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Short communication

Heat capacity of La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} by DSC

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ABSTRACT

Heat capacity measurements were carried out on La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} with differential scanning calorimetry in the temperature range 298–800 K. Enthalpy, entropy and Gibbs energy functions were computed. The heat capacity values of La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} at 298 K are 407, 439 and 461 $J\,K^{-1}\,mol^{-1}$, respectively.

1. Introduction

Rare earth elements are among the major fission products formed during irradiation of fuel in a nuclear reactor. The oxides of rare earths are highly soluble in uranium oxide and compounds of formula, RE_6UO_{12} (RE = rare earth), are known to exist in RE–U–O system [1,2]. These compounds crystallize in rhombohedral structure [3,4]. Thermodynamic properties such as heat capacity, enthalpy and Gibbs energy functions of these compounds are necessary to understand the behaviour of oxide fuels during irradiation. Thermal expansion of RE_6UO_{12} (RE = La, Sm, Eu) was measured by Jena et al. [5] and thermal diffusivity by Krishnaiah et al. [6]. There are no measured heat capacity data for these compounds. Therefore, heat capacity measurements on La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} were carried out by differential scanning calorimetry (DSC).

2. Experimental

2.1. Sample preparation

UO_2 of nuclear grade purity supplied by Nuclear Fuel Complex, Hyderabad, India and RE_2O_3 (RE = La, Sm, Eu) of 99.9% purity supplied by M/s. Indian Rare Earths were used for preparing the samples. RE_6UO_{12} compounds were prepared by combustion synthesis, which uses the large exothermicity of the chemical reaction between the fuel and an oxidant to energize the synthesis [7–11]. In our preparation citric acid was used as the fuel. UO_2 was heated at 873 K in air to convert it into U_3O_8. The RE_2O_3 powder was heated at 573 K in air to remove any adsorbed moisture. Stoichiometric quantities of U_3O_8 and RE_2O_3 were dissolved in nitric acid by heating at 353 K. Citric acid was added to the nitrate solution and mixed to get a clear solution. This mixture was then heated on a hot plate at 673 K. Combustion of the mixture took place with a flame. The resultant fine powder was ground, calcined at 1073 K in air for 4 h and compacted into pellets of 5 mm diameter with hydraulic press. The pellets were heated at 1473 K in air for 8 h. As the samples were heated in air only stiochiometric RE_6UO_{12} compounds are expected [5]. The sample pellets were then ground and X-ray diffraction analysis was performed on all the above mentioned samples, using Siemens D500 powder diffractometer using CuKα radiation monochromatized with curved graphite crystal placed in front of the NaI(Tl) scintillation detector. The scans were made in the range of $10^\circ \leq 2\theta \leq 80^\circ$. The X-ray diffraction patterns of La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} are shown in Fig. 1, which are in good agreement with the reported literature patterns [12–14]. The computed lattice parameter values listed in Table 1 are also in good agreement with the values reported in the literature [2,3,5,15]. The lattice parameter values also suggest that the RE_6UO_{12} compounds formed are stiochiometric. For DSC measurements, the powders of these samples were compacted into pellets of 5 mm in diameter and sintered at 1673 K in air for 8 h.

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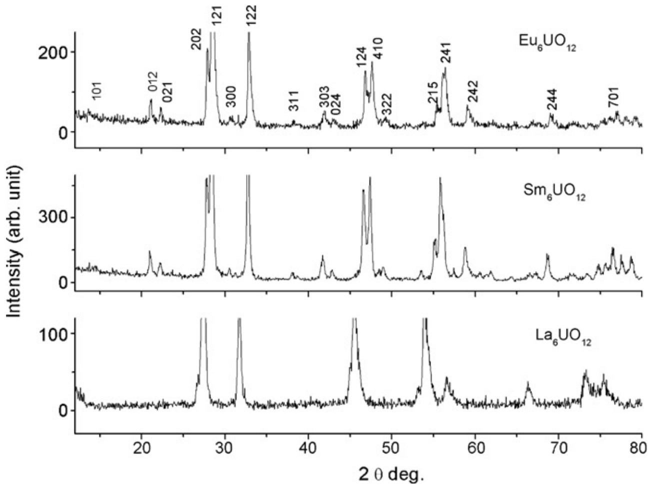

Fig. 1. Room temperature XRD patterns of RE$_6$UO$_{12}$.

2.2. Heat capacity measurements

A heat flux type differential scanning calorimeter (model number DSC821e/700 of M/s. Mettler Toledo GmbH, Switzerland) was used in this study. Pellet samples were hermetically sealed in 40 μl Al-pans. High purity argon was used as the purge gas at a flow rate of 50 ml min^{-1} and a heating rate of 10 K min^{-1} was employed in DSC measurements in the temperature range 298–800 K. A thin disc of sapphire was used as the heat capacity standard. A three-segment-heating programme was used. The first segment lasting for five minutes was an isothermal one at the initial temperature; the second segment was a dynamic one with a heating rate of 10 K min^{-1} and the final segment lasting for five minutes was another isothermal one at the final temperature. Temperature, heat and heat rate calibration of the DSC was carried out, as explained in our earlier work [16].

3. Results

Heat capacity data of sapphire given by National Institute of Standards and Technology, USA (NIST) were used for computing the heat capacities of the samples. Heat capacity of La$_6$UO$_{12}$, Sm$_6$UO$_{12}$ and Eu$_6$UO$_{12}$ measured by DSC and given in Tables 2–4, respectively are the mean of six measurements. The error in the heat capacity values by our DSC measurements had been earlier determined to be ±3% by measurements on ThO$_2$ samples [17]. However, the relative standard deviations among the present measurements are in the range of 1–3%. Hence the uncertainty in the measured heat capacity values has been estimated to be ±3%. The measured heat capacity of

Table 1
Crystal data for the RE$_6$UO$_{12}$ compounds measured by XRD

Crystal data at 298 K		Compound					
		Space Group-$R\bar{3}$					
		La$_6$UO$_{12}$		Sm$_6$UO$_{12}$		Eu$_6$UO$_{12}$	
		This study	Literature values	This study	Literature values	This study	Literature values
Hexagonal parameters	a (Å)	10.470 (3)	10.476 [2] 10.487 [5]	10.148 (3)	10.148 [3] 10.163 [5]	10.140 (4)	10.126 [15]
	c (Å)	9.970 (2)	9.988 [2] 9.963 [5]	9.620 (2)	9.630 [3] 9.641 [5]	9.569 (3)	9.601 [15]
Rhombohedral parameters	a_R (Å)	6.898 (3)	6.899 [2] 6.905 [5]	6.679 (3)	6.690 [5]	6.649 (4)	6.665 [15]
	α (degree)	98.78	98.72 [2] 98.81 [5]	98.92	98.85 [5]	98.95	98.87 [15]

Table 2
Thermodynamic functions of La$_6$UO$_{12}$

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})		$H_T^0 - H_{298}^0$ (J mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$G_T^0 - H_{298}^0/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
298	409	407	0	480	–480
300	409	407	816	483	–480
400	432	433	43,137	605	–497
500	445	444	87,140	703	–528
600	455	453	1,32,104	784	–564
700	465	464	1,78,025	855	–601
800	479	478	2,25,174	918	–637

Table 3
Thermodynamic functions of Sm$_6$UO$_{12}$

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})		$H_T^0 - H_{298}^0$ (J mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$G_T^0 - H_{298}^0/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
298	434	439	0	533	–533
300	434	439	880	536	-533
400	459	458	45,796	665	-550
500	473	476	92,527	769	-584
600	491	493	1,41,039	857	-622
700	513	511	1,91,307	935	-661
800	534	528	2,43,308	1,004	-700

Table 4
Thermodynamic functions of Eu_6UO_{12}

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})		$H_T^0 - H_{298}^0$ (J mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$G_T^0 - H_{298}^0/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
298	456	461	0	519	−519
300	457	462	923	522	−519
400	488	487	48,585	659	−538
500	498	500	97,997	769	−573
600	512	509	1,48,448	861	−614
700	521	518	1,99,790	940	−655
800	529	528	2,52,094	1,010	−695

La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} were least squares fitted to obtain the following polynomial in temperature.

$$C_{p,m}(La_6UO_{12})(\mathrm{J\,K^{-1}\,mol^{-1}}) = 558.18 - 3.0114 \times 10^{-1}\,T(\mathrm{K}) - 7.578036 \times 10^{6}\,T(\mathrm{K})^{-2} + 2.7 \times 10^{-4}\,T(\mathrm{K})^{2}(298\text{–}800\,\mathrm{K}) \quad (1)$$

$$C_{p,m}(Sm_6UO_{12})(\mathrm{J\,K^{-1}\,mol^{-1}}) = 385.73 + 1.8667 \times 10^{-1}T(\mathrm{K}) - 8.1902 \times 10^{4}T(\mathrm{K})^{-2} - 1.0 \times 10^{-5}T(\mathrm{K})^{2}(298\text{–}800\,\mathrm{K}) \quad (2)$$

$$C_{p,m}(Eu_6UO_{12})(\mathrm{J\,K^{-1}\,mol^{-1}}) = 556.94 - 1.3687 \times 10^{-1}\,T(\mathrm{K}) - 5.97721 \times 10^{6}\,T(\mathrm{K})^{-2} + 1.4 \times 10^{-4}\,T(\mathrm{K})^{2}(298\text{–}800\,\mathrm{K}) \quad (3)$$

The standard errors of the fit equations (1)–(3) are 1.6, 3.7 and 2.9 J K^{-1} mol^{-1}, respectively. The measured heat capacity of La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} along with the fit values are shown in Figs. 2–4, respectively. The heat capacity of La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} computed by Neumann–Kopp's law using the heat capacity data of UO_3 [18], La_2O_3, Sm_2O_3 and Eu_2O_3 [19] are also shown in Figs. 2–4, respectively. The heat capacity data of respective component oxides used for the computation are given below.

$$C_{p,m}(UO_3)(\mathrm{J\,K^{-1}\,mol^{-1}}) = 90.374 + 11.046 \times 10^{-3}\,T(\mathrm{K}) - 1.109 \times 10^{6}\,T(\mathrm{K})^{-2} \quad (4)$$

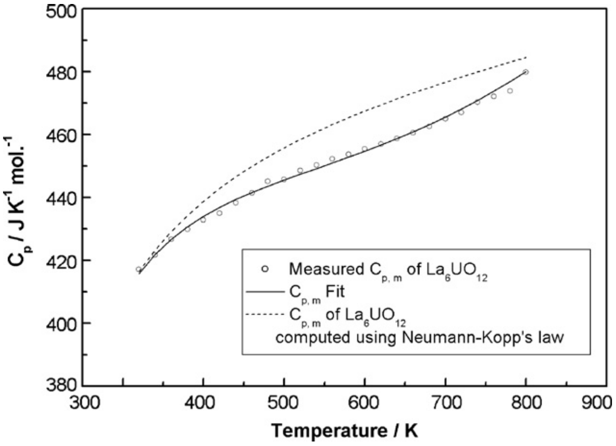

Fig. 2. Heat capacity data for La_6UO_{12}.

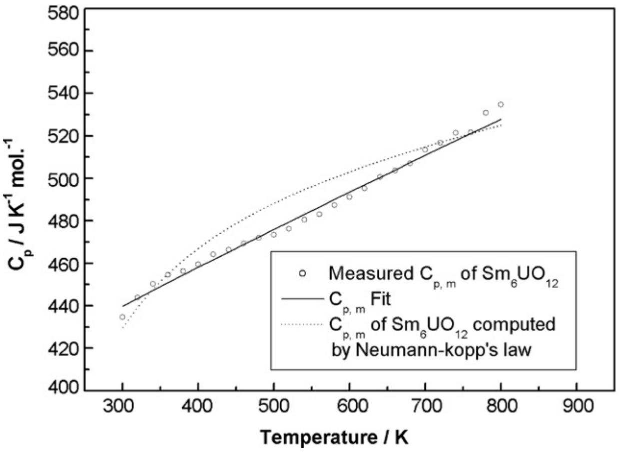

Fig. 3. Heat capacity data for Sm_6UO_{12}.

$$C_{p,m}(La_2O_3)(\mathrm{J\,K^{-1}\,mol^{-1}}) = 119.734 + 14.226 \times 10^{-3}\,T(\mathrm{K}) - 1.351 \times 10^{6}\,T(\mathrm{K})^{-2} \quad (5)$$

$$C_{p,m}(Sm_2O_3)(\mathrm{J\,K^{-1}\,mol^{-1}}) = 128.997 + 20.225 \times 10^{-3}\,T(\mathrm{K}) - 1.707 \times 10^{6}\,T(\mathrm{K})^{-2} \quad (6)$$

$$C_{p,m}(Eu_2O_3)(\mathrm{J\,K^{-1}\,mol^{-1}}) = 133.306 + 18.560 \times 10^{-3}\,T(\mathrm{K}) - 1.259 \times 10^{6}\,T(\mathrm{K})^{-2} \quad (7)$$

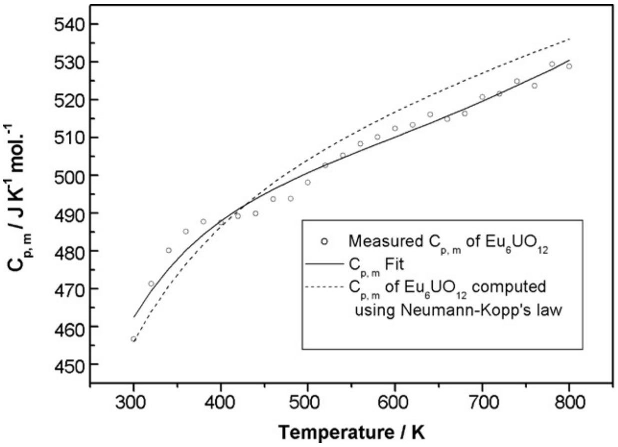

Fig. 4. Heat capacity data for Eu_6UO_{12}.

As can be seen in the figure the present data are in good agreement within ±3% with that computed using Neumann–Kopp's law using the heat capacity of their respective component oxides. From the heat capacity data, other thermodynamic functions such as enthalpy, entropy and Gibbs energy functions of La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} were computed and are given in Tables 2–4, respectively. The S^0_{298} values of La_6UO_{12}, Sm_6UO_{12} and Eu_6UO_{12} required for the computation of entropies and estimated by using Neumann–Kopp's law from the literature data [18,19] of their respective component oxides are 481, 533 and 519 $J\,K^{-1}\,mol^{-1}$, respectively.

4. Discussion

It is seen from Tables 2–4 that the heat capacity of RE_6UO_{12} increase in the order $Eu_6UO_{12} > Sm_6UO_{12} > La_6UO_{12}$. Also, the magnitude of increase in the heat capacity from La_6UO_{12} to Sm_6UO_{12} is higher than that from Sm_6UO_{12} to Eu_6UO_{12}. It is to be expected as the ionic radii decrease from La(III) to Eu(III) (due to lanthanide contraction) and hence the RE–O bond lengths. This is also evident from the measured room temperature lattice parameter from Table 1, which shows that the lattice parameter values decrease from La_6UO_{12} to Eu_6UO_{12}. Also, the magnitude of decrease in the lattice parameter values from La_6UO_{12} to Sm_6UO_{12} is higher than that from Sm_6UO_{12} to Eu_6UO_{12}. Shorter the RE–O bond length, higher will be the bond strength [20] and consequently higher will be the heat capacity.

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