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Short communication

Thermophysical properties of Dy_6UO_{12}

R. Venkata Krishnan, R. Babu, G. Panneerselvam, K. Ananthasivan, M.P. Antony, K. Nagarajan *

Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, Tamil Nadu, India

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Abstract

Dysprosium uranate (Dy_6UO_{12}) was prepared by citrate gel combustion and characterized by X-ray diffraction (XRD). A single phase with a rhombohedral structure was observed ($R\bar{3}$). The room temperature values of the lattice parameters "*a*" and "*c*" were found to be 9.9747 and 9.4370 Å, respectively. Heat capacity and enthalpy increment measurements were carried out by using a differential scanning calorimeter (DSC) and inverse drop calorimetry in the temperature range 298–800 K and 600–1700 K respectively. The thermal expansion characteristics were measured by using High Temperature XRD (HTXRD) in the temperature range 298–1973 K. The heat capacity data of Dy_6UO_{12} is being reported for the first time and its value at 298 K is 462 J K^{-1} mol^{-1}. The coefficient of lattice thermal expansion in the temperature range 298–1973 K along "*a*" and "*c*" axes are 13.28×10^{-6} and 9.35×10^{-6} K^{-1} respectively. These data are being reported for the first time as well.
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Keywords: C. Thermal expansion; Dysprosium uranate; Enthalpy increment; Heat capacity; Thermophysical properties

1. Introduction

RE_6UO_{12} (RE = rare earth) type of compounds with rhombohedral structure [1–9] are known to exist in the systems RE–U–O and are formed in the matrix of the mixed oxide ($(U, Pu)O_2$) during irradiation in the fast reactor (under transient conditions). Earlier, we have reported the experimentally determined values of the heat capacities of some of the RE_6UO_{12} (RE = La, Sm, Eu, Nd, Gd) type compounds [7,8]. Experimentally determined thermal expansion characteristics of RE_6UO_{12} (RE = La, Sm, Eu, Nd, Gd) were reported elsewhere [5,7]. No heat capacity and thermal expansion data has so far been reported in the literature for Dy_6UO_{12}. Therefore, in the present study the heat capacity of Dy_6UO_{12} was measured by using a DSC (298–800 K). The enthalpy increments of this compound were obtained by using a drop calorimeter (600–1700 K) and its thermal expansion characteristics were studied by using a HTXRD (298–1973 K). From the heat capacity data the thermodynamic functions viz., enthalpy, entropy and Gibbs energy functions were computed.

2. Experimental

UO_2 of nuclear grade purity supplied by M/s. Nuclear Fuel Complex, Hyderabad, India, and Dy_2O_3 (99.9% pure) procured from M/s. Indian Rare Earths were used in the preparation of Dy_6UO_{12}. The preparation method is described elsewhere [7,8]. The room temperature XRD pattern of Dy_6UO_{12} is shown in Fig. 1, which is in good agreement with the pattern reported in Refs. [6,9]. Heat capacity, enthalpy increment and thermal expansion characteristics were measured by using a heat flux type DSC (model number DSC821e/700, M/s. Mettler Toledo GmbH, Switzerland), a multi-detector high temperature drop calorimeter (MHTC-96 M/s. SETARAM) and a Philips-X'pert MPD system (equipped with the Büehler high vacuum heating stage) respectively. The details of these equipment and methods used in these measurements are described elsewhere [10–12].

3. Results and discussion

3.1. Heat capacity and enthalpy increment measurements

Measured values of the heat capacity and enthalpy increments are given in Table 1. The temperature dependence of enthalpy increment was arrived at by a least square regression analysis of the experimental values with two

* Corresponding author. Tel.: +91 44 27480098; fax: +91 44 27480065.
E-mail address: knag@igcar.gov.in (K. Nagarajan).

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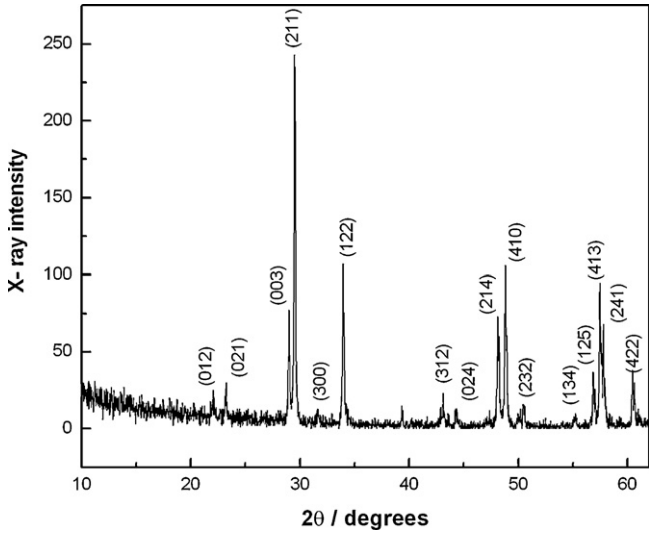

Fig. 1. Room temperature XRD pattern of Dy_6UO_{12}.

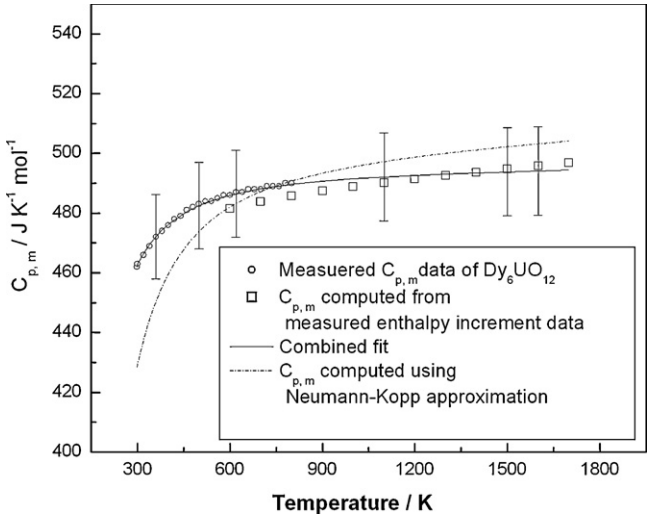

Fig. 2. Temperature dependence of the heat capacity data of Dy_6UO_{12}.

constraints. The constraints used in this analysis are: (i) $H_T - H_{298} = 0$ at 298 K and (ii) the derivative of the function at 298 K is equal to the value of heat capacity at 298 K obtained by DSC (462 J K^{-1} mol^{-1}). The resultant polynomial is given below (Eq. (1))

$$H_T - H_{298}/\mathrm{J\ mol^{-1}} = 481.161\,\mathrm{T} + 4.809 \times 10^{-3}\ \mathrm{T^2} + 1.931532 \times 10^{6}\ \mathrm{T^{-1}} - 1.5036 \times 10^{5}(600 - 1700\,\mathrm{K}) \quad (1)$$

By using Eq. (1), values of the heat capacity in the temperature range 600–1700 K were computed. These data were combined with the heat capacity values obtained by using DSC in order to arrive at an expression for the temperature dependence of heat capacity through least squares regression analysis (Fig. 2).

$$C_p\ /\mathrm{J\ K^{-1}\ mol^{-1}} = 492.49 + 1.72 \times 10^{-3}\,\mathrm{T} - 2.72214 \times 10^{6}\ \mathrm{T^{-2}}(298 - 1700\,\mathrm{K}) \quad (2)$$

The temperature dependence of the heat capacity of Dy_6UO_{12} was also computed by using Neumann–Kopp's approximation by using the values of the heat capacity of the constituent binary oxides viz., Dy_2O_3 [13] and UO_3 [13] and is shown in Fig. 2. From this figure, it is evident that the measured values of the heat capacity of Dy_6UO_{12} are in good agreement with that computed by using the Neumann–Kopp's approximation within ±3% except at lower temperatures (298–400 K). The values of the heat capacity measured by DSC are in good agreement with that computed by using the measured enthalpy

Table 1
Thermodynamic functions of Dy_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	Combined fit	Measured	Combined fit		
298	462	462		0	548	−548
300	463	463		925	551	−548
400	476	476		47965	686	−567
500	483	482		95930	793	−602
600	486	486	143,283	144,366	882	−641
700	488	488	191,564	193,078	957	−681
800	490	490	240,057	241,969	1022	−720
900		491	288,722	290,986	1080	−757
1000		491	337,537	340,096	1132	−792
1100		492	386,488	389,277	1178	−825
1200		493	435,563	438,517	1221	−856
1300		493	484,758	487,806	1261	−886
1400		494	534,066	537,137	1297	−914
1500		494	583,485	586,506	1331	−940
1600		494	633,011	635,907	1363	−966
1700		494	682,643	685,339	1393	−990

increment in the overlapping temperature range (600–800 K) as well within ±3%. From Eq. (2), other thermodynamic functions viz., enthalpy, entropy and Gibbs energy functions were computed and these are given in Table 1. The S^0_{298} values of Dy_6UO_{12} required for the computation of entropies were estimated from reported entropy data for its component oxides Dy_2O_3 [13] and UO_3 [13] by applying Neumann–Kopp's approximation.

3.2. Thermal expansion data of Dy_6UO_{12}

The lattice parameters of Dy_6UO_{12} were estimated by using NBSAIDS83 software. The diffraction pattern showed that this compound crystallized in a $R\bar{3}$ phase as reported by Hinatsu et al. [2] and Jena et al. [5,6]. All reflections were indexed based on hexagonal crystallographic axes; for the Miller indices, the relationship $-\ h + k + l = 3n$ was observed. The lattice was found to expand along the "a" and "c" axes. The variation in the value of the lattice parameter with temperature along these axes could be fit in to the following polynomials (Eqs. (3) and (4)) by a least squares regression analysis

$$a\ (\text{nm}) = 9.98301 + 4.0 \times 10^{-5}(T - 298) + 3.0575 \times 10^{-8}(T - 298)^2 \quad (3)$$

$$c\ (\text{nm}) = 9.4462 + 3.0 \times 10^{-5}(T - 298) + 1.8838 \times 10^{-8}(T - 298)^2 \quad (4)$$

From the above expressions the percentage thermal expansion $((a_T - a_{298})/a_{298}) \times 100)$ along "a" and "c" axes were computed and are shown in Fig. 3. The variation in the lattice parameters, coefficient of thermal expansion and percentage thermal expansion with temperature are given in Table 2. The variation in the lattice parameters along the c-axes is observed to be relatively lesser than that along the a-axes. A similar observation was reported in our earlier work on RE_6UO_{12} (RE = La, Nd and Sm) [5,7]. These observations could be explained based on the crystal structure of these compounds. In Dy_6UO_{12}, six oxygen atoms surround a uranium ion forming a distorted octahedron. Similarly, six oxygen atoms surround the Dy^{3+} ion forming a highly distorted octahedron. These octahedra UO_6 and DyO_6 share corners. Two edge sharing DyO_6 octahedron separate two UO_6 along the c-axes. Therefore it is summarized that the lesser degree of thermal expansion along the c-axes is due to the rigidity in the crystal as described above.

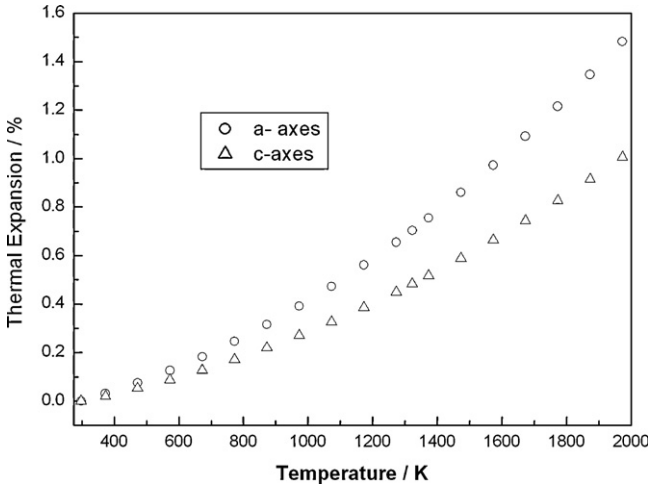

Fig. 3. Percentage thermal expansion of Dy_6UO_{12}.

Table 2
Thermal expansion characteristics of Dy_6UO_{12}.

T (K)	Lattice parameter a-axes (Å)	α_m a-axes (10^{-6} K^{-1})	Thermal expansion a-axes (%)	Lattice parameter c-axes (Å)	α_m c-axes (10^{-6} K^{-1})	Thermal expansion c-axes (%)
298	9.98301	3.02	0.000	9.4462	2.68	0.000
373	9.98598	3.48	0.030	9.4482	2.97	0.021
473	9.99048	4.09	0.075	9.4512	3.37	0.053
573	9.99559	4.70	0.126	9.4546	3.77	0.088
673	10.00131	5.32	0.183	9.4583	4.17	0.128
773	10.00764	5.93	0.246	9.4624	4.57	0.172
873	10.01459	6.54	0.316	9.4669	4.97	0.220
973	10.02214	7.15	0.391	9.4718	5.36	0.271
1073	10.03031	7.77	0.473	9.4771	5.76	0.327
1173	10.03909	8.38	0.561	9.4827	6.16	0.386
1273	10.04848	8.99	0.655	9.4887	6.56	0.450
1323	10.05340	9.30	0.704	9.4919	6.76	0.483
1373	10.05848	9.60	0.755	9.4951	6.96	0.518
1473	10.06909	10.22	0.861	9.5019	7.36	0.589
1573	10.08031	10.83	0.973	9.5090	7.75	0.665
1673	10.09215	11.44	1.092	9.5165	8.15	0.744
1773	10.10460	12.05	1.216	9.5244	8.55	0.828
1873	10.11766	12.67	1.347	9.5327	8.95	0.915
1973	10.13133	13.28	1.483	9.5413	9.35	1.007

$\alpha_m = (1/a_{298}) \times \{(a_T - a_{298})/(T - 298)\}$.

4. Summary

Dy_6UO_{12} was prepared by citrate gel-combustion and characterized by XRD. Heat capacity, enthalpy increment and thermal expansion measurements were carried out by using DSC, drop calorimetry and HTXRD respectively. The percentage thermal expansion along *c*-axes was found to be lower than that of *a*-axes due to rigidity along the *c*-axes. These high temperature thermophysical properties are not available in the literature and these are being reported for the first time.

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