Ac Conductivity for $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ with Pyrochlore-Type Composition

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Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama-shi 221-8686パイロクロア型組成を有する $\text{Eu}_2\text{Zr}_2\text{O}_7$ 及び $\text{La}_2\text{Ce}_2\text{O}_7$ の交流伝導度

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Ac conductivity (σ_{ac}) obtained from admittance of $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$, which have pyrochlore- and fluorite-type structure, respectively, was measured as a function of frequency in the range between 5 Hz and 13 MHz and in the temperature range between 573 and 1073 K. The frequency dependence of the σ_{ac} of these oxide-ion conductors showed a remarkably different behavior from that of the cation ones. By comparison of the σ_{ac} with other conductivity data obtained by dc four-probe and impedance spectroscopic methods, it was found that the σ_{ac} in the frequency range below 10^5 Hz was strongly influenced by space charge polarization at grain boundary and that the σ_{ac} obtained from high frequency plateau agreed with bulk conductivity, σ_{ib} , from impedance spectra and dc conductivity, σ_{dc} .

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1. Introduction

Oxide-ion conductors play an important role for various applications; oxygen sensor, oxygen pump, solid oxide fuel cell, etc. Among many materials showing oxide-ion conduction, fluorite (F)-type structure has been widely investigated, because the F-type structure can accept relatively large amounts of oxygen vacancy, from which pyrochlore (P)-type and rare-earth C-type (C) structures can be derived. In the P-type structure with a composition $\text{A}_2\text{B}_2\text{O}_7$ that belongs to space group $Fd\bar{3}m$ ($Z=8$), A^{3+} ion is located at 16c site, B^{4+} ion at 16d site, and O^{2-} ion at 8a and 48f sites. 8b site is vacant in the completely ordered P-type structure. The cubic C-type structure with a composition of A_2O_3 ($\text{AO}_{1.5}$) belongs to space group $Ia\bar{3}$ ($Z=16$), which can also be recognized as F-type structure with ordered oxygen vacancies on the anionic sublattice. Therefore, these oxides are very appropriate compounds in order to study the factors affecting on oxide-ion conduction from viewpoint of defect crystal chemistry.

Recently, the present authors have systematically investigated the relationship between crystal phases and oxide-ion conductivity for the various oxides with chemical formula of $(\text{A}, \text{B})\text{O}_{1.75}$ or $\text{A}_2\text{B}_2\text{O}_7$ ($\text{A}=\text{La}, \text{Y}$ and rare earth ions, $\text{B}=\text{Zr}, \text{Ce}$), and their solid-solution systems, which have F-type, P-type or C-type structures.^{1)–3)} Figure 1 shows the oxide-ion conductivity at 1073 K for $\text{A}_2\text{B}_2\text{O}_7$ ($\text{A}=\text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Y}, \text{Yb}$ and $\text{B}=\text{Zr}, \text{Ce}$) as a function of cation radius ratio, $r(\text{A}^{3+})/r(\text{B}^{4+})$. It can be seen that the crystal phases and the oxide-ion conductivities are strongly affected by both the cation radius ratio that is a measure of ordering of oxygen vacancy and the lattice constant that is a measure of unit cell free volume.²⁾ Consequently, the maximum oxide-ion conductivity was observed in the vicinity of the crystal phase boundary in these systems. Therefore, $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ that were boundary phases from F- to P-type, and from C- to F-type phase, respectively, were chosen in order to investigate the conduction mechanism in detail.

Although various methods for the electrical conductivity measurements are known, the present study focused frequency dependence of ac conductivity in relation with the conductivi-

Fig. 1. Dc conductivity (σ_{dc}) at 1073 K as a function of cation radius ratio in $\text{A}_2\text{Zr}_2\text{O}_7$ and $\text{A}_2\text{Ce}_2\text{O}_7$ ($\text{A}=\text{La}, \text{Y}$, and rare earth ions) systems.

ty data obtained from other methods: dc 4-probe method and impedance spectroscopy, in order to clarify the movement or displacement of oxide ion in oxide-ion conductors. It is known that the ac conductivity (σ_{ac}) of many cationic conductors obey the following relation in the usual frequency range $f=1$ Hz to 1 MHz:

$$\sigma_{ac} = \sigma(0) + \sigma'(\omega) \quad (1)$$

where $\sigma(0)$ is the ac conductivity extrapolated to zero frequency, which corresponds to the dc conductivity.⁴⁾ The dis-

persion term of conductivity, $\sigma'(\omega)$ is polarization conductivity at angular frequency (ω), which can be expressed in the form

$$\sigma'(\omega) = A\omega^s \quad (2)$$

where the parameter A and s are related to temperature-dependent properties. This relation is known as Universal Dielectric Response (UDR),⁵⁾ and can be applied to many cationic conductors of crystals and glasses.^{6)–9)} However, there have been only a few reports concerning the ac conductivity of oxide-ion conductors. Henn et al.¹⁰⁾ reported that σ_{ac} and $\sigma'(\omega)$ of single crystal Y-doped ZrO_2 obeyed Eqs. (1) and (2). On the other hand, Pimenov et al.¹¹⁾ observed a strong dispersion of σ_{ac} at a relatively high temperature for sintered specimens of Y-doped ZrO_2 and they have discussed that the dispersion of ac conductivity of the polycrystalline Y-stabilized zirconia in intermediate frequency region originated due to the contribution of grain boundary. However, there has not been an explicit relationship between the ac conductivity and the conductivity data obtained from dc and impedance spectroscopic methods. Therefore, in the present study, we investigated the ac conductivity of materials having pyrochlore-type composition with a relation to other conductivity data obtained from dc measurement and impedance spectroscopy.

2. Experimental procedures

Powder samples of $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ were synthesized by means of a solid-state reaction, using ZrO_2 (99.7%, TOSOH Co.), Eu_2O_3 (99.9%, Mitsuwa Chemicals Co.), La_2O_3 (99.99%, Wako Pure Chemicals Co.), CeO_2 (99.99%, High Purity Chemicals Co.) as starting materials.

The weighed powders were wet ball-milled for 16 h, using a milling pot made of synthetic resin and resin-coated balls, and ethanol as the dispersion reagent. After drying, the powder mixtures were calcined at 1373 K for 5 h in air. After sieving under 53 μm in mesh size, the powder samples were molded uniaxially under the pressure of 50 MPa and subjected to rubber press at 200 MPa. The compacts thus obtained were sintered at 1873 K for 10 h in air. The relative densities of the sintered specimens of $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$, which were estimated from the geometrical dimensions and weight, were 98.1 and 93.3%, respectively. Microstructure of the sintered specimens was observed by SEM (JSM-5200), after thermal etching at 1873 K for 1 h in air. Grain size of the thermal etched specimens was also estimated by intercept method with use of the surface micrographs of SEM.

The powdered samples were characterized by means of an X-ray diffraction (XRD) (model: RAD-A, Rigaku Co.) with monochromated $\text{Cu K}\alpha$ radiation. The lattice constant was determined from the XRD peaks by the least square method, using Si powder as the external standard.

Oxygen partial pressure, $p(\text{O}_2)$, dependence of the electrical conductivity was also measured in the range of 1.013×10^5 to 10.0 Pa at constant temperature of 1173 K.

The dc electrical conductivity (σ_{dc}) of the sintered specimens was measured by a dc four-probe method in the temperature range of 873 to 1273 K in air. The geometrical dimensions of the sintered bar for the dc conductivity measurements were 4×4 and ~ 30 mm length. Other electrical properties such as real and imaginary part of impedance, ac conductivity, (σ_{ac}) and dielectric constant (ϵ_r') were measured as a function of frequency by ac two-probe method in the temperature range from 573 to 1073 K in air. The ac conductivity was estimated from a real part of admittance. An impedance analyzer (4192A LF, Yokogawa-Hewlett-Packard Ltd.) was used for

these measurements in the frequency range of 5 Hz to 13 MHz. The dimension of the sintered disk for the ac conductivity measurements was 10 mm in diameter and 2 mm in thickness. For the all measurements, platinum electrode was attached to both sides of the specimen by firing at 1273 K for 1 h in air.

In this study, we deal with various kinds of conductivity. Therefore, it may be useful to summarize the various conductivity and their notations.

σ_{dc} : dc conductivity obtained by dc four-probe method.

σ_{ib} : bulk conductivity obtained from impedance spectra.

σ_{igb} : grain boundary conductivity obtained from impedance spectra.

σ_{total} : inverse value of $(\rho_{ib} + \rho_{igb})$, where ρ_{ib} and ρ_{igb} mean the resistivity of bulk and grain boundary estimated from impedance spectra, respectively.

$\sigma_{ac}(\omega)$: ac-conductivity obtained from a real part of admittance, which is a function of frequency of electric field.

σ_{ach} : ac-conductivity obtained from the plateau region at high frequency.

σ_{acl} : ac-conductivity obtained from the plateau region at low frequency.

3. Experimental results and discussion

Figure 2 shows XRD patterns of $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$. The XRD pattern of $\text{Eu}_2\text{Zr}_2\text{O}_7$ that contains superlattice lines besides diffraction lines of fluorite-type phase was successfully indexed according to pyrochlore (P)-type structure with cubic symmetry. The lattice constant was estimated to be $a = 1.056$ nm ($a = 0.5280$ nm for the F-type unit cell). On the other hand, $\text{La}_2\text{Ce}_2\text{O}_7$ has an oxygen-deficient fluorite (F)-type structure with cubic symmetry, of which the lattice constant was $a = 0.5569$ nm. The grain sizes of sintered specimens of $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ that were fired at 1873 K in air were estimated to be approximately 3 and 10 μm by SEM observation, respectively.

Oxygen partial pressure, $p(\text{O}_2)$, dependence of the electri-

Fig. 2. XRD patterns of $\text{Eu}_2\text{Zr}_2\text{O}_7$ (pyrochlore-type phase) and $\text{La}_2\text{Ce}_2\text{O}_7$ (fluorite-type phase).

Fig. 3. Arrhenius plots of various conductivities which are dc conductivity (σ_{dc}), bulk (σ_{ib}) and total conductivity (σ_{total}) estimated from impedance spectra, and ac conductivity from low frequency plateau (σ_{acl}) and from high frequency plateau (σ_{ach}) for a) $\text{Eu}_2\text{Zr}_2\text{O}_7$ and b) $\text{La}_2\text{Ce}_2\text{O}_7$.

cal conductivity was measured for $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ in order to clarify conduction carrier. Both compounds were independent on the $p(\text{O}_2)$ between 1.103×10^5 and 10.0 Pa, suggesting that their major conduction carriers were oxide-ions.

Figure 3 shows Arrhenius plots of $\log \sigma_{dc}$ for $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$, where σ_{dc} denotes the conductivity from the dc four-probe method. The σ_{dc} values of $\text{La}_2\text{Ce}_2\text{O}_7$ (F-type) were larger in the high temperature range, but became smaller in the low temperature range than that of $\text{Eu}_2\text{Zr}_2\text{O}_7$ (P-type), because the activation energy of $\text{La}_2\text{Ce}_2\text{O}_7$ (99.3 kJ/mol) was larger than that of $\text{Eu}_2\text{Zr}_2\text{O}_7$ (56.4 kJ/mol). The smaller activation energy for electrical conduction of the P-type phase than that of the F-type one was also observed by van Dijk et al.,^{(12),(13)} who explained the origin by assuming an existence of preferential conduction paths through the cation tetrahedron plane around the $48f$ oxygen sites in the P-type structure. In spite of the small activation energy in the P-type phase, the conductivity of $\text{Eu}_2\text{Zr}_2\text{O}_7$ showed low values in the high temperature range. This fact may be explained by considering that “free” oxygen vacancy in the F-type phase changed to “frozen” state in the P-type phase due to its ordered structure. This “frozen” oxygen vacancy means a decrease in the conduction carriers.

The bulk (σ_{ib}) and grain boundary conductivity (σ_{igb}) were estimated from the complex impedance plane plots. Figure 4 shows the impedance spectra of $\text{Eu}_2\text{Zr}_2\text{O}_7$ in the temperature range, 773 to 973 K, where the semicircle in the high frequency region corresponds to the σ_{ib} and that in the low frequency region does to the σ_{igb} .⁽¹⁴⁾ The σ_{ib} values for $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ are also plotted in Figs. 3(a) and (b), both of which approximately agreed with the σ_{dc} . The σ_{total} value was lower than the σ_{ib} in the high temperature range above 773 K, and approached to the σ_{ib} below 773 K. Although $\text{La}_2\text{Ce}_2\text{O}_7$ has

Fig. 4. Impedance spectra of $\text{Eu}_2\text{Zr}_2\text{O}_7$.

Fig. 5. $\log \sigma_{ac}$ of $\text{Eu}_2\text{Zr}_2\text{O}_7$ as a function of $\log f$.

also slightly lower σ_{total} than σ_{ib} , the temperature dependence of σ_{total} was almost same with that of σ_{ib} (Fig. 3(b)).

Figure 5 shows the $\log \sigma_{ac}$ of $\text{Eu}_2\text{Zr}_2\text{O}_7$ as a function of $\log f$ at various temperatures. The curves of $\log \sigma_{ac}$ of $\text{Eu}_2\text{Zr}_2\text{O}_7$ vs. $\log f$ strongly depended on the measuring temperatures. In the temperature below 773 K, where the ρ_{igb} could not be observed in the impedance spectra, the $\log \sigma_{ac}$ increased slightly and linearly with increase in the frequency up to 10^6 Hz, and then increased sharply in the frequency range of $f > 10^6$ Hz. Extrapolated value of the σ_{ac} to $f=0$ below 773 K agreed with the value of σ_{ib} . That fact means that the σ_{ac} in the temperature range below 773 K changes according to Eq. (1) and that the frequency dependence of $\log \sigma_{ac}$ can be explained by the UDR theory.⁽³⁾ However, in the

Table 1. Various Conductivity Data at 973 K for $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$

	$\text{Eu}_2\text{Zr}_2\text{O}_7$	$\text{La}_2\text{Ce}_2\text{O}_7$
σ_{dc}	4.54 (mS cm^{-1})	7.28 (mS cm^{-1})
σ_{ib}	3.68	5.15
σ_{igb}	0.837	3.84
σ_{total}	0.682	2.27
σ_{acl}	0.674	2.20
σ_{ach}	3.48	5.46

Remarks: Notations of conductivity are as follows,

σ_{dc} : dc conductivity obtained by dc four-probe method,

σ_{ib} : bulk conductivity from impedance spectra,

σ_{igb} : grain boundary conductivity from impedance spectra,

σ_{total} : inverse value of $(\rho_{\text{ib}} + \rho_{\text{igb}})$, where ρ_{ib} and ρ_{igb} are the resistivity of bulk and grain boundary from impedance spectra, respectively,

σ_{ach} : ac conductivity estimated from the plateau region at high frequency,

σ_{acl} : ac conductivity estimated from the plateau region at low frequency.

Fig. 6. $\log \epsilon_r'$ of $\text{Eu}_2\text{Zr}_2\text{O}_7$ as a function of $\log f$.

temperature range at and above 773 K, the $\log \sigma_{\text{ac}}$ showed each plateau in low ($f < 10^3$ Hz) and high frequency ($f > 10^6$ Hz) range and strong dispersion in the intermediate frequency range. In that temperature range, the values of σ_{acl} estimated from the low frequency plateau did not agree with that of σ_{ib} , but agreed with the total conductivity (σ_{total}) that was estimated from the inverse value of the total resistivity of both bulk (ρ_{ib}) and grain boundary (ρ_{igb}) observed in the impedance spectra, that is, $\sigma_{\text{total}} = 1/(\rho_{\text{ib}} + \rho_{\text{igb}})$ (Fig. 3(a)). On the other hand, it was found that the σ_{ach} estimated from the high frequency plateau agreed with both values of the σ_{dc} and σ_{ib} . Various conductivity data at 973 K obtained in the present study are summarized in Table 1.

Figure 6 shows the logarithmic values of relative dielectric constant (ϵ_r') of $\text{Eu}_2\text{Zr}_2\text{O}_7$ as a function of $\log f$ at various temperatures. Anomaly very large ϵ_r' was observed in the low frequency range ($< 10^4$ Hz) and temperature range above

Fig. 7. $\log \sigma_{\text{ac}}$ of $\text{La}_2\text{Ce}_2\text{O}_7$ as a function of $\log f$.

673 K. The ϵ_r' increased with increase in the measuring temperatures, accompanying the increase of the σ_{ac} at the same time. The occurrence of such a large dielectric constant may be ascribed to the polarization of mobile oxide-ion due to oxygen vacancy, i.e., the so-called space charge polarization. The ϵ_r' values abruptly decreased with increase in the frequency, because the polarization of space charge cannot follow with the frequency change.

Figure 7 shows $\log \sigma_{\text{ac}}$ of $\text{La}_2\text{Ce}_2\text{O}_7$ at various temperatures as a function of $\log f$. Alike to the case of $\text{Eu}_2\text{Zr}_2\text{O}_7$, the $\log \sigma_{\text{ac}}$ of $\text{La}_2\text{Ce}_2\text{O}_7$ showed two plateaus above 773 K, while the conductivity dispersion in the intermediate frequency range, 10^3 – 10^5 Hz was smaller than that of $\text{Eu}_2\text{Zr}_2\text{O}_7$. The σ_{ac} of the two plateaus at the low and high frequency also agreed with the σ_{total} and σ_{dc} , respectively (Fig. 3(b)). Small difference in the two conductivity values from the low and high frequency plateaus of $\text{La}_2\text{Ce}_2\text{O}_7$ can be ascribed to the smaller grain boundary resistivity than that of $\text{Eu}_2\text{Zr}_2\text{O}_7$. The conduction data at 973 K of $\text{La}_2\text{Ce}_2\text{O}_7$ are also given in Table 1.

As seen in the present experimental results, the frequency dependence of ac conductivity in the oxide-ion conductors was much different from that of cation conductors reported previously. Although Mizumoto and Hayashi⁹⁾ reported in their study concerning lithium ion conductors that the σ_{dc} values agreed with the σ_{total} estimated from impedance spectra, the present study concerning the two oxide-ion conductors, $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ showed that the σ_{dc} values rather agreed with the σ_{ach} estimated from the high frequency plateau and that the σ_{total} did with the σ_{acl} from the low frequency plateau, as also shown in Fig. 3 and Table 1. The conductivity dispersion in the intermediate frequency range was large for the material having larger grain boundary resistivity than the bulk resistivity (Fig. 4). Therefore, it can be assumed that the lower σ_{ac} than σ_{dc} in the low frequency range was ascribed to the polarization of space charge due to the presence of larger grain-boundary barrier. This assumption means that the one part of the mobile oxide-ions contributes to oxide-ion conduction and the other part does to the polarization at the grain

Fig. 8. Electric field dependence of $\log \sigma_{ac}$ (a) and $\log C_p$ (b) of $\text{Eu}_2\text{Zr}_2\text{O}_7$ as a function of $\log f$ at 773 K.

boundary barrier as the space charge. In the high frequency range, since the space charge can follow no longer with the frequency, the σ_{ach} at the high frequency range agreed with the bulk conductivity (σ_{ib}), that is, the dc conductivity (σ_{dc}). Vassen et al.¹⁵⁾ have reported the similar observations in the measurements of the impedance for $\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_{1.93}$ as a function of $\log f$. Dwivedi et al.¹⁶⁾ have also observed the similar relation between σ_{ac} and σ_{dc} for hole conduction in the (Ca, La) (Ti, Cr) O_3 system and discussed the contribution of grain boundary to ac conductivity.

It was tried to observe the electric field dependence of σ_{ac} in the range from 10 mV to 1 V at 773 K in order to investigate the behavior of space charge. As seen in Fig. 8(a), which shows the electric field dependence of $\log \sigma_{ac}$ of $\text{Eu}_2\text{Zr}_2\text{O}_7$ as a function of $\log f$, the increase of electric field decreased the dispersion degree in the intermediate frequency range, keeping the capacitance almost constant. Inversely, too weak electric field strength, e.g., 50 mV, increased the σ_{ac} in the lower frequency range < 100 Hz. The origin of the increase in σ_{ac} at such a very weak field strength is not clear at present stage. No electric field dependence of ac conductivity and capacitance could be observed for $\text{La}_2\text{Ce}_2\text{O}_7$, as can be seen in Figs. 9(a) and (b). The difference of electric field dependence between $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$ may be ascribed to the difference in their grain boundary resistivity.

These polarization effects at grain boundary have not been remarkable in the cation conductors of crystals and glasses, because the mobile cations with small ionic size occupy interstitial sites of close-packed larger anions.

4. Conclusion

Ac conductivity data for the oxide-ion conductors, $\text{Eu}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$, which has pyrochlore- and fluorite-type structure, respectively, were compared with the various

Fig. 9. Electric field dependence of $\log \sigma_{ac}$ (a) and $\log C_p$ (b) of $\text{La}_2\text{Ce}_2\text{O}_7$ as a function of $\log f$ at 773 K.

conductivity values obtained by means of dc four probe and impedance spectroscopic methods, in order to clarify the relation between their conductivities. The ac conductivity was strongly influenced by the space charge polarization due to mobile oxide-ions at the grain boundary. The frequency dependence of $\log \sigma_{ac}(\omega)$ showed two plateaus, where the one plateau in the high frequency region agreed with the bulk conductivity (σ_{ib} and σ_{dc}) and the other one of the low frequency region did with the σ_{total} that was the inverse value of the total resistivity of both bulk and grain boundary. The conductivity dispersion in the frequency range, $10^3 \text{ Hz} < f < 10^6 \text{ Hz}$ of $\text{Eu}_2\text{Zr}_2\text{O}_7$ with larger grain boundary resistivity was larger than that of $\text{La}_2\text{Ce}_2\text{O}_7$ with smaller grain boundary resistivity and became small with increase in the applying electric field.

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