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Thermal expansion and Debye temperature of rare earth-doped ceria

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Abstract

Thermal expansions of un-doped ceria and rare earth-doped ceria ($Ce_{1-x}M_xO_{2-x/2}$, M = La, Sm, Dy, Yb) were measured in the temperature range from 100 to 800 K by TMA. Debye temperatures of these compounds were measured at room temperature by an ultrasonic pulse method. The thermal expansion coefficients of rare earth-doped CeO_2 increased with increasing ionic radius of doped ions and its M content expect Dy ion. The Debye temperature of rare earth-doped ceria estimated from the longitudinal and transverse sonic wave velocities decreased with increasing M content, probably due to generation of oxygen vacancy by doping the rare earth elements. The relation between thermal expansion coefficient and Debye temperature was discussed.
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Keywords: Rare earth-doped ceria; Lattice parameter; Thermal expansion; Debye temperature

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1. Introduction

Rare earth-doped CeO_2 have received so far large attention as the solid electrolyte for high oxide ionic conductivity such as the solid oxide fuel cells and oxygen sensors [1–4]. Generally, these applications consist of some parts. For example, the solid oxide fuel cells are composed of an anode, a cathode, a solid electrolyte and interconnector. The composed materials at the interface need nearly the same thermal expansion coefficients, because they can be broken during heating and cooling cycles caused by mismatch among them. Therefore, thermal properties of doped ceria are very important for its application. So far, there have been some studies on the thermal expansion of the doped ceria [4–6], but systematic studies on the thermal expansion of doped ceria are lacking, and Debye temperature has not been studied yet.

In this paper, we investigate both the thermal expansion and Debye temperature of the doped ceria from the view of ionic radius of doped ionic species and its content. We selected four rare earth elements (La, Sm, Dy, Yb) for the doped ion to clarify the effect of ionic radius and oxygen vacancy on the thermal properties of doped ceria. The lattice parameters of the ceria doped with La or Sm increase with increasing La or Sm content. On the other hand, the lattice parameter of the Dy-doped ceria is independent of the Dy content and the lattice parameter of the Yb-doped ceria decreases with increasing Yb content. We measured the thermal expansion and Debye temperature of those doped ceria and discussed the thermal properties in this study.

2. Experimental

$Ce(NO_3)_3{\cdot}6H_2O$ and $M(NO_3)_n{\cdot}mH_2O$ (M = La, Sm, Dy, Yb) were used as the starting materials to prepare $Ce_{1-x}M_xO_{2-x/2}$ samples. Stoichiometric amounts of $Ce(NO_3)_3{\cdot}6H_2O$ and $M(NO_3)_n{\cdot}mH_2O$ were dissolved in the distilled water and the concentrations of Ce and M ions were determined by titration with EDTA. Mixed solution was added into a stirred oxalic acid solution to form the oxalate coprecipitate. The oxalate coprecipitate was vacuum-filtrated, washed with distilled water, and then dried 1 day at room temperature. The oxalate coprecipitate obtained was put into an alumina boat, and then heated up at 873 K for 1 h in air to decompose them. The oxide powders obtained were pressed and sintered at 1873 K for 8 h in air. All the samples prepared were characterized by X-ray powder diffractometer

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(XRD) using Cu Kα radiation with 40 kV–100 mA (RINT 2500 V, RIGAKU) at room temperature.

The linear thermal expansions of the samples were measured in the temperature range from 100 to 873 K in air at a heating rate of 2 K/min and a sampling time of 0.5 s by using TMA (Rigaku Thermo Plus TMA). Longitudinal (v_L) and transverse (v_T) sonic wave velocities of the samples were measured at room temperature to obtain Debye temperature by an ultrasonic pulse method using Toshiba-Tungalloy UML-L equipment. The frequency of oscillator used was 5 MHz.

3. Results and discussion

All the samples prepared were confirmed to be of a single phase having the fluorite crystal structure by XRD at room temperature. The lattice parameters of the samples were determined using the XRD results by a least square calculation after correcting of 2θ with Nelson–Riley's method. Table 1 shows the lattice parameters of CeO_2 and $Ce_{0.8}M_{0.2}O_{1.9}$ (M = La, Sm, Dy, Yb) at room temperature. The lattice parameters measured in this study are in good agreement with those reported by the previous works [7,8]. The lattice parameters as a function of doped ion content are summarized in Fig. 1. The lattice parameters of La- and Sm-doped CeO_2 increase linearly with increasing doped x content, whereas those of Yb-doped ceria decrease linearly with Yb content. The lattice parameters of Dy-doped ceria are nearly constant against Dy content. The lattice parameters in the same composition of $x = 0.1$ or 0.2 increase with increasing the ionic radius of the doped ion, suggesting that the ionic radius of the doped ion affects directly on the lattice parameter of the solid solution. The lattice parameter, a, of the rare earth-doped ceria is given by Hong and Virkar [9] as follows:

$$a = \left(\frac{4}{3}\right)^{1/2}\{xr_1 + (1-x)r_2 + (1-0.25x)r_3 + 0.25xr_4\} \times 0.9971 \qquad (1)$$

where x is the concentration of dopant, and r_1, r_2, r_3 and r_4 are the ionic radii of the doped rare earth ion, cerium ion (0.097 nm), oxygen ion (0.138 nm) and the oxygen vacancy (0.1164 nm), respectively. The correction factor, 0.9971, was introduced from the ratio of the lattice parameter (0.5411 nm) measured for un-doped ceria to that calculated from r_2 and r_3 (0.5427 nm). The straight line calculated by Eq. (1) is shown in Fig. 1. The lattice parameters measured in this study fit the calculated lines, and the slope reflects the ionic radius of doped ion.

Fig. 2 shows the linear thermal expansions of un-doped and 10 mol% rare earth-doped ceria measured by TMA. The normalized linear thermal expansion of all samples ($\Delta L/L_{298}$), where L_{298} is the sample length at 298 K and ΔL is the difference of the length between L_T and L_{298}, increases smoothly with increasing temperature in the range from 100 to 873 K. The increasing ratio also increases with increasing the temperature. The $\Delta L/L_{298}$ for all samples are about 0.6% at around 850 K.

To determine linear thermal expansion coefficients (α) of the solid solutions, we estimated the slopes of $\Delta L/L_{298}$ at 600 K, where the temperature is above the Debye temperature of the sample. The slope of $\Delta L/L_{298}$ against temperature, α, was calculated by a least square method from 1000 point data

Table 1
Lattice parameters of CeO_2 and $Ce_{0.8}M_{0.2}O_{1.9}$ (M = La, Sm, Dy, Yb) at room temperature

Sample	Lattice parameters (nm)		
	This study	Dirstine et al. [7]	Sameshima et al. [8]
CeO_2	0.54113 (±0.0001)	0.5411	0.5411
$Ce_{0.8}La_{0.2}O_{1.9}$	0.54776 (±0.0002)	0.5478	0.5474
$Ce_{0.8}Sm_{0.2}O_{1.9}$	0.54370 (±0.0001)	0.5439	0.5437
$Ce_{0.8}Dy_{0.2}O_{1.9}$	0.54112 (±0.0003)	–	–
$Ce_{0.8}Yb_{0.2}O_{1.9}$	0.53897 (±0.0003)	0.5391	0.5393

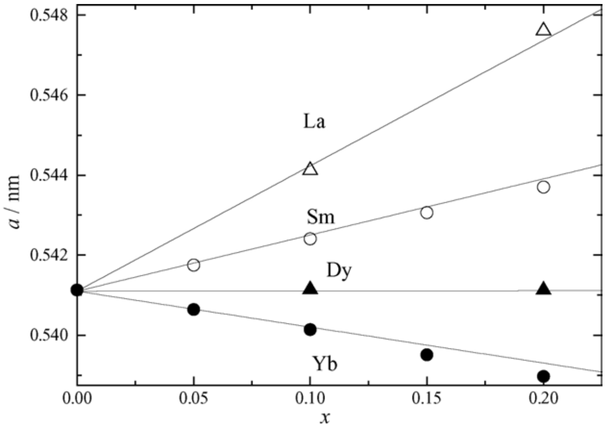

Fig. 1. Lattice parameters, a, of CeO_2 and $Ce_{1-x}M_xO_{2-x/2}$ (M = La, Sm, Dy, Yb, x = 0–0.2) as a function of doped x content at room temperature.

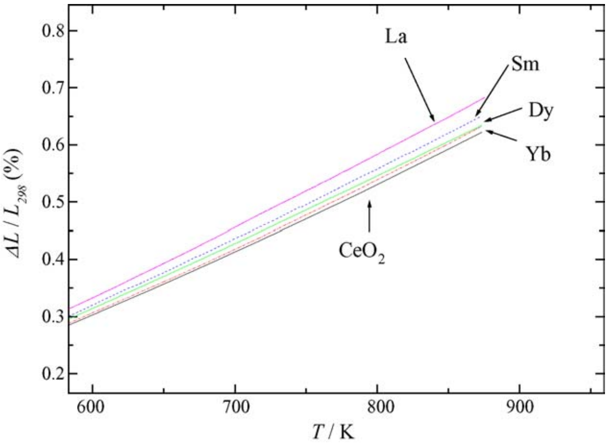

Fig. 2. Thermal expansions, $\Delta L/L_{298}$ (%), of CeO_2 and $Ce_{0.9}M_{0.1}O_{1.95}$ (M = La, Sm, Dy, Yb) as a function of temperature.

Table 2
Thermal expansion coefficients, α, of CeO_2 and $Ce_{0.8}M_{0.2}O_{1.9}$ (M = La, Sm, Dy, Yb)

Sample	This work		Sameshima et al. [6]
	α ($\times 10^{-6}$ K^{-1}) at 600 K	Ave. α ($\times 10^{-6}$ K^{-1}) at 298–800 K	Ave. α ($\times 10^{-6}$ K^{-1}) at 298–800 K
CeO_2	10.9	10.7	11.1
$Ce_{0.8}La_{0.2}O_{1.9}$	12.0	11.7	11.4
$Ce_{0.8}Sm_{0.2}O_{1.9}$	11.5	11.1	11.9
$Ce_{0.8}Dy_{0.2}O_{1.9}$	11.1	10.9	–
$Ce_{0.8}Yb_{0.2}O_{1.9}$	11.1	10.8	11.1

of $\Delta L/L_{298}$ in the temperature interval of 10–15 K at around 600 K, because the slope is considered to be approximately linear. For the all temperature range, the α as a function of temperature (T) was fitted by the following equation:

$$\alpha = b_0 + b_1 T + \frac{b_2}{T^2} \tag{2}$$

where b_0, b_1 and b_2 are the constants independent of temperature. Table 2 shows α at 600 K and the average α value between 298 and 800 K of CeO_2 and $Ce_{0.8}M_{0.2}O_{1.9}$ (M = La, Sm, Dy, Yb). Our average values are in good agreement with the previous ones calculated from measured values of ref. [6] by the present authors, except that of Sm-doped sample. Fig. 3 shows α of CeO_2 and $Ce_{1-x}M_xO_{2-x/2}$ (M = La, Sm, Dy, Yb) at 600 K as a function of doped x content. Each α of the solid solutions increases linearly with increasing doped ion content. The slope of the α depends on a kind of the doped ionic species and increases with increasing ionic radius of the doped ion, though the α of Dy- and Yb-doped samples is nearly the same. The slope of Yb-doped ceria is small, reflecting the effect of oxygen vacancy, because the ionic radius of Ce^{4+} (0.097 nm) is nearly the same as that of Yb^{3+} (0.0985 nm). On the other hand, large effect of the substitution on the thermal expansion coefficient is seen in La-doped ceria among the solid solutions in this study, mainly due to the size effect of ionic radius between Ce^{4+} and La^{3+} (0.116 nm).

The Debye temperatures (Θ_D) of the solid solutions at room temperature were estimated from the longitudinal (v_L) and transverse (v_T) sonic wave velocities of the samples measured by an ultrasonic pulse method. Debye temperature (Θ_D) was calculated by using the following Eq. (3):

$$\Theta_D = \left(\frac{h}{k_B a}\right)\left(\frac{3N}{4\pi}\right)^{1/3} v_m, \quad v_m^{-3} = \frac{1}{3}(v_L^{-3} + 2v_T^{-3}) \tag{3}$$

where h is the Plank's constant, k_B Boltzmann's constant, a lattice parameter and N is the atomic number of unit volume. The resultant Debye temperatures (Θ_D) of the solid solutions are shown in Fig. 4. Θ_D value of un-doped ceria is larger than those of the doped samples. Θ_D does not depend on the ionic radius, r, of doped ionic species, but decreases with increasing doped x content by about 13 K per 10% doped content. It is needed to prepare a single crystal of doped ceria for further discussion between Θ_D and the ionic radius of doped ceria. Fig. 5 shows Θ_D of $Ce_{1-x}Sm_xO_{2-x/2}$ as a function of doped x content. Θ_D decreases linearly with increasing doped x content. Similar tendency was observed for other doped elements. This decrease of Θ_D results from the generation of oxygen vacancy produced by the rare earth doping.

We obtained the thermal expansion coefficient and the Debye temperature of the rare earth-doped ceria in the same sample preparation procedure. Ruffa deduced the relation between α and Θ_D of a solid, previously [10], by using the Morse potential function and Debye model. Ruffa's equation

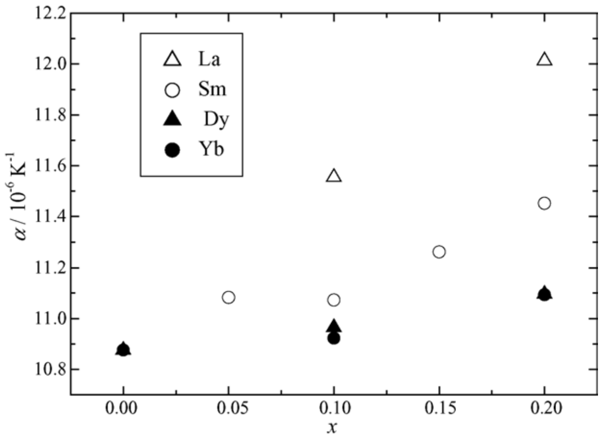

Fig. 3. Thermal expansion coefficients of CeO_2 and $Ce_{1-x}M_xO_{2-x/2}$ (M = La, Sm, Dy, Yb, x = 0–0.2) at 600 K as a function of doped x content.

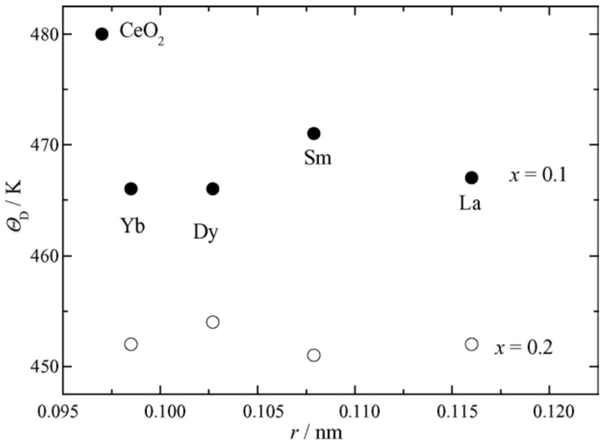

Fig. 4. Debye temperatures of CeO_2 and $Ce_{1-x}M_xO_{2-x/2}$ (M = La, Sm, Dy, Yb; x = 0.1, 0.2) as a function of ionic radius, r, of doped ions.

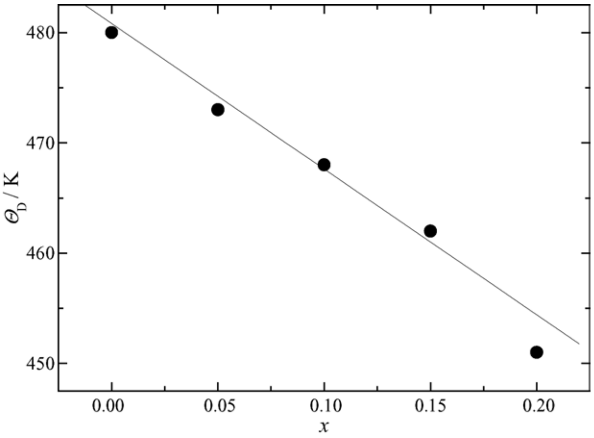

Fig. 5. Debye temperatures of $Ce_{1-x}Sm_xO_{2-x/2}$ ($x = 0$–0.2) as a function of doped x content.

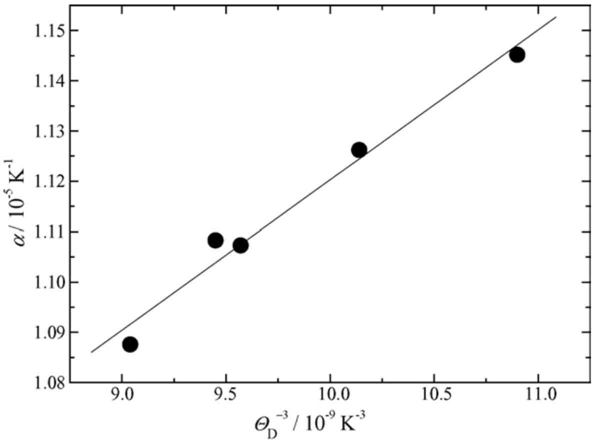

Fig. 6. Thermal expansion coefficients, α, of CeO_2 and $Ce_{1-x}Sm_xO_{2-x/2}$ ($x = 0$–0.2) at 600 K as a function of Θ_D^{-3}.

can be rewritten at constant temperature as follows:

$$\alpha \propto \Theta_D^{-3}$$

Fig. 6 shows the thermal expansion coefficients of CeO_2 and $Ce_{1-x}Sm_xO_{2-x/2}$ as a function of Θ_D^{-3}. Since Debye temperature was less dependent on temperature, we ignored the temperature dependence of Debye temperature in this study. The thermal expansion coefficient increases linearly with increasing Θ_D^{-3}. The experimental results are in good agreement with Ruffa's equation. This fact suggests that the thermal expansion coefficient is strongly related to the Debye temperature in the rare earth-doped ceria.

4. Summary

Thermal expansion and Debye temperature of CeO_2 and $Ce_{1-x}M_xO_{2-x/2}$ (M = La, Sm, Dy, Yb, $x = 0$–0.2) were obtained by using TMA and an ultrasonic pulse method, respectively, and the following conclusions were obtained.

1. The thermal expansion coefficient of CeO_2 was smaller than those of the rare earth-doped ceria at 600 K.
2. The thermal expansion coefficient of the rare earth-doped ceria increased with increasing doped ion content and ionic radius of the doped ionic species except Dy ion, due to the effect of oxygen vacancy and ionic size.
3. The Debye temperature of Sm-doped ceria decreased with increasing doped ion content.
4. The relation between the thermal expansion coefficient and the Debye temperature in the solid solutions obeyed Ruffa's theory on the thermal expansion of solid.

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