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Thermal conductivity of rare earth–uranium ternary oxides of the type RE_6UO_{12}

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Abstract

The knowledge of thermophysical properties of the rare earth uranium ternary oxides of the type RE_6UO_{12} (RE = La, Gd and Dy) is essential to understand the fuel performance during reactor operation and for modeling fuel behavior. Literature on the high temperature properties of this compound is not available and there is no report at all on the thermal conductivity of these compounds. Hence a study of thermal conductivity of this compound has been taken up. The compounds were synthesized by a solution combustion method using metal nitrates and urea. Thermal diffusivity of these compounds was measured by the laser flash method in the temperature range 673–1373 K. The specific heat data was computed using Neumann–Kopp's law. Thermal conductivity was calculated using the measured thermal diffusivity value, density and specific heat data for different temperatures. The temperature dependence of thermal conductivity and the implication of structural aspects of these compounds on the data are discussed here.

1. Introduction

Rare earths form a sizeable fraction of the fission products in the nuclear fission of fissile material in the reactor [1]. These fission products can interact with the fuel and can form various solid solutions as well as compounds. The formation of fuel-fission product compounds with complex crystal structures can alter the thermal behavior of the fuel. Thermal properties of uranium dioxide with fission products will be one of the preliminary data required for modeling the fuel performance during reactor operation. The thermal conductivity of the simulated fuel (UO_2) with various fission products dissolved in it has been measured [2]. The uranium oxide–lanthanide oxide systems were extensively investigated [3] in the past with respect to formation of non-stoichiometric ordered and disordered oxide phases, an aspect which is of great interest in nuclear technology. In fast reactors, where one usually talks of more than 10% burn up, the accumulation of fission products is considerably high. It is known that fission products form solid solutions with the host lattice only to a certain limited extent by the solubility of a particular element in the lattice and the ambient conditions (temperature, oxygen potential, etc.). In case of mixed oxides i.e., uranium–plutonium-oxide fuels, the fission distribution spectrum shifts towards the noble elements, because of which the oxygen potentials increase with burnup [4]. The formation of a family of iso-structural compounds represented by the formula $UO_3 \cdot 6REO_{1.5}$ or RE_6UO_{12} (RE = rare earth) due to the interaction between rare earth oxides and UO_3 has been reported [5]. This class of compounds shows an interesting feature that UO_3 species may be substituted with WO_3 or MoO_3 or NpO_3. In these systems, $UO_3 \cdot 6REO_{1.5}$, a uranium atom is surrounded by six oxygen atoms which form a distorted octahedron. All the U–O distances are 0.234 nm and in this structure a uranyl group does not exit [6]. The highly symmetrical coordination around the uranium atom may account for the remarkable thermal stability of these compounds.

Measurement of thermal expansion and the study of structural aspects using X-ray powder diffraction of

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RE_6UO_{12} type compounds were reported from our laboratory [7,8]. There is no report on the thermal conductivity of these compounds and hence the present work. This paper reports the chemical synthesis of three compounds of RE_6UO_{12} type, namely La_6UO_{12}, Gd_6UO_{12} and Dy_6UO_{12}, and the measurement of thermal conductivity using laser flash apparatus with a modified data acquisition system as a function of temperature.

2. Experimental

The uranium oxide obtained from Nuclear Fuel Complex, Hyderabad was heated to 800 °C to ensure the formation of U_3O_8. The lanthanum, dysprosium and gadolinium oxides obtained from Koch-Light Laboratories, England, were heated to constant weight in order to expel the absorbed moisture. The detailed procedure followed for the preparation of the compound is described in an earlier work [7]. Calculated amounts of these oxides to obtain the desired compounds were mixed, dissolved in nitric acid, and the solution thus obtained was subjected to combustion synthesis with urea. The formation of the compounds La_6UO_{12}, Gd_6UO_{12} and Dy_6UO12 was confirmed by powder X-ray diffraction [8]. After confirming the formation of the compound, the powder sample was compacted to 1 mm thick, 10 mm diameter pellets at 400 MPa, and sintered in air at 1500 °C for 10–15 h, to obtain pellets with density more than 90% theoretical. The XRD patterns recorded for these compounds are shown in Fig. 1. Density of the compounds was measured using the liquid immersion technique with di-butyl phthalate as the medium for displacement.

The sample discs were about 10 mm in diameter, thickness being in the range 0.9–1.2 mm. Since the RE_6UO_{12} compounds are translucent in nature, these samples were coated with platinum paste, followed by platinum black for better absorption of the laser light. The principle of the laser flash method and the applicability of this technique for ceramic materials are given elsewhere [9–12]. A general description of the experimental aspects can be found in the earlier reports from our laboratory [13–15]. In this method the samples are coated with platinum black, loaded on the sample holder, and placed in the constant temperature zone of the furnace and heated at different temperatures in flowing high purity argon gas atmosphere. A bundle of laser flash was given on the front surface of the pellet and the temperature rise on the rear side of the pellet was recorded as a transient signal using lead sulphide as the infrared detector. From the transient signal, $t_{1/2}$, the time taken for half of the maximum temperature rise on the rear side was obtained and the thermal diffusivity was calculated as described in the next section. The measurement was done in the temperature range of 673–1373 K.

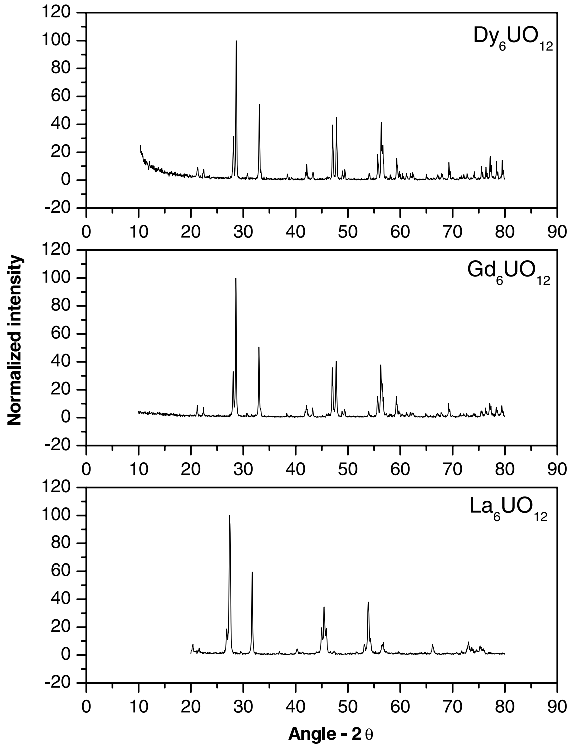

Fig. 1. XRD patterns of the compounds La_6UO_{12}, Gd_6UO_{12} and Dy_6UO_{12}.

3. Results and discussion

The thermal diffusivity was calculated using $t_{1/2}$ value obtained from the experiment using the formula:

$$\alpha = \frac{WL^2}{t_{1/2}}, \tag{1}$$

where α is thermal diffusivity, L is the thickness of the pellet and $t_{1/2}$ is the time taken for half of the maximum temperature rise. The factor W depends upon the degree of heat losses, and the value of W is 0.139 in the absence of heat loss; the values of W to be applied in the case of finite heat losses at high temperature are given in the literature [16]. The original equation for correction factors given by Cowan [16] was fitted to a polynomial and tabulated by Taylor and Maglic [17]. The values of thermal diffusivity thus obtained are tabulated in Tables 1–3 for La_6UO_{12}, Gd_6UO_{12}, and Dy_6UO_{12}, respectively. The corresponding thermal diffusivity plots were made against temperature and are shown in Fig. 2. It is observed that the thermal diffusivity value decreases with

Table 1
Thermal diffusivity, heat capacity, and thermal conductivity values of La_6UO_{12}

Temperature (K)	Thermal diffusivity $\times 10^7$ ($m^2 s^{-1}$)	Heat capacity ($J kg^{-1} K^{-1}$)	Thermal conductivity ($W m^{-1} K^{-1}$)
673	5.72	378.30	1.29
773	5.65	384.61	1.30
873	5.17	389.78	1.20
973	4.95	394.49	1.16
1073	4.82	399.18	1.15
1173	4.80	404.06	1.16
1273	4.83	409.13	1.18
1373	4.73	414.19	1.17

Table 2
Thermal diffusivity, heat capacity, and thermal conductivity values of Gd_6UO_{12}

Temperature (K)	Thermal diffusivity $\times 10^7$ ($m^2 s^{-1}$)	Heat capacity ($J kg^{-1} K^{-1}$)	Thermal conductivity ($W m^{-1} K^{-1}$)
673	5.26	342.85	1.36
773	5.30	348.60	1.39
873	5.34	353.58	1.42
973	5.12	358.09	1.38
1073	5.32	362.30	1.45
1173	4.81	366.30	1.33
1273	4.68	370.16	1.30
1373	4.42	373.92	1.24

Table 3
Thermal diffusivity, heat capacity, and thermal conductivity values of Dy_6UO_{12}

Temperature (K)	Thermal diffusivity $\times 10^7$ ($m^2 s^{-1}$)	Heat capacity ($J kg^{-1} K^{-1}$)	Thermal conductivity ($W m^{-1} K^{-1}$)
673	6.76	347.09	1.88
773	7.88	351.47	2.22
873	6.69	355.26	1.90
973	6.56	358.95	1.89
1073	5.53	362.88	1.61
1173	5.54	367.18	1.63
1273	5.18	371.81	1.54
1373	5.07	376.55	1.53

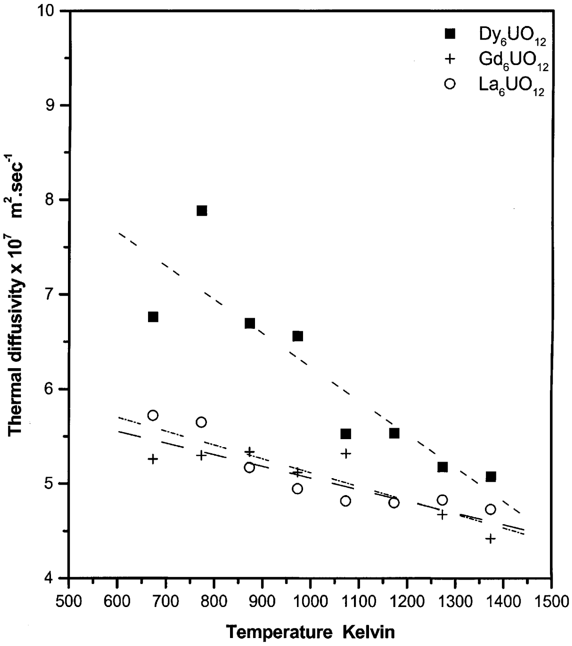

Fig. 2. Thermal diffusivity of compounds Gd_6UO12, Dy_6UO_{12} and La_6UO_{12} as a function of temperature.

increase in temperature for all these compounds. Thermal conductivity values for these compounds were calculated as a product of thermal diffusivity, heat capacity and density as given below:

$$\lambda = \alpha C d, \tag{2}$$

where λ is the thermal conductivity, α is the thermal diffusivity, C is the heat capacity and d is the density of the sample. Since the heat capacities of these compounds ($UO_3 \cdot 6REO_{1.5}$) are not available in the literature, the values were calculated using Neumann–Kopp's law based on the formula $UO_3 + 6 \times REO_{1.5}$. The heat capacity value of UO_3 is from the literature [18] and the heat capacity value of rare earth oxides is taken from the literature [19]. The thermal conductivity values were calculated as a product of the measured thermal diffusivity value, calculated heat capacity value above room temperature and the room temperature density value and the values are given in Tables 1–3. The plot of thermal conductivity as a function of temperature is shown in Fig. 3 for these three compounds. It is observed from the plot that the thermal conductivity values also decrease mildly with temperature rise. The uncertainty in the measurement of thermal diffusivity value using laser flash technique is ±5%. The standard reference material used in our studies is SS-304 and the estimated error in the measured thermal diffusivity data of this alloy is ±5%. The error propagation is estimated taking into account the errors in the measured thermal diffusivity value, room temperature density value and the calculated heat capacity value. The error thus estimated in the calculated thermal conductivity value is ±5.1%. This error is quite close to the expected limit of this technique. The thermal conductivity of these compounds can be seen to be very low, and probably it could be attributed to the complex structure of these compounds. It may be noted from Fig. 3 that the thermal

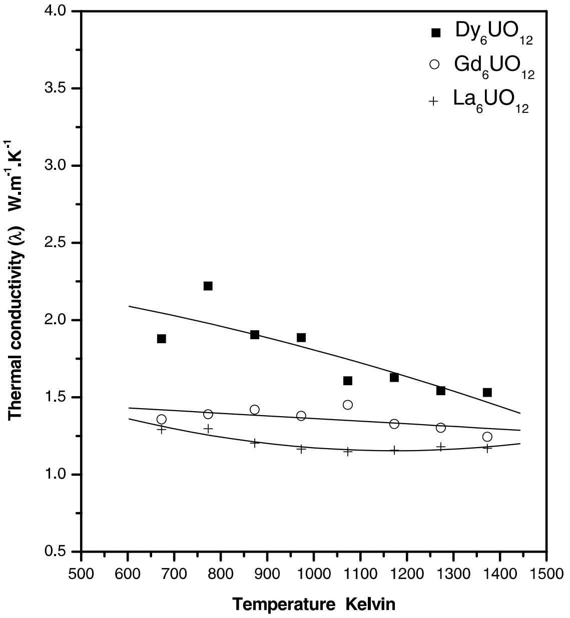

Fig. 3. Thermal conductivity of compounds Dy_6UO_{12}, Gd_6UO_{12} and La_6UO_{12} as a function of temperature.

conductivity for these compounds follows the following trend at any given temperature.

$$Dy_6UO_{12} > Gd_6UO_{12} > La_6UO_{12}. \quad (3)$$

In order to elucidate the heat transport behavior, the thermal resistivities of the present materials were obtained as reciprocal of thermal conductivities ($R = 1/\lambda$) and given in Table 4. Thermal resistivity is proportional to the mass difference (ΔM) between the host lattice and the impurity atoms [20]. It is also proportional to the difference in radii of the host lattice and the impurity atoms. In the present case, the host lattice can be thought to be the rare earth elements and the impurity to be uranium. The masses of the rare earth atoms La, Gd, Dy and U are 138.9, 151.96, 162.50, 238 amu and the ionic radii of La, Gd, Dy and U for six co-ordination are 0.1061, 0.0938, 0.0908, and 0.075 nm, respectively [21]. Since the thermal resistivity is directly related to squares of the ΔM and Δr, the effects will be mutually reinforcing. Variation of thermal resistivity as a function of temperature is shown in Fig. 4. There is a linear variation of the thermal resistivity as a function of temperature and it decreases along the lanthanide series. The ascending order of thermal resistivity variation is

$$Dy_6UO_{12} < Gd_6UO_{12} < La_6UO_{12}. \quad (4)$$

Linear variation of thermal resistivity of these compounds with temperature shows that the transport of heat in these solids is due to 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 thermal conductivity.

Table 4
Thermal resistivity of La_6UO_{12}, Gd_6UO_{12}, and Dy_6UO_{12} as a function of temperature

Temperature (K)	Thermal resistivity ($1/\lambda$, m K W^{-1})		
	La_6UO_{12}	Gd_6UO_{12}	Dy_6UO_{12}
673	0.8064	0.6986	0.5060
773	0.8160	0.7094	0.5276
873	0.8256	0.7202	0.5492
973	0.8352	0.7310	0.5708
1073	0.8449	0.7417	0.5924
1173	0.8545	0.7525	0.6140
1273	0.8641	0.7633	0.6355
1373	0.8737	0.7741	0.6571

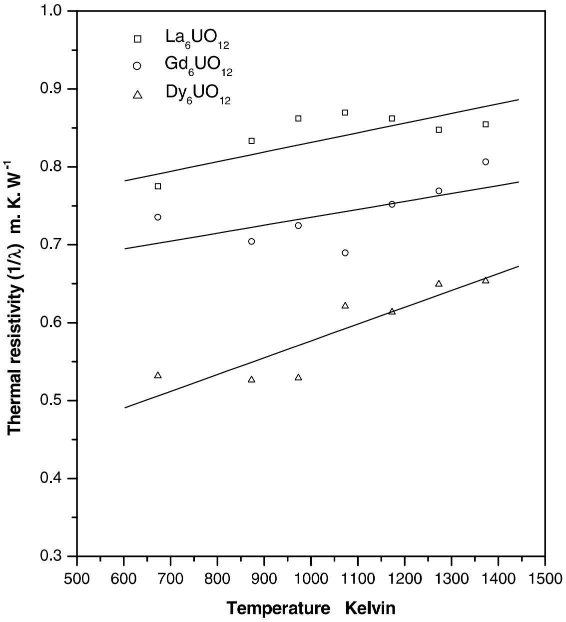

Fig. 4. Thermal resistivity of compounds Dy_6UO_{12}, Gd_6UO_{12} and La_6UO_{12} as a function of temperature.

4. Summary

The rare earth uranium ternary oxides of the type RE_6UO_{12} (RE = La, Gd and Dy) were synthesized by solution combustion method using metal nitrates and urea. Thermal diffusivity of these compounds was measured by laser flash method and specific heat data were computed using Neumann–Kopp's law. Their thermal conductivity was calculated using measured thermal diffusivity value, density and specific heat data. Thermal conductivity values show a mild decrease with temperature. The very low value of thermal conductivity can be attributed to the complex structure of these compounds.

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