Short communication

Synthesis, characterization and thermal expansion studies on europium titanate (Eu_2TiO_5)

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A B S T R A C T

The lattice thermal expansion characteristics of europium titanate (Eu_2TiO_5) have been studied by measuring the lattice parameter by high temperature X-ray diffraction technique (HT-XRD) in the temperature range 298–1573 K. Percentage linear thermal expansion and mean linear thermal expansion coefficients were computed from the lattice parameter data. The percentage linear thermal expansion in the temperature range 298–1573 K along *a*, *b* and *c* axes are 1.05, 1.15 and 0.95 respectively.

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1. Introduction

The thermal expansion of nuclear materials is an important parameter in determining their performance during the lifetime in the nuclear reactor. In addition, knowledge of the coefficient of thermal expansion is required in a number of equations derived from thermodynamics, which relate various physical properties (e.g., specific heats at constant volume and pressure). Thermal expansion data are also required to calculate the thermal conductivity as a function of the temperature. A research program on the investigation of various aspects of thorium lanthanides mixed oxide solid solution systems and the neutron absorber materials (RE_2O_3–TiO_2 systems) have been initiated in our laboratory. As a part of this program, determination of thermal expansion characteristics of the solid solutions containing different mol% of $LaO_{1.5}$ in ThO_2 [1] $NdO_{1.5}$ in ThO_2 [2] and thermophysical measurement on dysprosium and gadolinium titanate [3] were studied.

Lanthanides or their oxides as alloying constituents or as dispersions in stainless steel, aluminum and titanium can be used as control rod materials due to their capability in regulating the fission process by absorbing energetic neutrons [4]. Among the rare earth elements, europium, dysprosium and gadolinium have relatively large thermal neutron absorption cross-sections, and hence compounds of europium, dysprosium and gadolinium are considered as potential candidates for use in nuclear reactors as control rod materials [5–9]. TiO_2 has been used as the favorable host material for rare earth elements, due to its outstanding thermal properties, good mechanical resistance and high stability in corrosive environments [10–12]. Europium titanate has been successfully used in the PM-1 reactor as a control rod material [13]. In view of this, reliable data on the thermal expansion of europium titanate is of relevance in the arena of nuclear materials science. A careful perusal of literature revealed that data are not available on the thermal expansion behavior of Eu_2TiO_5. The present study is devoted to synthesis, characterization and measurement of thermal expansion of europium titanate in the temperature range 298–1573 K using high temperature X-ray diffractometry.

2. Experimental details

The europium oxide and titanium sponge (99.9%) used in this study were obtained from M/s Indian Rare Earths, India, J.K. Baker Chemical Co., Phillipsburg respectively. Europium titanate (Eu_2TiO_5) was prepared by standard solid-state synthesis (ceramic method) route as well as by wet chemical methods.

2.1. Solid-state synthesis

For solid-state synthesis, stoichiometric amounts of europium oxide and titanium sponge powders were mixed for about 1 h in an agate mortar. The homogeneous powder mix was compacted at a pressure of 500 MPa, using a uniaxial hydraulic press to get

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10 mm × 2 mm pellets. The green pellets were initially sintered at 1173 K for 8 h. The pellets were subsequently ground to get fine powders that were compacted again and heated at 1473 K for another 12 h to get final sintered pellets.

2.2. Wet chemical synthesis

For wet chemical synthesis, stoichiometric amounts of europium oxide and titanium sponge were dissolved in concentrated HNO_3. The solution was then evaporated to obtain dry powder. The powder was calcined at 1073 K for 8 h. The sample was then ground, compacted and sintered at 1473 K for 12 h. The phase characterization and lattice parameter measurements were carried out by X-ray diffraction technique.

2.3. X-ray diffraction studies

For characterization by X-ray powder diffraction, the sintered pellet was powdered to obtain ≈100 micron sized particles. The XRD experiment was performed using Ni filtered Cu Kα radiation (λ = 154.098 pm), in a Philips X'pert MPD system that is equipped with a graphite monochromator and a scintillation detector. The X-ray diffraction pattern was recorded in the two-theta range, $10° < 2\theta < 80°$. Peak positions and the relative intensities were estimated using a peak-fit program of the Philips X'pert Plus software. The calibration of the diffractometer was carried out using silicon and α-alumina standards obtained from the National Institute of Standards and Technology (NIST), USA.

2.4. Thermal expansion measurement

The thermal expansion behavior was studied from room temperature to 1573 K at a pressure of 10^{-6} mbar using the XRD–HDK 2.4 high temperature attachment in Philips X'pert MPD system. The detailed description of the HT-XRD procedure has already been described elsewhere [2]. The temperature of the sample was controlled within ±1 K. Before each run, the vacuum chamber was first evacuated to a pressure of about 10^{-6} mbar and then filled with high pure argon gas. The evacuation and argon filling cycle was repeated 4–5 times, before the X-ray patterns were recorded.

2.5. Lattice parameter estimation

The diffraction pattern indicated that the samples were single-phase orthorhombic (α-Pnam) structure. For orthorhombic structures, the lattice parameters a, b, c are related to the d-spacing by the following equation

$$\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{1}{d^2_{(hkl)}} \tag{1}$$

Hence, $d_{(hkl)}$, values corresponding to three principal reflections between $10°$ and $80°$ were calculated at each temperature. Three linear equations were set up by substituting the $d_{(hkl)}$ values and corresponding h, k, l values in the above mentioned equation. The lattice parameters a, b, c were computed by solving the three linear equations simultaneously. The procedure was repeated with d-spacings appropriate to different temperatures.

3. Results and discussion

The room temperature XRD pattern of europium titanate is shown in Fig. 1. It was observed from the XRD patterns that the europium titanate crystallizes into orthorhombic structure with space group Pnam (62). The lattice parameters of europium
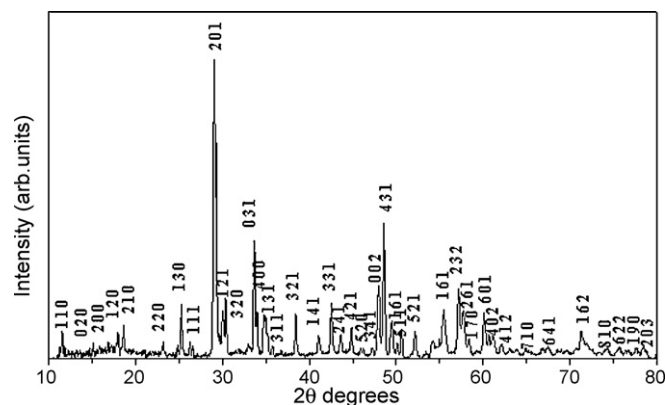

Fig. 1. Room temperature XRD pattern of the europium titanate.

titanate at room temperature are a = 1.0537 nm; b = 1.1303 nm; and c = 0.3779 nm. The diffraction patterns and the lattice parameter values are in good agreement with the literature data [14,15]. The lattice dimensions corresponding to different temperatures are listed in Table 1. For the purpose of estimating thermal expansion, the corrected lattice parameter data were fitted to a second-degree polynomial in the temperature increment (T-300). The variation of lattice parameters, a, b and c with temperature are given by the following equations:

$$a(nm) = 10.520 + 5.3073 \times 10^{-5}(T - 298)$$
$$+ 1.8106 \times 10^{-8}(T - 298)^2 \tag{2}$$

$$b(nm) = 11.284 + 5.5780 \times 10^{-5}(T - 298)$$
$$+ 2.4431 \times 10^{-8}(T - 298)^2 \tag{3}$$

$$c(nm) = 3.7733 + 1.1586 \times 10^{-6}(T - 298)$$
$$+ 1.8107 \times 10^{-9}(T - 298)^2 \tag{4}$$

Once the lattice parameter is known as a function of temperature, it is then possible to estimate the percentage thermal expansion (%TE), and the mean linear thermal expansion coefficient (MLTEC) by the following relations.

$$MLTEC(\alpha) = \left(\frac{1}{a_{298}}\right) \times \left\{\frac{(a_T - a_{298})}{T - 298}\right\}. \tag{5}$$

$$(\%)TE = 100 \times \left\{\frac{(a_T - a_{298})}{a_{298}}\right\}. \tag{6}$$

In the above expression, a_T represents the lattice parameter at temperature, T, and a_{298} the corresponding value at 298 K. The thermal expansion (%) and the mean linear coefficient of thermal expansion were obtained using above expressions. The percentages linear thermal expansion computed using Eq. (6) was fitted to second order polynomial in temperature and the expression for axes a, b and c are given below.

For a axis

Expansion (%) = $0.16488 + 5.0597 \times 10^{-4}T + 1.6934 \times 10^{-7}T^2$ (7)

for b axis

Expansion (%) = $0.16336 + 4.8878 \times 10^{-4}T + 2.1726 \times 10^{-7}T^2$ (8)

and for c axis

Expansion (%) = $0.15319 + 4.7002 \times 10^{-4}T + 1.4697 \times 10^{-7}T^2$ (9)
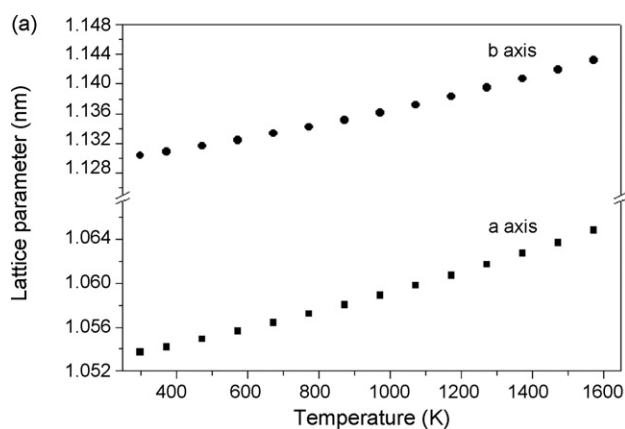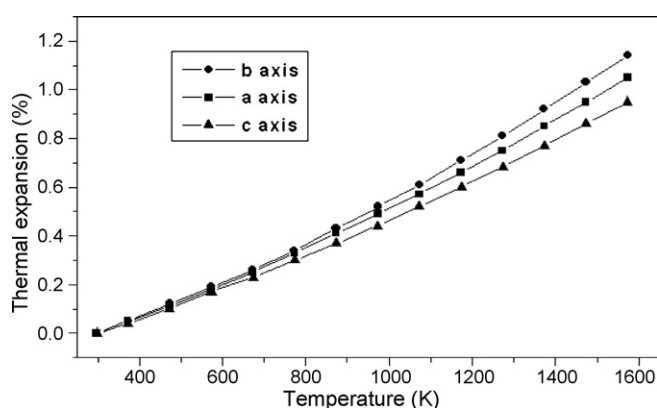
Table 1
The lattice parameters as a function of temperature, thermal expansion (%) and mean linear thermal expansion co-efficients of europium titanate

S. No.	T (K)	Lattice parameter (nm)			% Thermal expansion			Mean linear thermal expansion co-efficients (10^{-6} K^{-1})		
		a	b	c	a	b	c	a	b	c
1	298	1.0537	1.1303	0.3779	0.00	0.00	0.00	6.06	6.22	5.60
2	373	1.0542	1.1308	0.3781	0.05	0.05	0.04	6.32	6.55	5.82
3	473	1.0549	1.1316	0.3783	0.11	0.12	0.10	6.66	6.98	6.10
4	573	1.0556	1.1324	0.3785	0.18	0.19	0.17	7.01	7.41	6.39
5	673	1.0564	1.1333	0.3788	0.25	0.26	0.23	7.35	7.84	6.67
6	773	1.0572	1.1342	0.3790	0.33	0.34	0.30	7.69	8.28	6.96
7	873	1.0580	1.1351	0.3793	0.41	0.43	0.37	8.04	8.71	7.25
8	973	1.0589	1.1361	0.3796	0.49	0.52	0.44	8.38	9.14	7.53
9	1073	1.0598	1.1372	0.3799	0.57	0.61	0.52	8.72	9.57	7.82
10	1173	1.0607	1.1383	0.3802	0.66	0.71	0.60	9.07	10.01	8.10
11	1273	1.0617	1.1395	0.3805	0.75	0.81	0.68	9.41	10.44	8.39
12	1373	1.0627	1.1407	0.3808	0.85	0.92	0.77	9.75	10.87	8.68
14	1473	1.0637	1.1419	0.3811	0.95	1.03	0.86	10.10	11.30	8.96
15	1573	1.0648	1.1432	0.3815	1.05	1.14	0.95	10.44	11.74	9.25

In Fig. 2(a and b), the variation of lattice parameter as a function of temperature along the axes a, b and c are graphically displayed. In Fig. 3, the percentage linear thermal expansion estimated for europium titanate along the axes a, b and c are presented. From Fig. 2(a and b), it is observed that the lattice parameter of all three axes is increases progressively with increasing temperature. The percentage linear thermal expansions also increase progressively with increasing temperature. The average linear thermal expansion co-efficient was calculated by using the formula

$$\alpha = \frac{[\bar{\alpha}_a + \bar{\alpha}_b + \bar{\alpha}_c]}{3}. \tag{10}$$
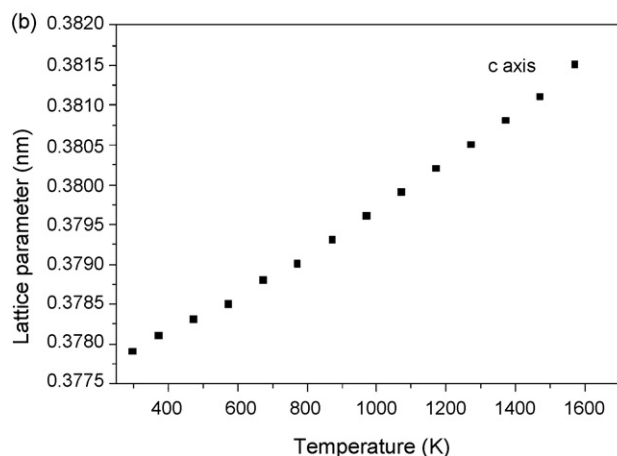
Fig. 2. (a and b) The variation of lattice parameters as function of temperature along the axes a, b and c are graphically displayed.

Fig. 3. The percentage linear thermal expansion estimated from the lattice parameter of europium titanate along the axes a, b and c are plotted.

Lattice parameters (a, b, c) as the function of temperature, percentage thermal expansion and the co-efficient of average linear thermal expansion of europium titanate are presented in Table 1. In Fig. 4, the average linear thermal expansion co-efficient of europium titanate is graphically displayed.

The average linear thermal expansion co-efficient computed using equation (10) was fitted to second order polynomial in temperature and the expression is given below.

$$\alpha = 4.9080 + 3.5378 \times 10^{-3}T + 1.6347 \times 10^{-9}T^2 \tag{11}$$
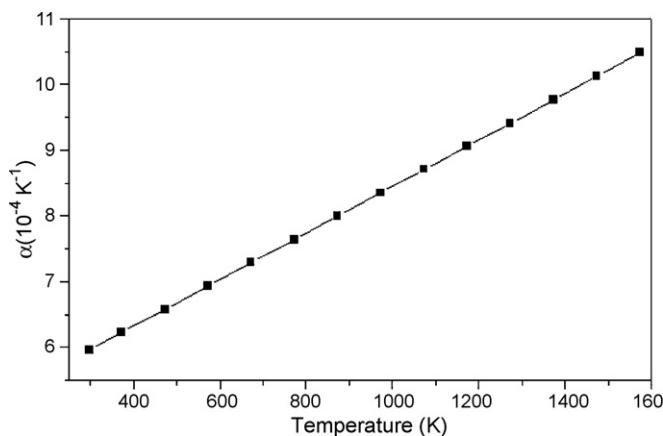
Fig. 4. Average linear thermal expansion co-efficient of Eu$_2$TiO$_5$ is presented.

At the outset, it must be mentioned that to the best of our knowledge, HT-XRD-based thermal expansion estimate for europium titanate are not available in the literature. The average coefficient of thermal expansion value obtained in the present study for europium titanate up to 1473 K is $10.12 \times 10^{-6}\,\text{K}^{-1}$; which is comparable to the value of $10.3 \times 10^{-6}\,\text{K}^{-1}$, reported by Paul et al. for Eu_2O_3 [16]. Hence the addition of TiO_2 does not significantly affect the thermal expansion characteristics of the europium titanate.

4. Conclusion

Europium titanate was prepared by ceramic route as well as wet chemical method. Thermal expansion characteristics were estimated by measuring accurately the temperature variation of lattice parameters in the temperature range 298–1573 K using HT-XRD for the first time. The mean linear thermal expansion coefficients in this temperature range, for a, b and c axes are $10.44 \times 10^{-6}\,\text{K}^{-1}$, $11.74 \times 10^{-6}\,\text{K}^{-1}$ and $9.25 \times 10^{-6}\,\text{K}^{-1}$, respectively.

Acknowledgements

References

[1] G. Panneerselvam, M.P. Antony, T. Vasudevan, J. Alloys. Compd. 415 (1–2) (2006) 26–30.
[2] G. Panneerselvam, M.P. Antony, T. Vasudevan, Thermochim. Acta 44 (2006) 109–115.
[3] G. Panneerselvam, R. Venkata Krishnan, M.P. Antony, K. Nagarajan, T. Vasudevan, P.R. Vasudeva Rao, J. Nucl. Mater. 327 (2004) 220.
[4] R.R. Suchomel, O. Hunter, J. Am. Ceram. Soc. 59 (1987) 149–152.
[5] V.D. Risovany, E.E. Varlashova, D.N. Suslov, J. Nucl. Mater. 281 (2000) 84.
[6] P.C.S. Wu, Europia as nuclear control material, WARD-292, Washington Advanced Reactors Division, 1973.
[7] A.E. Pasto, Europium oxide as a potential LMFBR Control material, ORNL-TM-4226, Oak Ridge national laboratory, 1973.
[8] W.E. Ray, Nucl. Eng. Des. 17 (1971) 337.
[9] H.E. Stevens, Nucl. Sci. Eng. 4 (1958) 373.
[10] R.J. Davis, Z. Liu, Chem. Mater. 9 (1997) 2311.
[11] Z. Liu, R.J. Davis, J. Phys. Chem. 98 (1994) 1253.
[12] M. Anpo, H. Nakaya, S. Kodama, Y. Kubokawa, K. Domen, T. Onishi, J. Phys. Chem. 90 (1986) 1633.
[13] D.R. Sprink, J.H. Schemel, J. Nucl. Mater. 49 (1973/74) 1–9.
[14] Powder diffraction files (Inorganic Phases), Joint Committee on Powder Diffraction Data (JCPDS), International Centre for Diffraction Data (1999). (ICDD card number: 82-1009).
[15] Hk. Muller-Buschbaum, J.P. Werner, J. Alloys Compd. 206 (1994) L11–L13.
[16] C.S. Wu Paul, Nucl. Tech. 39 (1978) 84–94.