



New Layered Perovskite Compounds, LiLaTiO_4 and LiEuTiO_4

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新規層状ペロブスカイト化合物 LiLaTiO_4 及び LiEuTiO_4

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New layered perovskite compounds, LiLnTiO_4 ($\text{Ln}=\text{La}$ and Eu), have been synthesized by an ion-exchange reaction from parent sodium compounds, NaLnTiO_4 . The crystal structures of LiLaTiO_4 and LiEuTiO_4 were determined by Rietveld analysis of the powder X-ray diffraction (XRD) patterns. The lithium ion-exchanged compounds retain the crystal symmetry of the parent phases. Although the framework of the perovskite layer of these compounds is the same as that of the parent compounds, there exists a fundamental difference. The lithium ions within the interlayer have a tetrahedral coordination because of small ionic radius for a rock-salt coordination. The structure of LiLaTiO_4 and LiEuTiO_4 consist of intergrowths of the perovskite sheets with the layers of Li-O in a tetrahedral coordination and those of Ln-O in a distorted rock-salt coordination. These compounds exhibit new phases analogous to the Ruddlesden-Popper phase. [Received June 23, 1995; Accepted November 13, 1995]

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1. Introduction

Ion-exchange reactions in inorganic solids can be used to provide metastable phases. An example is the synthesis of novel solid Brönsted acids, $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln}=\text{rare earth}$), from $\text{A}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{A}=\text{K}, \text{Rb}, \text{Cs}$) by an ion-exchange reaction.¹⁾

In the previous study, the crystal structures of layered perovskite compounds, NaLnTiO_4 , were determined.^{2),3)} These compounds show a sequential ordering of the cations of $[-\text{Ln}-\text{Ln}-\text{Na}-\text{Na}-]$. The characteristics of the crystal structure in these compounds are similar to those of ion-exchangeable layered perovskite, $\text{Na}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, with a triple perovskite layer.⁴⁾ It is of interest to study the ion-exchange reaction of the layered perovskites, NaLnTiO_4 , with a single perovskite layer because it is expected that these compounds are candidates for applications in catalysis and optical devices.

In this paper, we report the synthesis of new compounds, LiLaTiO_4 and LiEuTiO_4 , by an ion-exchange reaction from the parent sodium compounds. We also discuss the proposed structure of these compounds.

2. Experimental

The parent compounds, NaLaTiO_4 and NaEuTiO_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 ad-

ded to compensate for the loss due to the evaporation of the sodium component. The mixture was fired for 30 min at 900–1000°C in air. LiLaTiO_4 and LiEuTiO_4 were prepared by the ion-exchange reaction from parent compounds. The ion-exchange reaction of interlayer sodium ions in parent compounds with lithium ion was carried out in molten LiNO_3 at 300–310°C for 12h. The product was washed with distilled water and air-dried at room temperature. The completion of the ion-exchange reaction was confirmed by XRD and X-ray fluorescence analyses.

Powder XRD patterns were recorded on a Rigaku RAD-rA diffractometer, using $\text{Cu K}\alpha$ radiation which was monochromatized by a curved crystal of graphite. The data were collected in 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 achieved with the aid of the computer program CELL.⁵⁾ Data analysis was carried out by the Rietveld method, using the RIETAN-94 profile refinement program.⁶⁾ Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Mac Science thermal analyzer system 001 at a heating rate of 5°C min^{-1} in air.

3. Results and discussion

The ion-exchange compounds, LiLaTiO_4 and LiEuTiO_4 , are obtained in the form of light brownish-white crystallized powder. X-ray fluores-

cence analyses revealed the absence of sodium ion in both compounds. The XRD study of LiLaTiO_4 showed a tetragonal symmetry with only one systematic absence of $h+k=2n+1$ for $hk0$ reflections, indicating the possible space groups of $P4/n$ or $P4/nmm$. On the other hand, reflection conditions of LiEuTiO_4 are $k=2n$ for $0kl$ and $0k0$ reflections and $l=2n$ for $h0l$ and $00l$ reflections on the basis of an orthorhombic symmetry. The possible space groups are $Pbcm$ or $Pbc2_1$. These reflection conditions show crystal symmetry which is the same as those of the parent compounds, NaLaTiO_4 and NaEuTiO_4 . Despite the considerable difference in ionic radii between the lithium and rare earth ions, the symmetry of the ion-exchange compounds is practically unchanged. The Rietveld refinements for the ion-exchange compounds were, therefore, performed assuming the same structural model as that of the parent compounds.

Initial atomic positions were calculated by modifying the coordinates of the parent compounds. In the early refinement stage of ion-exchange compounds, the site assignment for lithium ions was not included. In the final refinement stage, the location of the lithium ion site was estimated using difference Fourier maps. However, it was not possible to locate the remaining lithium atoms from the difference Fourier maps because of their low atomic scattering factor. Therefore, several trial models were fitted to the profiles using the Rietveld program RIETAN.

The small size of the lithium ion leads to a large contraction along the stacking direction of perovskite layers. The spacing between the adjacent perovskite layers in both lithium compounds is about 0.14 nm. This interlayer distance is too small to allow the lithium ions to be in a rock-salt coordination. In addition, ninefold coordination of lithium atoms is unknown in oxides. In these compounds, there is only one possible crystallographic site for the lithium ion. The anomalously short lattice parameters obtained are due to a coordination change of the lithium atom, which is in a fourfold coordinate site. The refinement assuming this fourfold coordinate site of lithium atoms converged to $R_{wp}=13.4\%$, $R_p=10.2\%$, $R_I=3.4\%$, $R_F=1.9\%$ for LiLaTiO_4 and $R_{wp}=15.2\%$, $R_p=11.3\%$, $R_I=6.4\%$, $R_F=4.4\%$ for LiEuTiO_4 . The results of pattern fitting for LiLaTiO_4 and LiEuTiO_4 are shown in Fig. 1. The crystallographic data obtained from Rietveld refinement are listed in Table 1. The structural models for LiLaTiO_4 and LiEuTiO_4 are illustrated in Fig. 2. The coordination of Na-O observed in NaLaTiO_4 and NaEuTiO_4 is a rock-salt type.^{2),3)} In contrast, the lithium ions in both lithium compounds have a tetrahedral coordination. The lithium ion-exchanged compounds, LiLaTiO_4 and LiEuTiO_4 , consist of intergrowths of perovskite sheets with layers of Li-O in a tetrahedral coordination and those of Ln-O in a distorted rock-salt coordination. These compounds are new phases

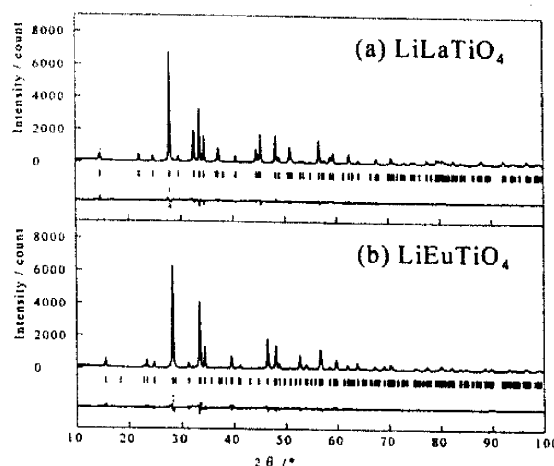


Fig. 1. X-ray powder pattern fitting for (a) LiLaTiO_4 and (b) LiEuTiO_4 . The calculated and observed patterns are shown as the top solid line and the dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The trace on the bottom is a plot of the difference between calculated and observed intensities.

Table 1. Crystallographic Data for LiLaTiO_4 and LiEuTiO_4

Sample	Atom	Site ^{a)}	x	y	z
LiLaTiO_4 P4/nmm (No. 129) a = 0.37718(2) nm c = 1.20829(6) nm	Li	2a	0.0	0.0	0.0
	La	2c	0.0	0.5	0.3802(4)
	Ti	2c	0.0	0.5	0.795(1)
	O(1)	4f	0.0	0.0	0.757(2)
	O(2)	2c	0.0	0.5	0.582(3)
	O(3)	2c	0.0	0.5	0.941(3)
Overall isotropic thermal parameter $Q = 0.1(2) \text{ nm}^2$					
LiEuTiO_4 Pbcm (No. 57) a = 1.14155(7) nm b = 0.5355(1) nm c = 0.5353(1) nm	Li	4c	0.49(2)	0.25	0.0
	Eu	4d	0.8810(4)	0.020(1)	0.25
	Ti	4d	0.290(1)	0.006(4)	0.25
	O(1)	4c	0.240(4)	0.25	0.0
	O(2)	4c	0.745(4)	0.25	0.0
	O(3)	4d	0.088(4)	-0.066(8)	0.25
Overall isotropic thermal parameter $Q = 0.4(1) \text{ nm}^2$					

a) Multiplicity and Wyckoff notation.

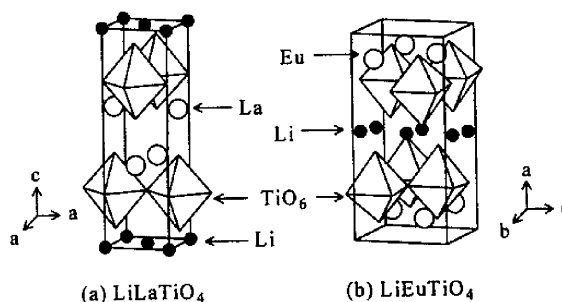


Fig. 2. Structural models of (a) LiLaTiO_4 and (b) LiEuTiO_4 .

analogous to the Ruddlesden-Popper phase.⁴⁾

As described in previous studies,^{2),3)} the charge imbalance between sodium and rare earth ion in parent compounds is compensated by a displacement of the titanium ion from the position of a regular octahedral center toward the sodium ions. Such a short Ti-O dis-

tance leads to less interaction between the sodium atoms of the interlayer and the apex oxygen atoms of the perovskite layers. Therefore, this structural feature may be a cause of ion-exchange reaction with other monovalent ions. The sodium ions in the parent compounds are readily exchanged with lithium ions in molten LiNO_3 , which leads to new layered oxides. The lithium compounds retain the same bond character as that of the parent compounds. In LiLaTiO_4 , the Ti-O bonds are classified into three types: i.e., a very short bond (0.177(4) nm) toward the interlayer, four normal bonds (0.194(1) nm) linked within the perovskite layer and a long bond (0.257(4) nm). These bond distances are similar to those of parent compounds. An important common structural feature for all the series of ion-exchangeable layered perovskite compounds is the presence of extremely short metal-oxygen bonds in the direction of the interlayer alkali metals between the perovskite layers.⁴⁾

DTA and TGA data showed decomposition at about 800°C, which was also confirmed by XRD measurement. The destruction of layered structure was observed above this temperature. The main degradation product is probably three-dimensionally linked perovskite structure, and a large amount of second phase was present. The lithium compounds, which are probably metastable, could only be obtained through the ion-exchange reaction. The difficulty in direct synthesis lies in the fact that the lithium compounds are unstable at high temperature. The lithium compounds do not exist in any hydrous form even when the compounds are washed

with distilled water. These results are in contrast to those of the parent sodium compounds which contain water molecules in the interlayer.⁷⁾ The differences in the hydration behavior can be explained by the small interlayer space which does not allow the insertion of water. The interaction between perovskite layers is much stronger for the lithium compound than for the sodium compound because of the smaller interlayer distance. Therefore, in the lithium compounds, the energetic gains obtained by hydration of lithium ions do not exceed the energy required to expand the interlayer space.

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