Dependence of the lithium ionic conductivity on the B-site ion substitution in $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ (*M*=Sn, Zr, Mn, Ge)

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Abstract

The dependence of the ionic conductivity on the B-site ion substitution in $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ (*M*=Sn,Zr,Mn,Ge) system has been studied. Same valence state and various electronic configuration and ionic radius of Sn^{4+}, Zr^{4+}, Mn^{4+} and Ge^{4+} ($4d^{10}$(0.69Å), $4p^6$(0.72Å), $3d^{10}$(0.54Å) and $3d^3$(0.54Å), respectively) induced the various crystallographic variation with substitutions. So it was possible to investigate the crystallographic factor which influence the ionic conduction by observing the dependence of the conductivity on the crystallographic variations. We found that the conductivity increased with decreasing the radii of B-site ions or vice versa and octahedron distortion disturb the ion conduction. The reason for this reciprocal proportion of conductivity on the radius of B-site ions has been examined on the base of the interatomic bond strength change due to the cation substitutions. The results were good in agreement with the experimental results. Therefore it could be concluded that the interatomic bond strength change due to the cation substitutions may be the one of major factors influencing the lithium ion conductivity in perovskite $(Li_{0.5}La_{0.5})$ TiO_3system

Key words : Perovskite structure; Lithium; Ionic conductivity; Conduction mechanism

1. Introduction

Recently perovskite structure oxide has been reported to show a lithium ion conductivity at room temperature[1-3]. Usually ionic conducting materials must contain tunnels of dimensions comparable to those of the mobile ions. ABO_3 perovskite structure is well known to have fcc-like close packing of A+3O ions with one fourth of octahedral sites occupied by B ions. Therefore there seems to exist no available space through which ion move. In case of lithium ion conduction perovskite structure, the A-site vacancies of

mobile ion are known to contribute to the lithium ion conductivity[4-5].

The first perovskite structure which exhibited the lithium ion conduction property was known as the A-site deficient $Ln_{1/2}Li_xNb_{1-x}Ti_xO_3$($Ln$=La, Nd and x≤0.1). However, the lithium ion conductivity of this material was not so high that little attention was paid on this perovskite ion conductor[1]. Recently Inaguma et al. have reported that perovskite $Li_{0.5}La_{0.5}TiO_3$ exhibited the lithium ion conductivity as high as 10^{-3} Scm^{-1} at room temperature, which was the one of highest lithium ion conductor[3]. This material has received a considerable attention due to the potential use as solid electrolytes in lithium ion battery. However the electronic conduction which appear due to the reduction of Ti^{4+} to Ti^{3+} with the intercalation of lithium prevent the use of this material as solid electrolyte[6]. Therefore it is very urgent research target to suppress the electronic conduction with maintaining the high ionic conductivity, but no considerable results has not been reported. Other studies have also been reported about this and related materials[7-10].

The ionic conduction mechanism has not been clarfied yet, only the following factors are known to affect the ionic conductivity:

■   the lithium and vacancy concentration in the A-site because the lithium ions move through the A-site vacancies.
■   the size of bottleneck which is the smallest cross-sectional area of an interstitial passageway. Therefore the conductivity decrease with the decrease of bottleneck size, and increase with the increase of bottleneck size. This bottleneck is reported to depend on the A-site ions substitutions and hydrostatic pressure.
■   the facilities of tilting of TiO$_6$ octahedron . It is suggested that the tilting of TiO$_6$ octahedra

actually occur during lithium motion in the perovskite. So conductivity increase with the TiO$_6$ octahedron tilting facility and vice versa.

In this research, we will investigate the dependence of the ionic conductivity on the B-site ion substitution in $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ (M=Sn,Zr,Mn,Ge) system. Same valence state and various electronic configuration and ionic radius of Sn^{4+}, Zr^{4+}, Mn^{4+} and Ge^{4+} (4d^{10}(0.69Å), 4p^6(0.72Å), 3d^{10}(0.54Å) and 3d^3(0.54Å), respectively) will induce the various crystallographic variations with substitutions. Therefore we expected   to find the crystallographic factor which influence the ionic conduction by observing the dependence of the conductivity on the crystallographic variations.

2.Experimental

Reagents   of   La$_2$O$_3$(Aldrich   Chem.   99.99%), Li$_2$CO$_3$(Aldrich Chem. 99.997%), TiO$_2$(Aldrich Chem. 99.99%), SnO$_2$(Aldrich Chem. 99.9%), ZrO$_2$(Yakuri Chem. 99.99%), GeO$_2$(Aldrich Chem. 99.998%) and MnO$_2$(Kanto Chem.) were used as starting materials. La$_2$O$_3$ dried at 800°C for 4 h to evaporate H$_2$O. These reagents were mixed in an agate mortar with ethanol. A stoichiometric mixture of the powder was calcined at 850°C for 10 h in air with several intermediate grindings. The calcined powder was ground, pressed into pellets with a diameter of 8 mm and a thickness of 1 to 2mm under a pressure of 40Mpa, fired at 1270-1320°C for 7 h with heating rate of 4°C/min in air and cooled to room temperature.

The sintered pellets were crushed into powders and heated to 500°C for 4 h to relieve the stress induced during crushing. The identification of the phases and the determination of the lattice parameters were carried out by powder X-ray diffraction with CuKα radiation using a Rikagu D/MA X-ⅢC. Silicon powder(99.99%)

was used as an internal standard in the determination of the lattice paremeters.

The lithium ionic conductivity of the sample with sputtered electrodes of Au was measured by an ac impedance method using a HP 4192a LF Impedance Analyzer over the frequency range from 5 to 13MHz. To calculate the activation energy, the impedances were measured over the temperature range from 273K to 323K. The lithium ionic conductivities were obtained by analyzing the impedance data, which were collected by IBM PC, using Boukamp companysoftware.

3. Result and discussion

3.1 Dependence of conductivity on the sintering temperature

Fig.1 shows the dependence of bulk conductivities and resistivities on the sintering temperature. Conductivity about 8.3×10^{-4} S/cm nearly does not change up to 1300℃, but above this temperature rapidly decrease. This decrease may arise from the evaporation of lithium, which decrease the carrier lithium ion concentration. Therefore, in this research,
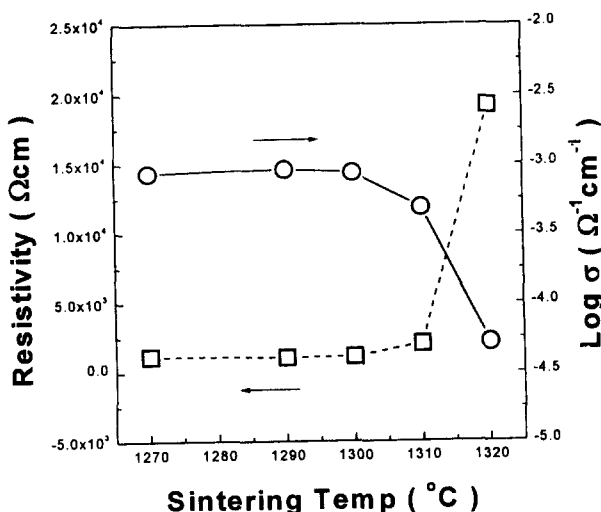
all samples were sintered on 1290℃ where little evaporation of lithium was estimated to occur.

3.2 Crystallographic change with B-site ions substitutions

Fig.2 shows the representative XRD patterns for the $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ (M=Sn,Zr,Mn,Ge) system. When Zr and Sn were substituted for Ti, no second phase was found up to 0.1mol% substitution, but in case of Mn second phase was observed over the 0.01mol% substitution. So Zr and Sn were substituted up to 0.1mol% at intervals of 0.02mol% and Mn up to 0.01mol% at intervals of 0.002mol%. Ge was substituted with same mol ratio of Mn in order to compare the ionic conductivity between Mn and Ge substitutions. The primitive cells were found to be cubic in all composition. Broad and weak superstructure and standard Si peaks are observed. No second phase and change of superstructures were observed through these substitutions.
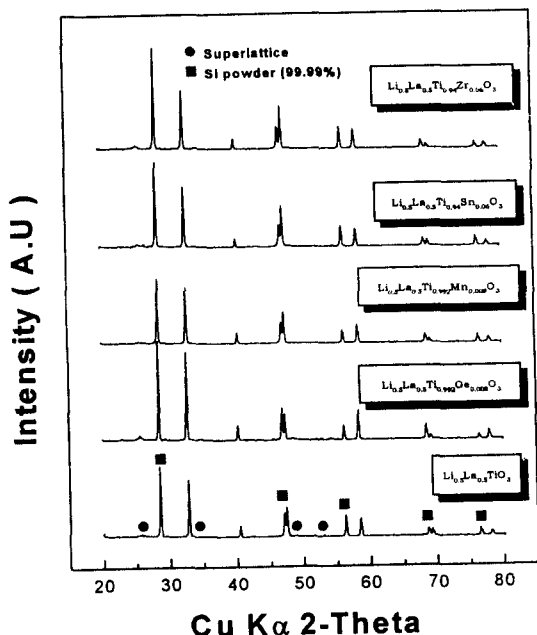

Fig.1. Dependence of bulk conductivity and resistivity on the sintering temperature.

Fig. 2. Representative XRD patterns for $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ (M=Sn,Zr,Mn,Ge)

Fig.3 shows the lattice parameters variation with B-site ion substitutions. Electron configuration of Sn^{4+} is $4d^{10}$. The full d orbital does not permit to form π bonds which tend to distort the octahedron, thus no distortion is expected to occur with substitution[11]. Although the distortion could be originated from the change of the tolerance factor, the amount of substitution is too small to affect the tolerance factor in this case (at most 0.1mol%). Because the ionic radius of Sn^{4+}(0.69Å) is larger than that of Ti^{4+}(0.605Å), the lattice parameter increase with substitution[12]. In case of Zr^{4+}, its electron configuration is $4p^6$(empty d orbital), so there exists π bond. Clear evidence of lattice distortion was not found with XRD because of a small amount of substitutions, but relatively smaller lattice constant of 0.1mol% substituted sample may be due to the distortion of octahedron. Lattice constant increase with the substitution of Zr^{4+} because its radius is 0.72Å(6C.N.). Electron configuration of Ge^{4+} is $3d^{10}$, which also has no π type bonds, so octahedron distortion will not occur. Lattice parameters decrease with substitution due to it's small ionic radius 0.54 Å(6 C.N). In case of Mn^{4+}, electron configuration is $3d^3$ and three electrons reside in d_{xy}, d_{yz}, d_{zx} the low energy states of octahedral crystal field t_{2g}. Therefore Mn^{4+} is expected to have a very high symmetry bounds in the octahedral and induce no distortion of octahedral. In considering the ionic radius of Mn^{4+}(0.54Å), which is same as that of Ge^{4+}, lattice parameters would have expected to decrease with the substitution of Mn^{4+}, but slightly increased as shown in Fig.3. This indicate that the valence state of Mn is not only Mn^{4+} but also Mn^{3+}. Electron configuration of Mn^{3+} is $4d^4$, so four electrons exist in the d-shell. In this case, two states(low and high spin) are possible. The ionic radius of low spin one is 0.58Å and that of high spin one which also induce Jahn-Teller distortion is 0.65Å. Therefore, there seems to exist high spin Mn^{3+} judged by slight lattice parameter increase, which will induce the octahedral distortion due to the π type bond and Jahn-Teller effect.
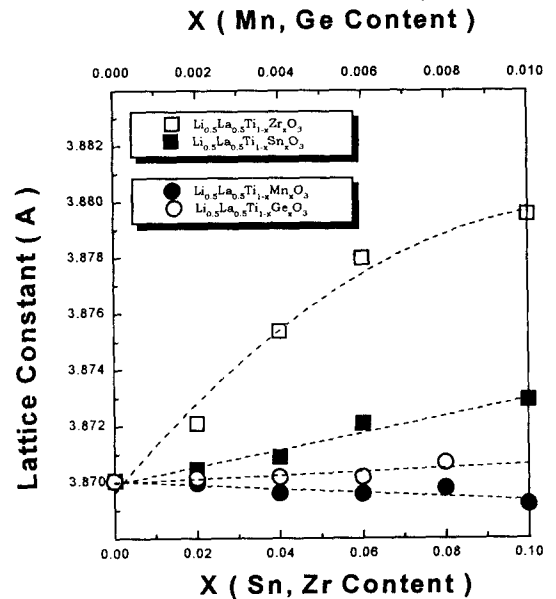
X (Mn, Ge Content)

X (Sn, Zr Content)

Fig. 3. Lattice parameters variation with B-site ion substitutions in $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$($M$=Sn,Zr, Mn,Ge).

3.3 Dependence of bulk conductivities on the B-site ion substitutions

Fig.4 shows the complex impedance plots for the bulks part of the B-site ion substituted samples and Fig.5 the calculated conductivities. As shown in Fig.5, conductivities decreased with the substitution of Sn^{4+}(0.69Å) and Zr^{4+}(0.72Å) , and the decrease was steeper for the Zr^{4+} substituted samples.

Especially the conductivity of 0.1mol% Zr^{4+} substituted samples was abnormally low. This is considered to have a relation with the distortion of octahedron estimated by the lattice parameter variations in Fig.3. Because octahedron distortion will contract the bottleneck, and make difficult for the lithium ion to
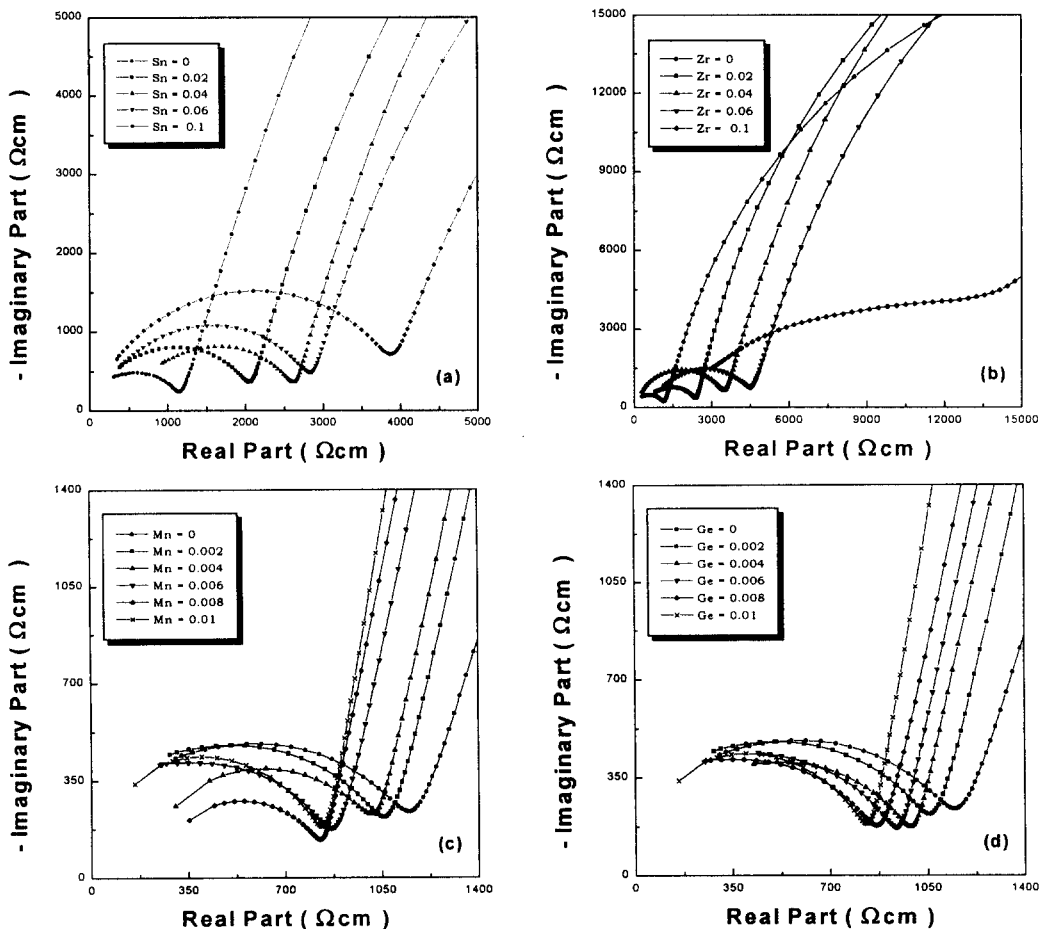
Fig. 4. Complex impedance plots of the bulk parts for (a) $(Li_{0.5}La_{0.5})Ti_{1-x}Sn_xO_3$, (b) $(Li_{0.5}La_{0.5})Ti_{1-x}Zr_xO_3$, (c) $(Li_{0.5}La_{0.5})Ti_{1-x}Mn_xO_3$, (d) $(Li_{0.5}La_{0.5})Ti_{1-x}Ge_xO_3$.

move to enter an adjacent A-site vacancy. Conductivities increased with the substitution of $Ge^{4+}(0.54\text{Å})$, but for the Mn substituted samples increased up to 0.008mol% and after that decreased. In case of Mn, two valence states $Mn^{4+}(0.54\text{Å})$ and $Mn^{3+}(0.65\text{Å}$ in high spin) might be thought to exist as it was shown through the lattice parameter variation in Fig.3. Therefore it looks like as if two ions exist, which make hard to discern the relationship between conductivity and the manganese substitution. So only considering the effects of Sn^{4+}, Zr^{4+} and Ge^{4+} substitution on the lithium ion conductivity, it could be concluded that the conductivity increase with decreasing the radii of B-site ions or vice versa and octahedron distortion disturb the ion conduction. After all the ions which have the only size effects of ions on the ionic conductivity are Sn^{4+} and Ge^{4+}. And considering the similarity of conductivities between Ge^{4+} and manganese substituted samples up to 0.008mol%, it may be deduced that Mn^{4+} dominate the conductivity up to 0.008mol% and after that Mn^{3+} which will diminish the ion conduction due to the Jahn-Teller distortion as well as the larger ionic radius. But the reason for this phenomena has not yet been known.

Why does the conductivity inversely depend on the ionic radius of B-site ions. We first considered about the relation of the bottleneck size and the B-site ion substitution. The size of bottleneck, lattice parameter minus diameter of oxygen ion, is proportional to the lattice parameter if there are no lattice distortion[3]. With the substitution of Sn^{4+} and Ge^{4+} no distortion was expected to occur (because of the small amounts of substitution, tolerance factor nearly did not change) as well as the observed primitive cell was cubic. Therefore, the increased lattice parameter with Sn^{4+} substitution will also increase the bottleneck size. Nevertheless the ionic conductivity decrease with Sn^{4+} substitutions. And it was same tendency for the case of Ge^{4+}, the shorter lattice parameter, the higher the conductivity. Therefore it was found that the variation of the conductivity with the B-site ion substitution was not due to the change of bottleneck size.
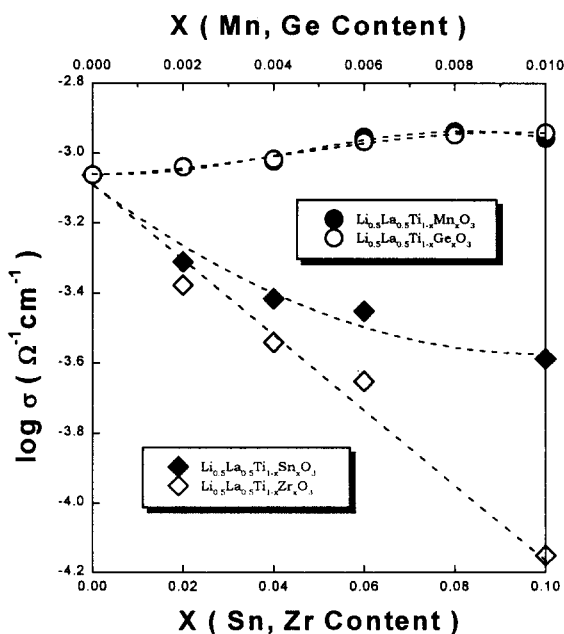
Conductivity was reported to decrease by the substitution of $(Mg_{1/2}W_{1/2})$ for Ti^{4+} (the average ionic radius of $(Mg_{1/2}W_{1/2})$: 0.66 Å, Ti^{4+} : 0.605 Å). And this was explained on the base of the reduction of free volume for lithium move[6]. However, the free volume in fact was increased by this substitution (the free volume was approximately estimated by calculating cell volume minus B-site ion volume: $57.48 Å^3$ for $(La_{0.63}Li_{0.1})TiO_3$, $59.34 Å^3$ for $(La_{0.63}Li_{0.1})(Mg_{1/2}W_{1/2})O_3$). We calculated and showed the dependence of free volume change on the Sn^{4+} and Ge^{4+} substitutions in Fig.6. Free volume increased with Sn^{4+} substitution and decrease with Ge^{4+} substitution. Therefore the change of free volume was on the contrary of the results of the conductivities, and not also the reason for the variation of the conductivity with the B-site ion substitution.

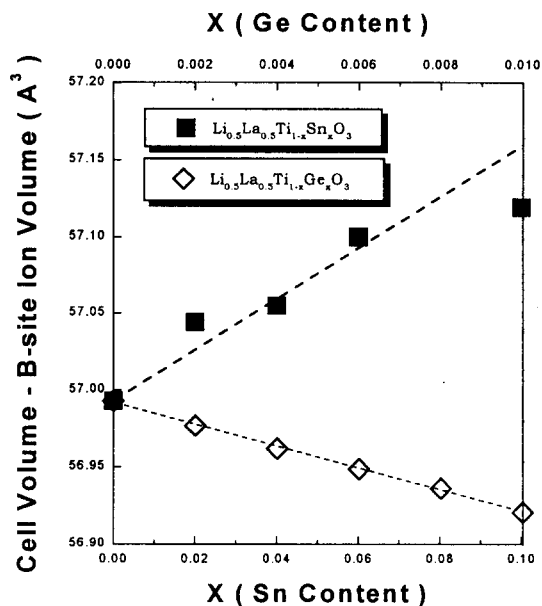Fig. 5. Conductivity dependence on the B-site ion substitutions for $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ ($M=$ Sn,Zr,Mn,Ge).

Fig. 6. Dependence of free volume change on B-site ion substitutions for $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ ($M=$ Sn,Zr,Mn,Ge).

Fig.7 shows the dependence of conductivities on temperature for Sn, Ge, substituted and undoped samples. The activation energies were 0.294eV and 0.265eV, larger and smaller than that of undoped one (0.280eV), for Sn^{4+} and Ge^{4+} substituted samples, respectively. Therefore it was found that the mobility of Ge^{4+} substituted sample increased, while that of Sn^{4+} substituted one decreased with substitutions. The reasons for this mobility change could be considered as follows. One reason may be the change of the facility of TiO_6 octahedron tilting. When lithium ion migrates from an A-site to a vacant site, the tilting of TiO_6 octahedron occur. So if Ge^{4+} substitution for Ti^{4+} facilitate the tilting of octahedron, lithium ion conduction will be enhanced, and the opposite phenomenon will occur in case of Sn substitution. It has not been known how the facility of TiO_6 octahedron tilting was influenced by the ions substitutions. But usually this octahedron tilting is empirically reported to depend on the lattice parameter and/or free volume[13,14]. That is the larger the lattice parameter(and/or free volume), the easier the tilting of octahedron and the higher the conductivity. But in this study Ge^{4+} substitution decrease the lattice parameter and free volume as shown in Fig.3 and 6, but increase the conductivity, and the opposite for Sn^{4+}. So the change of the facility of octahedron tilting by B-site ion substitution may not the reason for our results.

Therefore now we will discuss about the other possible reason. It is suggested that the bond strengths of A-O(σ_{A-O}) and B-O(π_{B-O}) bond in ABO_3 perovskite oxide are competing because they use the same 2p oxygen orbitals[15]. That is the strong A-O bond strength weaken the B-O bond and the weak A-O bond strength strengthen the B-O bond. And the bond strength depends on the interatomic distances. For example, in case of partly substituting Sr for Ba in $BaTiO_3$ (r_{Sr}^{2+} = 1.44 Å, r_{Ba}^{2+} = 1.61 Å), the interatomic
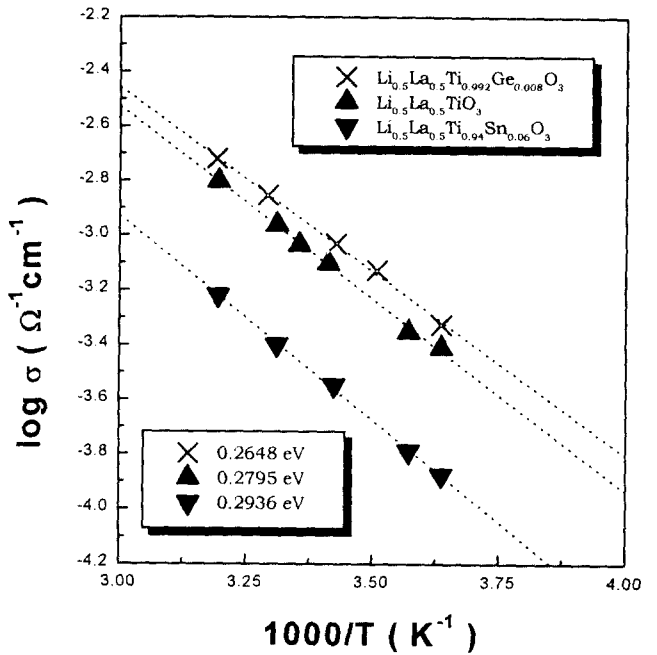

Fig. 7. Arrhenius plot of bulk conductivity for $(Li_{0.5}La_{0.5})TiO_3$, $(Li_{0.5}La_{0.5})Ti_{0.992}Ge_{0.008}O_3$, $(Li_{0.5}La_{0.5})Ti_{0.94}Sn_{0.06}O_3$.

distance of Sr-O is shorter than that of Ba-O, so σ_{Sr-O} bond is stronger than the σ_{Ba-O} bond, whereas the competing $\pi_{Ti-O}(Sr)$ bond becomes weaker with respect to $\pi_{Ti-O}(Ba)$. Therefore the Sr-Ba substitution weaken the π_{Ti-O} bond. It was reported that these change of the interatomic bond strength due to the variation of the interatomic distance induced by substituting the different ionic radius ions for A and/or B site ions affected the transition temperature and the evaporation of PbO[15.16]. These results could be applied to our system. When the Sn^{4+} substituted for Ti^{4+} in $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ system, the increased interatomic Ti-O bond distance weaken the bond strength(π_{Ti-O}), so the competing Li-O(σ_{Li-O}) bond is strengthened. Thereby the activation energy of lithium ion increase, the mobility decrease, so as a result the ionic conductivity decrease. In case of smaller B-site

ion substitution, for example Ge^{4+} substitution for Ti^{4+} in $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ system, the increased bond strength of $Ti-O$ (π_{Ti-O}) weaken the competing $Li-O$ (σ_{Li-O}) bond, decrease the activation energy of lithium ion, increase the ion mobility, and resultingly increase the lithium ionic conductivity. This suggestion is also quite in agreement with the results of lanthanide ions substitutions in $(Li_{0.5}Ln_{0.5})TiO_3$ (Ln=La,Pr,Nd,Sm) system[17]. Therefore the interatomic bond strength change due to the cation substitutions may be the one of the major factors influencing the lithium ion conductivity in perovskite $(Li_{0.5}La_{0.5})TiO_3$ system.

4. Conclusion

The conductivities study of the $(Li_{0.5}La_{0.5})$ $Ti_{1-x}M_xO_3$ (M= Sn,Zr,Mn,Ge) system have shown that the conductivity increase with decreasing the radii of B-site ions or vice versa and that octahedron distortion disturb the ion conduction. This reciprocal proportion of conductivity on the radius of B-site ions has been examined on the base of the bottleneck size, free volume and facility of TiO_6 octahedron tilting. But the results suggest that the conduction may involve other mechanism. Therefore we applied the interatomic bond strength change due to the cation substitutions. That is when the smaller B-site ion substituted for Ti^{4+} in $(Li_{0.5}La_{0.5})Ti_{1-x}M_xO_3$ (M=Sn, Zr,Mn,Ge) system, the decreased interatomic Ti-O bond distance strengthen the bond strength(π_{Ti-O}), and the competing Li-O(σ_{Li-O}) bond is weakened. Thereby the lithium ionic conductivity increase due to the decrease of the activation energy. In case of larger B-site ions and smaller lanthanide ions substitutions in $(Li_{0.5}Ln_{0.5})TiO_3$ system, the conductivities decrease could be explained as the

same reasoning. Therefore it could be concluded that the interatomic bond strength change due to the cation substitutions may be the one of major factors influencing the lithium ion conductivity in perovskite $(Li_{0.5}La_{0.5})TiO_3$ system.

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