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Thermophysical properties of $BaUO_3$

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Abstract

Thermophysical properties of $BaUO_3$, specifically melting point, thermal expansion coefficient, elastic moduli, Debye temperature, and thermal conductivity, have been studied. The longitudinal and shear sound velocities of $BaUO_3$ were measured by an ultrasonic pulse-echo method at room temperature, which enabled us to calculate the elastic properties and the Debye temperature. Microhardness measurements were made for $BaUO_3$ at room temperature using a micro-Vickers hardness tester. These mechanical properties of $BaUO_3$ differed from those of UO_2. The thermal conductivity was calculated from the measured density and thermal diffusivity and literature values of heat capacity. The thermal conductivity of $BaUO_3$ was about one-tenth that of UO_2. The thermophysical properties of $BaUO_3$ were found to be glass-like rather than like those of typical ceramics.

1. Introduction

In irradiated fuel, the presence of fission products affects the thermophysical properties of the fuel. In particular, the fission products precipitated in the fuel matrix, such as oxide and metallic inclusions, appear to have an influence on the thermal and mechanical properties of the fuel. The gray oxide phase with the perovskite type structure of $(Ba,Sr)(U,Pu,Zr,RE,Mo)O_3$ has been observed in irradiated MOX fuel [1,2]. Although several properties of the perovskite type compounds have been studied, little information on the properties of $BaUO_3$ is available.

On the other hand, for improvement of the economic and energetic efficiency of the nuclear power systems, we have been studying the utilization of thermoelectric materials to reuse exhaust heat from nuclear reactors. If high-performance thermoelectric materials of uranium compounds are developed and actually applied, the depleted uranium produced through a nuclear fuel cycle can be utilized efficiently. Ideal thermoelectric materials should have a low thermal conductivity and good electron transport properties (electrical conductivity and Seebeck coefficient). As a representation of ideal thermoelectric materials, the so-called phonon-glass electron-crystal (PGEC) behavior is proposed [3,4], in which phonon thermal conductivity approaches that of glassy materials while the electrons behave as in crystal structures.

In the present study, therefore, thermophysical properties of $BaUO_3$, specifically melting point, thermal expansion coefficient, elastic moduli, Debye temperature, and thermal conductivity, were examined. The paper also describes the relationships between the thermophysical properties of $BaUO_3$.

2. Experimental

$BaUO_3$ was prepared by mixing the appropriate amounts of UO_2 and $BaCO_3$ followed by reacting and sintering at 1223 K. The crystal structure of the sample was analyzed by a powder X-ray diffraction method using a Cu-Kα radiation at room temperature. For thermal and mechanical properties measurements, samples of appropriate shape were cut from the pellet. The densities of these samples were determined by hydrostatic weighing. The melting temperature of $BaUO_3$ was measured by the thermal arrest method under reduction atmosphere. The thermal expansion

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coefficient of $BaUO_3$ was evaluated by using a dilatometer in the temperature range from room temperature to about 700 K under reduction atmosphere. The longitudinal and shear sound velocities were measured by an ultrasonic pulse-echo method at room temperature to evaluate the elastic properties and Debye temperature of $BaUO_3$. The experimental technique and condition were the same as our previous studies [5–7]. The hardness measurement was also performed at room temperature using a micro-Vickers hardness tester. In the temperature range from room temperature to about 1200 K, the thermal conductivity of $BaUO_3$ was calculated from the measured density, literature values of heat capacity, and thermal diffusivity measured by a laser flash method using ULVAC TC-7000 in vacuum. The heat capacity of $BaUO_3$ was evaluated from Neumann–Kopp's law using the literature data [8] of UO_2 and BaO.

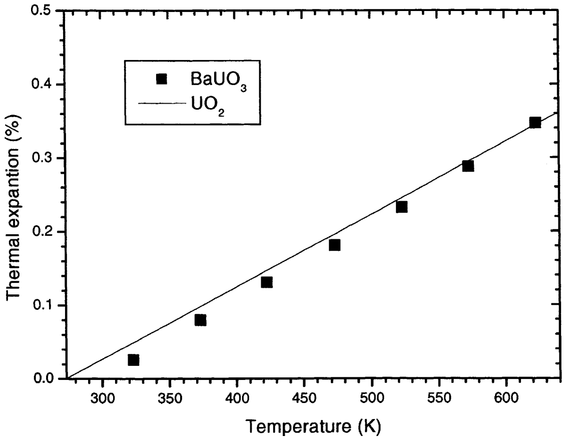

Fig. 1. Coefficient for thermal expansion from room temperature to about 700 K for $BaUO_3$.

3. Results and discussions

The powder X-ray diffraction pattern at room temperature of the sample showed single phase $BaUO_3$ with a perovskite type cubic structure. The lattice parameter and theoretical density of $BaUO_3$ were obtained from the X-ray diffraction analysis and are given in Table 1. The bulk densities of the samples were about 80% of the theoretical density. The O/M ratio of the $BaUO_3$ sample was not measured chemically, but the deviation from the stoichiometry appears to be small, since the lattice parameter of the $BaUO_3$ sample prepared in the present study, 0.4404 nm, was close to the previously reported value, in which the sample composition was found to be nearly stoichiometric ($a = 0.4408$ nm, $BaUO_{3.023}$) [9].

The thermal expansion from room temperature to about 700 K of $BaUO_3$ is shown in Fig. 1. It was confirmed that the thermal expansion of $BaUO_3$ nearly equaled that of UO_2 [10]. The melting temperature of $BaUO_3$ measured in the present study is shown in Table 1, together with the linear thermal expansion coefficient from room temperature to about 700 K. It is empirically confirmed that the thermal expansion coefficient varies inversely as the melting temperature for many substances [11]. The variations in the linear thermal expansion coefficient α_ℓ with the melting temperature T_m of perovskite type oxides and UO_2, ThO_2 are shown in Fig. 2. For some substances the following relationship between α_ℓ and T_m in K was reported [11]:

$\alpha_\ell \cdot T_m = 0.019$ (for metals),

$\alpha_\ell \cdot T_m = 0.019$ (for perovskite type oxides), and

$\alpha_\ell \cdot T_m = 0.030$ (for fluorite type oxides).

For $BaUO_3$ however the product of α_ℓ and T_m equaled 0.022, higher than that of other perovskite type oxides.

Table 1
Thermophysical properties of $BaUO_3$

Lattice parameter (nm)	a	0.4404
Bulk density (%T.D.)		82
Linear thermal expansion coefficient (K^{-1})	α_ℓ	1.101×10^{-5}
Melting temperature (K)	T_m	2450
Shear modulus	G	26.6
Young's modulus (GPa)	E	66.0
Bulk modulus	K	42.6
Poisson's ratio	ν	0.242
Vickers hardness (GPa)	H	5.46
Debye temperature (K)	θ_D	255.7

The longitudinal and shear sound velocities of $BaUO_3$ were measured at room temperature, and the elastic constants were evaluated. For isotropic media, the shear modulus G, Young's modulus E, and bulk

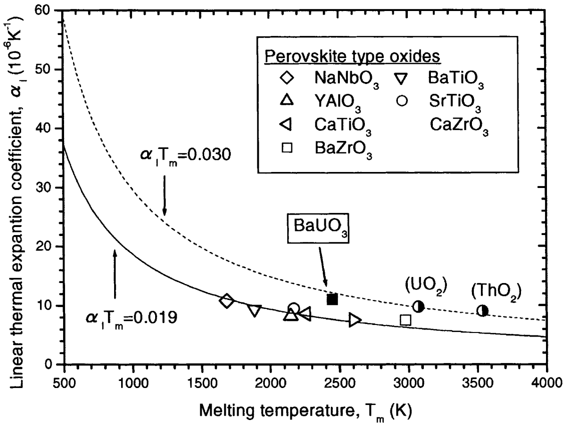

Fig. 2. Dependence of linear thermal expansion coefficient α_ℓ on melting temperature T_m for $BaUO_3$ and other materials.

modulus K can be written in terms of the longitudinal sound velocity V_L and shear sound velocities V_S [12] by

$$G = \rho V_S^2,$$

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

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

where ρ is the sample density. Poisson's ratio v can be expressed in terms of V_L and V_S as follows:

$$v = \frac{1}{2}\frac{V_L^2 - 2V_S^2}{V_L^2 - V_S^2}.$$

The values of G, E, K, and v calculated from the sound velocities are shown in Table 1.

For some substances, Young's moduli are proportional to $q(RT_m/V_m)$ [13] where q is the number of atoms in the chemical formula, T_m is the melting temperature in K, V_m is the molar volume and R is the gas constant. For pure metals we obtained the following relationship [14]:

$$E = 97.9q\left(\frac{RT_m}{V_m}\right)$$

which is in good agreement with the results of Frost and Ashby [13]. A comparison of Young's modulus is made between $BaUO_3$ and other substances in Fig. 3, indicating that the proportionality between E and $q(RT_m/V_m)$ of $BaUO_3$ is almost identical with that of SiO_2 glass.

Hardness is associated with the resistance of a material to plastic deformation. The value of Vickers microhardness obtained for $BaUO_3$ is given in Table 1. The hardness value was similar to that of UO_2 (6.4 GPa) [6].

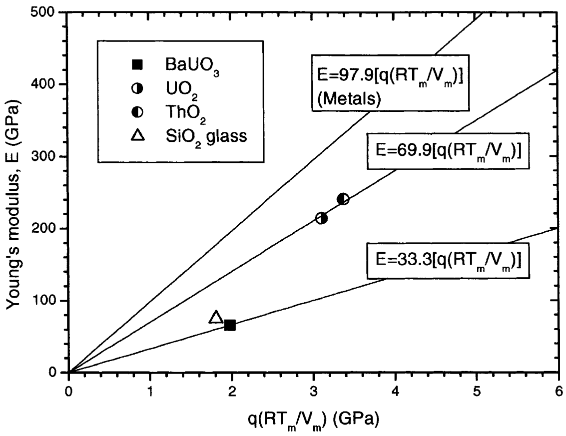

Fig. 3. Dependence of Young's modulus E on $q(RT_m/V_m)$ for $BaUO_3$ and other materials.

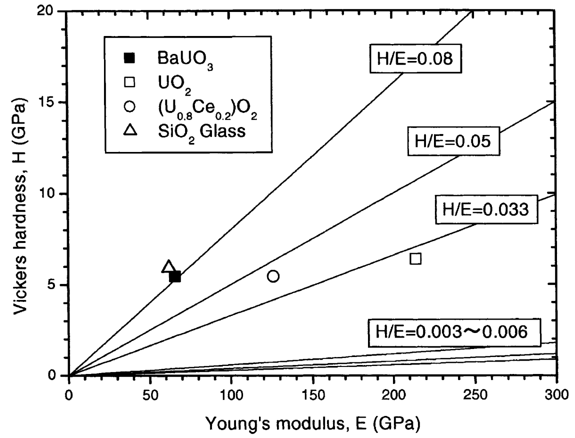

Fig. 4. Relationship between Young's modulus E and hardness H for $BaUO_3$ and other materials.

For some oxide and carbide ceramics, the hardness H was found to be proportional to Young's modulus E with the values of $H/E \approx 0.05$ [15].

We estimated the H/E for pure metals using the literature data [16] and obtained the values of 0.006, 0.003 and 0.004 for bcc, fcc and hcp metals, respectively [14]. The value of H for $BaUO_3$ is plotted in Fig. 4 as a function of Young's modulus E together with the other substances data [6]. As shown in this figure, it was found that the relationship between hardness and Young's modulus for $BaUO_3$ is similar to that of SiO_2 glass.

The Debye temperature θ_D for $BaUO_3$ can be calculated from the sound velocities and the lattice parameters. The Debye temperature θ_D is related to the longitudinal and shear sound velocities [17] as follows:

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

where h is the Plank 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 value of Debye temperature of $BaUO_3$ evaluated in the present study is shown in Table 1.

It is known that the Debye temperature θ_D can be related to the melting temperature T_m in K, the molar mass M and the molar volume V_m by the Lindemann relationship [18]. The relationships were reexamined for pure metals, and the ratios of θ_D to $(T_m/(MV_m^{2/3}))^{1/2}$ were estimated to be 1.42, 1.60 and 1.80 for bcc, fcc and hcp metals [14]. For perovskite type oxides the following relationship has been reported [19]:

$$\frac{\theta_D}{q^{5/6}(T_m/(MV_m^{2/3}))^{1/2}} = 1.60,$$

where q is the number of atoms in the chemical formulas. Fig. 5 shows this relationship for $BaUO_3$, obtained

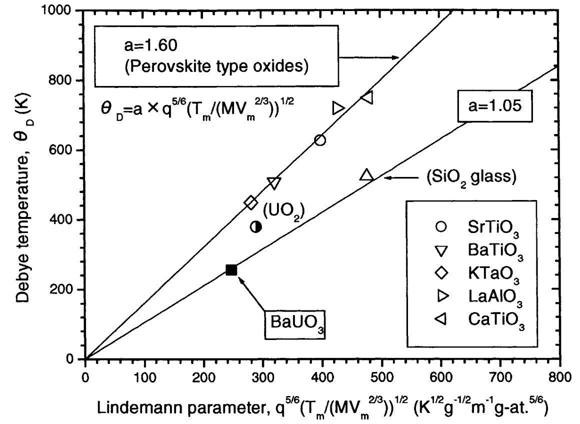

Fig. 5. Dependence of Debye temperature θ_D on $q(T_m/(MV_m^{2/3}))^{1/2}$ for $BaUO_3$ and other materials.

in the present study, together with the reported data [5,19,20]. The proportionality constant differs slightly between $BaUO_3$ and other perovskite type oxides. This further shows the glass-like tendency of $BaUO_3$.

The temperature dependence of the thermal diffusivity D of $BaUO_3$ is shown in Fig. 6. In this figure, solid and open squares are the data measured during heating and cooling, respectively. The thermal diffusivity of $BaUO_3$ was almost independent of the temperature. The temperature dependence of the thermal conductivity λ is shown in Fig. 7 together with those for other perovskite type oxides and SiO_2 glass [21–24]. The thermal conductivity was calculated from the measured thermal diffusivity D, specific heat capacity C_P and measured density d using the following relationship:

$$\lambda = DC_Pd.$$

The heat capacity of $BaUO_3$ was evaluated from Neumann–Kopp's law using the literature date [8] of UO_2 and BaO. The thermal conductivity of $BaUO_3$ was corrected to 100% of the theoretical density by using Schulz's equation [25]. As can be seen in the figure, the thermal conductivity of $BaUO_3$ was almost independent of the temperature, indicating that the mechanism of thermal conduction was not described by the simple phonon conduction theory. The thermal conductivity of $BaUO_3$ was markedly lower that those of other perovskite type oxides and was about one-tenth that of UO_2. In this aspect also, $BaUO_3$ is like glasses, in spite of its simple crystal structure.

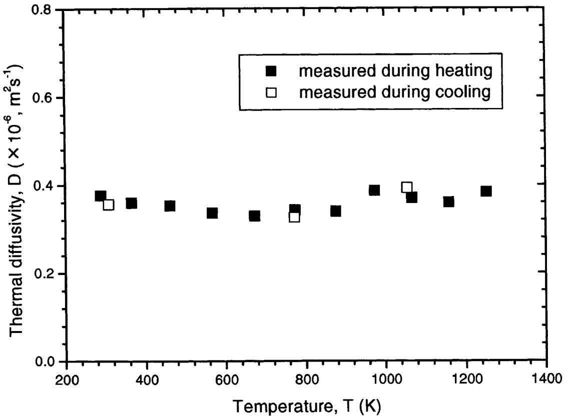

Fig. 6. Temperature dependence of thermal diffusivity for $BaUO_3$.

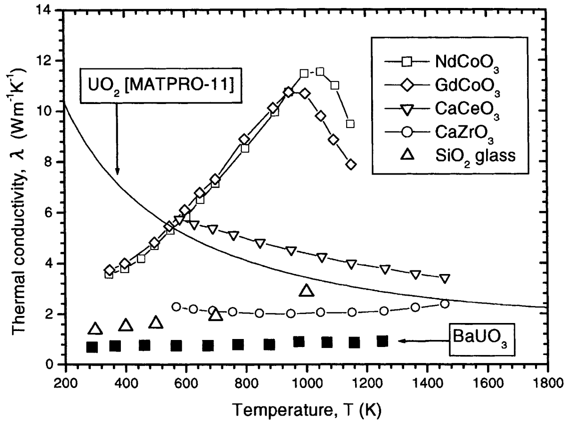

Fig. 7. Temperature dependence of thermal conductivity for $BaUO_3$ and other materials.

4. Summary

The relationships between the thermophysical properties of $BaUO_3$ have been studied. The linear thermal expansion coefficient α_ℓ from room temperature to about 700 K of $BaUO_3$ nearly equaled that of UO_2. The α_ℓ of $BaUO_3$ was higher than that of other perovskite type oxides. The elastic constants and Debye temperature of $BaUO_3$ were calculated from sound velocity measurements mode by the ultrasonic pulse-echo method. The relationship between hardness and Young's modulus of $BaUO_3$ resembled that for glass, particular SiO_2 glass, rather than those of ceramics. The thermal conductivity of $BaUO_3$ was evaluated from its thermal diffusivity measured by the laser flash method. The thermal conductivity of $BaUO_3$ was much lower than that of other perovskite type oxides – like SiO_2 glass – in spite of its simple crystal structure.

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