— Note —

Lithium Ion Conductivity in A-site Deficient Perovskites $\text{Sr}_{0.5}\text{La}_{0.05}\text{Li}_{0.35}\square_{0.1}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ and $\text{Sr}_{0.35}\text{La}_{0.15}\text{Li}_{0.35}\square_{0.15}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$

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A-site deficient perovskites $\text{Sr}_{0.5}\text{La}_{0.05}\text{Li}_{0.35}\square_{0.1}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ and $\text{Sr}_{0.35}\text{La}_{0.15}\text{Li}_{0.35}\square_{0.15}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ were synthesized, and their structures and lithium ion conductivities were investigated. Both compounds have cubic symmetry (space group; $Pm\bar{3}m$) and the A- and B-site ions are randomly distributed. The ionic conductivities for the bulk part at 300 K are $6.8 \times 10^{-4} \text{ S cm}^{-1}$ for $\text{Sr}_{0.5}\text{La}_{0.05}\text{Li}_{0.35}\square_{0.1}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ and $7.2 \times 10^{-4} \text{ S cm}^{-1}$ for $\text{Sr}_{0.35}\text{La}_{0.15}\text{Li}_{0.35}\square_{0.15}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$, respectively, which are higher than that of $\text{Sr}_{0.5}\text{Li}_{0.5}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ ($5.5 \times 10^{-4} \text{ S cm}^{-1}$). The ionic conduction of their compounds was found to be based on the vacancy process as was observed for other perovskite-type lithium ion conductors.

Key Words : Lithium Ion Conductivity, Perovskite, Vacancy, Percolation

1 Introduction

Research on lithium ion conducting solid electrolytes is of great interest because of their potential application in high energy batteries, chemical sensors, separators and so on. Among them much attention has been recently paid to lithium ion conducting perovskites due to their high conductivity. Latie *et al.*¹⁾ and Belous *et al.*²⁾ first reported lithium ion conductivity in perovskite-type oxides $\text{Ln}_{1/3}\text{Li}_x\text{Nb}_{1-x}\text{Ti}_x\text{O}_3$ ($\text{Ln} = \text{La}$ and Nd) and $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$, respectively. Since a perovskite lanthanum lithium titanate was found to show high lithium ion conductivity $10^{-3} \text{ S cm}^{-1}$ at room temperature,³⁾ lithium ion conducting perovskites was again evoked and many researches concerning the high lithium ion conductivity in perovskite-type oxides have been made. The study on lithium ion conductivity in perovskite-type oxides is still important in the solid state chemistry and solid state ionics by the following experimental results: (1) Cation conductivity other than proton has not been known in the perovskite-type oxides. (2) Highest lithium ion conductivity, which is comparable to that of $\text{Li}^+/\beta\text{-alumina}$,⁴⁾ is attained in the crystal with higher crystal symmetry. (3) The importance of vacancy/carrier ratio has experimentally been confirmed.⁵⁻⁸⁾ (4) Site percolation model has been found to hold for the lithium ion-conducting path through A-sites.^{7,9,10)} (5) Activation energy is simply related to the size of lattice, *i.e.*, the bottleneck formed by the four oxygen ions.¹¹⁻¹⁴⁾ (6) Covalency of the host lattice is indispensable to the migration of lithium ions.¹⁵⁾

Recently, there were several reports on the Sr-based lithium ion conducting perovskites.^{9,16,17)} One of aims of their researches is to obtain higher ionic conductivity than La-based compounds, for example, $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$. This idea is based on the result (5).

The adoption of Sr^{2+} , which is larger than La^{3+} will dilate the bottleneck size and cause a reduction of the activation energy for ionic conduction, resulting in higher ionic conductivity. In our earlier work,⁹⁾ perovskite-type oxides $\text{Sr}_p\text{Li}_{1-p}\text{Ti}_p\text{Ta}_{1-p}\text{O}_3$ were synthesized and the ionic conductivity was elucidated. Resultingly, the variation of the lithium ion conductivity at room temperature versus p in $\text{Sr}_p\text{Li}_{1-p}\text{Ti}_p\text{Ta}_{1-p}\text{O}_3$ could be explained by the view of the site percolation for simple cubic lattice and the maximum conductivity at 300 K ($5.5 \times 10^{-4} \text{ S cm}^{-1}$) was observed when $p = 0.5$. The conductivity was, however, less than that of $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$.

In this study, in order to investigate the vacancy process in addition to site percolation in the ionic conduction and enhance the ionic conductivity in $\text{Sr}_p\text{Li}_{1-p}\text{Ti}_p\text{Ta}_{1-p}\text{O}_3$, we attempted the introduction of vacancy in A-sites by the substitution of La^{3+} ion for Li^+ ions ($3\text{Li}^+ \rightarrow \text{La}^{3+} + 2\square$) (case 1) and Sr^{2+} plus Li^+ ions ($\text{Sr}^{2+} + \text{Li}^+ \rightarrow \text{La}^{3+} + \square$) (case 2). As the first attempt, we synthesized A-site deficient perovskites $\text{Sr}_{0.5}\text{La}_{0.05}\text{Li}_{0.35}\square_{0.1}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (case 1) and $\text{Sr}_{0.35}\text{La}_{0.15}\text{Li}_{0.35}\square_{0.15}\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (case 2) (abbreviated as SR50LA5 and SR35LA15 below) and the structure and lithium ion conductivity were investigated.

2 Experimental

Samples were prepared by a conventional solid state reaction. Starting materials were $\text{SrCO}_3(3\text{N})$, $\text{Li}_2\text{CO}_3(3\text{N})$, $\text{La}_2\text{O}_3(4\text{N})$, $\text{TiO}_2(3\text{N})$ and $\text{Ta}_2\text{O}_5(3\text{N})$. The amount of metal in reagent La_2O_3 was determined by quantitative analysis using EDTA. Starting materials were mixed in an agate mortar with ethanol. The mixed powders were calcined at 1073 K for 4 h, 1273 K for 12 h and 1373 K for 12 h in air with intermediate grindings. The calcined powder was pressed into a pellet (10 mm in diameter and 1 to 2 mm in thickness) and fired at 1523 K for 6 h

in air. The phase identification and determination of lattice parameter of samples were performed by powder X-ray diffraction analysis with $\text{CuK}\alpha$ radiation using Rigaku or Mac Science X-ray diffractometers equipped with a graphite monochromator. Si powder (5N) was used as an internal standard in the determination of the lattice parameter. Crystal structure of SR50LA5LI35 was also analyzed using Rietveld analysis program, RIETAN,¹⁸⁾ and data was collected by accumulating counts for 1 sec at 0.02 degree intervals in the range $2\theta = 20$ to 120 degree. The lithium ion conductivity of the samples with electrodes of gold paste was measured by ac impedance method using a Hewlett Packard 4192A impedance analyzer over the frequency range from 5 Hz to 13 MHz and temperature range from 238 K to 500 K.

3 Results and Discussions

Figures 1(a) and (b) show the powder X-ray diffraction patterns for SR50LA5 and SR35LA15, respectively. These patterns indicate that both compounds possess simple cubic perovskite-type structure the same as $\text{Sr}_p\text{Li}_{1-p}\text{Ti}_p\text{Ta}_{1-p}\text{O}_3$ does. A small amount of impurity phases, e.g. LiTaO_3 was observed. No extra peaks ascribed to superstructure were observed. The lattice parameters at room temperature (290 K) for SR50LA5 and SR35LA15 are 392.70 ± 0.03 and 391.44 ± 0.02 pm, respectively. The difference in parameter is thought to be originated from the average size of A-site ion radii estimated from the data after Shannon (Sr(XII): 144 pm and La(XII): 138 pm¹⁹⁾). Figure 2 shows the X-ray diffraction profile fit and difference patterns of SR50LA5 using space group $Pm\bar{3}m$. The crystal data, the refined values of atomic parameters are listed in Table 1. Here, we supposed that Sr, La in ideal A-sites (1a site) and Ti and Ta in B-sites (1b

Fig. 1 Powder X-ray diffraction patterns for (a) SR50LA5 and (b) SR35LA15.

Fig. 2 Calculated (continuous line), observed (points) X-ray diffraction patterns, and expected peak positions (vertical markers) for SR50LA5. The residuals are shown below the diffraction patterns.

Table 1 Crystallographic data for SR50LA5.

Atom	x/a	y/a	z/a	$100B/\text{nm}^2$
Sr,La	1a	0.0	0.0	0.0
Li	8g	x^*	x^*	x^*
Ti,Ta	1b	0.5	0.5	0.5
O	3c	0.0	0.5	0.5

$x^* = 0.14 \pm 0.12$. Occupation factors are Sr,La, 0.55;

Li, 0.35. Space group $Pm\bar{3}m$ (No.221);

$a = 392.785 \pm 0.002$ pm; $Z = 1$, $R_{wp} = 6.93\%$, $R_p = 5.15\%$,

$R_e = 2.48\%$, $R_i = 2.50\%$, $R_F = 1.93\%$

site) are randomly distributed. According to a potential calculation, the stable position for Li is displaced from 1a site and is on 8g site.¹⁵⁾ When this model was adopted, slightly better reliable factor was obtained than that obtained when Li is on 1a site ($R_{wp} = 7.00\%$) or on the bottleneck (3d site) ($R_{wp} = 6.97\%$). Since the error of fractional coordinate was fairly large and the isotropic atomic displacement parameter B of Li was not refined (B was fixed to be zero, because B had a minus value) due to the small scattering factor of Li, neutron diffraction experiments are necessary to refine more precisely.

Figure 3 shows the complex impedance plots for SR50LA5 measured by using blocking Au electrodes at 300 K. The plots for SR35LA15 showed the same tendency. As shown in Fig.3, a semi-circle in the high frequency region and spike can be observed. The semi-circle is attributed to the bulk part of the sample when considering the associated capacitance; the capacitance has a magnitude of 100 pF. Figure 4 shows the Arrhenius plots for lithium ion conductivity from 238 K to 500 K for SR50LA5 and SR35LA15. The lattice parameters, ionic conductivities at 300 K and the pre-exponential factors and the activation energies for ionic conduction were summarized in Table 2. The pre-exponential factor σ_0 , activation energy $E_{a\sigma T}$ and $E_{a\sigma}$ were obtained from a least squares fit of the conductivity data below 400 K to the formulae $\sigma T = \sigma_0 \exp(-E_{a\sigma T}/k_B T)$ and $\sigma = A \exp(-E_{a\sigma}/k_B T)$. The ionic conductivities for the bulk part at 300 K of SR50LA5 ($6.8 \times 10^{-4} \text{ S cm}^{-1}$) and SR35LA15 (7.2

Fig. 3 Complex impedance plots of SR50LA5 at 300 K.

Fig. 4 Temperature dependence of the logarithmic bulk ionic conductivity for SR50LA5 (open circles) and SR35LA15 (open squares).

Table 2 Data regarding the lattice parameters, lithium ion conductivities at 300 K, pre-exponential factors σ_0 and activation energies E_a for SR50LA5 and SR35LA15.

Sample	Lattice constant /pm	Conductivity (300 K)/S cm ⁻¹	σ_0 /S cm ⁻¹ K	$E_{a\sigma T}$ /eV	$E_{a\sigma}$ /eV
SR50LA5	392.70 ± 0.03	6.8 × 10 ⁻⁴	8.8 × 10 ⁴	0.34	0.31
SR35LA15	391.44 ± 0.02	7.2 × 10 ⁻⁴	7.6 × 10 ⁴	0.33	0.31

× 10⁻⁴ S cm⁻¹) are higher than that of Sr_{0.5}Li_{0.5}Ti_{0.5}Ta_{0.5}O₃ (5.5 × 10⁻⁴ S cm⁻¹). This implies that lithium ion conduction in them is based on the vacancy process that lithium ions migrate via vacancies in A-sites as in other perovskite-type lithium ion conductors. When considering the simple vacancy process that a lithium ions migrate via vacancies in A-sites and site percolation in the same way as we considered for La_{2/3-x}Li_{3x}□_{1/3-2x}TiO₃, the conductivity can be described by the following relation.⁷⁾

$$\sigma \propto m(1-m)(n-n_c)^2 \quad (1)$$

Here, m represents the ratio of the concentration of lith-

ium to the concentration of lithium plus vacancy n . n_c represents the percolation threshold for simple cubic lattice (0.3117).²⁰⁾ The values of right side of the equation for SR50LA5 and SR35LA15 are 3.3×10^{-3} and 7.4×10^{-3} , respectively. Though we could expect that the conductivity of SR35LA15 was more than twice of that of SR50LA5 from these values, in fact almost same values were obtained as seen in Table 2. Furthermore, the activation energies for ionic conduction and σ_0 are also same. These results imply that the conductivity can not be explained under the assumption that the circumstances of conduction pass are average in these compounds. The presence of two kinds of atom, Sr and La on A-sites may cause the local distortion^{5,10)} and influences the conductivity, e.g. it is thought that the bottleneck around La is narrower than that around Sr, which decreases the conductivity. We will synthesize other relative compounds, elucidate the ionic conduction more detail.

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