Lithium Ion Mobility and Activation Energy for Lithium Ion Conduction in A-Site Deficient Perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$

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A サイト欠損型ペロブスカイト $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ のリチウムイオン伝導におけるリチウムイオン移動度と活性化エネルギー

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The lithium ion conductivity of perovskite-type solid-solutions $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ was measured by the ac impedance method and the activation energy for conduction was determined. The lithium ion mobility was calculated in order to discuss the conductivity behavior. While the ordering at the A-sites as well as the tetragonal distortion lowered the mobility for tetragonal perovskites ($x \leq 0.06$), the mobility decreased with decreasing the lattice parameter for cubic perovskites ($0.075 \leq x \leq 1/6$). The logarithm of the mobility was found to decrease linearly with increasing the activation energy. It was concluded that the lithium ion mobility was the major factor in influencing lithium ion conduction in this solid-solution system.

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1. Introduction

Much attention has been paid to lithium ion conductors because of their potential applications as solid electrolytes in high energy density batteries and electrochemical devices. Recently, the lithium ion conductors, such as $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$,^{2),3),10),11)} $\text{Ln}_{1/2}\text{Li}_{1/2}\text{TiO}_3$ (Ln=La, Pr, Nd and Sm)^{1),3),8),9),12)} and $\text{La}_{1/3-x}\text{Li}_{3x}\text{NbO}_3$,⁴⁾ derived from A-site deficient perovskites have been reported. Their high lithium ion conductivity is considered to be attributed to the presence of many equivalent sites available for lithium ion migration.

We have prepared the perovskite-type solid-solutions $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ ($x \leq 1/6$) by substituting 3Li^+ for La^{3+} in the A-site deficient perovskite $\text{La}_{1/3}\text{TaO}_3$ and measured the lithium ion conductivity at room temperature.⁵⁾ The maximum conductivity of $7 \times 10^{-3} \text{ S} \cdot \text{m}^{-1}$ was found at a composition of $x=0.06$ which differed from the composition with the maximum carrier concentration. In the present paper, we investigated the ordering at A-sites, lithium ion mobility and activation energy, in order to find out the major factor in influencing lithium ion conduction.

2. Experimental

La_2O_3 (4N), Li_2CO_3 (3N) and Ta_2O_5 (3N) supplied from Nacalai Tesque Inc. were used as starting materials. These reagents were weighed, mixed in an alumina mortar with ethanol, dried and calcined in air at 973 K for 12h. After grinding, the calcined powder was uniaxially pressed at 30 MPa and then isostatically pressed at 200 MPa into a pellet with 15 mm in diameter and 2 mm in thickness. The pellet was put into a Pt container together with the calcined powder of the same composition and fired at 1773 or 1823 K for 48h in air. After regrinding, a repressed pellet was sintered under the same conditions as mentioned above. Sintered samples were polished and were characterized as follows.

Identification of crystalline phases and determination of lattice parameters were carried out by X-ray powder diffraction (XRD; Rigaku, RAD-rA) analysis using $\text{Co K}\alpha$ radiation. Au paste was painted on both faces of the sample as

blocking electrodes. An ac impedance method was used to determine bulk conductivity. The measurement was carried out in air over the temperature range from room temperature to 673 K and the frequency range from 5 Hz to 13 MHz, using a YHP4192A impedance analyzer.

3. Results and discussion

3.1 Ordering of cations and vacancies at the A-sites

In the previous paper,⁵⁾ we have reported the presence of ordering of cations and vacancies at the A-sites in the tetragonal perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ ($x \leq 0.06$). The present paper describes the composition dependence of an order parameter (δ). The crystal structure of $\text{La}_{1/3}\text{TaO}_3$ has been determined.⁶⁾ In Fig. 1, lanthanum ions statistically occupy two thirds of the A_1 -sites in the (002) plane. All of the A_2 -sites in the (001) plane and one third of the A_1 -sites are vacant. The similar distribution of cations and vacancies is expected to occur in the ordered phases of the solid-solutions $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$.

Abe and Uchino⁷⁾ have investigated the structure of the A-site deficient perovskite $\text{La}_{2/3}\text{TiO}_{3-\lambda}$. We applied their

Fig. 1. A model proposed for the unit cell of the tetragonal perovskite $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ (perfectly ordered).

method to $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$ and determined δ on the following assumptions.

(a) Lanthanum and lithium ions occupy only the A_1 -sites in the ordered phase ($\delta=1$).

(b) The distribution of vacancies, lanthanum and lithium ions is random at each of the A_1 - and A_2 -site in partially ordered phases ($0 < \delta < 1$); this results in a tetragonal unit cell with a dimension of $a' \times a' \times 2c'$ as shown in Fig. 1. Equation (1) was used to estimate the value of δ .

$$I^{\text{sup}} \propto \{(1/3-x)f_{\text{La}} + 3xf_{\text{Li}}\}^2 \delta^2 \quad (1)$$

It must be noticed that δ is a relative parameter because no effects of atomic displacement and tilting of TaO_6 octahedra are included in Eq. (1). Here, I^{sup} is the intensity of superstructure lines and f_{La} and f_{Li} are atomic scattering factors of lanthanum and lithium, respectively. The intensity of fundamental structure lines is independent of δ . We calculated the intensity of the superstructure line of (001) and the fundamental structure line of (010) and then obtained the relationship between their intensity ratio and δ . We determined δ by comparing the calculated and observed intensity ratios. The values of δ for $x=0.025$, 0.05 and 0.06 are, respectively, 0.46, 0.34 and 0.31.

Figure 2 shows the relationship between the tetragonal distortion (c'/a') and order parameter (δ). Substitution of 3Li^+ for La^{3+} reduced both the tetragonal distortion and order parameter, and led to cubic symmetry at $x=0.075$. A distorted bottleneck for lithium ion transport may result from the tetragonal distortion. Therefore, we expect that lanthanum and lithium ions and vacancies should not be distributed statistically at the A-sites and that the potential difference between the A_1 - and A_2 -sites should occur.⁸⁾

3.2 Lithium ion conductivity and mobility at room temperature

In the previous paper⁵⁾ on the perovskites $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$, we have studied the relationship between the lithium ion conductivity at room temperature and estimated effective carrier concentration, and showed that the composition dependence of the conductivity markedly differed from that of the effective carrier concentration.

Itoh et al.⁹⁾ found that the lithium ion conductivity was related to the lattice parameters of the perovskites (Ln , Li) TiO_3 , where Ln is La , Pr , Nd or Sm . Furthermore, for $\text{La}_{2/3-x}\text{Li}_x\text{TiO}_3$ ^{2),3),10)} in which little variation in the lattice parameter was observed with increasing x , the activation energy for lithium ion conduction was almost independent of x . The dependence of the effective carrier concentration on the conductivity was able to be explained on the assumption that the lithium ion mobility was independent of x . On the other hand, for $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$, marked decrease in lattice parameters was observed with increasing x . Contraction of the bottleneck size for lithium ion transport is con-

Fig. 2. Relationship between the tetragonal distortion (c'/a') and order parameter (δ) for the perovskites $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$.

Fig. 3. Lithium ion conductivity, σ (○) and mobility, u (●) at room temperature as a function of composition for the perovskites $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$.

sidered to significantly decrease the lithium ion mobility.

We calculated the lithium ion mobility for $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$ and compared with the lithium ion conductivity as follows. The lithium ion conductivity (σ) is given by Eq. (2),

$$\sigma = e \cdot C \cdot u \quad (2)$$

where e is the electronic charge, C is the effective carrier concentration and u is the carrier mobility. The effective carrier concentration in the perovskites $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$ can be calculated by Eq. (3).⁵⁾

$$C = \{3x(2/3-2x)(2/3+x-f_c)^2\} \cdot \{(2/3+x)^2 V_p\}^{-1} \quad (3)$$

Here, f_c is the threshold of site percolation and V_p is the volume of the perovskite primitive cell ($V_p = a_p^3$). If all the lithium ions and vacancies at the A-sites contribute to conduction, the lithium ion mobility can be estimated by Eq. (4).

$$u = \sigma V_p (2/3+x)^2 \cdot \{3x(2/3-2x)(2/3+x-f_c)^2 e\}^{-1} \quad (4)$$

Figure 3 shows the composition dependence of the conductivity measured at room temperature and estimated mobility. The variation in the lithium ion mobility is very similar to that in the conductivity. The lithium ion mobility was maximum at $x=0.06$ where the maximum conductivity was seen. a_p was nearly constant in the tetragonal perovskites and was larger in the tetragonal perovskites than in the cubic perovskites.⁵⁾ It is, therefore, expected that the lithium ion mobility should be nearly constant in the tetragonal perovskites and should be higher in the tetragonal perovskites than in the cubic perovskites. However, the lithium ion mobility decreased with decreasing x in the tetragonal perovskites, as seen in Fig. 3; this is attributed to the tetragonal distortion. In the cubic perovskites, no ordering was observed at the A-sites and a_p decreased with increasing x . This decrease in a_p lowered the lithium ion mobility.

3.3 Temperature dependence of the lithium ion conductivity

In the previous section, we have mentioned that the lithium ion conductivity at room temperature is predominantly controlled by the lithium ion mobility in the perovskites $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$. In this section, in order to clarify the effect of the lithium ion mobility on the conductivity, we estimate the activation energy for lithium ion conduction and discuss the relationship among the lithium ion conductivity, mobility and activation energy.

Figure 4 shows temperature dependence of the lithium ion conductivity for $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$ in the Arrhenius formalism. For simplicity, part of the obtained data are included in Fig. 4. For the perovskites $\text{La}_{1/3-x}\text{Li}_x\text{TaO}_3$, it is apparent that the activation energy for lithium ion conduction

Fig. 4. Arrhenius plots of the conductivity for the perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$.
 $\circ$ $x=0.025$, $\bullet$ $x=0.06$, $\triangle$ $x=1/12$, $\blacklozenge$ $x=0.1$, $\blacksquare$ $x=0.12$, $\blacktriangle$ $x=1/6$.

Fig. 5. Relationship between the activation energy, E_a and lattice parameter, a_p for the perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$.
 $\circ$ tetragonal structure, $\bullet$ cubic structure.

Fig. 6. Relationship between the activation energy, E_a and lithium ion mobility, u at room temperature for the perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$.

is dependent of composition (x). The activation energy was estimated from these conductivity data up to 573 K.

Figure 5 shows a relationship between the activation energy for lithium ion conduction and lattice parameter (a_p). In the cubic perovskite structures, the activation energy decreases with increasing a_p . For the perovskites (Ln, Li) TiO_3 (Ln: La, Pr, Nd or Sm), Itoh et al.⁹⁾ have indicated that the lattice parameters increase with increasing ionic radius of Ln, leading to decrease in the activation energy.

For the perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, the lattice parameters are varied with the number of La acting as a spacer. Thus, it is considered that the lattice parameter dominates the activation energy and conductivity for $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ as well as (Ln, Li) TiO_3 although different ions are included in the two systems. However, in the tetragonal perovskites ($\circ$), the activation energy increases with increase in the tetragonal distortion. As described above, the ordering was observed to occur at the A-sites in the tetragonal structures. The ordering at the A-sites or tetragonal distortion should give rise to difference in the lattice potential between the A_1 - and A_2 -sites. Noting that a_p includes no factor due to the ordering at the A-sites in the tetragonal structures, the deviation from the linear relation between E_a and a_p should be ascribed to the distortion of the bottleneck.

Figure 6 shows a relationship between the activation energy and lithium ion mobility at room temperature calculated from Eq. (4). It can be seen that the logarithm of the lithium ion mobility decreases linearly with increase in the activation energy.

From Figs. 5 and 6, the lithium ion mobility depends on the lattice parameter and controls the lithium ion conductivity for the cubic perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$. For the tetragonal perovskites, the ordering at the A-sites raises the activation energy for lithium ion conduction.

4. Conclusions

We prepared the perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ by solid state reaction and discussed the ordering at the A-sites, lithium ion mobility and activation energy for lithium ion conduction; the conclusions are as follows.

(1) For the tetragonal perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, the order parameter and tetragonal distortion increased with decreasing x .

(2) The variation in the lithium ion mobility with x was found to be similar to that in the conductivity.

(3) For the cubic perovskites, a linear relationship was observed between the activation energy for lithium ion conduction and logarithmic mobility.

(4) The lithium ion mobility increases with increasing lattice parameter for the cubic perovskites. The lattice parameter is considered to control the bottleneck size for lithium ion transport.

(5) The ordering of cations and vacancies at the A-sites raises the activation energy and reduces the lithium ion mobility. This results from the distortion of the bottleneck for lithium ion transport.

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