Journal of Thermal Analysis, Vol. 37 (1991) 2643-2648

THERMAL DIFFUSIVITY AND THERMAL CONDUCTIVITY STUDIES ON THE ZIRCONATE, CERATE AND URANATE OF BARIUM

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(Received January 17, 1991)

The thermal diffusivity and thermal conductivity of the zirconate, cerate and uranate of barium were investigated by employing the laser flash technique. The variation in the thermal resistivity as a function of temperature was examined and the heat transport behaviour of these materials is discussed.

Introduction

Thermal diffusivity and thermal conductivity information is essential in order to evalueate heat flow and temperature variations in materials operable at elevated temperatures and to understand their thermal performance. With reference to the area of refractory materials, there is growing interest in the properties and applications of selected compounds of barium as well as those of other alkaline earth elements. In the "oxide" type of nuclear fuels, barium, which is a fission product element, is known to react with another fission product, zirconium, to form a barium zirconate ($BaZrO_3$) phase [1]. As a result of the high-temperature reaction between barium and the urania fuel, the formation of barium uranate ($BaUO_4$) may also occur [2]. In addition to its relevance in the area of nuclear fuels, barium zirconate is also of considerable importance as an oxide ceramic [3]. It is a candidate for use as a refractory coating material for space vehicles [3, 4] and is also used as an additive in the preparation of ceramic capacitor bodies. Another compound of barium, barium cerate ($BaCeO_3$), is likewise of considerable interest, not only because of its formation in reactor fuels

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from the interaction of the fission products barium and cerium, but also in view of its possible development as a ceramic coating material and a solid electrolyte. Thermal diffusivity and thermal conductivity information on the zirconate, uranate and cerate of barium is necessary to understand their thermal behaviour and performance. In the present work, thermal diffusivity measurements were carried out on barium zirconate, cerate and uranate, employing the laser flash technique. Thermal conductivity data were obtained from the thermal diffusivity values by utilizing the already available heat capacity information.

Experimental

In order to prepare the zirconate, cerate and uranate of barium, an appropriate amount of barium carbonate was mixed with the corresponding metal oxide, namely ZrO_2, CeO_2 or U_3O_8. The reaction mixtures were ground thoroughly for 4 hours and pelletized, and the pellets were heated in air at 1373 K for 12 hours. The pellets were again ground thoroughly and the "grinding-pelletisation-heating" cycle was repeated three times in order to facilitate the uniform progress of the reaction and to ensure homogenization. The pellets were finally heated at 1823 K for 26 hours in the case of the zirconate, at 1453 K for 40 hours in the case of the uranate, and at 1500 K for 36 hours in the case of the cerate. The formation of the required barium zirconate, cerate and uranate was verified by X-ray diffraction, for which a Siemens model D 500 powder diffractometer was utilized. The sample densities for barium zirconate and cerate were measured by the liquid immersion technique, with dibutyl phthalate as the immersion liquid. The sample densities were found to be 5.85 $g \cdot cm^{-3}$ and 5.91 $g \cdot cm^{-3}$, which correspond to 93.9% and 92.9% theoretical for barium zirconate and cerate, respectively. The specimen density of barium uranate was determined from dimensional and weight measurements. The density was found to be 6.56 $g \cdot cm^{-3}$, which corresponds to 86.0% theoretical.

Thermal diffusivity measurements as a function of temperature were carried out by the laser flash technique [5]. Salient features of the laser flash technique, experimental methodology, and application for measurements on various materials have been discussed in several earlier reports [6–9]. In the present work, a pulsed ruby laser,with a pulse time of 0.8 ms, was employed to deliver the laser flashes, the pulse energies being selectable in the range from 5 to 25 J. A super kanthal furnace was used to heat the sample to the various temperatures at which the laser flash measurements were made, and

the present measurements were carried out in an argon atmosphere. A lead sulphide infrared detector, together with a transient wave form recording unit, was used to monitor the rear surface temperature of the sample consequent to the laser flash. Both the front and rear surfaces of the sample were coated with a thin layer of platinum, and a 'type B' thermocouple was used for measurement of the ambient temperature of the sample. The thermal diffusivity (D) was obtained from the relationship

$$D = W \cdot \frac{l^2}{t_{1/2}} \tag{1}$$

where l is the sample thickness, $t_{1/2}$ is the time taken for the rear surface of the sample to attain half the maximum rise in temperature and W is a dimensionless parameter which depends on the heat losses fromthe sample. In the present work, the heat losses were taken into account and the parameter W was determined by utilising the method of Cowan [10]. The present samples were about 10 mm in diameter, the thickness being in the range from 0.8 to 1.4 mm. The thermal diffusivity measurements were carried out over the temperature range from 573 to 1515 K for barium zirconate and cerate, and from 573 to 1425 K for barium uranate.

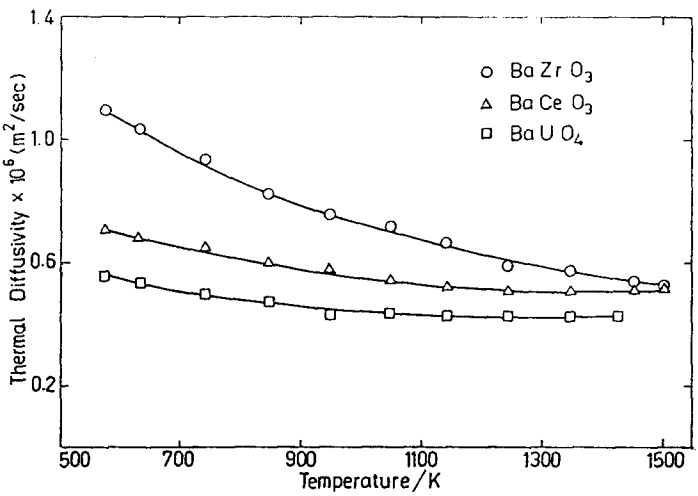

Fig. 1 Thermal diffusivity of barium zirconate, cerate and uranate as a function of temperature

Results and discussion

Figure 1 shows the thermal diffusivity data obtained for barium zirconate, cerate and uranate as a function of temperature. For the zirconate,

the thermal diffusivity decreases gradually as the temperature is increased throughout the present temperature range. For barium cerate and uranate, the thermal diffusivity decreases as the temperature is increased up to about 1200 K, and thereafter does not vary much. The thermal diffusivities are seen to follow the sequence zirconate > cerate> uranate.

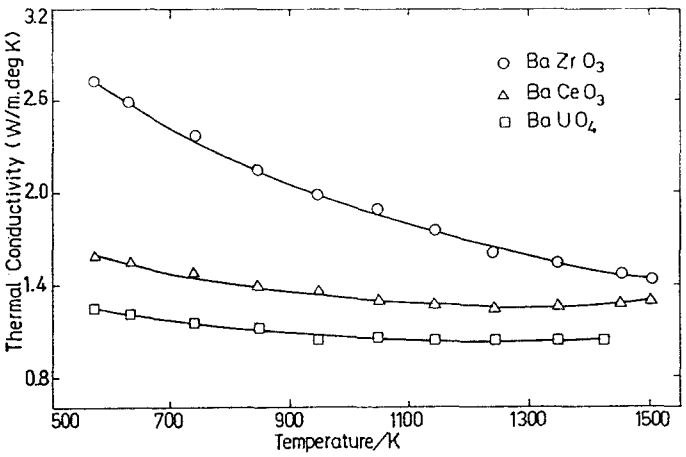

Fig. 2 Thermal conductivity of barium zirconate, cerate and uranate as a function of temperature

From the thermal diffusivity values, the thermal conductivity was obtained via the relationship

$$K = DCd \tag{2}$$

where K is the thermal conductivity, C is the heat capacity at constant pressure and d is the density. The necessary heat capacity values were taken from the data reported earlier for these materials by our laboratory [11–13]. The thermal conductivities of these materials as a function of temperature are shown in Fig. 2. It is seen that the thermal conductivities lie within the range from 1 to 3 w/m·deg, which is generally characteristic of low thermal conductivity oxide ceramics. The thermal conductivities are seen to follow the sequence zirconate > cerate > uranate. To examine the heat transport behaviour, the thermal resistivity (R) of these materials was obtained as $R = \frac{1}{K}$. The variation in the thermal resistivity as a function of temperature is shown in Fig. 3. The thermal resistivity of the zirconate increases linearly with increase of temperature throughout the present temperature range.

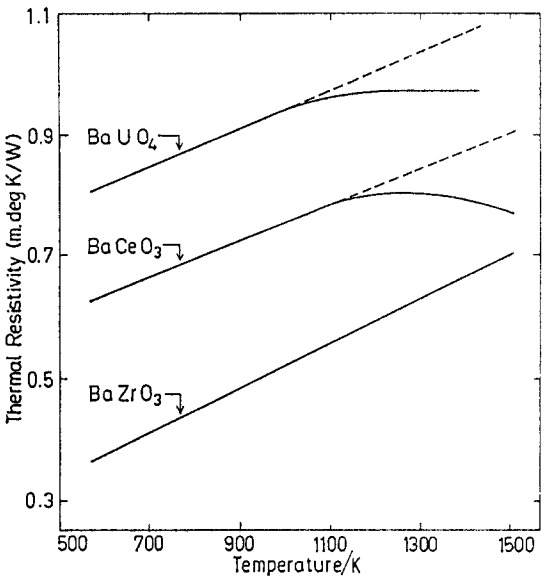

Fig. 3 Variation of the thermal resistivity of the barium compounds as a function of temperature

The thermal resistivity of the uranate increases linearly with increase of temperature from 573 to 1050 K, and attains constancy beyond 1200 K. It is seen that the lattice thermal conduction is responsible for the transport of heat in these materials. In the lattice mode of heat transport, it is known that, as the temperature is increased, the phonon mean free path decreases gradually, resulting in a linear increase in thermal resistivity, or, conversely a corresponding decrease in thermal conductivity [14]. Eventually, at high temperatures, as the phonon mean free path approaches values of the order of interatomic distances, the thermal conductivities of the materials approach the lowest limits and the corresponding thermal resistivities approach the highest limits beyond which no variation can be seen. The thermal resistivity behaviour of barium zirconate and uranate can be understood on the basis of the considerations discussed above. In the case of barium cerate, however, it is noted that up to a temperature of about 1150 K the thermal resistivity increases linearly with increase of temperature and thereafter slowly decreases as the temperature is further raised. In this case, while the lattice conduction accounts for the behaviour up to 1150 K, it is considered that the radiative component of heat conduction (also known as the photon thermal conductivity) is responsible for the mild increase in thermal conductivity or decrease in thermal resistivity at higher temperatures

[15, 16]. These observations are considered useful in facilitating an understanding of the thermophysical behaviour of the present materials; hence, further investigations have been undertaken on the heat transport properties of other alkaline earth-based oxide ceramics.

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The authors gratefully acknowledge the technical assistance of R. Kandan and S. Munusamy during the course of this work.

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Zusammenfassung — Mit der Laserflash-Technik wurde die Temperaturleitfähigkeit und die Wärmeleitfähigkeit von Bariumzirkonat, -zerat und -uranat untersucht. ES wurde die Wärmewiderstand als eine Funktion der Temperatur untersucht und das Wärmetransportverhalten dieser Substanzen besprochen.