Relationship between Pre-Exponential Factor and Activation Energy of Conductivity in Sintered $\text{Ln}_{9.33+x/3}\text{Si}_{6-x}\text{M}_x\text{O}_{26}$ (Ln = La, Nd, Sm, M = Al, Gd) with Apatite-like Structure

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Electrical conductivity of a series of $\text{Ln}_{9.33+x/3}\text{Si}_{6-x}\text{M}_x\text{O}_{26}$ (Ln = La, Nd and Sm, M = Al and Ga) sinters was examined. The pre-exponential factor and activation energy of the ionic conduction were well related by Meyer-Neldel rule, i.e., $G = G_0 \exp(\Delta E/kT_0) \exp(-\Delta E/kT)$. Most of the sinters were composed with an apatite-like phase in major and sub-products such as LnSiO_5 and Ln_2O_3 in minor proportions. The single phases with apatite-like structure were obtained for the composition of $x = 1.5$. At this composition, the activation energy increased with a decrease in the ionic radius of Ln. The lowest activation energy and highest pre-exponential factor were observed for the combination of Ln = La and M = Al. This result was interpreted by considering the formation of the 4e sites for oxygen with under occupancy and oxygen ion interstitials surrounded with six 6h(La) sites.

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1. Introduction

Solid-state electrolytes with high ionic conductivity form the basis of electric devices, such as oxygen pumps, sensors and fuel cells, which have a huge marked potential. Recently, it was found that some apatite-like rare earth silicates exhibited a quite high oxide-ion conductivity.^{1)–6)} The La_2O_3 - SiO_2 phase diagram reported by Bondar⁷⁾ suggested that the phases below 1775°C in the relevant composition range were composed with $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and La_2SiO_5 and $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ is not an equilibrium phase according to this diagram. In fact a single phase of $\text{Ln}_{10}(\text{SiO}_4)_6\text{O}_3$ could not be obtained even by the sintering at 1550–1850°C.³⁾ Tao and Irvine reported that a single phase $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ could be synthesized by a sol-gel process.⁸⁾ However, the obtained sinters were not dense and the relative density was no more than 69% for those sintered at 1400°C for 20 h and 80% at 1500°C for 22 h. Mazza and Ronchetti⁹⁾ have been reported the ternary phase diagram, La_2O_3 - SiO_2 - Al_2O_3 at 1300°C and suggested that the $\text{La}_{14}\text{Si}_9\text{O}_{39}$ compound extended its stability range in the interior of the phase diagram, forming a solid solution of the type $\text{La}_{14+x/3}\text{Si}_{9-x}\text{Al}_x\text{O}_{39}$, which was stable from $x = 0$ to $x = 1.5$. The electrical conductivity of $\text{La}_{9.33+x/3}(\text{SiO}_4)_{6-x}(\text{AlO}_4)_x\text{O}_2$ ($0 \leq x \leq 2$) was examined and Al-doping resulted a conductivity enhancement by 1–2 orders of magnitude for intermediate x -values.¹⁰⁾ They explained this conductivity enhancement from the viewpoint of the La vacancy created by the Al-doping. However, the conduction mechanism involved has not been clarified in detail. The electrical characteristics are influenced by several factors such as quality of phase, impurities, sub-product, grain boundary, porosity and so on. To clarify the reason for the abnormally high ionic conductivity of the materials, it is desired to know the electrical properties of family compounds in which the elements have different ionic radii and coordination numbers.

Therefore, in this work, a series of the related compounds, Ln_2O_3 - M_2O_3 - SiO_2 (Ln = La, Nd and Sm, M = Al and Ga), were examined in detail by XRD, SEM, solid-state ^{29}Si NMR and ac impedance analyses and the oxide ion conduction was systematically discussed in terms of thermal activation process.

2. Experimentals

Reagent grade of La_2O_3 , Nd_2O_3 , Sm_2O_3 , Al_2O_3 , Ga_2O_3 and amorphous SiO_2 were used as starting materials. These materials were mixed with a prescribed ratio by dry ball-mill using YSZ balls in nylon pot. The mixed powders were heat-treated and compressed in a disc at 300 kg/cm² and finally sintered at 1600°C for 5 h in ambient air. The morphology of the sintered discs was observed with SEM (JEOL, JSM-5310). The discs on which of both the sides were painted with Au paste were lead with Au wire and then heated at 700°C in ambient air. Then the conductivity of the disks in ambient air was determined by using impedance/gain-phase analyzer (Solartron SI1260). The sinters in powders were examined with XRD ($\text{K}\alpha$ Cu, Rigaku RINT2200V) and solid-state ^{29}Si NMR (JEOL JNM-CMX300) at 59.74 MHz (rotation: 4 kHz). Chemical shifts are quoted relative to poly-dimethylsilane.

3. Results and discussion

The mixtures in discs were sintered at several temperatures in ambient air and their outer and fractured surfaces were observed with SEM. Some of the results are shown in **Figs. 1** and **2**. In some sinters, closed pores were found but any through pores could not be detected. The sinters were composed with an apatite-like crystalline phases in major and Ln_2O_3 and Ln_2SiO_5 were detected in minor proportions. The concentration of the minor proportions depended on the composition of the starting materials. The XRD patterns of $\text{Ln}_{9.33+x/3}(\text{SiO}_4)_{6-x}(\text{MO}_4)_x\text{O}_2$ are shown in **Figs. 3–5**. For $x = 0$ (Fig. 3), further to the apatite-like phase, Ln_2SiO_5 sub-phase were detected and its peak intensity decreased with an increase in the x -value. For $x = 1.5$ (Fig. 4), all the observed signals with the relative intensity higher than 5% were assigned with an apatite-like crystal with hexagonal ($P6_3/m$ and/or $P-1$). It should be noted that in La-system the most intense peaks at $2\theta = 30.5^\circ$ for M = Ga and 30.6° for M = Al are not single peaks but have their shoulders at 30.6° and 30.7° , respectively, and this leaves no doubt that the La-system have a similar crystalline systems as the Sm and Nd-systems. When the x -value increased to 2.0 (Fig. 5), Ln_2SiO_5 could be detected but on the other hand Ln_2O_3 phase newly appeared. It is thus concluded that a highest quality of

Surface

Cross Section

Fig. 1. SEM photographs of the surfaces and cross-sections of $\text{Ln}_{9.33+x/3}\text{Si}_{6-x}\text{Al}_x\text{O}_{26}$ sinters with $x=0$ to 2.0.

Fig. 2. SEM photographs of the cross-sections of $\text{Ln}_{9.83}\text{Si}_{4.5}\text{M}_{1.5}\text{O}_{26}$ sinters, where the combinations of (Ln, M) = (La, Ga), (Nd, Al) and (Nd, Ga).

the sinters with an apatite-like crystal was observed for $x=1.5$. **Figure 6** shows the estimated lattice parameters of the apatite-like crystals with hexagonal, $P6_3/m$ (SG: 176). In common to the Ln and M, the lattice parameters were monotonically increased with an increase both in the x -values and the ionic radius.

The electrical conductivity of the sinters in ambient air was examined by ac impedance analysis. In the complex impedance plots, arcs and spike were observed in a high and low frequency ranging from 10 MHz to 100 Hz. The total resistances were estimated from the intercept of the spike and/or the arcs in the lower frequency end on the Z' axis. The conductivity was determined from the total resistance. The temperature dependence of the G was well expressed by Arrhenius relationship.

$$G = G_0 \exp(-\Delta E/kT) \quad (1)$$

where G , T , G_0 , ΔE and k are conductivity, absolute temperature, pre-exponential factor, activation energy and Boltzmann constant, respectively. The pre-exponential factor and the activation energy of the sinters were estimated using Eq. (1). The relationship between the activation energies and pre-exponential factors of the conductivity in each series of the sinters is shown in **Fig. 7**. It was confirmed that the relationship could be described with the following equation.

$$G = G_{00} \exp(\Delta E/kT_0) \exp(-\Delta E/kT) \quad (2)$$

where T_0 is a constant called “compensation temperature” and G_{00} is newly defined pre-exponential factor. This phenomenological relationship is known as “Meyer-Neldel rule” since this relationship was observed by Meyer and Neldel (1937) for the

Fig. 3. XRD powder patterns of $\text{Ln}_{9.33}\text{Si}_6\text{O}_{26}$ ($\text{Ln} = \text{La}, \text{Nd}$ and Sm) sintered at 1600°C for 5 h.

Fig. 4. XRD powder patterns of $\text{Ln}_{9.83}\text{Si}_{4.5}\text{M}_{1.5}\text{O}_{26}$, where (Ln, M) = (La, Al), (La, Ga), (Nd, Al), (Nd, Ga) and (Sm, Al), sintered at 1600°C for 5 h.

Fig. 5. XRD powder patterns of $\text{Ln}_{9.996}\text{Si}_{44.0}\text{M}_{2.0}\text{O}_{26}$, where (Ln, M) = (La, Al), (La, Ga), (Nd, Al), (Nd, Ga) and (Sm, Al), sintered at 1600°C for 5 h.

conductivity of disordered oxide semiconductors exposed to an oxygen atmosphere.^{11),12)} At present, the reason why the

Fig. 6. Lattice parameters of the $\text{Ln}_{9.33+x/3}\text{Si}_{6-x}\text{Al}_x\text{O}_{26}$ with the different x -values and (Ln, M) combinations determined by the corresponding XRD patterns.

Fig. 7. Relationship between the activation energies and pre-exponential factors (G_0) of the conductivity in each series of the sinters. The plots denoted by circles correspond to the $x = 1.5$ in each series of sinters.

relationship expressed by Eq. 3) is not well realized. By adopting a random walk approach for the migration of oxygen ions, it is shown that the Meyer–Nelder rule follows if one assumes spatially randomly varying activation energies for jumps with an exponential probability distribution, $p(\Delta E')$.

$$p(\Delta E') \propto \exp(-\Delta E'/kT_0) \quad (3)$$

where $\Delta E'$ is the energy difference between the energy of barrier (ε_0) and site energies (ε), which varies between zero and maximum activation energy ΔE equal to the conductivity activation energy. For a random walk model with equal energy maximum and randomly varying minima, the distribution of site energies, i.e. minimum energies is expressed as follows,

$$p(\varepsilon) \propto \exp(\varepsilon/kT_0) \quad (4)$$

since $\Delta E' = \varepsilon_0 - \varepsilon$ where ε_0 is the energy of the barrier (the maximum).

The observed results in the present study strongly suggested that the Meyer–Nelder rule was applicable for the mixtures of apatite type oxide and sub-products such as Ln_2O_3 and Ln_2SiO_5 . The existence of Ln_2SiO_5 resulted in a decrease in the pre-exponential factor, mainly, i.e. the decrease in the concentration of mobile oxygen ions in bulk. In addition, it seems that the existence of Ln_2O_3 results in the decrease in pre-

Table 1. ^{29}Si -NMR Data for the Series of Lanthanoid Silicates

Sample	Sintering temp. ($^{\circ}\text{C}$)	Chemical shift (ppm)	Relative intensity (%)	Phase (XRD)
La_2SiO_5	1600	-83.3	100	La_2SiO_5
$\text{La}_{10}\text{Si}_6\text{O}_{27}$	1600	-77.8, -82.4, -85.4	43.6, 49.0, 7.4	Apatite, La_2SiO_5
$\text{La}_{9.33}\text{Si}_6\text{O}_{26}$	1600	-77.1, -82.2, -85.8	68.7, 26.4, 4.9	
$\text{La}_{9.67}\text{Si}_6\text{O}_{26.5}$	1600	-78.4, -83.5, -87.5	79.1, 12.9, 8.0	Apatite, La_2SiO_5
$\text{La}_{9.5}\text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{26}$	1600	-77.6, -81.7	79.0, 21.0	Apatite, La_2SiO_5
$\text{La}_{9.67}\text{Si}_5\text{AlO}_{26}$	1600	-77.6, -81.1	86.0, 14.0	Apatite
$\text{La}_{9.83}\text{Si}_{4.5}\text{Al}_{1.5}\text{O}_{26}$	1600	-77.6	100	Apatite
$\text{La}_{10}\text{Si}_4\text{Al}_2\text{O}_{26}$	1600	-77.1, -81.4	90.5, 9.5	Apatite, La_2O_3

exponential factor and increase in activation energy, i.e. the decrease in the concentration of mobile oxygen ions and the increase in the difference of $\Delta E'$ in Eq. (4). The compensation temperature T_0 for La, Nd and Sm-systems decreased with an increase in the ionic radius of the Ln-ions ($\text{La} < \text{Nd} < \text{Sm}$).

Lippmaa, et al.^{(13),(14)} studied on the ^{29}Si isotropic chemical shift in the series of solid silicates. The ^{29}Si chemical shifts in the silicates is observable in the range between -60 to -120 ppm with well-separated ranges for monosilicates (Q^0), disilicates and chain end groups (Q^1), middle groups in chains (Q^2), chain branching sites (Q^3), and the three-dimensional cross-linked framework (Q^4). It seems that the phase homogeneity of the sinters reflects to the ^{29}Si NMR signals. The ^{29}Si NMR data for the series of lanthanoid silicates are summarized in **Table 1**. Only single peaks was observed at -83.3 ppm for La_2SiO_5 with monoclinic structure (P121/c1) and at -77.6 ppm for the samples with $\text{La}_{9.83}\text{Si}_{4.5}\text{Al}_{1.5}\text{O}_{26}$ indicating that the $[\text{SiO}_4]^{4-}$ units in each of the lanthanoid silicates are chemically equivalent. Both the values of chemical shift seem to belong to the Q^1 sub-division. In some compositions, more than one chemical shifts were observed at < -80 ppm, most probably due to distortions and/or displacements in some of $[\text{SiO}_4]^{4-}$ units arising from cation vacancies, oxygen interstitials and/or due to the coexistence of sub-formed silicates such as La_2SiO_3 and $\text{La}_2\text{Si}_2\text{O}_7$.

By the comparison of the XRD and ^{29}Si NMR signals, a highest quality in composite of the sinters is expected for $x = 1.5$. The XRD results of $x = 1.5$ are shown in Fig. 4 and the observed signal with the threshold intensity $> 1\%$ were assigned to the apatite-like crystal structure with P63/m. In Fig. 7, the characteristics of the sinters for $x = 1.5$ were indicated with open circles. For that composition, the estimated activation energy increased with a decrease in the ionic radius of Ln-ion. The lowest activation energy and a higher pre-exponential factor were observed for the $x = 1.5$ compositions in the La-system. For the Nd and Sm-systems, the activation energies and logarithm of the pre-exponential factors seem to be in a linear relationship, hence follow the Meyer-Nelder rule. For the La-system only the characteristics for the $x = 1.5$ compositions were clearly deviated from the Meyer-Neldel relationship. The expected crystal structures of $\text{La}_{9.84}\text{Si}_6\text{O}_{26}$ and $\text{La}_{9.83}\text{Si}_{4.5}\text{Al}_{1.5}\text{O}_{26}$ were illustrated in **Fig. 8**.

The total number of the elements in the unit cell is 42 and 50 for $\text{La}_{9.84}\text{Si}_6\text{O}_{26}$ and $\text{La}_{9.83}\text{Si}_{4.5}\text{Al}_{1.5}\text{O}_{26}$, respectively.⁽¹⁵⁾ In the latter case, the 6h sites for Si are partially replaced with Al and the 4e sites for O are in under occupancy. It seems that the partial replacement of Si with Al induces the change of the O-site from 2a (fully occupied) to 4e (half occupied) situating along the c-lattice. Assuming the number of mobile oxide-ions is uninfluenced by the partial replacement of Si with Al, activation energy for the migration of oxide-ions would be decreased with the change from 2a-site to 4e-site. Replacing Al with Ga resulted in the cell volume and this could decrease in activation energy. But on the contrary the replacement increased the activation energy. Therefore it is deduced that the oxygen ions bound with the M^{3+} ions are not mobile oxygens.

A large pre-exponential factor was observed for $x = 1.5$, La-Al, and a similar tendency was observed for $x = 1.5$, La-Ga (Fig. 7). The observed large values may be due to the higher coordination number of La with O than the other lanthanoid systems, resulting that the oxide ion interstitials surrounded with the six 6h sites are occupied with La. The effects of the coordination number of oxygen and ionic radius of Ln were considered. The cluster structures of La, Nd and Sm sites are interpreted from the crystal structures. The numbers of coordinating oxygen are 7 and 9 for 6h(La) and 4f(La), 7 and 9 for 6h(Nd) and 4f(Nd), and 6 and 6 for 6h(Sm) and 4f(Sm), respectively. If the oxygen locating at the 2a sites becomes mobile by thermal activation, activation energy should be related to the Ln(6h)-O(2a) distance. The distance between Ln(6h)-O(2a) is expected to 0.290, 0.271 and 0.247 nm for La, Nd, and Sm in $\text{Ln}_{10}\text{Si}_6\text{O}_{26}$ (the number of atoms in the unit cell was assumed to be 42), respectively. The increase in the activation energy was related to the number of coordinated oxygen and the distance between Ln(6h)-O(2a). In fact the migration energy of oxygen located at the 2a site is in a linear relationship with the reciprocal value of the sum of radii of Ln and O, i.e., $1/(r'_{\text{Ln}} + r_0)$ that is lowest in the case of La.

4. Conclusion

A series of $\text{Ln}_{9.33+x/3}\text{Si}_{6-x}\text{Al}_x\text{O}_{26}$ with apatite-like crystal structure with hexagonal was examined because of their high oxide ion conductivity. In appearance, the characteristics of

Fig. 8. Expectable crystal structures of apatite-like oxides.

the conductivity of the sinters were not related to the composition and also to the estimated lattice parameters. Phenomenally, the relationship between the pre-exponential factor and the activation energy of the conductivity is expressed with Meyer–Neldel rule for a series of the sinters composed with apatite-type oxide and sub-products. The XRD results suggested that the sinters with $x = 1.5$ for $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ and $\text{M} = \text{Al}$ and Ga , were composed with apatite-like phase in high levels of quality. The activation energy of the conductivity decreased with an increase in the ionic radius of Ln . A novel high conductivity of $\text{La}_{9.83}\text{Si}_{4.5}\text{Al}_{1.5}\text{O}_{26}$ sinter is due to the high coordination number of Ln -ions in 6h sites for oxygen and the existence of half occupied 4e sites for oxygen.

References

- 1) S. Nakayama, H. Aono and Y. Sadaoka, *Chem. Lett.*, 431–432 (1995).
- 2) S. Nakayama, T. Kageyama, H. Aono and Y. Sadaoka, *J. Mater. Chem.*, 5, 1801–1805 (1995).
- 3) S. Nakayama and M. Sakamoto, *J. Eur. Ceram. Soc.*, 18, 1413–1418 (1998).
- 4) L. L. Reina, E. R. Losilla, M. M. Lara, S. Bruque and M. A. G. Aranda, *J. Mater. Chem.*, 14, 1142–1149 (2004).
- 5) J. E. H. Sansom, D. Riching and P. R. Slater, *Solid State Ionics*, 139, 205–210 (2001).
- 6) N. Takeda, Y. Itagaki, H. Aono and Y. Sadaoka, *Sens. and Actuators*, B115, 455–459 (2006).
- 7) L. A. Bondar, *Izv. Akad. Nauk SSSR, Neorg Mater.*, 15, 1008 (1979); *Inorg. (Engl Transl)*, 15, 793 (1979).
- 8) S. Tao and J. T. S. Irvine, *Mater. Res. Bull.*, 36, 1245–1248 (2001).
- 9) D. Mazza and S. Ronchetti, *Mater. Res. Bull.*, 34, 1375–1382 (1999).
- 10) E. J. Abram, D. C. Sinclair and A. R. West, *J. Mater. Chem.*, 11, 1978–1979 (2001).
- 11) R. Dewsberry, *J. Phys. D: Appl. Phys.*, 8, 1797–1805 (1975).
- 12) J. C. Dyre, *J. Phys. C: Solid State Phys.*, 21, 2431–2434 (1988).
- 13) E. Lippmaa, M. Maegi, A. Samson, G. Engelhard and A.-R. Grimmer, *J. Am. Chem. Soc.*, 102, 4889–4893 (1980).
- 14) J. E. H. Sansom, J. R. Tolchard, M. S. Islam, D. Apperley and P. R. Slater, *J. Mater. Chem.*, 16, 1410–1413 (2006).
- 15) ICSD-files; #99940, #30585.