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THERMAL DIFFUSIVITY AND THERMAL CONDUCTIVITY STUDIES ON EUROPIUM, GADOLINIUM AND LANTHANUM PYROHAFNATES

M.V. KRISHNAIAH, P. SRIRAMA MURTI and C.K. MATHEWS

Radiochemistry Programme, Indira Gandhi Centre for Atomic Research,
Kalpakkam 603102 (India)

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ABSTRACT

The measurement of thermal properties forms an important aspect of the research on materials of interest in nuclear technology. In particular thermal diffusivity and thermal conductivity data are of relevance in the quantitative evaluation of the heat flow and temperature variations in materials operating at high temperatures. Since isotopes of several lanthanide elements and hafnium have high neutron absorption cross-sections, their compounds are potential candidates for control rod applications. In this paper, our studies on rare earth pyrohafnates $R_2Hf_2O_7$ (where R represents a rare earth), which are 2:1 solid solutions of hafnium dioxide and a rare earth sesquioxide, are reported. Thermal diffusivity and thermal conductivity data obtained on europium, gadolinium and lanthanum pyrohafnates, employing a laser flash apparatus set up in our laboratory and covering the temperature range 600–1300 K, are presented.

INTRODUCTION

The study of thermal properties forms an important aspect of the research on materials of interest in nuclear technology. Thermal diffusivity and thermal conductivity data are of relevance in the quantitative evaluation of the heat flow and temperature variations in materials operating under variable temperature gradients. Rare earths and hafnium occupy an important place in nuclear technology for neutron absorption and control rod applications [1]. As a part of the work on the study of rare earth and hafnium containing compounds for such applications, investigations were carried out on the heat transport properties of rare earth pyrohafnates $R_2Hf_2O_7$ (where R is a rare earth), which are 2 : 1 solid solutions of hafnium dioxide and a rare earth sesquioxide and can also be represented as $R_2O_3 \cdot 2HfO_2$. Thermal diffusivity and thermal conductivity studies carrried out on europium, gadolinium and lanthanum pyrohafnates employing a laser flash apparatus set up in our laboratory are presented here.

EXPERIMENTAL

Europium, gadolinium and lanthanum pyrohafnates used in this work were prepared by the method of mechanical mixing and sintering. Hafnium dioxide and the appropriate rare earth sesquioxide were mixed in the desired proportions, ground thoroughly and pelletized at a pressure of 300 MPa. The pellets were presintered for 8 h at 1373 K. The pellets were then crushed to a powder and the process of pelletization and presintering was repeated once again as this was found to improve the sinterability. Final sintering of the pellets was carried out at 1873 K in air for 16 h. The formation of single phase, f.c.c. rare earth pyrohafnates was indicated by X-ray diffraction examination for which a Siemens D-500 X-ray diffractometer was employed.

The bulk densities of europium, gadolinium and lanthanum pyrohafnate pellets employed in this work were found to be 8.07, 8.23 and 7.30 g cm^{-3}, respectively as determined using the liquid immersion method with dibutyl phthalate as the immersion liquid. These densities correspond to 92.5% of the theoretical in the case of gadolinium pyrohafnate and to 92.0% of the theoretical for europium and lanthanum pyrohafnates. Samples with diameters of about 10 mm and thicknesses of 0.7 to 1.3 mm were used.

The thermal diffusivities of the rare earth pyrohafnates were measured using the laser flash technique [2] which is especially useful for ceramic materials and when the data is required over a range of temperatures. The principle and general details of this technique have been described by several earlier investigators [2,3–5]. A schematic diagram of the apparatus set up in our laboratory is shown in Fig. 1. A pulsed ruby laser with a pulse duration of 0.8 ms was used to apply an energy pulse on the front surface of the thin disc-shaped sample. The transient temperature response at the rear surface of the sample was measured using a lead sulphide IR detector. The sample was positioned inside the alumina muffle tube of a kanthal furnace which was used to heat the sample to various temperatures at which the laser flash measurements were carried out. The muffle tube was provided with

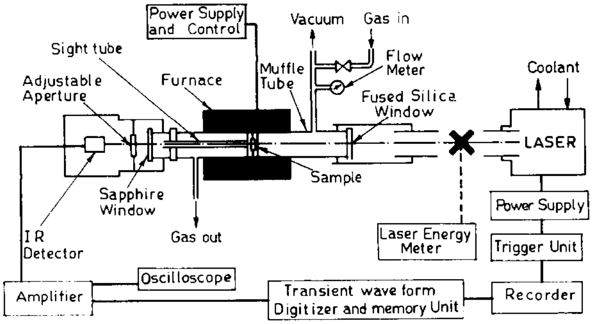

Fig. 1. A schematic diagram of the laser flash apparatus.

leak tight couplings and the measurements were carried out in an argon atmosphere. In order to prevent the direct transmission of the laser beam through the sample and to increase the absorption of the laser energy, the front surface of the sample was coated with a thin layer of platinum using 'DEMETRON' platinum paste. A sight tube located between the sample and the IR detector cut off stray light and provided optical guidance for a clear viewing of the rear surface of the sample by the detector. The output of the detector was amplified and recorded using a transient wave form digitizer-cum-storage unit coupled to a strip chart recorder. A trigger unit was used to synchronize the wave form storage unit with the firing of the laser flash. The relationship between the thermal diffusivity D, time t and temperature rise ΔT at the rear surface can be given as

$$\frac{\Delta T}{\Delta T_{\max}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \tag{1}$$

and

$$D = SL^2/t_{1/2} \tag{2}$$

where L is the sample thickness, $\Delta T_{\max}$ is the maximum rise in temperature at the rear surface, $t_{1/2}$ is the time required for the rear surface of the sample to attain a temperature rise equal to half of the maximum rise and S is constant which depends on the degree of radiative heat losses from the sample. In the absence of radiative heat losses, the value of S is 0.139. In this work, the thermal diffusivities were obtained using eqn. (2). When significant radiative heat losses occurred, the value of S was obtained using the method of Cowan [6]. This involves the measurement of the ratio $H_{5t_{1/2}}/H_{t_{1/2}}$ where $H_{5t_{1/2}}$ and $H_{t_{1/2}}$ represent the temperature rise values corresponding to the times $5t_{1/2}$ and $t_{1/2}$, respectively. A circular aperture of variable diameter which was located between the IR detector and the sample was useful in regulating the amount of radiation falling on the detector, especially at high temperatures.

RESULTS AND DISCUSSION

The variation in the thermal diffusivities of gadolinium, europium and lanthanum pyrohafnates as a function of temperature is shown in Fig. 2. It is seen that in all cases the thermal diffusivity decreases with an increase in temperature up to about 1000 K and thereafter remains relatively constant. The thermal conductivities K were determined from the product of thermal diffusivity, heat capacity and density. The heat capacity values were obtained using the Neumann–Kopp relationship [7] and heat capacity data for hafnium dioxide [8] and the rare earth sesquioxides [9]. The thermal conductivity values were also corrected to the theoretical density using the

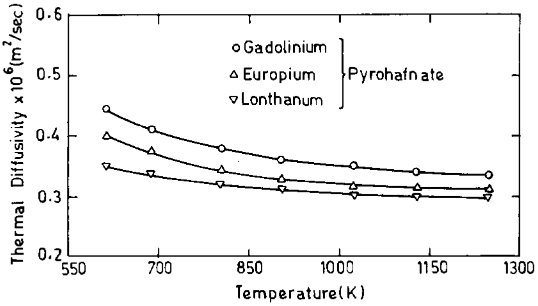

Fig. 2. Thermal diffusivity of rare earth pyrohafnates as a function of temperature.

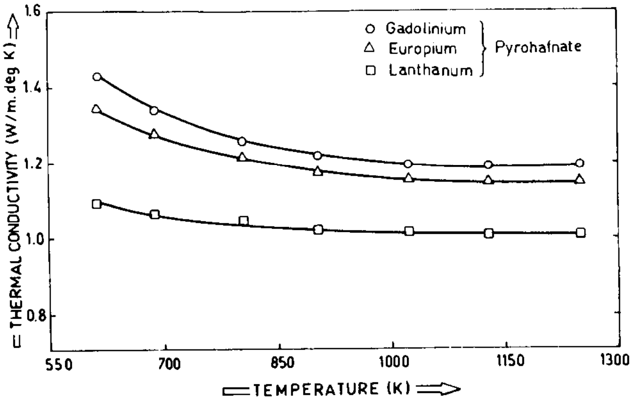

Fig. 3. Thermal conductivity of rare earth pyrohafnates as a function of temperature.

Maxwell–Eucken relationship discussed in detail by Biancheria [10]. The variation in the thermal conductivities of the pyrohafnates as a function of temperature is shown in Fig. 3. The thermal conductivities of europium and gadolinium pyrohafnates are similar and the thermal conductivity of lanthanum pyrohafnate is somewhat lower. In all cases the thermal conductivity decreases gradually with an increase in temperature up to 1000 K beyond which the variation with temperature is much less. In the temperature range 600–1300 K, the thermal conductivity values of the pyrohafnates are seen to be in the range 1.5–1.0 W m^{-1} K^{-1} which is generally characteristic of low thermal conductivity oxides [11]. Measurement of the heat transport properties of other candidate materials for neutron absorber applications is in progress.

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REFERENCES

1 W.K. Anderson, Nuclear applications of yttrium and the lanthanons, in F.H. Spedding and A.H. Daane (Eds.), The Rare Earths, Krieger, Huntington, NY, 1971, p. 522.
2 W.J. Parker, R.J. Jenkins, C.P. Butler and G.L. Abbott, J. Appl. Phys., 32 (1961) 1679.
3 Y. Takahashi and M. Murabayashi, J. Nucl. Sci. Technol., 12 (1975) 133.
4 R.E. Taylor, High Temp. High Pressures, 11 (1979) 43.
5 F. Righini and A. Cezairliyan, High Temp. High Pressures., 5 (1973) 481.
6 R.D. Cowan, J. Appl. Phys., 34 (1963) 926.
7 R.A. Swalin, Thermodynamics of Solids, Wiley-Interscience, New York, 1972.
8 O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry, Pergamon, Oxford 1967.
9 C.E. Holley, Jr., E.J. Hubber, Jr., and F.B. Baker, in L. Eyring (Ed.), Progress in the Science and Technology of The Rare Earths, Vol. 3, Pergamon, Oxford, 1968, p. 343.
10 A. Biancheria, Trans. Am. Nucl. Soc., 9 (1966) 15.
11 W.D. Kingery, Introduction to Ceramics, Wiley, New York, 1960.