Oxide-ion conduction and dielectric relaxation in the fluorite-type $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) system.

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The electrical conductivity and dielectric properties of the $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) system which have a cubic fluorite-type structure were investigated in order to clarify a dynamic property of oxygen vacancy in oxide-ion conductors. The frequency dependences of dielectric constants (ϵ_r') were successfully explained by the superposition of Debye-type polarizations and electrolyte-electrode interfacial polarizations. The ac conductivity (σ_{ac}) agreed with the calculated values using the dielectric parameters. It was found that the compositional dependence of dielectric properties was similar to that of σ_{ac} .

Key words: Dielectric relaxation, Fluorite-type compound, Oxide-ion conduction, Oxygen defect

1. Introduction

Oxide-ion conductors have an important role in oxygen sensors, oxygen pumps and solid oxide fuel cells (SOFCs) etc. Among many oxide-ion conductors, aliovalent cation-doped ZrO_2 has been widely studied from various viewpoints such as electrochemistry, crystallography and solid-state chemistry in recent years. However, the dominant factors for oxide ion conduction have not been clear.

It is generally accepted that when ZrO_2 was doped with Ln_2O_3 (Ln: rare earth), oxygen vacancy could be introduced into the oxygen sublattice based on the following defect reaction according to Kröger Vink notation,

However, the oxygen vacancy introduced by doping of the aliovalent cation is not necessarily free, but may be bound to the doped cation by such defect associate pairs as $[\text{Ln}_{\text{Zr}}' - \text{V}_\text{O}^\bullet]'$ and $[\text{Ln}_{\text{Zr}}' - \text{V}_\text{O}^\bullet - \text{Ln}_{\text{Zr}}']$ due to coulomb interaction. Although the oxide ion conduction must be influenced by the defect associate, the relationship between oxide-ions and associated pairs has not been investigated in detail. If the defect associates behaved as an electric dipole at fairly high temperatures, Debye-type relaxation would be observed. In fact, our research group has reported in the previous paper that the frequency dependence of dielectric constant of YSZ was successively explained by assuming the contribution of both interfacial polarization of electrolyte and electrode and Debye-type relaxation.¹⁾ The present research is focused to study the compositional dependence of the dielectric relaxation with the relation to the oxide-ion conductivity in the $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) system having a cubic fluorite-type structure.

2. Experimental

Powder samples of the present system, $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) were synthesized by a solid-state reaction method, using ZrO_2 (99.7 %, TOSOH Co.) and Ln_2O_3 (99.9 %, High Purity Chemicals Co.) except Yb_2O_3 (99.99 %, High Purity Chemicals Co.) as starting materials.

The weighed powders were wet ball-milled for 24 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 1273 K for 10 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, which were estimated from the geometrical dimensions and weight, were over 95 % of theoretical density.

The powder samples were characterized by means of X-ray diffraction (XRD) (Multiflex, Rigaku) with monochromated Cu K α radiation. The lattice constant was determined using the XRD peaks by the least-squares method. The unit cell free volume (V_f) was calculated using a following equation,

$$V_f = a^3 - 4 \times 4/3 \times (M_{\text{cation}}^3 + 2 \times r_0^3 - 0.1 \times r_{\text{Vo}}^3), \quad (2)$$

where a , M_{cation} , r_0 , r_{Vo} denote the lattice constant, the mol fraction of cation, the ionic radii of oxygen and oxygen vacancy, respectively. The free volume means a free space in the crystal structure.

The dc electrical conductivity (σ_{dc}) of the sintered specimens was measured by the four-probe method in

the temperature range of 773 to 1173 K in air. The geometrical dimensions of the sintered bar for the dc conductivity measurements were 4×4 mm² in cross-sectional area and ~30 mm in length.

Dielectric constant (ϵ_r') and dielectric loss factor (ϵ_r'') were observed as a function of frequency by the ac two-probe method in temperature range of 573 to 1173 K in air. An impedance analyzer (4192A LF, Yokogawa-Hewlett-Packard, Japan) was used for these measurements in the frequency range of 5 Hz to 13 MHz.

The electrical conductivity (σ_{imp}) was also obtained from the intercept of the real plane in the impedance spectra. The dimensions of the sintered disk for the dielectric and ac conductivity measurements were 10 mm in diameter and 2 mm in thickness. For all the measurements, a platinum electrode was attached to both sides of the specimen by firing at 1223 K for 30 min in air.

Kaleida Graph (Synergy Software) was used for the numerical calculation of the dielectric parameter.

3. Results and discussion

It was confirmed by the XRD experiments that the $Zr_{0.8}Ln_{0.2}O_{1.9}$ ($Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu$) system were single phases of a cubic fluorite-type structure. Figure 1 shows the lattice constants and the unit cell free volume as a function of the ionic radius of Ln^{3+} . The values of ionic radius of Ln^{3+} used in the present study are summarized in Table 1. The lattice constant and unit cell free volume increased linearly with increasing ionic radii of Ln^{3+} .

Figure 2 shows Arrhenius plots of the electrical conductivity (σ_{dc}) of the $Zr_{0.8}Ln_{0.2}O_{1.9}$ system measured by the dc four-probe method in air. The temperature dependence of conductivity (σ) can be described by,

$$\sigma = \sigma_0 \exp(-E_a/RT), \quad (3)$$

where pre-exponential term (σ_0) is a measure of the number of mobile ions and E_a denotes the activation energy. The E_a values for the $Zr_{0.8}Ln_{0.2}O_{1.9}$ system are summarized in Table 2. The activation energies for the electrical conduction were in the range from 89 to 107 kJ mol⁻¹, which have a tendency to decrease until the Er doped system, and then to increase with decrease in the ionic radii of the dopants. Stafford et al.³⁾ have reported that the activation energies for oxide ion conduction of the 12 mol% Gd_2O_3 , Nd_2O_3 , Y_2O_3 or Yb_2O_3 doped ZrO_2 systems were estimated to be 107, 116, 108 or 102 kJ mol⁻¹, respectively. Their results concerning the activation energy agreed with those of the present study.

Figure 3 shows the dc electrical conductivity (σ_{dc}) at several temperatures as a function of the ionic radius of Ln^{3+} in the $Zr_{0.8}Ln_{0.2}O_{1.9}$ system. The conductivity decreased gradually with increasing ionic radius of the dopant, that is, with increasing unit cell free volume which means a free space in the crystal structure. On the other hand, the σ_{dc} showed the maximum values in the vicinity of the ionic radius of Ln^{3+} , 0.994 and 1.066 Å. It has been reported that the oxide-ion conductivity has a close relation with the

unit cell free volume.⁴⁾⁻⁷⁾ It may be reasonable for oxide ion to move more easily in the larger space. However, the idea of unit cell free volume has not been successfully applied to the present $Zr_{0.8}Ln_{0.2}O_{1.9}$ system. Therefore, the decrease in the conductivity in the $Zr_{0.8}Ln_{0.2}O_{1.9}$ systems may be ascribed to other origins such as ordering of oxygen vacancy.

Fig.1 Lattice constant and unit cell free volumes as a function of ionic radius of Ln^{3+} in $Zr_{0.8}Ln_{0.2}O_{1.9}$ system.

Table 1. Ionic radius (Å) of various elements used in the present study²⁾.

Zr^{4+}	0.84
Nd^{3+}	1.109
Sm^{3+}	1.079
Eu^{3+}	1.066
Gd^{3+}	1.053
Dy^{3+}	1.027
Ho^{3+}	1.015
Er^{3+}	1.004
Tm^{3+}	0.994
Yb^{3+}	0.985
Lu^{3+}	0.977

Fig.2 Arrhenius plots of σ_{dc} for $Zr_{0.8}Ln_{0.2}O_{1.9}$ system.

Table 2. Activation energy of electrical conduction for the $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ system.

Ln	Ea(kJ mol ⁻¹)
Nd	107.01
Sm	104.91
Eu	101.88
Gd	101.47
Dy	97.31
Ho	96.9
Er	89.79
Tm	90.02
Yb	91.73
Lu	94.28

Fig. 3 $\log \sigma_{dc}$ as a function of ionic radius in $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ system.

Figure 4 shows the angular frequency (ω) dependence of dielectric constant (ϵ_r') of $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ at 773 K in air. The ϵ_r' values of all samples were anomalously large in low frequency, and showed large dispersion in the intermediate frequency region and high frequency region. Figure 5 typically shows a result of numerical analysis for the frequency dependence of the observed ϵ_r' for $\text{Zr}_{0.8}\text{Ho}_{0.2}\text{O}_{1.9}$ at 773 K on the basis of following equation.

$$\epsilon_r' = \epsilon_{r\infty} + \sum_i \frac{\epsilon_{r0i} - \epsilon_{r\infty}}{1 + (\omega\tau_{0i})^2} + \frac{\epsilon_r(0)}{\omega^s} \quad (4)$$

where ω , ϵ_{r0i} and τ_{0i} represent the angular frequency ($=2\pi f$, f : frequency), the dielectric constant at low frequency limit due to the i -th Debye-type polarization and the i -th dipole relaxation time, respectively. $\epsilon_{r\infty}$ represents the dielectric constant at high frequency limit. $\epsilon_r(0)$ is defined as the dielectric constant due to the interfacial polarization at low frequency limit. Frequency exponent (s) was introduced to generalize a function of frequency. The first two terms of the right side in Eq. (4) represent the Debye-type dispersion. The numerical calculation of the frequency dependence of ϵ_r' clarified the presence of two Debye-type relaxations for all the samples. These dipoles were named Dipole 1 and 2 in order of increasing the frequency: therefore, the dielectric parameters of the Dipoles are denoted as ϵ_{r01} and ϵ_{r02} , and τ_{01} and τ_{02} ,

Fig. 4 Frequency dependence of ϵ_r' for $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ at 773 K.

Fig. 5 The numerical analysis of ϵ_r' for $\text{Zr}_{0.8}\text{Ho}_{0.2}\text{O}_{1.9}$ at 773 K.

respectively. It can be speculated that the two observed dipoles correspond to the dopant-vacancy associates; $[\text{Ln}_{\text{Zr}}'\text{V}_\text{O}^-]$ and $[\text{Ln}_{\text{Zr}}'\text{V}_\text{O}^- - \text{Ln}_{\text{Zr}}']$, according to our previous study.¹⁾ The dielectric parameters at 773 K are summarized in Table 3. It was confirmed that the exponent of frequency (s) was around unity for all the samples. Although the physical meaning of s has not been clarified, the s value may have a close relation to the charging mechanism of oxide ion to electrode. Figure 6 shows the observed ϵ_{r01} and ϵ_{r02} values at 773 K as a function of the ionic radius of Ln^{3+} in the $\text{Zr}_{0.8}\text{Ln}_{0.2}\text{O}_{1.9}$ system. The ϵ_{r02} values decreased with increasing the ionic radius of the dopant. Especially, the decrease in the ϵ_{r02} values with increasing ionic radius of the dopant was the similar tendency to that of σ_{dc} . On the other hand, the ϵ_{r01} and ϵ_{r02} showed two maximum values with increase in the ionic radius. These facts mean that the sample having the larger Debye-type dipoles show also the high σ_{dc} value, and that the presence of the dopant-vacancy pair is not an origin of the decrease in oxide-ion conductivity.

Table 3. Dielectric parameter of $Zr_{0.8}Ln_{0.2}O_{1.9}$ at 773 K.

	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	Lu
$\epsilon_r(0)$	7.50×10^{10}	2.23×10^9	1.02×10^9	1.05×10^9	1.12×10^{10}	3.57×10^9	1.26×10^9	1.59×10^{10}	1.48×10^{10}	1.66×10^{10}
$\epsilon_{r\infty}$	81.7	113	91.8	92.6	115	87.3	97.6	98.9	153	99.3
s	1.54	1.19	1.18	1.17	1.35	1.20	1.16	1.29	1.32	1.32
ϵ_{r01}	186	569	2.49×10^3	2.52×10^3	1.30×10^3	250	174	473	1.12×10^3	352
ϵ_{r02}	9.19×10^5	2.32×10^6	6.16×10^6	4.42×10^6	9.79×10^6	1.48×10^7	1.11×10^7	8.78×10^6	1.15×10^7	1.22×10^7
$\tau_{01}(s)$	1.45×10^{-6}	1.29×10^{-6}	6.73×10^{-7}	4.93×10^{-6}	1.23×10^{-6}	2.68×10^{-7}	3.31×10^{-7}	5.62×10^{-7}	4.82×10^{-7}	2.67×10^{-7}
$\tau_{02}(s)$	3.28×10^{-3}	1.64×10^{-3}	3.7×10^{-3}	2.64×10^{-3}	1.62×10^{-3}	1.41×10^{-3}	1.91×10^{-3}	1.08×10^{-3}	1.39×10^{-3}	1.09×10^{-3}

Fig. 6 $\log \epsilon_r$ as a function of ionic radius in $Zr_{0.8}Ln_{0.2}O_{1.9}$ system at 773 K. Fig. 7 Frequency dependences of σ_{ac} for $Zr_{0.8}Ho_{0.2}O_{1.9}$ at 773 K: observed σ_{ac} ($\circ$), calculated σ_{ac} (—).

Figure 7 typically shows the frequency dependence of σ_{ac} for $Zr_{0.8}Ho_{0.2}O_{1.9}$ at 773 K. The σ_{ac} values showed a strong dispersion in the intermediate-frequency region. In order to understand the frequency dependence of σ_{ac} , the numerical analysis was carried out using the following equation,

$$\sigma_{ac} = \omega \epsilon_0 \epsilon_r'' = \omega \epsilon_0 \left\{ \sum_i \frac{(\epsilon_{r0i} - \epsilon_{r\infty}) \omega \tau_i}{1 + (\omega \tau_i)^2} + \frac{\sigma(0)}{\epsilon_0 \omega^s} \right\} \quad (5)$$

where only the $\sigma(0)$ value must be estimated from the numerical analysis of dielectric loss factor (ϵ_r'') using following equation,

$$\epsilon_r'' = \sum_i \frac{(\epsilon_{r0i} - \epsilon_{r\infty}) \omega \tau_i}{1 + (\omega \tau_i)^2} + \frac{\sigma(0)}{\epsilon_0 \omega} \quad (6)$$

The calculation result for the frequency dependence of σ_{ac} is also shown as solid line in Fig. 7. Prior to the calculation of σ_{ac} , ϵ_r'' was first analyzed using Eq. (6), and then σ_{ac} was calculated according to Eq. (5). As seen in Fig. 7, the calculated σ_{ac} values agreed with the observed values. This fact suggests that the large dispersion of σ_{ac} in the intermediate-frequency region originates from the relaxation of Debye-type dipoles.

4. Conclusion

It was confirmed by XRD experiments that the $Zr_{0.8}Ln_{0.2}O_{1.9}$ ($Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu$) systems were single phases of a cubic fluorite-type structure. The lattice constant and unit cell free volume increased linearly with increasing the ionic radii of the dopant. On the other hand, the electrical conductivity (σ_{ac}) gradually decreased with increasing the ionic radius of the

dopant. The numerical analyses of the frequency dependence of ϵ_r'' showed the two kinds of Debye-type relaxations for all the samples. The calculated σ_{ac} values agreed with the observed values, suggesting that the large dispersion of σ_{ac} in the intermediate-frequency region may originate from the relaxation of Debye-type dipole.

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