Dielectric Relaxations in the $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ System

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Dielectric relaxations were investigated for the solid-solution system $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ ($0.0 \leq x \leq 0.5$), which is a typical oxide-ion conductor. The dielectric constants showed anomalously large values at low frequencies and high temperatures. Computer simulation clarified that the anomalously large dielectric constant (ϵ_r') originated from the superimposition of both Debye-type polarization and interfacial polarization between electrolyte and electrode. Two kinds of Debye-type relaxation observed were ascribed to defect associates, $(\text{Sm}_{\text{Ce}}'-\text{V}_{\text{O}}^{\bullet\bullet})^{\bullet}$ and $(\text{Sm}_{\text{Ce}}'-\text{V}_{\text{O}}^{\bullet\bullet}-\text{Sm}_{\text{Ce}}')^{\times}$. The Debye-type polarization was also confirmed by analyzing the dielectric loss factor (ϵ_r''). When the oxide-ion conductivity decreased in the heavy Sm-doped samples, the Debye-type polarization also disappeared, suggesting that ordering of oxygen vacancy suppressed the electric field response of Debye-type polarization.

[Received January 9, 2007; Accepted February 15, 2007]

Key-words: Oxide-ion conductivity, Dielectric constant, Debye-type polarization, Oxygen vacancy, Defect associate

1. Introduction

Oxide-ion conductors play an important role in oxygen sensors, oxygen pumps and solid oxide fuel cells (SOFCs) etc. Among many oxide-ion conductors, aliovalent cation-doped CeO_2 has been widely studied from various viewpoints such as electrochemistry, crystallography and solid-state chemistry in recent years. Inaba and Tagawa¹⁾ have summarized the many papers concerning the ceria based solid electrolytes. Eguchi et al.^{2,3)} reported that the oxide-ion conductivity of Sm- and Gd-doped ceria showed the highest conductivity among the 20 atom% doped cerias because of the close ionic-radii of Sm^{3+} and Gd^{3+} to the radius of Ce^{4+} .

The oxide-ion conduction has a close relation with an electric dipole polarization of oxygen vacancy. However, most of studies concerning dielectric properties of the oxide-ion conductors have been carried out using the electric modulus M^* ($=1/\epsilon^*$) in order to avoid overlap with dielectric constant at low frequency. Sarkar and Nicholson^{4,5)} studied electric field relaxations in the $\text{CeO}_2\text{-Ln}_2\text{O}_3$ ($\text{Ln}=\text{Y}, \text{La}$) systems in a relatively low temperature range and reported that two relaxation processes observed in the lightly Ln-doped CeO_2 were due to a long range migration of free oxygen vacancies and to an orientation relaxation of the charged associated defects $(\text{Ln}_{\text{Ce}}'-\text{V}_{\text{O}}^{\bullet\bullet})^{\bullet}$. Kim⁶⁾ also investigated dielectric relaxations of $\text{Li}_2\text{B}_4\text{O}_7$ single crystal which was Li ion conductor, using the electric modulus spectroscopy. On the other hand, Wang and Nowick⁷⁾ observed the dielectric relaxation in Y-doped CeO_2 using Thermally Stimulated Depolarization Current (TSDC) method, where two relaxation peaks were observed, which were ascribed to the associated defects (low temperature range) and the long range vacancy migration (high temperature range).

It is generally accepted that when CeO_2 was doped with Sm_2O_3 , oxygen vacancy could be introduced into the oxygen sublattice sites 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 because of a defect associate pair $[\text{Sm}_{\text{Ce}}'-\text{V}_{\text{O}}^{\bullet\bullet}]^{\bullet}$ due to coulomb interaction. Although the oxide ion con-

duction must be influenced by the defect associate, the relation 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, the present authors have reported in the previous paper that the frequency dependence of dielectric constant of $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ was successively explained by assuming the contribution of both interfacial polarization of electrolyte and electrode and Debye-type relaxation.⁸⁾ The present research is concerning the dielectric relaxation of the Sm-doped CeO_2 ($\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$) system having a cubic fluorite-type structure, in order to study the compositional dependence of the dielectric relaxation in the relation with the oxide-ion conductivity.

2. Experimental procedures

Powder samples of Sm-doped CeO_2 ($\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$, $0.0 \leq x \leq 0.5$) were synthesized by a solid-state reaction, using CeO_2 (99.9%, High Purity Chemicals Co.), Sm_2O_3 (99.9%, Furuuchi Chemicals Co.) as starting materials.

Weighed powders were wet ball-milled for 16 h, using a milling pot made of synthetic resin and resin-coated balls, and ethanol as dispersion reagent. The dried powder mixtures were calcined at 1273 K for 5 h in air. After sieving under $53 \mu\text{m}$ in mesh size, the powder samples were uniaxially molded under the pressure of 50 MPa and then subjected to rubber press under 200 MPa. Compacts thus obtained were sintered at 1873 K for 10 h in air. Relative densities of the sintered specimens, which were estimated from their geometrical dimensions and weight, were between 93 and 96%, where the sample with the higher Sm content showed the higher relative density. The powdered samples were characterized by means of an X-ray diffraction (XRD) (model: RAD-A, Rigaku Co.) with monochromated Cu $K\alpha$ radiation. Lattice constant was determined from XRD peaks by a least square method, using Si powder as an external standard. Microstructures of the sintered specimens were observed by SEM (JSM-5200), after thermal etching at 1873 K for 1 h in air.

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 sintered bar for the dc conductivity measurements were 4×4 and ~ 30 mm length.

In the parallel circuit model composed of capacitor (C) and resistor (R), ac currents (I) can be separated into a charging current ($j\omega\epsilon_r''C_0V$) (j : imaginary unit) and a loss current ($\omega\epsilon_r''C_0V$), as shown by a following equation.

$$I = (j\omega\epsilon_r' + \omega\epsilon_r'') C_0 V, \quad (2)$$

where ω , ϵ_r' , ϵ_r'' , and C_0 denote the angular frequency ($=2\pi f$), the dielectric constant (relative permittivity), the dielectric loss factor, and the capacitance in vacuum, respectively. Using the relation of $C_0 = \epsilon_0 A/d$ (ϵ_0 : permittivity in vacuum, A : area of electrode and d : distance between electrodes), the current density (J) can be related to the complex admittance (Y^*) as follows,

$$J = (j\omega\epsilon' + \omega\epsilon'') E = (j\sigma'' + \sigma') E = Y^* E \quad (3)$$

Therefore, we get a following relation,

$$\sigma' = \omega\epsilon'' \text{ and } \sigma'' = \omega\epsilon', \quad (4)$$

where σ' is loss current conductivity (conductance), which was named ac conductivity (σ_{ac}), and σ'' is conductivity due to charging current (susceptance). These parameters were obtained as a function of frequency by ac two-probe method in the temperature range from 573 to 1073 K in air. The impedance analyzer (4192A LF, Yokogawa-Hewlett-Packard Ltd., Japan) was used for these measurements in the frequency range of 5 Hz to 13 MHz. The dimension of sintered disk for 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 1223 K for 30 min in air.

3. Results and discussion

XRD experiments confirmed that the $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ system was a single phase of cubic fluorite-type structure in the composition range, $0.0 \leq x \leq 0.4$. The sample with $x = 0.50$ was assigned to a rare-earth C-type structure because of coexistence of super structure lines in the XRD pattern. **Figure 1** shows the observed and calculated lattice constants as a function of the composition (x). The calculated values of lattice constant were obtained by use of a following equation, according to Hong and Virkar.⁹⁾

$$a_{\text{calc.}} = \frac{4}{\sqrt{3}} [xr_{\text{Sm}} + (1-x)r_{\text{Ce}} + (1-0.25x)r_{\text{O}} + 0.25xr_{\text{VO}}] \times 0.9971, \quad (5)$$

where r_{Sm} , r_{Ce} , r_{O} and r_{VO} are ionic radii of Sm^{3+} (0.1079 nm in 8 coordination and 0.102 nm in 7 one), Ce^{4+} (0.097 nm in 8 coordination), oxide-ion (0.138 nm) and oxygen vacancy (0.1164 nm), respectively, and 0.9971 is a multiplication factor in order to fit the calculated value for the observed one of pure CeO_2 . The calculation of lattice constant was proceeded on the basis of following two models. In the model I, the ionic radius of 8-coordinated Sm^{3+} was used. In the model II, it is supposed that 7-coordinated Sm^{3+} partially occurred due to the incorporation of oxygen vacancy. The model I and II are shown as the broken and solid lines in Fig. 1, respectively. The observed lattice constant agreed with the model II for $x < 0.3$, but showed the intermediate value between the model I and II for $x \geq 0.3$, as shown in Fig. 1.

Figure 2 shows $\log \sigma_{ac}$ at 773 K as a function of f for the composition range, $0.0 \leq x \leq 0.5$. The $\log \sigma_{ac}$ values increased with increasing frequency. For the composition range, $0.1 \leq x \leq 0.3$, $\log \sigma_{ac}$ showed 2 plateaus in the intermediate and high frequency regions. The dispersion of $\log \sigma_{ac}$ became small at

Fig. 1. Lattice constant as a function of composition (x). The observed value (●) and calculated value according to Model 1 (---) and Model 2 (—)

Fig. 2. Frequency dependence of $\log \sigma_{ac}$ at 773 K for the $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ system, where the numbers of marks mean the composition (x).

$x = 0.4$ and then almost disappeared at $x = 0.5$.

Figure 3 shows frequency dependence of dielectric constant (ϵ_r') at 773 K in the composition range, $0.0 \leq x \leq 0.5$. The ϵ_r' value of CeO_2 ($x = 0.0$) was small (~ 100) and did not show the frequency dependence. The ϵ_r' values of Sm-doped sample in the low frequency range were anomalously large and showed step-like behavior for the frequency, which disappeared for the sample with $x \geq 0.4$. In the previous paper, we supposed that ϵ_r' of the 10 atm% Sm-doped samples was composed of both Debye-type polarization and electrolyte-electrode interfacial polarization (space charge polarization) that depends on the inverse of frequency.⁸⁾ The apparent dielectric constant (ϵ_r') can be given as a following equation, assuming the presence of plural relaxation times.

$$\epsilon_r' = \epsilon_{r\infty} + \sum_i \frac{\epsilon_{r0i}}{1 + (\omega\tau_{oi})^2} + \frac{\epsilon_r(0)}{\omega^s}, \quad (6)$$

Fig. 3. Frequency dependence of ϵ'_r at 773 K for the $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ system, where the numbers of marks mean the composition (x).

Fig. 5. $\log \sigma_{dc}$ and $\epsilon(0)$ at 773 K as a function of the composition (x).

Fig. 4. Frequency dependence of the observed and calculated values of ϵ'_r at 773 K for the sample with $x=0.2$; Observed value (○) and calculated one (—).

Fig. 6. Frequency dependence of ϵ''_r at 773 K for the sample with $x=0.2$.

where ϵ_{r0i} and τ_{oi} represent 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 dielectric constant at high frequency limit. $\epsilon_{r(0)}$ is defined as a dielectric constant due to the interfacial polarization at low frequency limit, which corresponds to susceptance ($\epsilon' = \sigma''/\omega$) in Eq. (4). Frequency exponent (s) was introduced to generalize a function of frequency. The first two terms of the right side in Eq. (6) represent the Debye-type dispersion, where ρ_{r0} in the second term was used in place of $(\rho_{r0} - \epsilon_{r\infty})$ in the usual Debye's equation, because $\rho_{r0} \gg \epsilon_{r\infty}$ in the present study. **Figure 4** typically shows the frequency dependence of observed and calculated ϵ'_r at 773 K obtained by the computer simulation on the basis of Eq. (6) for the sample with $x=0.2$. The observed and calculated values agreed well with each other. Two kinds of the Debye-type relaxation were found in the frequency dependence of ϵ'_r ; for example, the lower relaxation-frequency ($f_{01}(\epsilon'_r)$) of the sample with $x=0.2$ at 773 K was 154 Hz and the higher one ($f_{02}(\epsilon'_r)$) was 2.2×10^5 Hz. For the sample with $x \geq 0.4$, the Debye-type polarization dis-

appeared in low temperature range, and only the interfacial polarization remained. The frequency dependence of ϵ'_r at fairly high temperatures could not be analyzed because of too complex behaviors. On the other hand, as it was expected that $\epsilon_{r(0)}$ must have a close relation with σ_{dc} , both values at 557 K were plotted as a function of the composition, as shown in **Fig. 5**. The similar compositional dependence between $\epsilon_{r(0)}$ and σ_{dc} suggests that the higher σ_{dc} accelerate the larger charging currents.

Figure 6 typically shows frequency dependence of dielectric loss factor (ϵ''_r) at 773 K for the sample with $x=0.2$. According to the assumption for ϵ'_r , it was supposed that ϵ''_r includes a contribution of the conduction term ($\sigma/\omega\epsilon_0$) in addition to the Debye-type dipole. Therefore, the apparent ϵ''_r can be given by a following equation,

$$\epsilon''_r = \sum_i \frac{\epsilon_{r0i}\omega\tau_{oi}}{1 + (\omega\tau_{oi})^2} + \frac{\sigma}{\omega\epsilon_0}, \quad (7)$$

where the first term of the right side means the plural Debye-type peaks. Equation (7) also suggests that the subtraction of $\sigma/\omega\epsilon_0$ from ϵ''_r value will give Debye-type relaxation peaks.

Figure 6 shows a comparison of the observed ε_r'' with the calculated one for the sample with $x=0.2$, where two upward arrows show the Debye-type relaxation frequencies, f_{01} (ε_r'') and f_{02} (ε_r'') for the lower and the higher relaxation frequencies estimated from the analysis of ε_r'' at 773 K, respectively. **Figure 7** shows the two Debye-type relaxation peaks obtained by the subtraction of $\sigma/\omega\varepsilon_0$ from ε_r'' value at 773 K. The values of f_{01} (ε_r'') and f_{02} (ε_r'') were estimated to be 84 and 2.3×10^5 s⁻¹, respectively, which approximately agreed with the values obtained from ε_r' . **Table 1** summarized these dielectric relaxation parameters at 773 K in the $\text{Ca}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ system. The dielectric constants at low frequency limit (ρ_{r01} and ρ_{r02}) due to the Debye-type polarization abruptly decreased, and the frequency exponent(s) increased in the composition $x \geq 0.4$, suggesting that there may be other factors in the heavy doped samples.

The computer simulation of the frequency dependence of ε_r' and ε_r'' revealed the presence of two kinds of Debye-type relaxation process, one of which may occur due to the dipole moment of defect associates such as $(\text{SmCe}'-\text{V}_{\text{O}}'')^{\bullet}$ in the high frequency range. The another relaxation process observed in the low frequency range above 573 K for the samples with $x \geq$

0.1 may be ascribed to such an associate type as a neutral trimer of $(\text{SmCe}'-\text{V}_{\text{O}}''-\text{SmCe}')^{\times}$. The neutral trimer having large ε_r' values is not a linear associate, but a bended one, because the linear trimer will not show any effective dipole moment. In the high temperatures, the decrease in ε_{r01} and ε_{r02} can be understood by considering that a following equilibrium reaction for the defect associates will proceed to right hand,

Therefore, when temperature increased, the equilibrium shifted to the right side and therefore the dielectric constant decreased and the conductivity increased at the same time. The lowering of conductivity in the low frequency in Fig. 2 may be ascribed to occurrence of the mobile dimmer associates, which do not contribute to the oxide-ion conductivity, but do to the dielectric constant. It should be noted that the frequency region showing the conduction dispersion almost agreed with that showing Debye-type relaxation. In the heavy doped samples with $x \geq 0.3$, it happens for V_{O}'' and SmCe' to order, resulting in the rare earth C-type phase for $x=0.5$. The ordering of V_{O}'' and SmCe' decrease both the Debye-type polarization and the oxide-ion conductivity. Therefore, the decrease in oxide-ion conductivity for the heavy doped samples is not due to the defect associates, but due to the ordering of oxygen vacancy.

Pimenov et al.¹⁰⁾ suggested that the plateau which was observed in the frequency dependence of the dielectric constant for ceramic sample of 4 mol% Y_2O_3 doped ZrO_2 originated from the grain boundary, even if the single crystal sample showed the similar plateau in the dielectric constant. Moreover, they have also reported that the frequency dependence of the observed dielectric constant can not be explained by the universal dielectric response,

$$\varepsilon'(\omega) = \varepsilon_{\infty} + A\omega s^{-1} \tan(\pi/2)/\varepsilon_0, \quad (10)$$

which describes a monotonously decreasing function at low frequencies. As suggested in the present study, the plateau or step-like behavior in the frequency dependence of the dielectric constant of Y-doped ZrO_2 should be rather ascribed to the Debye-type relaxation. We would like to emphasize that although the plural semicircles in the complex impedance plane have often been attributed to bulk conductivity, grain boundary and electrode contact relaxation in order from high frequency region to low frequency one, this interpretation

Fig. 7. Two Debye-type relaxation peaks obtained by the subtraction of $\sigma/\omega\varepsilon_0$ from ε_r'' values at 773 K for the sample with $x=0.2$, where f_{01} and f_{02} represent the relaxation frequencies obtained from ε_r'' .

Table 1. Dielectric Relaxation Parameters at 773 K in the $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ System Obtained from Frequency Dependence of Dielectric Constant (ε_r')

x	0.05	0.1	0.2	0.3	0.4	0.5
$\varepsilon_r(0)$	1.39×10^7	1.85×10^8	4.32×10^8	3.39×10^8	2.46×10^8	5.01×10^7
s	0.93	1.05	1.11	1.10	1.45	1.67
ε_{r01}		1.57×10^6	1.51×10^7	1.36×10^7	2.67×10^6	2.08×10^4
ε_{r02}	7.6×10^4	5.81×10^4	2.84×10^4	2.75×10^4	82.0	90.8
ε_r	90.9	49.7	73.0	80.3	68.7	72.2
τ_{01} (s)		2.71×10^{-3}	1.03×10^{-3}	9.88×10^{-3}	2.11×10^{-3}	1.32×10^{-3}
τ_{02} (s)	1.20×10^{-6}	6.84×10^{-7}	7.27×10^{-7}	4.30×10^{-6}	2.14×10^{-7}	1.27×10^{-7}
f_{01} (s ⁻¹)			154	16.1	75.5	121
f_{02} (s ⁻¹)	1.33×10^5	2.35×10^5	2.19×10^5	3.70×10^4	7.45×10^5	1.26×10^6

may be not necessarily correct.

4. Conclusions

The dielectric relaxations were investigated for the system $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-\delta}$ ($0.0 \leq x \leq 0.5$), which is a typical oxide-ion conductors. A single phase of cubic fluorite-type structure in the composition range, $0.0 \leq x \leq 0.4$, while the sample with $x=0.5$ transformed to a rare-earth C-type structure. Computer simulation of dielectric constant (ϵ_r') and dielectric loss factor (ϵ_r'') clarified that the anomalously large values of ϵ_r' originated from the superimposition of both Debye-type polarization and interfacial polarization between electrolyte and electrode. Two kinds of Debye-type relaxation were ascribed to defect associates, $(\text{SmCe}'-\text{V}_\text{O}^{\bullet\bullet})^*$ and $(\text{SmCe}'-\text{V}_\text{O}^{\bullet\bullet}-\text{SmCe}') \times$. When the oxide-ion conductivity decreased in the heavy Sm-doped samples, the Debye-type polarization also disappeared, suggesting that the ordering of oxygen vacancy suppressed the electric field response of Debye-type polarization.

Acknowledgements This study was supported by the Scientific Frontier Research Project from the Ministry of Education, Science, Sport and Culture, Japan.

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