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Thermomechanical properties of calcium series perovskite-type oxides

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ABSTRACT

The thermomechanical properties of polycrystalline samples of $CaTiO_3$, $CaZrO_3$, and $CaHfO_3$ were studied. The thermal expansions were measured using a dilatometer in the temperature range from room temperature to 1273 K, and the thermal expansion coefficients were calculated from the slope of the thermal expansion curves. The longitudinal and shear sound velocities as well as the micro-hardness were measured at room temperature. The elastic moduli and the Debye temperature were evaluated from the measured sound velocities. The relationships between these properties of the calcium series perovskite-type oxides were studied.

1. Introduction

The ABO_3 perovskite-type oxides have potentials to be attractive functional materials because they have various unique properties such as high-temperature superconductivity, ferro-magnetism, ferro-, pyro- and piezo-electrics properties [1–3]. In the perovskite-type oxides, $CaTiO_3$ is important in nuclear engineering because it is one of the major phases of Synroc which is a titanate ceramic designed for the immobilizing high-level radioactive waste [4]. When utilizing $CaTiO_3$-based materials as the nuclear materials, the thermomechanical properties should be understood. In addition, the thermomechanical properties of some of the strontium series perovskite-type oxides such as $SrTiO_3$ and $SrZrO_3$ have been widely and systematically studied. However, those of $CaTiO_3$ as well as other calcium series perovskite-type oxides, $CaZrO_3$ and $CaHfO_3$ have not been studied in details. In the present study, therefore, we collected the data of the thermomechanical properties (thermal expansion, elastic moduli and micro-hardness) of $CaTiO_3$ as well as $CaZrO_3$, and $CaHfO_3$. The present paper will be a first report, in which the thermomechanical properties of the calcium series perovskite-type oxides were systematically investigated.

2. Experimental

The polycrystalline sample of $CaHfO_3$ was prepared by solid-state reactions. 50 mol% $CaCO_3$ powders (purity 98%, Nacalai Tesque Co. Ltd.) and 50 mol% HfO_2 powders (purity 98%, Kojundo Chemical Laboratory Co. Ltd.) were mixed in an agate mortar for 30 min and the mixture was pressed into a green pellet. The green pellet was sintered at 1273 K for 10 h in air, followed by heating at 1773 K for 40 h in air. After that, the obtained powders were put into a 20-mm diameter graphite die and given a spark plasma sintering (SPS, Sumitomo coal mining Dr Sinter SPS-1020 apparatus) at 1673 K under an argon-flow atmosphere. The powders of $CaTiO_3$ (purity 99%) and $CaZrO_3$ (purity 98%) were supplied from Aldrich Chemical Company and Kojundo Chemical Laboratory Co. Ltd., respectively. The polycrystalline bulk-samples of $CaTiO_3$ and $CaZrO_3$ were also prepared by the SPS method as mentioned above. The SPS temperatures for $CaTiO_3$ and $CaZrO_3$ were 1373 and 1473 K, respectively. All the bulk-samples thus obtained were heated at 1273 K for 24 h to compensate oxygen loss occurred during SPS.

The powder X-ray diffraction (XRD) analysis was performed using Cu-Kα radiation at room temperature using Rigaku Rint2000; the crystal structures of the sample were evaluated from the XRD patterns. The bulk densities were calculated from the measured weight and dimensions.

In the temperature range from room temperature to 1273 K, the thermal expansion coefficient was evaluated using a dilatometer (BRUKER TD5000SA) under an argon-flow atmosphere with the flow rate of 100 ml/min. The longitudinal and shear sound velocities were measured through the ultrasonic pulse-echo method at room temperature in air using KARL DEUTSCH Echometer1062, which enables us to evaluate the elastic moduli and Debye temperature. For an isotropic medium, the shear modulus G, Young's modulus E, bulk modulus B, and Debye temperature θ_D can be calculated from the longitudinal sound velocity V_L and shear sound velocity V_S as follows:

$$G = \rho V_S^2, \quad (1)$$

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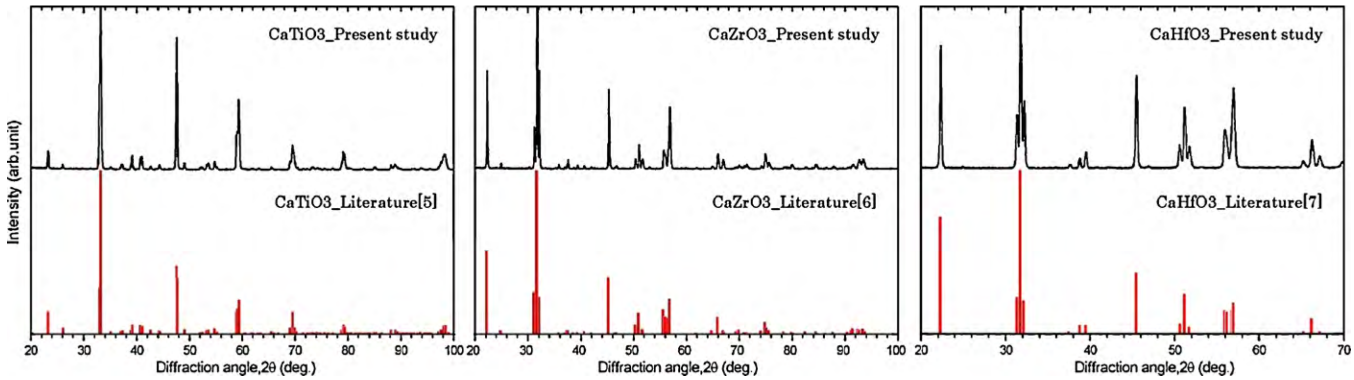

Fig. 1. The XRD patterns of the polycrystalline samples of $CaTiO_3$, $CaZrO_3$, and $CaHfO_3$, together with the literature data [5–7].

$$E=\frac{G(3V_L^2-4V_S^2)}{V_L^2-V_S^2}, \tag{2}$$

$$B=\rho\left(V_L^2-\frac{4}{3}V_S^2\right), \tag{3}$$

$$\theta_D=\left(\frac{h}{k_B}\right)\left[\frac{9N}{4\pi V(V_L^{-3}+2V_S^{-3})}\right]^{1/3}, \tag{4}$$

where ρ is the sample density, h is the Planck constant, k_B is the Boltzmann constant, N is the number of atoms in a unit cell, and V is the unit cell volume. The Vickers hardness H_V was measured by loading a diamond pyramid-type (with apex 136) indenter into the sample surface at room temperature in air, using the micro-Vickers hardness tester (Matsuzawa Seiki MHT-1). The applied load and loading time were chosen to be 9.8 N and 15 s, respectively; and the measurements were repeated 14 times for each sample. The H_V was calculated from the following equation:

$$H_V=\frac{2P_H\ \sin(\phi/2)}{d^2}, \tag{5}$$

where ϕ is the indenter apex angle, P_H is the applied load, and d is the mean length of diagonal of the indentation trace.

3. Results and discussion

The XRD patterns are shown in Fig. 1, together with the literature data [5–7]. The calcium series perovskite-type oxides prepared in the present study are indicated to be the orthorhombic structure at room temperature. The XRD patterns of our samples were well consistent with the literature data [5–7]. The lattice parameters and the samples' bulk densities of the calcium series perovskite-type oxides are summarized in Table 1. The density values were above 95% of the theoretical densities.

In the early 1920s, Goldschmidt proposed a "tolerance factor" to study the stability of perovskites, ABX_3 [8]. The tolerance factor t is defined as:

$$t=\frac{r_A+r_O}{\sqrt{2(r_B+r_O)}}, \tag{6}$$

where r_A, r_B, and r_O are the ionic radius of each atom. The coordination numbers of A and B atoms are 12 and 6, respectively. Generally speaking, t determines the stability of the perovskite phase for a given set of anions and cations. Ordinarily, the value of t is within 0.75–1.1. For the perovskite-type oxides, the cubic structure has a value near 1 [9]. As the value of t shifts from 1, the geometric distortion becomes larger. The values of the tolerance factor of the calcium series perovskite-type oxides are summarized in Table 1. The Shannon's values of the ionic radius [10] were used to evaluate the values of t in the present study.

The thermal expansion curves of the $CaTiO_3$, $CaZrO_3$, and $CaHfO_3$ samples are shown in Fig. 2. It was revealed that $CaTiO_3$ exhibited the highest thermal expansion in the calcium series perovskite-type oxides. The average thermal expansion coefficients (α_l) were evaluated from the slopes of the thermal expansion curves. The α_l values for $CaTiO_3$, $CaZrO_3$, and $CaHfO_3$ determined in the present study are summarized in Table 1. The present results of $CaTiO_3$ and $CaZrO_3$ agreed well with the previously reported values, $11.7\times10^{-6}\,K^{-1}$ [11] and $6.5\times10^{-6}\,K^{-1}$ to $8.5\times10^{-6}\,K^{-1}$ [12], respectively. It is empirically confirmed that the linear thermal expansion coefficient varies inversely as the melting temperature for many substances [13]. The reference data of the melting temperature (T_m) of $CaTiO_3$, $CaZrO_3$ and $CaHfO_3$ [11,12,14] are summarized in Table 1. $CaTiO_3$, of which the melting temperature was the lowest in the calcium series perovskite-type oxides, indicated the highest linear thermal expansion coefficient. $CaZrO_3$ and $CaHfO_3$, of which the melting temperatures were quite similar, indicated the

Table 1
Crystallographic data and thermomechanical properties of the calcium series perovskite-type oxides.

		$CaTiO_3$	$CaZrO_3$	$CaHfO_3$
Tolerance factor	t	0.966	0.914	0.918
Crystal system (*RT*)		Orthorhombic	Orthorhombic	Orthorhombic
Lattice parameters (*RT*) (nm)	a	0.53828	0.55936	0.57242
	b	0.54460	0.80089	0.79847
	c	0.76391	0.57704	0.55746
Density (g/cm^3)	ρ	3.87	4.46	6.66
%TD	η	96.0%	96.8%	95.8%
Average linear thermal expansion coefficient (K^{-1})	α_l	11.05×10^{-6}	8.38×10^{-6}	8.38×10^{-6}
Melting temperature (K)	T_m	2262 [11]	2618 [12]	2713 [14]
Young's modulus (GPa)	E	260 ± 2	224 ± 1	244 ± 1
Shear modulus (GPa)	G	104 ± 1	89.5 ± 0.3	97.6 ± 0.4
Bulk modulus (GPa)	B	172 ± 2	149 ± 2	163 ± 2
Debye temperature (K)	θ_D	760 ± 3	631 ± 1	538 ± 1
Vickers hardness (GPa)	H_V	9.5 ± 0.5	8.1 ± 0.1	8.9 ± 0.9

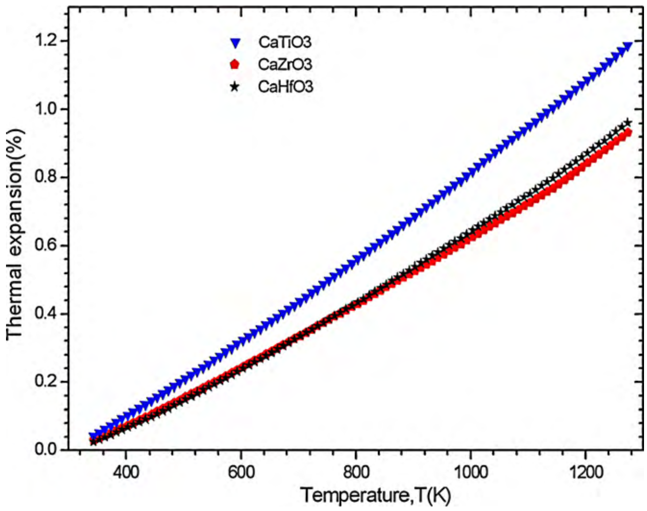

Fig. 2. The thermal expansion curves of the calcium series perovskite-type oxides in the temperature range from room temperature to 1273 K.

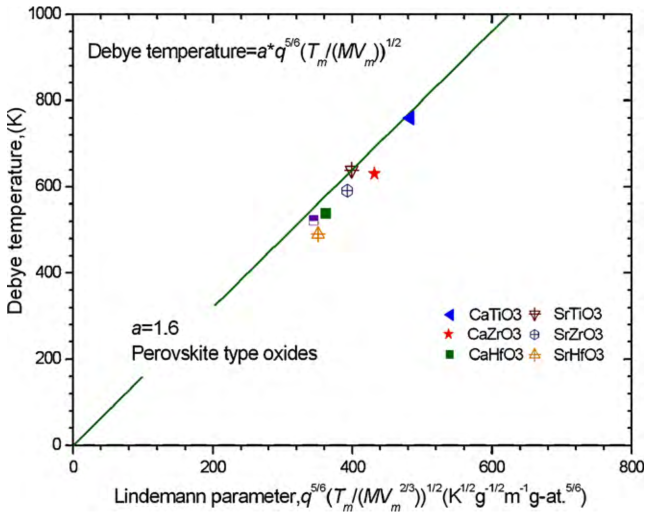

Fig. 3. Relationship between the Debye temperature θ_D and the Lindemann parameter $q^{5/6}(T_m/(MV_m^{2/3}))^{1/2}$ for the perovskite-type oxides.

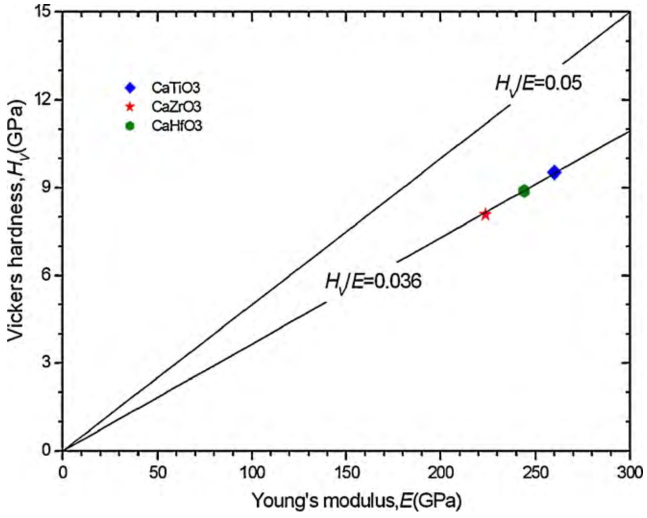

Fig. 4. Relationship between the Young's modulus E and the Vickers hardness H_V for the calcium series perovskite-type oxides.

close values of the linear thermal expansion coefficient. As for the calcium series perovskite-type oxides, it was concluded that the magnitude relation of linear thermal expansion coefficient was explained from the viewpoint of melting temperature.

The elastic moduli and the Debye temperature of the calcium series perovskite-type oxides at room temperature are summarized in Table 1. The elastic moduli of $CaTiO_3$ obtained in the present study agreed with the literature values (E: 266.4 GPa, G: 106.9 GPa, B: 175.3 GPa) [15]. The bulk moduli of $CaZrO_3$ agreed with the reported results obtained through single-crystal X-ray diffraction measurements (B: 154 GPa) [16]. The elastic moduli of $CaZrO_3$ and $CaHfO_3$ agreed with the results of the cubic phase calculated by employing a first principles method (E: 221.8 GPa, G: 87.9 GPa, B: 154.8 GPa) [17] and (E: 231 GPa, G: 89 GPa, B: 192 GPa) [18], respectively. The experimental data of the orthorhombic phase of $CaHfO_3$ are not available until now. Based on the sound velocity reported by Sinelnikov et al. [15], the Debye temperature of $CaTiO_3$ are calculated to be 761 K, which is in good agreement with our results. The Debye temperature of $CaHfO_3$ was close to the calculated value for the cubic phase (522 K) [18].

$CaTiO_3$ exhibited the highest elastic moduli and $CaZrO_3$ the lowest elastic moduli in the calcium series perovskite-type oxides. It is known that the Young's modulus becomes small as the tolerance factor deviates from 1 [19]. From the values of the tolerance factor shown in Table 1, it can be seen that the substance with the smaller value of t showed the smaller Young's modulus. This fact indicates that the geometric distortion of the crystal affects the Young's modulus.

The Debye temperature θ_D is known to be related to the melting temperature T_m (K), the molar mass M, and the molar volume V_m by the Lindemann relationship [20]. The relationship for the perovskites is [21]:

$$\theta_D = a \cdot q^{5/6}\left(T_m/(MV_m^{2/3})\right)^{1/2} \quad a = 1.60, \tag{7}$$

where a is the proportionality constant and q is the number of atoms in the chemical formula. Fig. 3 shows the relationship between the Debye temperature and the Lindemann parameter of the calcium series perovskite-type oxides, together with the data of the strontium series perovskite-type oxides [9]. As shown in Fig. 3, all of the calcium and strontium series perovskite-type oxides showed a good agreement with Eq. (7). In addition, as the constituent element of these substances shifted to heavier (from Ti to Hf or Ca to Sr), the θ_D decreased sequentially. These results showed that the Debye temperatures of the perovskite-type oxides were closely related with the mass of the constituent elements.

The values of the Vickers hardness of $CaTiO_3$, $CaZrO_3$, and $CaHfO_3$ are summarized in Table 1. The hardness provides the information of the resistance of a material to plastic deformation. For various materials, the Vickers hardness is also known to be associated with the Young's modulus E. For some oxides and carbides, the hardness H_V was found to be proportional to the Young's modulus E with H_V/E of approximately 0.05 [22]. For the strontium series perovskite-type oxides, H_V/E has been reported to be 0.03 [19]. The relationship between Young's modulus E and hardness H_V of calcium series perovskite-type oxides in this present study is shown in Fig. 4. The proportional constants of all of the three calcium series perovskite oxides were close to 0.036. The proportional constants were in good agreement with the result for the strontium series perovskite-type oxides.

4. Conclusions

The thermal expansion coefficient, elastic moduli, Debye temperature and micro-hardness of $CaTiO_3$, $CaZrO_3$, and $CaHfO_3$ were examined and the relationships between these properties of the calcium series perovskite-type oxides were studied. The linear thermal expansion coefficients were related to the melting temperature, that is the α_l varied inversely as the T_m. The tendency of the elastic moduli of $CaTiO_3$, $CaZrO_3$ and $CaHfO_3$ were explained in terms of the tolerance factor, indicating that the geometric distortion of the crystal affected on the Young's modulus. The Debye temperatures of $CaTiO_3$, $CaZrO_3$, and $CaHfO_3$ were systematically varied with the mass of the constituent elements. The proportionalities between the Young's modulus E and the Vickers hardness H_V were about 0.036 which was well consistent with the value for strontium series perovskite-type oxides (0.03) reported previously [17].

Acknowledgements

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