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Combustion synthesis and thermal expansion measurements of the rare earth–uranium ternary oxides RE_6UO_{12} (RE = La, Nd and Sm)

Hrudananda Jena, R. Asuvathraman, K.V. Govindan Kutty *

Materials Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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Abstract

Rare earth–uranium ternary oxides were synthesized by a solution combustion route. The starting materials were the corresponding metal nitrates and urea. In these preparations, the metal nitrates act as oxidizer and urea as fuel. Highly exothermic decomposition of the metal nitrate–urea complexes on heating at about 500 K leads to a combustion process yielding RE_6UO_{12} fine powders. Thermal expansion measurements of these compounds were carried out in the temperature range of 298–1173 K by high temperature X-ray powder diffractometry. The observed axial thermal expansion behaviour is explained on the basis of the crystal chemistry of the compounds. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Uranium and rare earth (RE) oxides have pivotal importance in nuclear industry. The properties of these compounds and their interaction products at high temperature are of interest in the solid state chemistry of oxide nuclear fuels. The RE oxides exhibit considerable solid solubility in the nuclear fuel material UO_2. A notable feature of the RE–U–O system is the existence of compounds of the formula RE_6UO_{12} [1,2]. By heating the mixtures of the oxides of U and RE in the atomic ratio 1:6 in air or oxygen at temperatures above 1273 K, the compounds of the general composition $UO_3 \cdot 6REO_{1.5}$ are formed. The crystal structure of the compounds is rhombohedral [3,4], which is closely related to the fluorite type structure. The solid state synthesis [2] involves heating of pressed pellets of reactants at 1473 K in air for 3 days, followed by grinding, repelletising and further heating at 1473 K for 2 days, and slow cooling to room temperature in 3 days. RE_6UO_{12} can be conveniently synthesized by a solution route involving combustion of the metal nitrates along with urea as fuel. This method of combustion synthesis [5,6] is an example of self-propagating high temperature synthesis. The method makes use of highly exothermic reactions involving complexes of the reactants, which often produce a flame due to spontaneous combustion. This then yields the desired product or its precursor in a finely powdered form. A large amount of gas evolved during the combustion reaction leads to give a highly porous product. The temperature of the flame is possibly higher than 1000 K. Since the heat generated is large, volatile impurities, if any, are vaporized resulting in formation of pure crystalline or nanocrystalline products. The main advantage of the combustion synthesis is the simplicity of the process, short reaction time and the absence of energy intensive steps. The first step is a mixing of solutions, which ensures molecular level contact of reactants and formation of homogeneous products. If the reactants are mixed in the solid state, prolonged

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* Corresponding author. Tel.: +91-4114 40 398; fax: +91-4114 40 365.

E-mail address: kvg@igcar.ernet.in (K.V. Govindan Kutty).

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grinding in suitable media, and heating at high temperatures with intermittent grinding would be needed for the product to form. Even then, impurity phases like unreacted material can be present in the product. We have successfully adopted the urea combustion synthesis for the preparation of RE uranates for the first time. This paper reports the synthesis and thermal expansion measurements of these compounds in the temperature range of 298–1173 K by employing high temperature X-ray powder diffractometry. The axial expansion behaviour of the compounds, and the variation of percentage thermal expansion with the atomic number of the RE elements are discussed.

2. Experimental

2.1. Chemicals

Nuclear grade U_3O_8 was obtained from Nuclear Fuel Complex, Hyderabad, India. La_2O_3, Nd_2O_3 and Sm_2O_3, and analytical reagent grade urea were supplied by SD Fine Chemicals, Mumbai, India. Y_2O_3 was obtained from Indian Rare Earths, Mumbai. Eu_2O_3 and Gd_2O_3 were procured from Leico Industries, USA.

2.2. Materials synthesis and characterization

U_3O_8 and RE_2O_3 (RE = La, Nd, Sm, Eu, Gd and Y) were heated at 773 K for 5 h to remove moisture and other gaseous impurities. Calculated amounts of these compounds were dissolved in concentrated HNO_3.The nitrate solutions of both the metals were mixed and boiled for a few minutes. To the hot solution, the calculated amount of urea crystals were added. The mixture was heated on a hot plate; after a few minutes the solution in the glass beaker frothed, fumed and burst into bright flame forming an orange coloured fluffy mass of powder. The freshly prepared powder was scraped from the glass beaker, transferred to a silica crucible and heated in air at 773 K for 4 h to remove NO_2 and other volatile species sticking to the product. The fully dried and completely degassed powder was ground in an agate mortar and transferred to an alumina crucible, and heated in air at 1273 K for 5 h and successively at 1473 K for 8 h. X-ray diffraction analysis of the as-prepared and sintered samples was carried out in all cases.

The X-ray diffraction analysis of the samples was performed with a 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 $10° \leqslant 2\theta \leqslant 80°$ with a scan rate of 0.02°/s and a counting time of one second per step. To eliminate systematic errors in scattering angles, the observed values were corrected with those of silicon standard. The NBS AIDS83 software was used to calculate precise lattice parameters.

2.3. High temperature X-ray powder diffractometry

A Siemens D500 X-ray diffractometer coupled with a Seifert HDK2.1 high temperature attachment was used for axial thermal expansion measurements in the temperature range 298–1173 K. The high temperature stage and experimental details are described in detail elsewhere [7]. The powder sample is mounted as a thin layer on a tantalum strip that was resistively heated at programmed rates. The sample temperature was monitored with a thermocouple spot-welded to the rear of the sample carrier strip. All measurements were carried out in a vacuum of about 10^{-5} Torr. The XRD patterns of the samples were recorded at room temperature, then the temperature was subsequently increased in steps of 100 K to higher temperatures. The XRD patterns up to 1173 K were recorded. The lattice parameters were obtained from the XRD data at each temperature. The maximum error in the measured lattice parameter values was 0.005 Å. The lattice parameters, l, were fitted against temperature (in Kelvin) to the polynomial expression:

$$l = x + yT + zT^2. \tag{1}$$

The average axial expansion coefficient, α_l, between the temperatures, T_1 and T_2, was calculated by the equation

$$\alpha_l = \frac{l_2 - l_1}{l_1(T_2 - T_1)}, \tag{2}$$

where l_1 and l_2 are the lattice parameters at temperatures T_1 and T_2, respectively. Similarly, the average volume expansion coefficient, α_v, was also calculated. The average linear expansion coefficient, $\bar{\alpha}$, was calculated by the following expression

$$\bar{\alpha} = \frac{\alpha_v}{3} = \frac{2\alpha_a + \alpha_c}{3}. \tag{3}$$

3. Results and discussion

3.1. Combustion synthesis

Urea forms complexes with most metal cations [8]. The probable complexes of uranyl nitrate with urea can be represented as $UO_2 \cdot (NO_3)_2 \cdot CO(NH_2)_2 \cdot H_2O$, or $UO_2 \cdot (NO_3)_2 \cdot (CO(NH_2)_2)_n$, ($n$ = 2–6). On heating, the anhydrous complexes decompose to $UO_2 \cdot (NO_3)_2 \cdot CO(NH_2)_2$ and urea molecules. In the case of $UO_2 \cdot (NO_3)_2 \cdot CO(NH_2)_2 \cdot H_2O$, the water molecule is released in the first step of thermal decomposition and subsequently the urea molecule is released from the complex. On further heating the complex decomposes to UO_3 and other unidentified products [9]. It is probable that oxidation–reduction reactions involving urea molecules and nitrate groups occur. This process is supported by the mass spectra of the evolved gases, as reported in the literature [9]. With RE nitrates, urea forms complexes through the carbonyl oxygen [10]. On thermal decomposition of these complexes, the RE oxide, NH_3, CO_2, NO_2 and O_2 are formed as products. Thus the metal nitrate–urea mixtures can ignite at high heating rates and generate the high temperatures required for the formation of RE uranates with the evolution of gaseous byproducts. It is believed that the complex first decomposes exothermally, and then NH_3 and NO_2 react, giving rise to N_2, O_2 and H_2O [11,12]. The appearance of flame during heating is influenced by the quantity of urea added. The combustion of urea can be represented as follows:

$$CO(NH_2)_2 + 1.5O_2 \rightarrow CO_2 + 2H_2O + N_2 \qquad (4)$$

If the amount of urea added to the system is insufficient, the combustion does not occur. A large amount of fumes are evolved instead. Substoichiometric amount of urea is insufficient for the complex formation and hence, the amount of ammonia released during decomposition of the intermediate will be inadequate for burning. This results in evolution of copious fumes. It is essential to add ~10 moles of urea to 2 moles of reactants, so that complex formation, ignition and sustenance of burning are achieved. The overall reaction during combustion may be represented as

$$UO_2(NO_3)_2 + 6RE(NO_3)_3 + 2CO(NH_2)_2 \rightarrow RE_6UO_{12} + 12N_2 + 2CO_2 + 4H_2O + 22O_2. \qquad (5)$$

The gaseous mixture has not been fully analyzed. Fumo et al. [11,12] reported nitrogen and oxygen to be

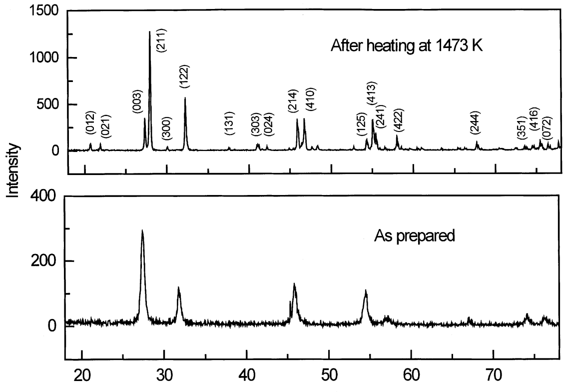

Fig. 1. Powder X-ray patterns of the as-synthesized and annealed Nd_6UO_{12}.

Table 1
Crystal data for the RE_6UO_{12} compounds measured by X-ray powder diffraction (RE = La, Nd and Sm)

Crystal data at 298 K	Compound					
	La_6UO_{12}		Nd_6UO_{12}		Sm_6UO_{12}	
	This study	Ref. [2]	This study	Ref. [3]	This study	Ref. [3]
Hexagonal parameters	$a = 10.487 \pm 0.008$ Å $c = 9.963 \pm 0.007$ Å	$a = 10.476 \pm 0.001$ Å $c = 9.988 \pm 0.001$ Å	$a = 10.255 \pm 0.006$ Å $c = 9.748 \pm 0.001$ Å	$a = 10.254$ Å $c = 9.748$ Å	$a = 10.163 \pm 0.006$ Å $c = 9.641 \pm 0.003$ Å	$a = 10.148$ Å $c = 9.630$ Å (Calculated values)
Rhombohedral parameters	$a = 6.905 \pm 0.004$ Å	$a = 6.899 \pm 0.003$ Å	$a = 6.754 \pm 0.003$ Å	–	$a = 6.690 \pm 0.004$ Å	–
	$\alpha = 98.81 \pm 0.02°$	$\alpha = 98.72 \pm 0.01°$	$\alpha = 98.79 \pm 0.01°$	–	$\alpha = 98.85 \pm 0.01°$	–
X-ray density in g/cm³	6.632 ± 0.008	6.630 ± 0.001	7.267 ± 0.006	7.270	7.692 ± 0.007	7.728

the gaseous products in the preparation of iron substituted perovskites by the combustion synthesis using urea as fuel. This points to the oxidation of urea by the nitrogen dioxide evolved from the decomposition of metal nitrates, giving nitrogen, carbon dioxide and water.

3.2. Phase characterization

The compounds RE_6UO_{12} (RE = La, Nd, Sm, Eu, Gd and Y) have been synthesized by urea combustion synthesis for the first time. X-ray diffraction patterns of the as-prepared products showed the formation of fine crystalline RE_6UO_{12} powders. After heating the material at 1473 K for 8 h, more crystalline single-phase materials were obtained. X-ray diffraction patterns of the as-prepared and sintered powders are given in Fig. 1. The diffraction patterns of all the compounds could be indexed on the R $\overline{3}$ space group, as reported by Hinatsu et al. [2]. All reflections were indexed based on hexagonal crystallographic axes; for the Miller indices, the relationship $-h+k+l=3n$ was observable. They have also studied the crystal structure of La_6UO_{12} prepared by the conventional ceramic route. The room temperature lattice parameters reported by Hinatsu et al. [2] and Bartram et al. [3,13] are quite comparable with our results. The lattice parameters and the X-ray density of the three compounds covered in the thermal expansion study (La_6UO_{12}, Nd_6UO_{12} and Sm_6UO_{12}) are given in Table 1. The lattice parameters a and c decrease with decreasing ionic radii of RE ion. This trend is also seen in the unit cell volume of the compounds. The variation of the measured lattice parameters a and c with the trivalent ionic radii for 6-fold coordination [14] of the RE elements is delineated in Fig. 2. The lattice parameters are the ones measured by us for the six compounds prepared by combustion synthesis. The unit cell volume

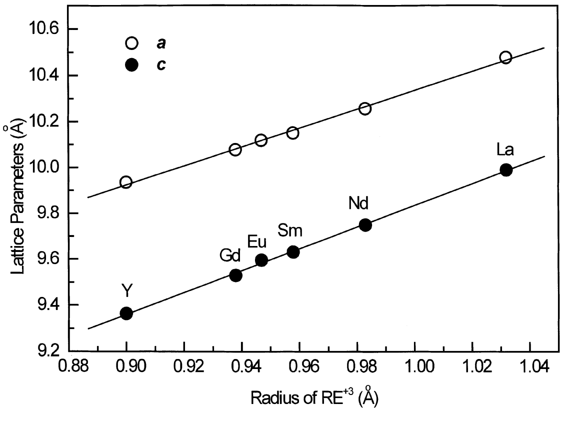

Fig. 2. The measured hexagonal lattice parameters a and c versus the ionic radius of the trivalent RE element for the compounds RE_6UO_{12}.

Table 2
Coefficients of the equation $l = x + yT + zT^2$ used to fit the lattice parameters, a (x_1, y_1, z_1) and c (x_2, y_2, z_2) against temperature (in Kelvin)

Compound	x_1	y_1	z_1	x_2	y_2	z_2
La_6UO_{12}	10.477 ± 0.001	$5.670 \times 10^{-6} \pm 2.268 \times 10^{-6}$	$7.506 \times 10^{-8} \pm 1.643 \times 10^{-9}$	9.938 ± 0.001	$8.832 \times 10^{-5} \pm 2.622 \times 10^{-6}$	$-3.382 \times 10^{-9} \pm 2.207 \times 10^{-9}$
Nd_6UO_{12}	10.226 ± 0.002	$9.495 \times 10^{-5} \pm 9.577 \times 10^{-6}$	$7.565 \times 10^{-9} \pm 6.941 \times 10^{-9}$	9.717 ± 0.007	$1.059 \times 10^{-4} \pm 2.617 \times 10^{-6}$	$-2.207 \times 10^{-8} \pm 2.047 \times 10^{-9}$
Sm_6UO_{12}	10.126 ± 0.001	$1.285 \times 10^{-4} \pm 1.703 \times 10^{-6}$	$-1.471 \times 10^{-8} \pm 1.149 \times 10^{-9}$	9.610 ± 0.001	$1.103 \times 10^{-4} \pm 2.403 \times 10^{-6}$	$-2.170 \times 10^{-8} \pm 1.622 \times 10^{-9}$

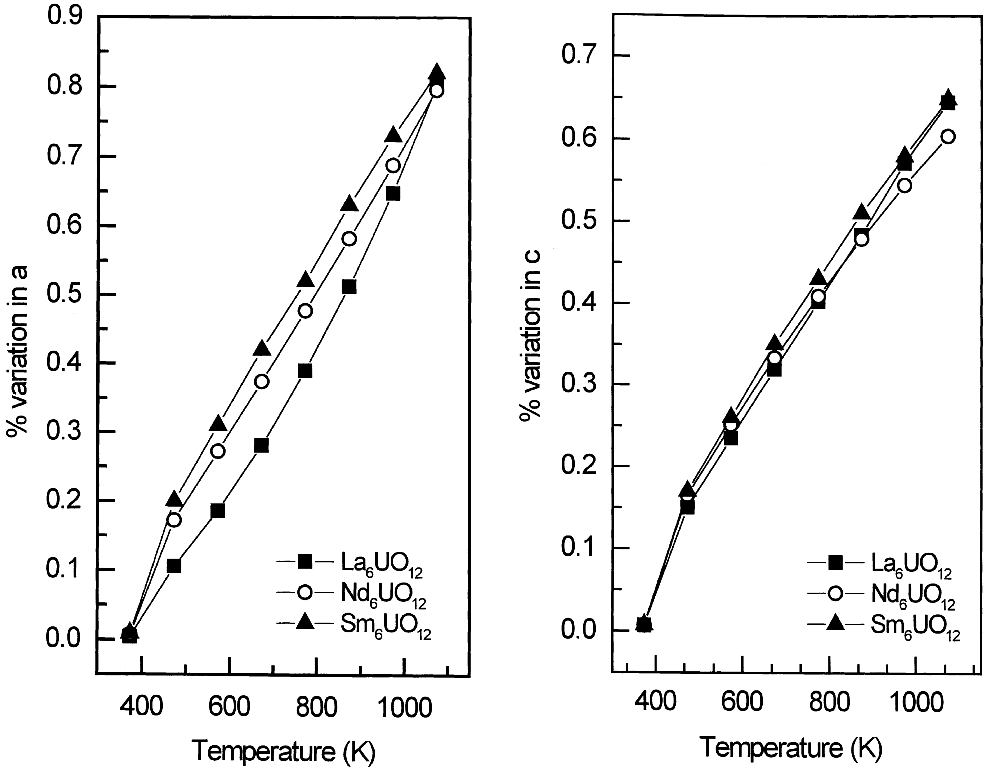

Fig. 3. Percentage linear expansion along the hexagonal axes versus temperature for the compounds RE_6UO_{12} (RE = La, Nd and Sm).

calculated from the *a* and *c* values were used to compute the X-ray density of the materials.

3.3. Thermal expansion

The lattice parameters were calculated from the measured reflection angles at different temperatures. All the three compounds expand along the *a* and *c* axes with increasing temperature. The measurements could be carried out only up to 1173 K on account of the onset of sample degradation at higher temperatures in the X-ray diffraction chamber under the measuring conditions employed. The measured *a* and *c* values were fitted against temperature. Table 2 shows the coefficients of the polynomial expression. Fig. 3 shows the variation of percentage linear thermal expansion along the axes against temperature. The percentage of variation along the *c* axis is found to be lower than that along the *a* axis. The observed expansion behaviour can be explained in terms of the crystal structure and bonding of the compounds. The chemical bonding in these compounds can be considered to be predominantly ionic. In the structure [2] of La_6UO_{12}, six oxygen atoms surround a uranium ion, which forms a distorted octahedron. Similarly, six oxygen atoms surround the lanthanum ion in a highly distorted octahedral fashion. Hence, both La^{+3} and U^{+6} are six coordinated in La_6UO_{12}. The corners of UO_6 octahedra are shared by LaO_6 octahedra. Two edge shared LaO_6 octahedra separate two UO_6 octahedra along *c* axis; this gives rigidity along this axis. Nd_6UO_{12} and Sm_6UO_{12} appear to be isostructural with La_6UO_{12}. In the RE_6UO_{12} compounds, as the RE^{+3} ionic radius decreases the cation–cation distance decreases, which gives rise to increased coulombic repulsion and hence higher thermal expansion. Table 3 shows the average linear thermal expansion coefficients along the hexagonal crystallographic axes for the three compounds between room temperature and 1000 K. At very high temperatures the lanthanum compound tends to show larger expansion values (Fig. 3), probably due to oxygen loss from the compound under the measurement conditions. The measured expansion

Table 3
The average linear expansion coefficient along the hexagonal axes between room temperature and 1000 K for the RE_6UO_{12} compounds

Compound	α_a (10^{-6} K^{-1})	α_c (10^{-6} K^{-1})
La_6UO_{12}	9.78 ± 1.11	8.28 ± 1.00
Nd_6UO_{12}	10.14 ± 0.89	7.95 ± 0.36
Sm_6UO_{12}	10.79 ± 0.85	8.51 ± 0.49

coefficients are in the range 8–10 × 10^{-6} K^{-1}, and hence these compounds can be categorized as high thermal expansion materials, as per the broad classification of materials based on thermal expansion [15].

4. Summary

The RE uranium ternary oxides RE_6UO_{12} (RE = La, Nd, Sm, Eu, Gd and Y) were synthesized by solution combustion method by using metal nitrates and urea. The lattice parameters of these compounds were measured and compared with the literature data. Thermal expansion coefficients of La_6UO_{12}, Nd_6UO_{12} and Sm_6UO_{12} were measured by high temperature X-ray powder diffractometry. The average linear expansion coefficients along the hexagonal axes were found to increase with temperature.

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