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Letter to the Editors

Investigation of the thermal conductivity of selected compounds of gadolinium and lanthanum

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Abstract

As a part of the development of rare earth based ceramic materials for nuclear applications, the thermal conductivity of gadolinium zirconate, lanthanum zirconate and gadolinium aluminate was investigated employing the laser flash technique and covering a temperature range from 650 to 1400 K. Based on the temperature dependence of the thermal resistivity, the heat transport behaviour of these materials was briefly examined. © 1997 Elsevier Science B.V.

1. Introduction

Investigation of thermal conductivity forms an important aspect of the current research and developmental work on high temperature materials. Information on thermal conductivity as a function of temperature is essential in order to evaluate the heat flow and temperature variations in materials operable under temperature gradients and also to understand the thermal performance of such materials. As a part of the work program for the development of rare earth based materials of interest in nuclear technology, thermal conductivity studies were taken up on selected compounds of gadolinium and lanthanum. Gadolinium zirconate and gadolinium aluminate are currently under development as candidate materials for neutron absorption and control rod applications. Lanthanum zirconate is also of interest as a high temperature container material and as a candidate host material for fixation of radioactive waste. In the present work, thermal conductivity studies were carried out on gadolinium zirconate ($Gd_2Zr_2O_7$), lanthanum zirconate ($La_2Zr_2O_7$) and gadolinium aluminate ($GdAlO_3$) employing the laser flash technique and covering a temperature range from 650 to 1400 K.

2. Experimental

The preparation of the compounds was carried out starting from the aqueous route and adopting a novel procedure for powder synthesis. Nitrate solutions of gadolinium, lanthanum and aluminium were obtained by dissolving gadolinium oxide (Gd_2O_3), lanthanum oxide (La_2O_3) and aluminium metal in nitric acid. The zirconium nitrate solution was obtained by dissolving zirconium nitrate in double-distilled water and acidifying the solution with dilute nitric acid. Subsequent preparation of the oxide powders was carried out following the urea combustion method as described in detail by Kingsley and Patil [1]. In order to prepare gadolinium zirconate ($Gd_2Zr_2O_7$), appropriate quantities of gadolinium nitrate and zirconium nitrate solutions were mixed with urea and the solution was slowly evaporated to a state of viscous paste. When this material was taken to a temperature of 773 K in a furnace, further dehydration occurred followed by vigorous frothing, combustion and formation of a fine powdery product. The oxide powder thus obtained was ground well, pelletised and the pellets were presintered at 1173 K for 12 h. Final sintering of the pellets was carried out at 1773 K for 20 h. Sintered pellets of lanthanum zirconate ($La_2Zr_2O_7$) and gadolinium aluminate ($GdAlO_3$) were also obtained adopting a similar preparation procedure as in the case of gadolinium zirconate. The final sintering temperature was

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1823 K in the case of lanthanum zirconate and 1753 K in the case of gadolinium aluminate. The formation of single phase (cubic pyrochlore) zirconates of gadolinium and lanthanum and also single-phase (orthorhombic perovskite) gadolinium aluminate was verified by X-ray diffraction for which a Siemens model D 500 powder diffractometer was employed. The measurement of the bulk densities of the samples was carried out by liquid immersion technique utilising dibutyl phthalate as the immersion liquid. Bulk densities of gadolinium zirconate, lanthanum zirconate and gadolinium aluminate were found to be 6.32, 5.54 and 6.86 g/cm^3, respectively, and these densities correspond to 90.5%, 91.6% and 92.3% theoretical, respectively. It is noted that bulk densities of the present materials lie within a narrow band of 91.5 ± 1% and hence are fairly close to each other.

Thermal diffusivity measurements on the present materials were carried out as a function of temperature employing the laser flash technique [2]. Salient features of the laser flash technique and application of this technique for the measurement of thermal diffusivity of a variety of materials was discussed in several earlier reports [3–5]. In the present work a ruby laser with a pulse time of 0.8 ms and pulse energy selectable in the range 5 to 25 J was used for the laser flashing of the samples. A kanthal furnace was employed for performing measurements at various temperatures. The present samples were about 10 mm in diameter, the thickness being in the range 1.0 to 1.3 mm. The front surface of the sample was coated with a thin layer of platinum to overcome the problem of transparency of the sample to laser radiation and also to ensure uniform absorption of the energy of the laser pulse by the sample. A lead sulphide infrared detector together with a signal digitiser-cum-memory unit was used for monitoring the transient temperature variation at the rear surface of the sample. The measuring unit was interfaced with a personal computer to enable on-line data acquisition and processing. Detailed description of the laser flash apparatus in our laboratory and the method of measurement of thermal diffusivity had been presented in earlier papers from our laboratory [6–8].

3. Results and discussion

The variation of the thermal diffusivity of the present materials as a function of temperature is shown in Fig. 1. It is seen that the thermal diffusivity of lanthanum and gadolinium zirconates decreases gradually as the temperature increases. The thermal diffusivity of gadolinium aluminate decreases as the temperature increases from 650 to about 1000 K, beyond which there is a sluggish tendency to increase. It is noted that the thermal diffusivity of gadolinium aluminate is higher than that of lanthanum and gadolinium zirconates throughout the present temperature range. Among the zirconates, the thermal diffusivity of lanthanum zirconate is seen to be higher than that of the gadolinium analogue.

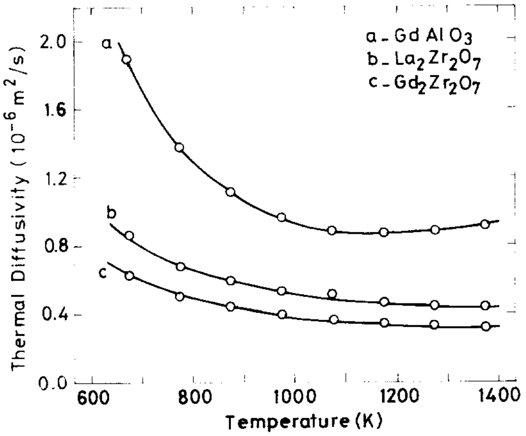

Fig. 1. Variation of the thermal diffusivity of $GdAlO_3$, $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ as a function of temperature.

From the present thermal diffusivity data, thermal conductivity values for the present materials were obtained employing the relationship

$$K = DCd,$$

where K is the thermal conductivity, D is the thermal diffusivity, C is the heat capacity, and d is the density. As experimental heat capacity data are not available, heat capacity values for the present materials were obtained utilising the heat capacity data of the constituent binary oxides (namely, gadolinium oxide, lanthanum oxide, alumina and zirconia) and employing Neumann–Kopp's rule [9]. Experimental heat capacity data for the constituent binary oxides were taken from the compilation of Kubaschewski et al. [10]. The thermal conductivity of the present materials as a function of temperature is shown in Fig. 2. It is seen that the thermal conductivity of lanthanum and gadolinium zirconates decreases as the temper-

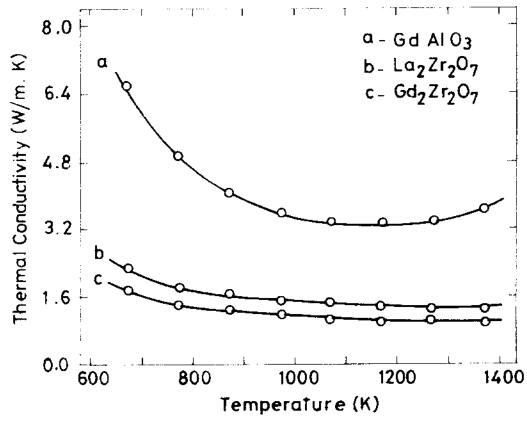

Fig. 2. Variation of the thermal conductivity of $GdAlO_3$, $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ as a function of temperature.

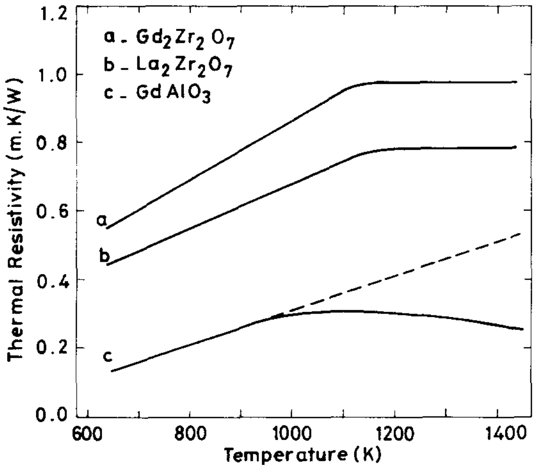

Fig. 3. Variation of the thermal resistivity of $GdAlO_3$, $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ as a function of temperature.

ature increases from 650 to 1150 K and thereafter remains constant at higher temperatures. The thermal conductivity of gadolinium aluminate decreases as the temperature is increased from 650 to 1000 K. Further increase in temperature is seen to result in an increase in thermal conductivity. It is also noted that the thermal conductivity of gadolinium aluminate is higher than that of the zirconates of lanthanum and gadolinium. Among the zirconates, the thermal conductivity of lanthanum zirconate is seen to be higher than that of gadolinium zirconate.

In order to elucidate the heat transport behaviour, the thermal resistivity (R) of the present materials was obtained as reciprocal of the thermal conductivity. Variation of the thermal resistivity as a function of temperature is shown in Fig. 3. It is seen that the thermal resistivity of lanthanum zirconate as well as gadolinium zirconate increases linearly when the temperature is increased up to about 1150 K and thereafter remains constant, thereby indicating that the heat transport in these materials is by lattice thermal conduction, also known as phonon conduction. In the lattice mode of heat transport it is known that, as the temperature increases, the phonon mean free path decreases gradually (as a result of increased phonon–phonon scattering), resulting in a linear increase in the thermal resistivity, or a corresponding decrease in the thermal conductivity. Eventually, at high temperatures, as the phonon mean free path gets lowered to values of the order of interatomic distances, the thermal conductivity of the material approaches the lowest limit and the corresponding thermal resistivity approaches the highest limit beyond which no variation can be seen. Heat transport in the present zirconates can thus be understood on the basis of the considerations discussed above. In the case of gadolinium aluminate, however, it is seen that the thermal resistivity increases linearly up to a temperature of about 1000 K and thereafter decreases slowly as the temperature is increased further. While lattice thermal conduction is responsible for the behaviour up to 1000 K it is considered that the radiative component of heat conduction, also known as photon thermal conductivity, is responsible for the mild increase in thermal conductivity or corresponding decrease in thermal resistivity at temperatures beyond 1000 K. The radiative contribution to the thermal conductivity is well known in ceramic oxide materials and discussions on the role of the radiative (photon) thermal conductivity in the transport of heat in ceramic materials had been presented by Kingery [11], Hyland [12], Bentsen et al. [13], and Kawakubo and Yamamoto [14]. Further work is in progress in our laboratory on the preparation of other rare earth bearing ceramic materials of interest in nuclear technology and investigation of their heat transport properties.

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