Molecular Dynamics Simulation of the High Lithium Ion Conductor, $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$

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高リチウムイオン伝導体, $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ の分子動力学シミュレーション

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Molecular dynamics (MD) simulation was carried out on the high Li ion conductor, $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$, using the partially ionic model (PIM). MD simulation of the Li ion conductivity with the variation of mobile ion size under high pressure revealed that this compound had the optimum lattice size for Li ion conduction and that the skeletal lattice was too small for Li^+ ion to show the highest conductivity.

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1. Introduction

In recent years, many solid Li ion conductors have been developed for their potential application in solid state devices, mainly as solid electrolytes in rechargeable Li ion batteries. In some solid ion conductors, Li ion conductivity has been as high as $10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at room temperature.^{1)–7)} However, this value was lower than about 1/10 that of the liquid electrolytes, and in order to use these conductors as solid electrolytes we have to improve their ionic conductivity. The perovskite-type Li ion conductor, $\text{La}_{2/3-x}\text{Li}_x\text{TiO}_3$, is one of these promising fast Li ion conductors. $\text{La}_{2/3-x}\text{Li}_x\text{TiO}_3$ has a cation deficient perovskite structure in which Li, La, and a vacancy are distributed in the A-site, as shown in Fig. 1. In this study, the bottleneck is defined as the 3c site with the space group $Pm3m$ surrounded by four oxide ions in the structure. Ion migration is known to occur through the conduction path composed of Li ions and the vacancy. According to previous studies, Li ion conduction depends on the vacancy and carrier concentration.⁸⁾ $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$, whose vacancy and carrier concentration are optimized, shows Li ion conduction of $1.1 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at room temperature.⁷⁾ Several investigations of the transport mechanism of the perovskite-type Li ion conductors such as this compound have been carried out because of its simple structure and the high Li ion conductivity.^{4)–21)} However the relationship between the lattice size and Li ion conductivity has not been understood completely.

In $\text{Ln}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ ($\text{Ln} = \text{La, Pr, Nd, and Sm}$), conductivity decreases with the average ionic radius of the A-site ion¹¹⁾ and the pressure.^{12),13)} These results are considered to be caused by the contraction of the bottleneck due to the pressure or the substitution of the A-site ion. However, in $(1-x)\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_{3-x}\text{ATiO}_3$ ($\text{A} = \text{Sr, Ba and Pb}$), Li ion conductivity did not always increase with x , while the lattice parameter always increased with x . In $(1-x)\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_{3-x}\text{BaTiO}_3$, Li ion conductivity decreases continuously with x and in $(1-x)\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_{3-x}\text{ATiO}_3$ ($\text{A} = \text{Sr and Pb}$), Li ion conductivity showed the maximum when the lattice parameter was about 0.388 nm.^{7),9)} The authors suggested that the decrease in Li ion conductivity in these solid

solutions was due to the local distortion of the crystal structure caused by the ion substitution. On the other hand, in $\text{Li}^+\beta\text{-Al}_2\text{O}_3$ a decrease in the ion conductivity due to the lattice expansion has been observed.²²⁾ It is noted that the ion conductivity of $\text{Li}^+\beta\text{-Al}_2\text{O}_3$ was lower than that of $\text{Na}^+\beta\text{-Al}_2\text{O}_3$ and $\text{Ag}^+\beta\text{-Al}_2\text{O}_3$ under ambient pressure, even though the width of the conduction plane was almost the same in all the compounds. Furthermore, the ion conductivity of $\text{Li}^+\beta\text{-Al}_2\text{O}_3$ increased with pressure, while that of $\text{Na}^+\beta\text{-Al}_2\text{O}_3$ and $\text{K}^+\beta\text{-Al}_2\text{O}_3$ decreased with pressure.^{23),24)} These results indicate that the lattice size of $\beta\text{-Al}_2\text{O}_3$ under ambient pressure is too large for Li ion conduction and that

Fig. 1. Schematic figure of perovskite structure and schematic representation of the arrangement of A-site and oxide ions projected on {100}.

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it is suitable for Li ion conduction by the pressure. Therefore, $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ may also have a lattice size suitable for Li ion conduction, and in $(1-x)\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_{3-x}\text{ATiO}_3$ ($A=\text{Sr}, \text{Ba}$ and Pb) the large framework due to the lattice expansion may cause the decrease in Li ion conductivity. However, it is difficult to research the relationship between Li ion conduction and lattice size by ion substitution because other factors that influence Li ion conduction such as carrier concentration and bond character were simultaneously varied with the substitution of ions. If we can estimate the suitable lattice size and Li ion conductivity in the optimized structure, it would be useful in the design of novel fast ion conductors.

Molecular dynamics (MD) simulation can be used to investigate the relationship between ion migration and structural or chemical factors (bond covalence, lattice size, mobile ion size, etc.) because it allows us to change such factors independently and to explore ion dynamics at the atomic level under variable conditions. In the present study, we observed the motion of ions, mainly the Li ion, in $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ using MD simulation and will discuss the relationship between the bottleneck size and the ion migration. This paper follows the following organization: In Section 2, we will describe the systems, methods, conditions, and potential parameters used in the present simulation and experimental procedures. In Section 3, we will present the results and discuss the following issues: (1) the reproducibility of the physical properties in MD simulation using the partially ionic model (PIM),²⁵⁾ (2) the influence of lattice size on Li ion migration as obtained from the MD simulation (by changing Li ion size under various pressures), and (3) the estimation of the optimum lattice size and Li ion conductivity in the optimized structure. Finally, the conclusions from the present work are described.

2. Simulation and experimental procedures

The interatomic potential of PIM is expressed by²⁵⁾

$$U_{ij} = \frac{z_i z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp \left[\frac{(a_i + a_j - r_{ij})}{(b_i + b_j)} \right] - \frac{c_i c_j}{r_{ij}^6} + D_{ij} \{ \exp [-2\beta_{ij}(r_{ij} - r_{ij}^*)] - 2 \exp [-\beta_{ij}(r_{ij} - r_{ij}^*)] \}. \quad (1)$$

The first term in Eq. (1) represents the Coulomb interaction where z_i and z_j are the effective charges of the ions i and j , respectively, and r_{ij} is the interatomic distance between the ions. The second term represents the short-range repulsion potential. The parameters a_i and a_j reflect the ionic radii, and b_i and b_j reflect the hardness of the ions. The quantity f_0 is a constant 6.9478×10^{-11} N. The third term represents the dipole-induced dipole dispersion potential based on the Van der Waals interaction. The specific parameters of each ion, a_i , b_i , and c_i , were determined by the trial and error method. The last term in the PIM represents the Morse potential which relates to the covalent bond. Here the bond directionality is ignored. D_{ij} , β_{ij} , and r_{ij}^* are the specific parameters of the bond between the i and j ions. In the PIM, the effective charge of ions influenced by the bond covalency is reduced from the nominal ionic valence. In the preset study z_{Ti} determined from the previous studies on SrTiO_3 and TiO_2 , which have almost the same Ti-O bond length as $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$. According to the angle integrate photoemission experiment²⁶⁾ and the band calculation based on the augment plane wave method for SrTiO_3 ,²⁷⁾ the number of d electrons in Ti ion was estimated to about +1.5, that is, the effective charge of Ti ion is +2.5. Furthermore the MD simulation for TiO_2 polymorphs (brookite, anatase and rutile) reproduced its physical

Table 1. Potential Parameters of Each Ion and Ion Pair for PIM

Ion	The number of ions	z (e)	a (nm)	b (nm)	$c \times 10^3$ ($\text{kJ}^{1/2} \cdot \text{nm}^3 \cdot \text{mol}^{-1/2}$)
O	540	-1.267	0.19265	0.018	84
Ti	180	+2.400	0.11158	0.010	0
La	108	+2.000	0.17070	0.010	29
Li	36	+1.000	0.10010	0.008	8
Ion pair		D ($\text{kJ} \cdot \text{mol}^{-1}$)	β (nm^{-1})	r^* (nm)	
Ti-O		260	20	0.188	

properties and structures well when the z_{Ti} and z_{O} was +2.4 and -1.2, respectively.²⁸⁾ Therefore z_{Ti} in this system was reduced to +1.2 from +4.0. Since the ionicity of the La-O bond calculated from the difference of electron negativities between O and La ions is about 75 percent,²⁹⁾ the z_{La} was also reduced to +2.0 from +3.0. The z_{Li} was constant, the normal valence being +1.0. The z_{O} was determined at -1.274 to keep the charge neutralization in the system. Other potential parameters were determined by the trial and error method to reproduce the compressibility, thermal expansion and structure at room temperature. All the parameters are listed in Table 1.

La, Li and vacancy were distributed randomly in A-sites in the simulation cell which has 864 particles. The number of each ions are also shown in Table 1. The simulations were carried out using the program, MXDORTO developed by Kawamura³⁰⁾ in which a rapid convergence was achieved by the Ewald method. The Verlet algorithm was applied for the atomic motions. Periodic boundary conditions were used with the MD basic cell. All the simulations were carried out under constant temperature and pressure, which were controlled by the scaling of particle velocities and basic cell parameters, respectively. A period of one simulation was 200 ps (100000 steps) at 2 fs time steps. The diffusion coefficient of the lithium ion, D^{Li} , was calculated from the time dependence of the mean square displacement (MSD), $\langle \Delta r(t)^2 \rangle$, using the Einstein relation

$$\langle \Delta r(t)^2 \rangle = A + 6D^{\text{Li}}t \quad (2)$$

where A is a constant. Lithium ion conductivity, σ , was calculated from D^{Li} using the Nernst-Einstein equation. The pair correlation function is expressed as the following equation,

$$g_{ij}(r) = \sum_j \frac{N_j}{N_i} \frac{n_{ij}(r - \Delta r/2; r + \Delta r/2)}{4\pi(N_i N_j / V) r^2 \Delta r} \quad (3)$$

where V is the volume of a unit cell and N_i and N_j is the number of ions i and j in a unit cell, respectively. The n_{ij} is the number of ion j in the area between sphere 1 (its radius is $r - \Delta r$) and sphere 2 (its radius is $r + \Delta r$), whose center is ion i . In this study, Δr is 0.001 nm.

The $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ polycrystalline sample for the investigation of physical properties and structure was prepared by the conventional solid state reaction technique. Powders of La_2O_3 (99.9%), Li_2CO_3 (99.9%) and TiO_2 (99.9%) were used as the starting materials. The mixture was calcined at 1373 K for 12 h, sintered at 1423 K for 5 h in air, and quenched to room temperature so that the arrangement of lanthanum ions was in the disordered state. Thermal expansion was measured using a high temperature X-ray diffractometer (Mac Science MPX¹⁸ X-ray diffractometer) from 300 K to 1200 K. Both sides of the sample were pasted with gold as electrode, and Li ion conductivity was measured in the temperature range from 238 K to 625 K by the ac impedance method using a HP 4192 impedance analyzer in the frequency range 5 Hz–13 MHz.

3. Results and discussions

3.1 Reproducibility of physical properties in MD simulation using PIM

Table 2 shows the structural data of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ obtained by MD simulation and experiment at 300 K. The lattice parameter (cube root of volume of perovskite unit cell), a_p , and density, d , obtained by MD simulation was in accord with experimental value. In this simulation, the a , b , and c parameters were same within thermal fluctuations. The MD simulation could reproduce the cubic structure of actual $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ at 300 K.

Figure 2 shows the temperature variation of the density of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ in the experiment and the simulation using the PIM. The bulk thermal expansion coefficients, α , determined by the simulation and experiment were 3.09×10^{-5} and 2.66×10^{-5} , respectively. The α obtained by the PIM was in good agreement with experimental one.

Figure 3 shows the volume change of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ under hydrostatic pressure calculated by the MD simulation with the experimental data of SrTiO_3 .³¹⁾ The compressibility of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ obtained from the MD simulation is considered to be comparable to that of SrTiO_3 , though the compressibility, κ , of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ is unknown (Because the compressibility of perovskite titanates are

almost the same, i.e., $5.68 \times 10^{-12} \text{ Pa}^{-1}$ for SrTiO_3 and $7.8 \times 10^{-12} \text{ Pa}^{-1}$ for BaTiO_3).³¹⁾ The initial compressibility, κ , which was obtained by the extrapolation of the linear part of the data in the low pressure region, was $6.06 \times 10^{-12} \text{ Pa}^{-1}$. The result in MD simulation shows good agreement with the experimental one of SrTiO_3 . Therefore thermal expansion, compressibility, and crystal structure at room temperature were reproduced in this simulation using the PIM.

Since Li ion motion is most interesting in this simulation, we observed Li ion motion by the trajectory plot. Figure 4 shows the trajectory plots of Li, O and La ions at 300 K. At 300 K the Li ions were found to migrate from A-site to adjacent A-site through the bottleneck. Furthermore, we calculated the pair correlation function to investigate the distribution of ions. Figure 5 shows $g_{\text{Ti-Ti}}(r)$, $g_{\text{Ti-O}}(r)$,

Table 2. Crystal Structure Obtained by MD Simulation and Experiment

	PIM	Exp.
a_p/nm	0.387(8)	0.38777(2)
a/nm	0.390(8)	-
b/nm	0.385(6)	-
c/nm	0.387(7)	-
$d/\text{g}\cdot\text{cm}^{-3}$	5.147(4)	5.1436(9)

Fig. 2. Temperature dependence of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ density obtained by the simulation and experiment.

Fig. 3. Pressure dependence of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ volume obtained by simulation and experiment for SrTiO_3 .

Fig. 4. Trajectory plots of Li, La and O ions projected on {100} plane for $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ at 300 K.

Fig. 5. Pair correlation function for ion pairs, Ti-Ti, O-Ti, La-Ti, and Li-Ti, at 300 K.

$g_{\text{Ti-La}}(r)$ and $g_{\text{Ti-Li}}(r)$ at 300 K. While the $g_{\text{Ti-Ti}}(r)$, $g_{\text{Ti-O}}(r)$ and $g_{\text{Ti-La}}(r)$ showed clear peaks at the distance between each equivalent position, the peaks of the $g_{\text{Ti-Li}}(r)$ were connected. The $g_{\text{Ti-Li}}(r)$ begin to increase at $r=0.25$ and is not zero at every r value in $r>0.25$. Since the distance between the bottleneck and the Ti ion is 0.27 nm, Li ions are found to exist at various positions between the A-site and bottleneck and are indicated to migrate in this simulation cell.

Figure 6 shows the time dependence mean square displacement (MSD) of La, Ti, O and Li ions at 300 K. While each MSD of the La, Ti and O ions showed no time dependence, that of Li ion increased with time. The Li ion apparently diffused at 300 K in this simulation. The curvature of the time dependence MSD is found to be due to the simulation condition.

Table 3 shows the D^{Li} at 300 K, 500 K and 1000 K estimated in each MD simulation for three simulation cells with different arrangements of A-site ions and obtained by the experiment. As shown in this table, the D^{Li} obtained by MD simulation was smaller than that obtained by experiment at each temperature. The difference in among the three simulation cells was larger at low temperatures and decreased with the increase in temperature. The large difference in D^{Li} among the three simulation is mainly attributed to the simulation condition, since the difference in D^{Li} decreased with increasing temperature. At low temperature the precise D^{Li} could not be estimated under this simulation condition owing to an insufficient number of particles and/or simulation steps, but at high temperature the precise D^{Li} could be estimated under this condition because of increasing the D^{Li} with increasing temperature. Though the arrangement of A-site ions may influence ion diffusion, the precision of D^{Li} in this simulation is not enough to evaluate the influence. Accordingly, we consider that the difference between the experiment and the MD simulation at low temperatures is caused by the insufficient number of particles and/or simulation steps, and the D^{Li} obtained at high temperatures (≥ 500 K) can be used for the

quantitative discussion.

3.2 Influence of lattice size and mobile ion size on Li ion migration

In MD simulation, by manipulating the variable conditions, those factors which influence Li ion conductivity can be independently controlled. In order to understand the relationship between Li ion conduction and lattice size, we executed MD simulations in which Li ion size was changed under various pressures and investigated the resulting variations of Li ion conductivity. In this Section, the simulations were executed under the pressures of 0, 10 and 50 GPa with various a_{Li} values ($a_{\text{Li}}=0.0801, 0.0851, 0.0901, 0.0951, 0.1001, 0.1101$ and 0.1201 nm) which reflect the radius of Li ion, and discuss the variation of D^{Li} for each condition.

Table 4 shows the average interatomic distance of O-O ion pair, $r_{\text{O-O}}$, and Li-O ion pair, $r_{\text{Li-O}}$. The $r_{\text{O-O}}$ was independent of a_{Li} , but $r_{\text{Li-O}}$ decreased with a_{Li} . Figure 7 shows the variation of the effective radius of Li ion, R_{Li} , calculated by Eq. (4),

$$R_{\text{Li}} = r_{\text{Li-O}} - \frac{1}{2} r_{\text{O-O}} \quad (4)$$

As shown in this figure, R_{Li} decreased linearly with a_{Li} in the range $a_{\text{Li}} \leq 0.1001$. Therefore we could change the Li ion size only by changing a_{Li} while keeping the lattice size constant. The gradual variation of R_{Li} in $a_{\text{Li}} > 0.1001$ was caused by excess size of the Li ion. In this simulation cell the lattice parameter at 300 K was about 0.389 nm, and the distance between the oxide ion and the cation at the A-site is calculated at 0.505 nm. Therefore, the Li ion can not

Fig. 6. Time dependence of the mean square displacement (MSD) of La, Li, Ti and O ions at 300 K.

Table 3. Diffusion Coefficients of Li Ion on MD Simulation and Experiment at 300 K, 500 K and 1000 K

T (K)	Diffusion coefficient (cm^2s^{-1})			
	Configuration A	Configuration B	Configuration C	Exp.
300	$1.4(9) \times 10^{-9}$	$1.5(1) \times 10^{-7}$	$2.7(9) \times 10^{-8}$	8.65×10^{-9}
500	$1.95(1) \times 10^{-7}$	$6.36(6) \times 10^{-7}$	$1.96(3) \times 10^{-7}$	1.30×10^{-6}
1000	$0.88(4) \times 10^{-6}$	$1.62(6) \times 10^{-6}$	$2.69(9) \times 10^{-6}$	-

Table 4. Average Interatomic Distances under Ambient Pressure in MD Simulation

a_{Li} (nm)	Average interatomic distance	
	O-O (nm)	Li-O (nm)
0.0801	0.275	0.242
0.0851	0.275	0.244
0.0901	0.275	0.252
0.0951	0.275	0.258
0.1001	0.275	0.264
0.1101	0.275	0.269
0.1201	0.275	0.271

Fig. 7. Variation of effective ionic radius of Li ion, R_{Li} , with a_{Li} .

detach freely from O ions when $R_{Li} \geq 0.131$ nm and the variation of R_{Li} in $a_{Li} > 0.1001$ is gradual.

Figure 8 shows the variation of ionic conductivity with a_{Li} at 1000 K under various pressures. Under ambient pressure, the ionic conductivity attained a maximum $1.41 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at $a_{Li} = 0.0951$. This compound was found to be the optimum mobile ion size for Li ion migration. The ionic conductivity at $a_{Li} = 0.0901$ and $a_{Li} = 0.0851$ attained their maximum under 10 GPa and 50 GPa, respectively. This suggests that the pressure approaches the framework size in the direction which is more suitable for ion conduction, similarly as in $\text{Li}^+\beta\text{-Al}_2\text{O}_3$,²³⁾ when the mobile ion size is too small for the framework size. When a_{Li} is 0.0901 nm, the framework size is most suitable under about 10 GPa and contracted to the smaller size than suitable under 50 GPa. The pressure under which the ionic conductivity was maximum increased with a_{Li} in the range, $0.0851 \leq a_{Li} \leq 0.0951$ thus the suitable framework size varies with the mobile ion size and this compound seems to have a suitable framework size for each mobile ion size. The effect of pressure for ion conduction disappeared at $a_{Li} = 0.0801$. The change of framework size in this pressure range is not enough to affect ion conduction. A pressure of more than 50 GPa would be required in order to optimize the framework for the Li ion at $a_{Li} = 0.0801$.

Figure 9 shows the trajectory plots of ions on {100} plane at 1000 K under ambient pressure for $a_{Li} = 0.1201$, $a_{Li} = 0.0951$, and $a_{Li} = 0.0801$. When $a_{Li} = 0.0951$ nm the Li ions migrated freely, though they tended to stay at the A-site or bottleneck at $a_{Li} = 0.1201$ and 0.0801. These results were supported by the pair correlation function.

Figure 10 shows the pair correlation function, $g_{Li-Ti}(r)$ for $a_{Li} = 0.0801$, $a_{Li} = 0.0951$, and $a_{Li} = 0.1201$ at 1000 K under ambient pressure. When $a_{Li} = 0.0801$, the peak was observed at $r_{ij} = 0.27$ nm which is the distance between the Ti ion and bottleneck. When $a_{Li} = 0.1201$, the peak was observed at $r_{ij} = 0.34$ nm which is the distance between the Ti ion and the A-site. On the other hand, for $a_{Li} = 0.0951$ the peaks are broadened. These represent that at $a_{Li} = 0.0951$ Li ions migrate freely in the simulation cell, and at $a_{Li} = 0.1201$ and $a_{Li} = 0.0801$ Li ions tend to stay around the A-site and the vicinity of bottleneck, respectively. Figure 11 shows the $g_{Li-Ti}(r)$ at 1000 K under ambient pressure and 50 GPa for $a_{Li} = 0.0851$. The $g_{Li-Ti}(r)$ under ambient pressure showed that the Li ion was distributed in the vicini-

Fig. 9. Trajectory plots of Li, La and O ions projected on {100} plane for $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ at 1000 K under ambient pressure. Upper plot, middle plot, and lower plot is $a_{Li} = 0.1201$ nm, $a_{Li} = 0.0951$ nm and $a_{Li} = 0.0801$ nm, respectively.

Fig. 8. Variation of ionic conductivity with repulsion parameter of Li ion, a_{Li} , under ambient pressure, 10 GPa, and 50 GPa at 1000 K.

Fig. 10. Pair correlation function between Li and Ti ions at $a_{Li} = 0.1201$ nm, $a_{Li} = 0.0951$ nm and $a_{Li} = 0.0801$ nm at 1000 K under ambient pressure.

Fig. 11. Pair correlation function between Li and Ti ions at 1000 K under ambient pressure and 50 GPa ($a_{\text{Li}}=0.0851$ nm).

ty of the bottleneck. Under 50 GPa, the peaks were observed at 0.27 nm and 0.32 nm. The position where Li ions mainly stay varies from bottleneck to A-site with increasing pressure, because the distance between the B-site and bottleneck and B-site and A-site under 50 GPa are 0.276 nm and 0.338 nm, respectively. These results imply that in this simulation the decrease in a_{Li} has the same effect on the ion conduction as the lattice expansion.

When $a_{\text{Li}}=0.1201$ nm, Li ions wander around the A-site, and few Li ions migrate through the bottleneck due to its large size. When mobile ion size is too large for the framework size, the ion can not migrate through the bottleneck and the ion conductivity decreases for this compound. When $a_{\text{Li}}=0.0801$ nm, Li ions stayed around the bottleneck and migrated from bottleneck to bottleneck without passing the A-site. The potential at bottleneck and A-site are found to increase and decrease with decreasing a_{Li} , respectively. Stabilizing the potential for Li ion at the bottleneck by decreasing a_{Li} is reasonable, because the short range repulsion decreases with decreasing a_{Li} . The increase in the potential energy at the A-site with the lattice expansion was suggested by the energetic calculation.¹³⁾ Inaguma et al. reported that the potential energy around the A-site increases with an increase in the lattice parameter, and that the lowest energy path gradually swerves from the A-site.¹³⁾ Since the lattice expansion has the same effect on Li ion migration as the decrease in a_{Li} in this simulation, the decrease in ion conductivity is considered to be due to the interruption of the ion conduction at the A-site when mobile ion size is excessively small.

3.3 Estimation of Li ion conductivity in the optimized structure

The optimum lattice size for Li ion conduction is an important information for the design of new Li ion conductors. In this Section we estimated the optimum lattice size and Li ion conductivity in the optimized structure using MD simulation.

Figure 12 shows the variation of ionic conductivity with the lattice parameter, a_p , at 1000 K. In this case, a_{Li} was fixed to 0.0901 nm because Li ion conductivity apparently attains a maximum in the pressure range between 0 and 50 GPa when $a_{\text{Li}}=0.0901$ nm. As shown in this figure, at $a_p=0.3799$ nm Li ion conductivity attained a maximum value, $4.5 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$, which was about 3 times higher than that reproduced physical properties. The R_{Li} at $a_{\text{Li}}=0.0901$ is estimated as 0.120 nm in Fig. 7, and the ionic radius of the Li ion for coordination 12 is estimated to within 0.125 nm by extrapolation of the variation of ionic radius of the coordination number.³²⁾ If the ionic radius of the Li ion in the ac-

Fig. 12. Variation of perovskite parameter, a_p , with ionic conductivity, σ , for $a_{\text{Li}}=0.0901$ nm at 1000 K.

tual $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ assumes 0.125 nm, the optimum bottleneck size predicted by this simulation study is 0.412 nm. This value is larger than the actual $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ ($a_p=0.3877$ nm). By the extrapolation of the relationship between a_p and the activation energy, E_a , for $\text{Ln}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ ($\text{Ln}=\text{La}, \text{Pr}, \text{Nd}, \text{Sm}$)¹¹⁾⁻¹³⁾ to $E_a=0$, the optimum lattice parameter is calculated as 0.3945 nm. This value is in good agreement with that predicted by this MD simulation. Consequently, it is indicated that $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ has an optimum bottleneck size and that ionic conductivity increases by the optimization of the crystal structure.

4. Conclusions

The simulation using the PIM could simultaneously reproduce the crystal structure at room temperature and its physical properties (thermal expansion, compressibility, and Li ion migration). But Li ion conductivity could not be reproduced quantitatively due to the insufficient number of calculation steps and/or simulation cells. The observation of Li ion motion using MD simulation for various a_{Li} under high pressure revealed that the decrease in Li ion conductivity with lattice contraction and lattice expansion was due to the interruption of Li ion migration at the bottleneck and at the A-site, respectively. According to the investigation of Li ion conductivity at various lattice sizes, Li ion conductivity at 1000 K attained $4.5 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at $a_p=0.3799$ nm when a_{Li} was 0.0901 nm. This value was 3 times larger than that of the simulation using parameters reproducing physical properties. Furthermore, the suitable lattice size predicted by MD simulation was 0.412 nm, which is larger than the actual lattice parameter, 0.3877 nm, of $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$. These simulations indicated that $\text{La}_{0.6}\text{Li}_{0.2}\text{TiO}_3$ has an optimum lattice size, and that the ionic conductivity becomes several times higher by extending the framework structure.

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References

- 1) H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka and G. Adachi, *J. Electrochem. Soc.*, **140**, 1827-33 (1993).
- 2) J. Kennedy and Z. Zhang, *J. Electrochem. Soc.*, **135**, 859-62 (1988).

- 3) J. Fu, *Solid State Ionics*, **96**, 195-200 (1997).
- 4) Y. Inaguma, Y. Matsui, Y. J. Shan, M. Itoh and T. Nakamura, *Solid State Ionics*, **79**, 91-97 (1995).
- 5) A. G. Belous, G. N. Novitskaya, S. V. Polyanetskaya and Y. I. Gornikov, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **23**, 470-72 (1987).
- 6) Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, T. Uchida, M. Ikuta and M. Wakihara, *Solid State Commun.*, **86**, 689-93 (1993).
- 7) Y. Inaguma, L. Chen, M. Itoh and T. Nakamura, *Solid State Ionics*, **70/71**, 196-202 (1994).
- 8) Y. Inaguma and M. Itoh, *Solid State Ionics*, **86-88**, 257-60 (1996).
- 9) T. Katsumata, Y. Matsui, Y. Inaguma and M. Itoh, *Solid State Ionics*, **86-88**, 165-69 (1996).
- 10) Y. Inaguma, Y. Matsui, J. Yu and M. Itoh, *Mater. Res. Soc. Symp. Proc.*, **453** (1997) pp. 623-28.
- 11) M. Itoh, Y. Inaguma, W. H. Jung, L. Chen and T. Nakamura, *Solid State Ionics*, **70/71**, 203-07 (1994).
- 12) Y. Inaguma, J. Yu, Y. J. Shan, M. Itoh and T. Nakamura, *J. Electrochem. Soc.*, **142**, L8-L11 (1995).
- 13) Y. Inaguma, Y. Matsui, J. Yu, Y. J. Shan, M. Itoh and T. Nakamura, *J. Phys. Chem. Solids*, **58**, 843-52 (1997).
- 14) J. S. Lee, K. W. Yoo, T. S. Kim and H. J. Jung, *Solid State Ionics*, **98**, 15-26 (1997).
- 15) C. León, M. L. Lucía, J. Santamaría, M. A. París, J. Sanz and A. Váres, *Phys. Rev.*, **B54**, 184-89 (1996).
- 16) C. León, J. Santamaría, M. A. París, J. Sanz, J. Ibarra, L. M. Torres and A. Váres, *Phys. Rev.*, **B56**, 5302-05 (1997).
- 17) C. León, M. L. Lucía, J. Santamaría and F. Sánchez-Quesada, *Phys. Rev.*, **B57**, 41-47 (1998).
- 18) J. L. Fourquet, H. Duroy and M. P. Crosnier-Lopez, *J. Solid State Chem.*, **127**, 283-94 (1996).
- 19) A. D. Robertson, S. G. Martin, A. Coats and A. R. West, *J. Mater. Chem.*, **5**, 1405-12 (1995).
- 20) P. Birke, S. Scharner, R. A. Huggins and W. Weppner, *J. Electrochem. Soc.*, **144**, L167-69 (1997).
- 21) M. Oguni, Y. Inaguma, M. Itoh and T. Nakamura, *Solid State Commun.*, **91** 627-30 (1994).
- 22) Y. F. Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.*, **29**, 2453-75 (1967).
- 23) R. H. Radzilowski and T. Kummer, *J. Electrochem. Soc.*, **118**, 714-16 (1971).
- 24) K. Itoh, K. Kondo, A. Sawaoka and S. Saitoh, *Jpn. J. Appl. Phys.*, **14**, 1237-39 (1975).
- 25) K. Kawamura, *Proc. the 13th Taniguchi Sym., Kashikojima Japan*, No. 6-9 (1990) pp. 87-97.
- 26) R. Courths, B. Cord and H. Saalfeld, *Solid State Commun.*, **70**, 1047-51 (1989).
- 27) K. Takegahara, *J. Electron Spectros. Relat. Phenom.*, **66**, 303-20 (1994).
- 28) D. W. Kim, N. Enomoto, Z. Nakagawa and K. Kawamura, *J. Am. Ceram. Soc.*, **79**, 1095-99 (1996).
- 29) L. Pauling, "The Nature of Chemical Bond," Cornell University Press, New York (1960).
- 30) K. Kawamura, MXDORTO, Japan Chemistry Program Exchange, #029.
- 31) L. R. Edwards and R. W. Lynch, *J. Phys. Chem. Solids*, **31**, 573-74 (1970).
- 32) R. D. Shannon, *Acta Cryst.*, **A32**, 751 (1976).