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INVESTIGATION OF THE THERMAL CONDUCTIVITY OF SELECTED RARE EARTH ALUMINATES

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Abstract

As a part of the thermophysical property studies on rare earth based oxide ceramics thermal conductivity of the aluminates of samarium and dysprosium was investigated employing laser flash technique and covering a temperature range from 673 to 1373 K. Heat transport behaviour was briefly examined by analysing the variation of thermal resistivity as a function of temperature.

Keywords: laser flash technique, rare earth aluminates, thermal conductivity

Introduction

Rare earth based ceramic oxides occupy an important place among the materials having high temperature applications [1]. Preparation as well as study of the thermophysical properties of selected rare earth based oxide materials is undertaken as a part of the solid state work in our laboratory. Rare earth aluminates ($MAlO_3$ where *M* represents rare earth element) are currently under development to serve as neutron absorber materials, flux-suppressers, high temperature container materials and solid electrolytes. Information on the thermal conductivity is necessary for evaluating the heat flow and temperature variations in these materials and for understanding their thermal performance.

Thermal conductivity studies carried out on samarium aluminate ($SmAlO_3$) and dysprosium aluminate ($DyAlO_3$) employing the laser flash technique and covering a temperature range from 673 to 1373 K are reported here.

Experimental

Preparation of the rare earth aluminates was carried out adopting the hydroxide coprecipitation method. The nitrate solutions of aluminium and of the corresponding rare earth, with known concentrations, were mixed in the desired pro-

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portion and the mixed hydroxide was precipitated by the addition of ammonia solution. The mixed hydroxide was converted into the oxide form by thermal decomposition at 1073 K. The oxide powder was then compacted into pellets and the pellets were presintered at 1173 K for 10 h. The pellets were crushed, ground to a fine powder and the process of pelletisation and presintering was repeated once again. The pellets were then subjected to final sintering at 1673 K for 12 h. Formation of the single phase (orthorhombic perovskite) rare earth aluminates was verified by X-ray diffraction employing Siemens D 500 powder diffractometer and also by scanning electron microscopy utilising Philips SEM 501. Figure 1 shows the X-ray powder diffraction patterns and Figs 2 and 3 show the SEM micrographs of the present materials. The bulk densities of the samarium and dysprosium aluminate samples were found to be 6.81 and 6.94 g cm^{-3} which correspond to 95.1 and 90.1% theoretical respectively. The density measurements were carried out by liquid immersion method using dibutyl phthalate as the immersion liquid. The samples were about 9 mm in diameter, the thickness being in the range of 0.6–0.8 mm.

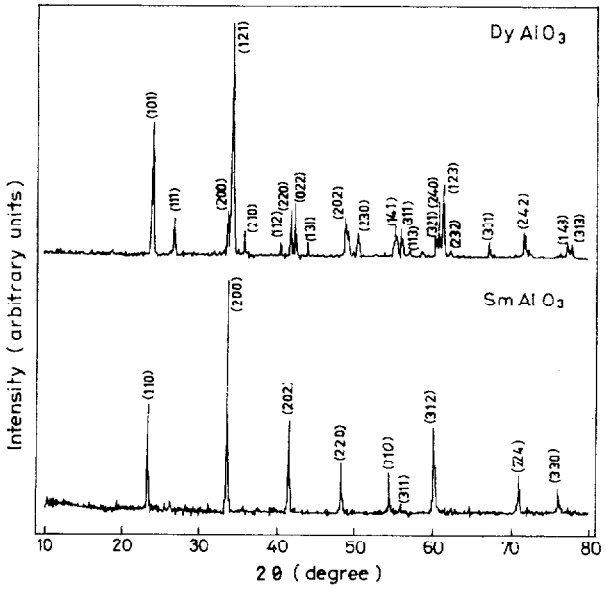

Fig. 1 X-ray diffraction patterns for samarium and dysprosium aluminates

Thermal diffusivity measurements on the samples were carried out employing the laser flash technique [2]. Important features of the laser flash technique and application of this technique for the measurement of the thermal diffusivity of a number of materials were described in several earlier reports [2–5]. In the present work a ruby laser with a pulse time of 0.8 ms and pulse energy selectable in the range 5–25 J was utilised for the laser flashing of the samples. The front

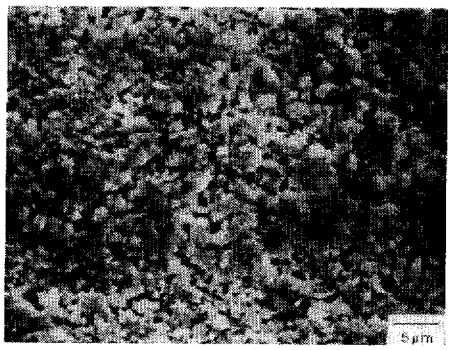

Fig. 2 Scanning electron micrograph of samarium aluminate

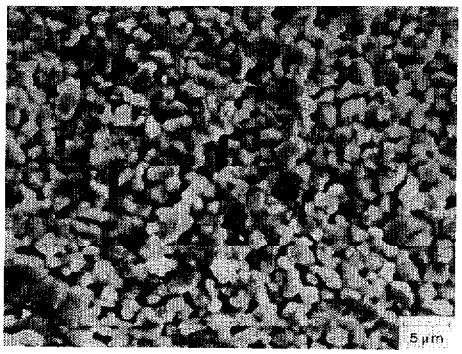

Fig. 3 Scanning electron micrograph of dysprosium aluminate

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. Detailed description of the laser flash apparatus in our laboratory, method of measurement of thermal diffusivity and evaluation of thermal conductivity had been presented in earlier papers from our laboratory [6, 7].

Results and discussion

Variation of the thermal diffusivity of the rare earth aluminates as a function of temperature is shown in Fig. 4. It is seen that the thermal diffusivity of $SmAlO_3$ is higher than that of $DyAlO_3$. The diffusivity in both the cases is seen to decrease gradually as temperature increases from 673 to 1073 K beyond which the variation appears to be not much discernable. Thermal conductivity (K) was determined from the thermal diffusivity using the relationship:

$$K = DCd \tag{1}$$

where D is the thermal diffusivity, C is the heat capacity and d is the density.

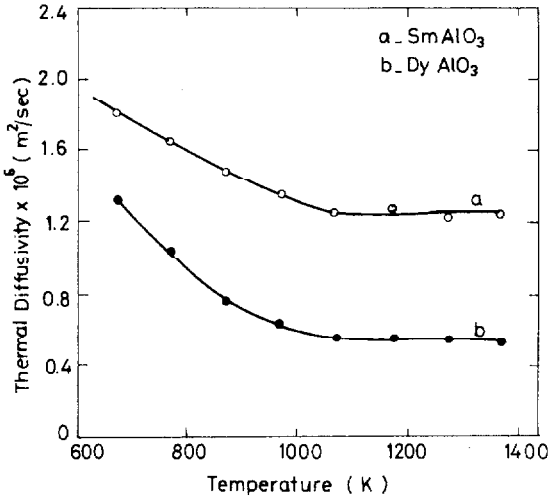

Fig. 4 Thermal diffusivity of samarium and dysprosium aluminates as a function of temperature

The heat capacity data for the present aluminates were obtained by employing the Neumann Kopp's law of additivity of the heat capacity of the constituent binary oxides (namely Al_2O_3 and M_2O_3 where M is rare earth). For this purpose the heat capacity values of Al_2O_3 and Sm_2O_3 were taken from the compilation of Kubaschewski *et al.* [8] and the values for Dy_2O_3 were taken from the compilation of Knacke *et al.* [9]. This method of estimation of heat capacities was adapted as no experimental data are available on the heat capacity of the present aluminates. Porosity correction was carried out and thermal conductivity values corresponding to theoretical density were obtained by employing Maxwell-Eucken relationship

$$K_o = K_p\left(\frac{1+\beta P}{1-P}\right) \tag{2}$$

where P is fractional porosity, K_o and K_p represent the thermal conductivity values corresponding to zero porosity and porosity P and β is shape factor. The value of β is taken as 0.5 for the present porosity range from the recommendation of Biancheria [10].

The variation of the thermal conductivity as a function of temperature is shown in Fig. 5. It is seen that the thermal conductivity of $SmAlO_3$ is higher than that of $DyAlO_3$. Thermal conductivity of both the aluminates decreases as the temperature increases from 673 to 1073 K. Further increase in temperature re-

sults in a mild increase in the thermal conductivity of $SmAlO_3$ and no significant variation in the case of $DyAlO_3$.

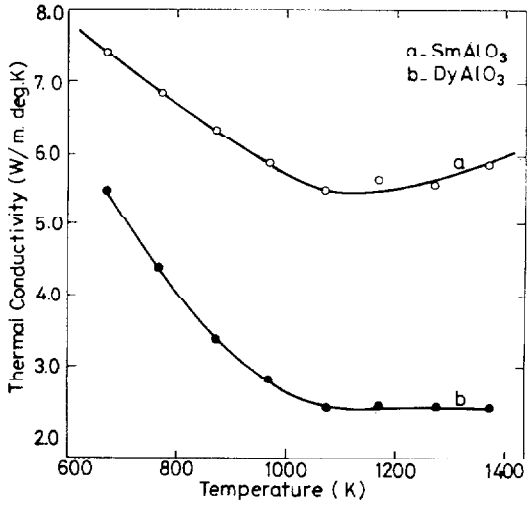

Fig. 5 Thermal conductivity of samarium and dysprosium aluminates as a function of temperature

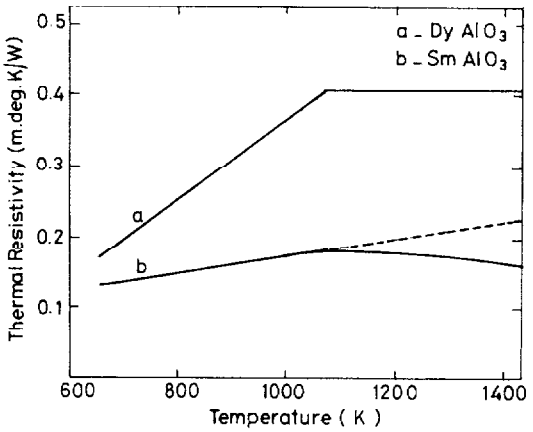

Fig. 6 Thermal resistivity of samarium and dysprosium aluminates as a function of temperature

Thermal resistivity (R) of the aluminates as a function of temperature was obtained as reciprocal of thermal conductivity (R=1/K) and shown in Fig. 6. It is seen that thermal resistivity of $DyAlO_3$ increases linearly as the temperature increases from 673 to 1073 K and thereafter remains constant. This indicates that the heat transport is by lattice thermal conduction, also known as phonon conduction. In the lattice mode of heat transport, as the temperature increases the

phonon mean free path decreases gradually (as a result of 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 becomes reduced to values of the order of interatomic distances the thermal conductivity approaches the lowest limit and the corresponding thermal resistivity approaches the highest limit beyond which no further variation would be noticeable. Heat transport in $DyAlO_3$ can thus be understood on the basis of the considerations discussed above.

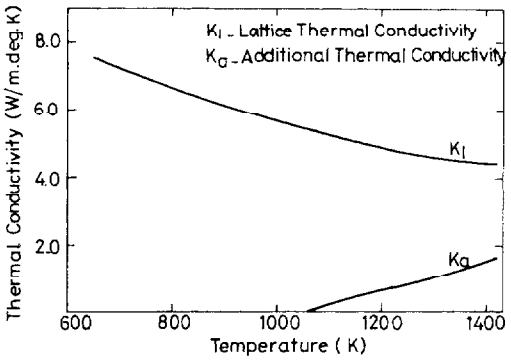

Fig. 7 Lattice thermal conductivity and additional thermal conductivity of samarium aluminate as a function of temperature

In the case of $SmAlO_3$ however, it is noted that while the thermal resistivity increases linearly up to a temperature of 1073 K, it decreases slowly as the temperature is increased further. While lattice thermal conduction can explain the behaviour up to 1073 K, it is considered that an additional contribution to the thermal conductivity, electronic or radiative in nature, is responsible for the mild increase in thermal conductivity (Fig. 5) or corresponding decrease in thermal resistivity (Fig. 6) at temperatures beyond 1073 K. The reciprocal of the extended thermal resistivity line (shown in dashes) for $SmAlO_3$ in Fig. 6 gives the lattice thermal conductivity component (K_l) and the difference ($K-K_l$) gives the additional thermal conductivity component (K_a).Variation of these two components K_l and K_a as a function of temperature is shown in Fig. 7. Further studies are in progress on the thermal conductivity of other rare earth based ceramic oxide materials for technological applications.

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