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Crystal structure determination and ionic conductivity of layered perovskite compounds $NaLnTiO_4$ (Ln = rare earth)

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Abstract

The layered perovskite compounds $NaLnTiO_4$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Y and Lu) were synthesized by the solid state reaction. The crystal structure of these compounds were determined by the Rietveld analysis. Single phases of the compounds (except for Ln = Lu) could be prepared only under very restricted preparation conditions. The composition of $NaLuTiO_4$ was not a single phase under the conditions employed in this study. Compounds $NaLnTiO_4$ have a tetragonal symmetry for Ln = La–Nd, while an orthorhombic symmetry is observed for Ln = Sm–Lu. The stabilization of $NaLnTiO_4$ is discussed on the basis of the relative sizes of the rare earth and the alkali metal ions. The lowering of the symmetry is considered to be introduced by the mismatch between TiO_2 and LnO_2 layers. Ionic conductivities attributed to the interlayer sodium ions were observed at high temperatures. The magnitude of ionic conductivity of $NaLaTiO_4$, with a single perovskite layer, was much higher than that of $Na_2La_2Ti_3O_{10}$, with a triple perovskite layer. This high ionic conductivity is due to the weak interaction between the perovskite layer and interlayer sodium ions.

Keywords: Layered perovskite; Titanate; Crystal structure; Rietveld analysis; Ionic conductivity

1. Introduction

The layered perovskite compounds $NaLnTiO_4$ (Ln = La, Nd, Sm, Gd, Dy, Y, Tm and Lu) were first prepared by Blasse [1]. The X-ray powder diffraction patterns were successfully indexed on a tetragonal unit cell. Blasse claimed from the indexing that the interlayer cations in $NaLnTiO_4$ are ordered between the two available interlayer sites. This compound is of particular interest because it is the only $AA'BO_4$ compound which contains ordered A-site cations. These layered perovskite compounds could be suitable systems with which to investigate two-dimensional physical peoperties such as luminescence and ionic conductivity attributed to the A-site cations. However, there has been no direct evidence that such ordering really exists. The crystal structure of $NaLnTiO_4$ remains unknown.

In this study we present the synthetic conditions required for the formation of $NaLnTiO_4$ and discuss the proposed structure of these compounds. We also present the ionic conductivities attributed to the interlayer sodium ions at high temperatures. Based on the comparison between $NaLaTiO_4$ with a single perovskite layer and $Na_2La_2Ti_3O_{10}$ with a triple perovskite layer, we discuss the mechanism of ionic conductivitive behavior in layered perovskite compounds.

2. Experimental details

Compounds $NaLnTiO_4$ were prepared by a conventional solid-state reaction. The starting materials were a mixture of sodium carbonate, rare earth oxide and titanium oxide. An excess amount of sodium carbonate (30 mol%) was added to compensate for the loss due to the evaporation of the sodium component. Sodium carbonate can also act as an oxidizing flux [2]. The reactants were ground, pelletized and then fired in an open alumina crucible. The firing temperature of mixture was 900–1000°C for Ln = La–Gd, and 1050°C for Ln = Y and Lu. The mixtures were fired for 30 min.

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After reaction the solid product was washed with methanol and air dried.

Chemical analyses were carried out by the energy-dispersion and wavelength-dispersion fluorescent X-ray methods. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RAD-rA diffractometer using Cu-K_α radiation which was monochromatized by a curved crystal of graphite. The data were collected by a step-scanning mode in the 2θ range of 5°–100° with a step width of 0.02° and a step time of 4 s. Indexing of the powder XRD patterns obtained was accomplished with the aid of the computer program CELL [3]. Structural refinements were performed with a Rietveld program RIETAN [4] on an ACOS2010 computer at Niigata University.

The ionic conductivities of $NaLaTiO_4$ and $NaEuTiO_4$ were measured by a complex impedance technique, using a Hewlett Packard LF impedance analyzer 4192A at the frequencies 5 Hz to 13 MHz in the temperature range 200–500°C. Powder samples were compressed into a pellet at 400 MPa and silver paste was used as the electrode.

3. Results and discussion

The preparation of $NaLnTiO_4$ was described previously by Blasse [1] and Linares and Blanchard [5]. First the $NaLnTiO_4$ was prepared by a method and under conditions similar to those used by these authors. The resulting products were not single-phase but mixtures of $NaLnTiO_4$ and $Na_2Ln_2Ti_3O_{10}$. The synthetic conditions for $NaLnTiO_4$ were investigated in detail in order to obtain single phase materials. After some trial and error we found that $Na_2Ln_2Ti_3O_{10}$ is formed preferentially at high reaction temperatures. To prepare single phase $NaLnTiO_4$, the reaction conditions had to be modified slightly. A low reaction temperature was necessary to obtain the single-phase. The reaction temperature was decreased to 900–1000°C for Ln = La–Gd and 1050°C for Ln = Y. It was found to be necessary to hold the reaction temperature within the range 900–1000°C for Ln = La–Gd and at 1050°C for Ln = Y, since the intermediate compound remains below this temperature range. The diffraction pattern of the intermediate compound can be indexed using an orthorhombic cell with lattice parameters related to those of a pseudocubic perovskite.

The approximate cell parameters were expressed as $2^{1/2}a_p \times 2^{1/2}a_p \times 2a_p$, where a_p is the lattice parameter of the pseudocubic structure. The thermal stability of the intermediate compound is very sensitive to the size of the rare earth ions. The decomposition temperature of the intermediate compounds increases when going from lighter rare earths to heavier ones. For example, the intermediate compounds of Ln = Eu decomposed on heating at about 850°C, whereas those of Ln = Y decomposed at about 1050°C. The single phase compound of Ln = Lu could not be obtained under the preparation conditions used in this study, probably because of the high decomposition temperature of the intermediate compound. Extended heat treatment at a low reaction temperature (i.e. 900°C) was found to be ineffective. The product showed an asymmetric broadening toward the lower side diffraction angle of the XRD pattern. It seems that the broadening is caused by a structural disorder of interlayer cations. As mentioned above, the single-phase sample of $NaLnTiO_4$ was obtained under quite restricted preparation conditions.

Chemical analyses by fluorescent X-ray methods show that the atomic ratio of the single-phase material exhibits stoichiometric composition within experimental error. In an earlier study [6] the space group of $NaLnTiO_4$ was reported to be *P4mm* with tetragonal symmetry, although the refinement of the crystal structure was unsuccessful. Linares and Blanchard [5] pointed out that the symmetry of the rare earth site in the $NaLnTiO_4$ (except for Ln = La) is lower than C_{4v} symmetry because the number of lines observed in the emission spectra of $NaLnTiO_4$:Eu is much greater than expected for C_{4v} symmetry. Therefore, we reexamined the indexing of the XRD patterns of $NaLnTiO_4$ by means of the CELL program. The powder XRD patterns obtained for $NaLaTiO_4$ and $NaEuTiO_4$ are shown in Fig. 1. For Ln = La, Pr and Nd, the XRD

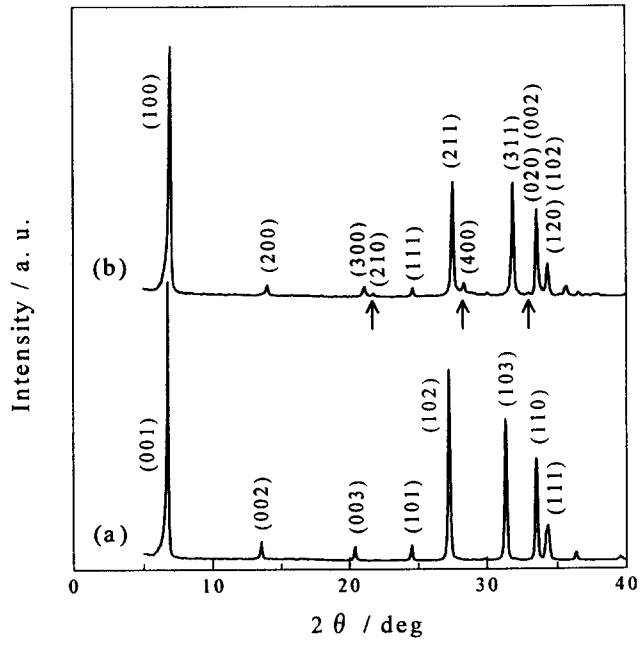

Fig. 1. Powder X-ray diffraction patterns for (a) $NaLaTiO_4$ and (b) $NaEuTiO_4$. Arrows represent the superlattice reflections on the basis of orthorhombic symmetry.

pattern exhibits a simple diffraction pattern without superlattice reflections. The pattern clearly indicates that $hk0$ reflections with $h+k=2n+1$ are systematically absent. All the peaks can be indexed to a tetragonal cell with the $P4/nmm$ space group. However, the XRD patterns for Ln = Sm–Lu are apparently distinguishable from the tetragonal phase. The XRD patterns showed weak extra reflections which could not be explained by refererence to the tetragonal cell with $P4mm$ or $P4/nmm$ space groups. These results clearly indicate that $NaLnTiO_4$ (Ln = Sm–Lu) has a symmetry lower than tetragonal. The reflection conditions found are $k=2n$ for $0kl$ and $0k0$ reflections and $l=2n$ for $h0l$ and $00l$ reflections on the basis of orthorhombic symmetry. These conditions lead to the $Pbcm$ and $Pbc2_1$ space groups.

In this study, we adopted $Pbcm$ space group with higher symmetry than $Pbc2_1$, because some of the standard deviations for structural parameters became fairly large (sometimes one order of magnitude larger than that of $Pbcm$) in the case of $Pbc2_1$ space group for the Rietveld refinement. This space group explains the weak reflections in the XRD patterns. As an example, the results of the pattern fitting for $NaLaTiO_4$ and $NaEuTiO_4$ are shown in Figs. 2 and 3. The structural model for $NaLaTiO_4$ and $NaEuTiO_4$ is illustrated in Fig. 4. Typical crystallographic data finally refined by the Rietveld method are listed in Table 1. The atomic coordinates are very precise, but the atomic temperature factors B are less so. We note that the Bragg peaks with strong l character fitted relatively poorly compared with other peaks. Such discrepancies could result from the occurrence of some stacking faults and a structural disorder in this layered formation due to periodicity of the stacking direction of a perovskite slab.

It is interesting to examine the variation of the lattice parameters and c/a ratios in $NaLnTiO_4$ compounds with the size of the rare earth ion. The c/a ratio is a useful parameter in determining the structural type of K_2NiF_4 phase. The variations of the lattice parameter c and the c/a ratio are illustrated in Fig. 5. The variation of lattice parameter a with the size of the rare earth ions [7] is smaller than that of c/a ratio. Substitution of a larger rare earth ion by a smaller one leads to a decrease in lattice parameter c and c/a ratio. If the BO_6 octahedra were regular and all the A–O distances were identical in the A_2BO_4 compound, the theoretical value of c/a ratio was found to be 3.41. In general, the c/a ratio of K_2NiF_4-type compound is usually found to be 3.3 ± 0.1 [8]. $NaLaTiO_4$ and $NaLuTiO_4$ have unusually high (3.45) and low (3.16) c/a ratios, respectively. If the octahedra in tetragonal $NaLaTiO_4$ are regular, the cell parameter of a would be in the range 0.390–0.396 nm. The observed value (0.377 nm) is much smaller. The high c/a ratio observed for $NaLaTiO_4$ is caused by this a small value of the cell parameter a. Ganguly and Rao [8] presumed from the lattice parameters of $NaLaTiO_4$ that there is a considerable pressure on the Ti–O equatorial distances of the TiO_6 octahedra in $NaLaTiO_4$.

As shown in the refinement results of the crystal structure for $NaLaTiO_4$, the apparent compression of bond is due to the deviation of the titanium ion from

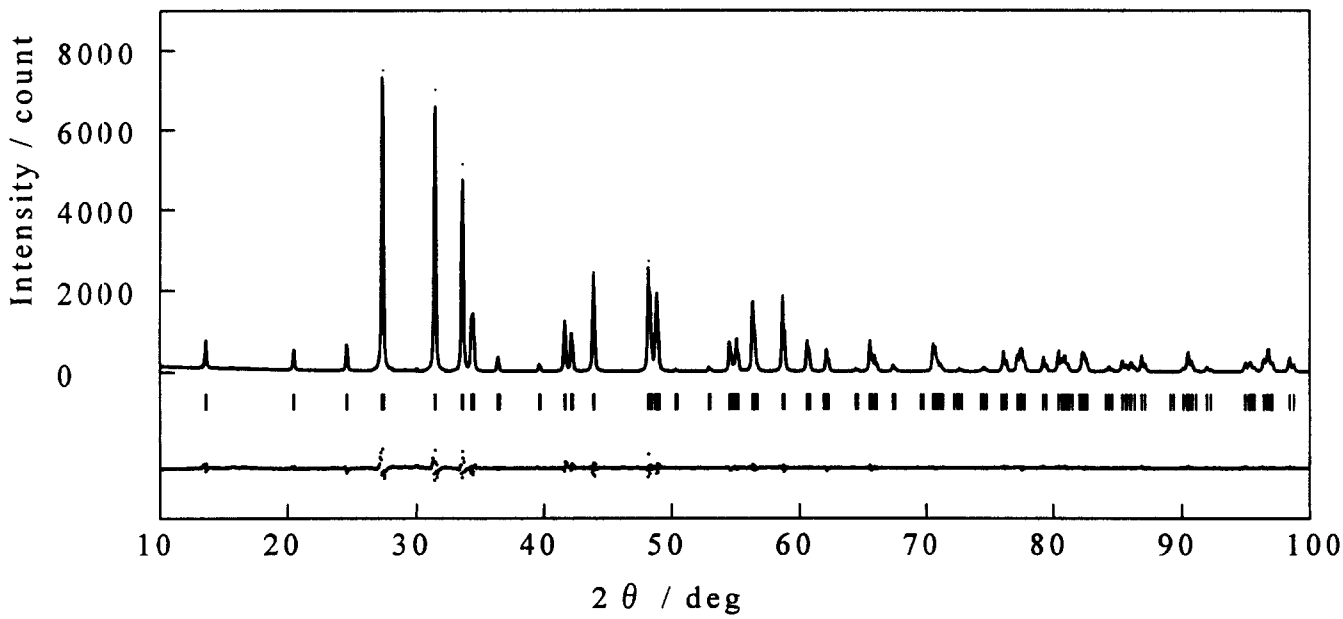

Fig. 2. X-Ray powder pattern fitting for $NaLaTiO_4$. The calculated and observed patterns are shown on the top solid line and the dots above the peaks, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities.

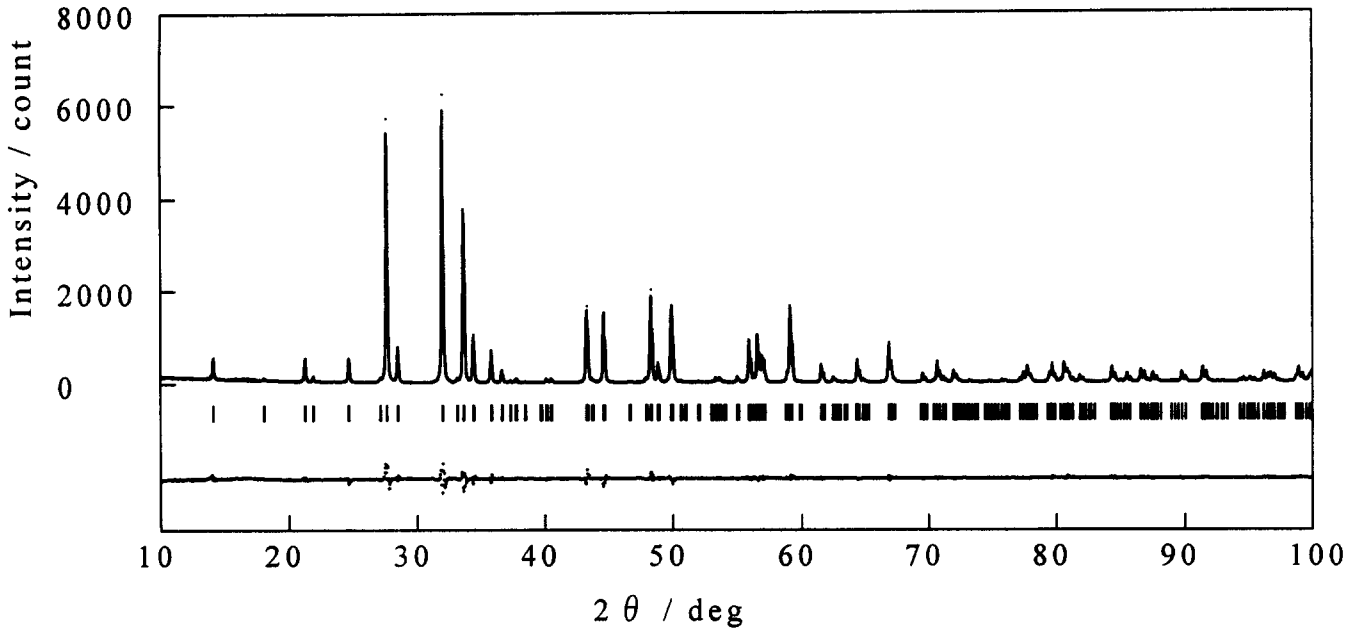

Fig. 3. X-Ray powder pattern fitting for $NaEuTiO_4$.

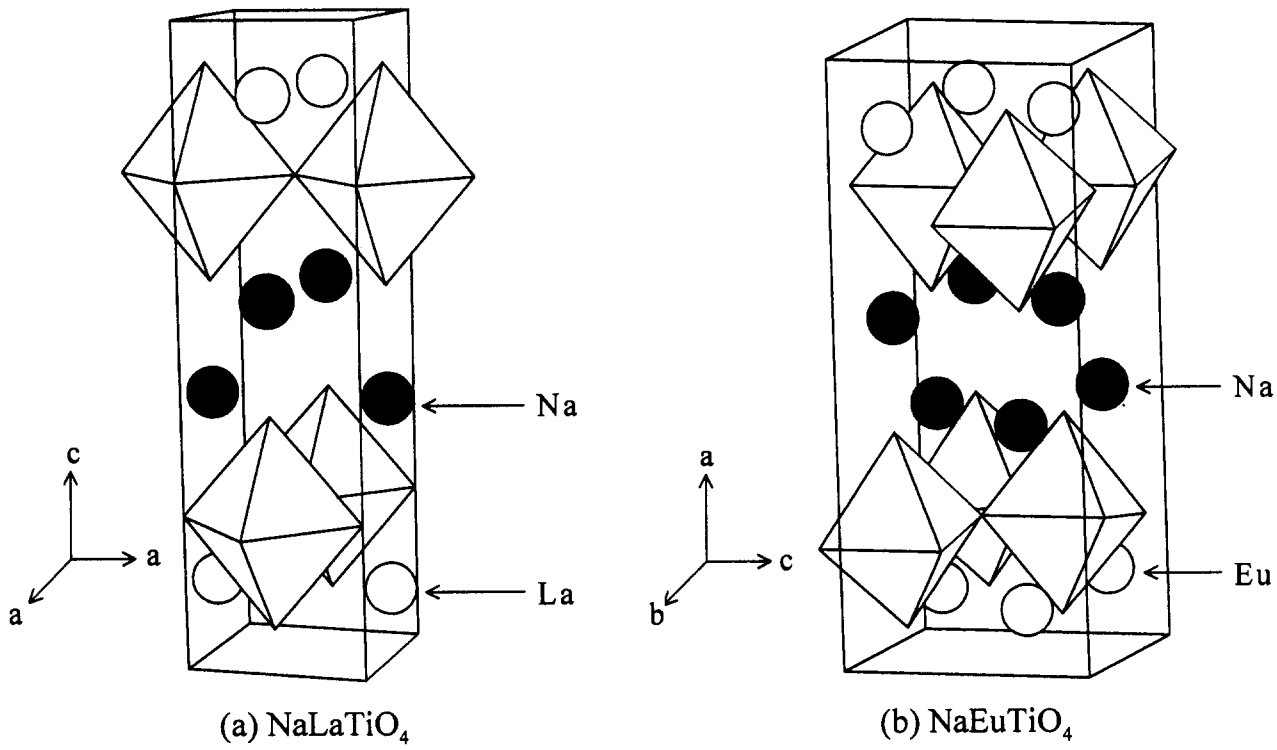

Fig. 4. Structural models of (a) $NaLaTiO_4$ and (b) $NaEuTiO_4$.

the octahedral center. The Ti–O equatorial distance (0.1935(4) nm) is similar to that observed for Sr_2TiO_4, in contrast to Ti–O apical distances with abnormally short (0.170(2) nm) and long bonds (0.265(2) nm). The ordering of the A-site cations in $NaLnTiO_4$-type compounds is due to the large charge difference between sodium and the rare earth ions. The charge imbalance between sodium and the rare earth ions both located at the interlayer is compensated by a displacement of the titanium ions from the position of the regular octahedral center toward the sodium ions. The deformation of TiO_6 octahedra can be regarded as spontaneous distortion rather than constrained compression. Such a distortion of TiO_6 octahedra in these compounds contrasts with that of the Ruddlesden–Popper phase, $Sr_3Ti_2O_7$, which has an almost

Table 1
Crystallographic data for $NaLnTiO_4$ (Ln = La, Eu, Gd and Y)

Sample	Atom	Site[a]	x	y	z	B (nm^2)
$NaLaTiO_4$	Na	2c	0.0	0.5	0.585(1)	0.015(4)
P4/nmm (No. 129)	La	2c	0.0	0.5	0.8890(2)	0.001
a = 0.377404(5)nm	Ti(1)	2c	0.0	0.5	0.2755(6)	0.001
c = 1.30146(2)nm	O(1)	2c	0.0	0.0	0.243(1)	0.003(4)
R_{wp} = 10.47%	O(2)	2c	0.0	0.5	0.072(2)	0.002(6)
R_F = 1.64%	O(3)	4d	0.0	0.5	0.406(2)	0.006(6)
$NaEuTiO_4$	Na	4d	0.5876(9)	0.0118(35)	0.25	0.010(3)
Pbcm (No. 57)	Eu	4d	0.8925(2)	0.0185(5)	0.25	0.002(1)
a = 1.25436(2)nm	Ti(1)	4d	0.2664(4)	0.0069(18)	0.25	0.005
b = 0.53285(4)nm	O(1)	4c	0.2190(19)	0.25	0.0	0.015(8)
c = 0.53281(4)nm	O(2)	4c	0.7547(18)	0.25	0.0	0.003(6)
R_{wp} = 10.80%	O(3)	4d	0.0711(16)	−0.0536(45)	0.25	0.005
R_F = 2.09%	O(4)	4d	0.3996(15)	0.0386(44)	0.25	0.005
$NaGdTiO_4$	Na	4d	0.5896(11)	0.0157(41)	0.25	0.008(3)
Pbcm (No. 57)	Gd	4d	0.8925(2)	0.0217(6)	0.25	0.001(1)
a = 1.24727(4)nm	Ti(1)	4d	0.2652(5)	0.0075(21)	0.25	0.005
b = 0.53349(6)nm	O(1)	4c	0.2130(20)	0.25	0.0	0.015(8)
c = 0.53361(5)nm	O(2)	4c	0.7570(21)	0.25	0.0	0.005
R_{wp} = 10.40%	O(3)	4d	0.0716(18)	−0.0729(63)	0.25	0.007(8)
R_F = 1.73%	O(4)	4d	0.3970(16)	0.0368(53)	0.25	0.005
$NaYTiO_4$	Na	4d	0.5905(9)	0.0154(36)	0.25	0.023(3)
Pbcm (No. 57)	Y	4d	0.8931(2)	0.0298(8)	0.25	0.004(1)
a = 1.22134(3)nm	Ti(1)	4d	0.2610(5)	0.0111(17)	0.25	0.005(1)
b = 0.53517(3)nm	O(1)	4c	0.2062(16)	0.25	0.0	0.010(6)
c = 0.53509(3)nm	O(2)	4c	0.7571(17)	0.25	0.0	0.010(6)
R_{wp} = 9.75%	O(3)	4d	0.0703(15)	−0.0809(50)	0.25	0.012(7)
R_F = 2.25%	O(4)	4d	0.3980(14)	0.0568(49)	0.25	0.011(5)

[a] Multiplicity and Wyckoff notation.

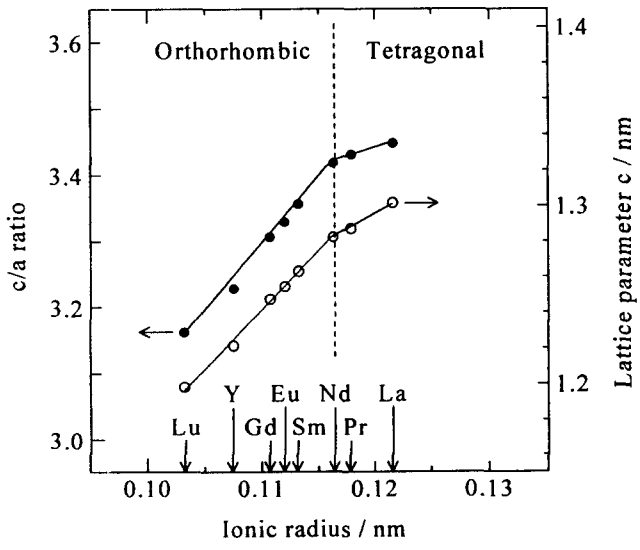

Fig. 5. Variation of lattice parameter c and c/a ratio in $NaLnTiO_4$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Y and Lu) as a function of ionic radius of the rare earth ion.

regular TiO_6 octahedral structure [9]. Blasse and Van Den Heuvel [6] suggested from the IR and Raman spectra of $NaLnTiO_4$ (Ln = La, Gd and Y) that the position of the Ti atom in the TiO_6 octahedra is shifted from the regular central position. The structural refinement results obtained here strongly support their prediction.

The stability of the A_2BO_4 structure is often described in terms of a tolerance factor [10], defined as

$$t = \Psi_A / \sqrt{2}\beta_B \quad (1)$$

where Ψ_A and β_B are invariant values related with A–O and B–O distances in the case of nine- and six-fold coordination of A and B cations, respectively. The calculated tolerance factors of the $NaLnTiO_4$ compounds are given in Table 2. The calculated tolerance factor t(La) of $NaLaTiO_4$ is 0.940. Since the Ti–O–Ti bond is bent considerably from the ideal

Table 2
Lattice parameters and t values for $NaLnTiO_4$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Y and Lu)

Compound	a	b	c	c/a ratio[a]	t(Ln)
$NaLaTiO_4$	3.77404(5)	—	13.0146(2)	3.45	0.940
$NaPrTiO_4$	3.75708(7)	—	12.8711(3)	3.43	0.921
$NaNdTiO_4$	3.75149(8)	—	12.8319(3)	3.42	0.914
$NaSmTiO_4$	12.6292(2)	5.3215(6)	5.3210(5)	3.36	0.903
$NaEuTiO_4$	12.5436(2)	5.3285(4)	5.3281(4)	3.33	0.900
$NaGdTiO_4$	12.4727(4)	5.3349(6)	5.3361(5)	3.31	0.895
$NaYTiO_4$	12.2134(3)	5.3517(3)	5.3509(3)	3.23	0.878
$NaLuTiO_4$	11.9809(8)	5.3583(8)	5.3603(7)	3.16	0.862

[a] The c/a ratio of orthorhombic samples were calculated using the value of the primitive cell.

bond angle of 180°, the effective Ti–O bond distance is reduced. Therefore, t(La) for $NaLaTiO_4$ is close to unity required from the ideal tetragonal geometry, giving an excellent matching of La–O and Ti–O bond lengths. This result is consistent with the fact that the space group of $NaLaTiO_4$ was found to be $P4/nmm$ with tetragonal symmetry. The tolerance factor also explains the change in the symmetry from tetragonal to orthorhombic for $NaLnTiO_4$ (Ln = Sm–Lu). The occurrence of orthorhombic symmetry is ascribable to the mutual tilting of TiO_6 octahedra. The tetragonal structure is assumed to be stable within the limits $1.02 > t > 0.85$ [10]. The tolerance factors t(Ln) for $NaLnTiO_4$ compounds seem to lie on the tetragonal side of boundary tetragonal–orthorhombic transition. TiO_2 slabs are separated by the sodium and rare earth ions in the stacking sequence TiO_2-NaO-NaO-TiO_2-LnO-LnO-. If an A_2BO_4-type compound has $t < 1$, the A–O distance is expected to be increased. The decrease in tolerance factor t(Ln) with decreasing ionic radius of the rare earth ions causes the mismatch between TiO_2 and LnO_2 layers. A considerable energy would be required to stretch the Ln–O bond in the Ln–O layer because of the high charge on the rare earth ions. However, the Na–O interaction is weaker than the Ln–O interaction. The Na–O bond is readily stretched because of the weak interaction. As a result, the slight mismatch between TiO_2 and LnO_2 layers is compensated by the tilting of TiO_6 octahedra.

Fig. 6 shows the temperature dependence of the ionic conductivities for $NaLaTiO_4$ and $NaEuTiO_4$, together with that for $Na_2La_2Ti_3O_{10}$ [11] as a reference. Before measuring the ionic conductivity, it was confirmed by a dc polarization method that the electrical conduction for both samples was mainly ionic. It is interesting to compare the ionic conductivity of $NaLaTiO_4$ with that of $Na_2La_2Ti_3O_{10}$. The ionic conductivity of $NaLaTiO_4$ with a single perovskite layer was much higher than that of $Na_2La_2Ti_3O_{10}$ with a triple perovskite layer. This result suggests that the thickness of the perovskite layer is a fairly important factor in the ionic conductivity of layered titanate

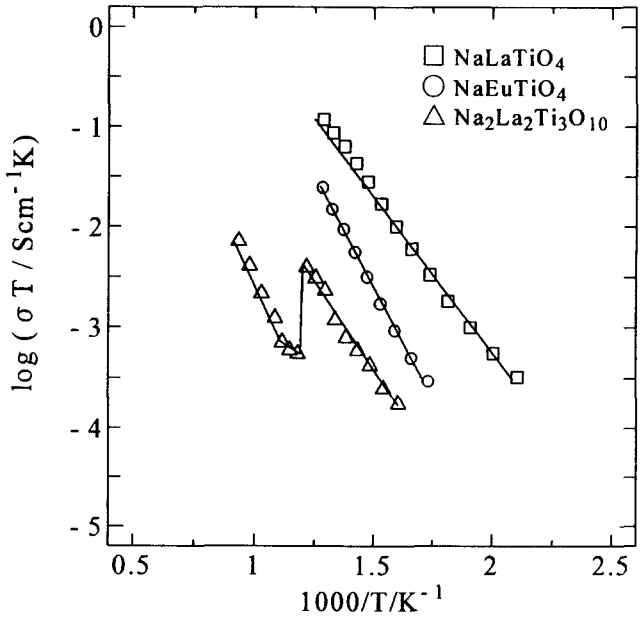

Fig. 6. Temperature dependence of ionic conductivity of $NaLaTiO_4$, $NaEuTiO_4$ and $Na_2La_2Ti_3O_{10}$.

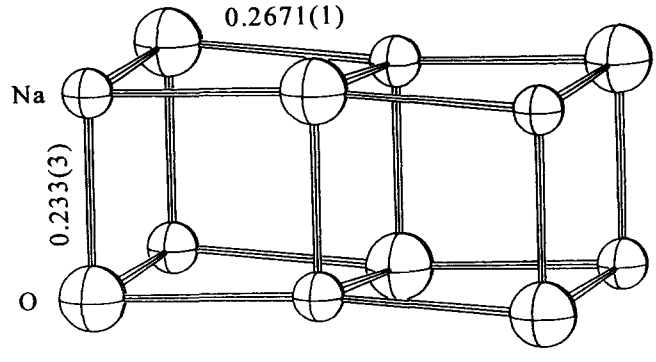

Fig. 7. Environment around sodium atoms in $NaLaTiO_4$.

compounds. This is in contrast to the case of the corresponding layered niobate compounds [12]. The high ionic conductivity observed for $NaLaTiO_4$ is due to a weak interaction between the perovskite layer and interlayer sodium ion.

Fig. 7 shows the environment around sodium ion located between the two perovskite layers in $NaLaTiO_4$. Although the interlayer cations in $NaLaTiO_4$ and $Na_2La_2Ti_3O_{10}$ have the same rock-salt type coordination, there is a relatively large difference for the Na–O bond along the *c*-axis between the two compounds. The bond distance in $NaLaTiO_4$ (0.233 nm) is longer than that for $Na_2La_2Ti_3O_{10}$(0.228 nm). This bond charcter may be reflected in the ionic conductivities for each compounds. In $NaLnTiO_4$ compounds the (LnO) layer is positively charged and the (NaO) layer is negatively charged. Therefore, the perovskite layers are thought to be electrically neutral. As a result the interaction between the perovskite layer and interlayer cation is relatively weak. The perovskite layers of $Na_2La_2Ti_3O_{10}$, however, are negatively charged and separated by interlayer sodium ions, leading to a strong interaction between perovskite slabs and interlayer sodium ions. The strong Na–O bonding would reduce the mobility of the interlayer sodium ion. The measured ionic conductivity of $NaEuTiO_4$ is lower by approximately one order of magnitude than that of $NaLaTiO_4$. This difference is probably due to the orthorhombic distortion, resulting in a small-sized bottleneck in the interlayer space.

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