na<sup>+</sup> and La<sup>3+</sup> ions leads the Ti atom to displacement from the center of the TiO<sub>6</sub> octahedron toward the Na interlayer in NaLaTiO<sub>4</sub>.<sup>11</sup> Consequently, the TiO<sub>6</sub> octahedron is cooperatively distorted along the *c*-axis as follows. The Ti atom is bonded to the apical O atoms with a short Ti–O<sub>3</sub> bond length of 1.70 Å and long Ti–O<sub>3</sub> bond length of 2.65 Å, and the O<sub>1</sub>–Ti–O<sub>1</sub><sup>ii</sup> bond angle, cf. Table 2, is bent from the ideal bond angle of 180°. Further distortion of the

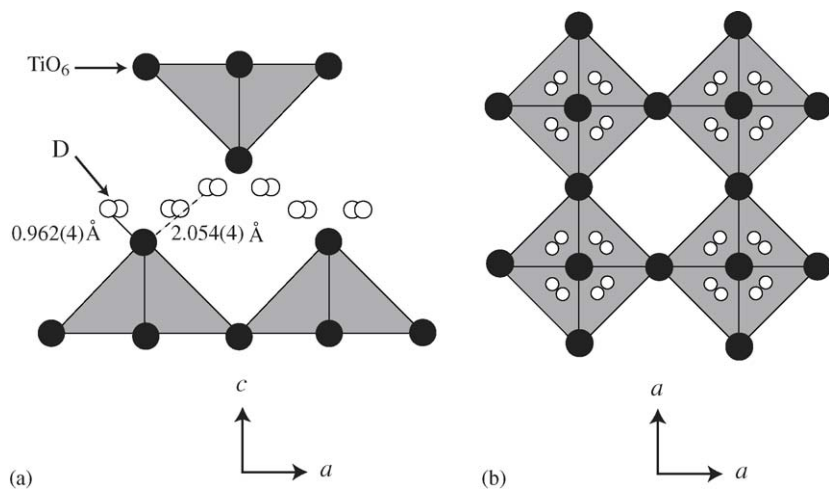


Fig. 3. Schematic illustrations of the location of protons viewed along the (a) *a*- and (b) *c*-axes.

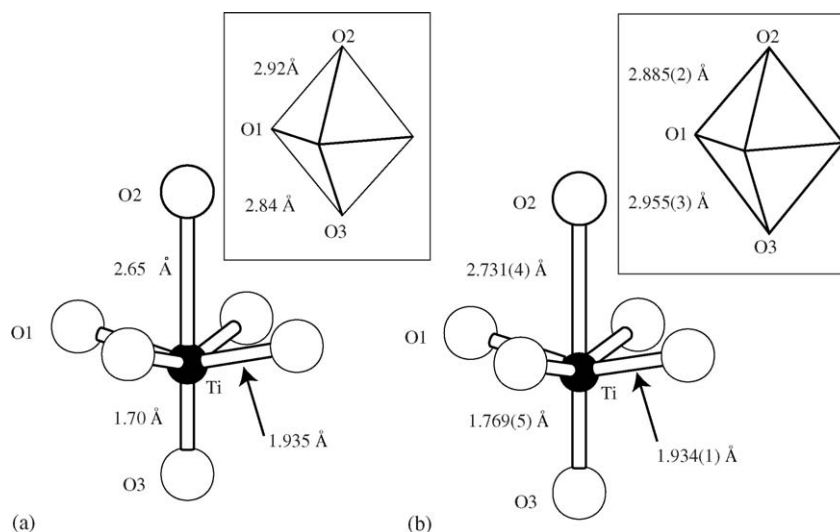


Fig. 4. Schematic illustrations of  $\text{TiO}_6$  octahedra in (a)  $\text{NaLaTiO}_4$  and (b)  $\text{DLaTiO}_4$ . The O1–O2 and O1–O3 distances in  $\text{NaLaTiO}_4$  and  $\text{DLaTiO}_4$  are shown in inserted boxes.

Table 2

Selected interatomic distances (Å) and bond angles ( $^\circ$ ) of  $\text{NaLaTiO}_4$  and  $\text{DLaTiO}_4$

	$\text{NaLaTiO}_4^a$	$\text{DLaTiO}_4$
Interatomic distances		
D–O3	–	0.962(4)
D–O3 <sup>ib</sup>	–	2.054(4)
Ti–O1( $\times 4$ )	1.935	1.934(1)
Ti–O2( $\times 1$ )	2.65	2.731(4)
Ti–O3( $\times 1$ )	1.70	1.769(5)
O1–O2	2.81	2.885(2)
O1–O3	2.74	2.955(3)
Bond angles		
O1–Ti–O1 <sup>iib</sup>	154.7	148.4(2)

<sup>a</sup> Reference 11.

<sup>b</sup> Symmetry codes: (i)  $1/2 - x, -1/2 + y, 1 - z$ ; (ii)  $1 + x, y, z$ .

$\text{TiO}_6$  octahedron along the  $c$ -axis was observed after the ion-exchange of  $\text{Na}^+$  ions with protons. That is, both the Ti–O apical bond lengths of  $\text{DLaTiO}_4$  were lengthened, whereas the Ti–O equatorial bond lengths were hardly changed, and the O1–Ti–O1<sup>ii</sup> bond angle was more narrowed, compared to those of  $\text{NaLaTiO}_4$ . As a result, the O1–O3 distance, which is shorter than the O1–O2 distance in  $\text{NaLaTiO}_4$ , became longer than the O1–O2 distance after the ion-exchange reaction, as seen in Fig. 4. These indicate that the protonation modified not only the interlayer structure but also the  $\text{TiO}_6$  octahedral layer structure.

#### 4. Conclusion

Neutron diffraction study has concluded the crystal structure of  $\text{DLaTiO}_4$  ( $\text{HLaTiO}_4$ ) prepared by the ion-exchange reaction of  $\text{NaLaTiO}_4$  as follows:  $\text{DLaTiO}_4$  was crystallized in the same space group,  $P4/nmm$ , as parent  $\text{NaLaTiO}_4$ . The protons in the interlayer were statistically located at the sites

different from the Na atom sites in the parent  $\text{NaLaTiO}_4$ , i.e., eight equivalent sites around the apical O atom of the  $\text{TiO}_6$  octahedron, and covalently bonded to the apical O atom of  $\text{TiO}_6$  the octahedron. Furthermore, the analytical results suggested the formation of the hydrogen bond to bridge the  $\text{TiO}_6$  octahedral layers. In addition to the modification of the interlayer structure accompanied with the shrinkage of the interlayer space, the protonation influenced the  $\text{TiO}_6$  octahedral layer structure. Namely, the expansion of Ti–O apical bond lengths by the protonation resulted in the further distortion of the  $\text{TiO}_6$  octahedron.

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