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Letter to the Editors

Bulk and lattice thermal expansion of $Th_{1-x}Ce_xO_2$

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Abstract

Bulk and lattice thermal expansion studies on $Th_{1-x}Ce_xO_2$ ($x = 0.0$, 0.04, 0.08 and 1.0) were carried out by dilatometry and high-temperature XRD from room temperature to 1123 K and to 1473 K, respectively. The average linear thermal expansion coefficients, $\bar{\alpha}$, of ThO_2, $Th_{0.96}Ce_{0.04}O_2$, $Th_{0.92}Ce_{0.08}O_2$ and CeO_2 were found to be 9.04×10^{-6}, 9.35×10^{-6}, 9.49×10^{-6} and 11.58×10^{-6} K^{-1}, respectively, between 293 and 1123 K. The average lattice thermal expansion coefficients, $\bar{\alpha}_a$, were 9.54×10^{-6}, 9.85×10^{-6}, 10.01×10^{-6} and 12.06×10^{-6} K^{-1}, respectively, between 293 and 1473 K in this series of compounds. The substitution of 4 and 8 mol% Ce^{4+} at Th^{4+} sites in ThO_2 has a noticeable influence on the thermal expansion behavior. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Of late, a research program on investigation of various aspects of thorium-based systems has been initiated in our laboratory. As part of this program, the thermal expansion behavior of ThO_2 containing 2 wt% UO_2 by high-temperature XRD was investigated recently [1]. The preparation and bulk thermal expansion studies of $BaThO_3$ and $SrThO_3$ were also reported by us recently [2]. Yamashita et al. [3] reported the thermal expansion studies, by high-temperature XRD, on a number of actinide dioxides. There are not many reports on the thermodynamic and transport properties in the ThO_2–PuO_2 system. It was observed by Freshley and Mattys [4] that ThO_2 and PuO_2 form an ideal solid solution in the whole composition range. A critical evaluation of the thermal and thermodynamic properties of ThO_2, $Th_{1-y}U_yO_2$ and $Th_{1-y}Pu_yO_2$ was made by Bakker et al. [5]. They observed that the thermodynamic and thermal expansion data of mixed oxides in the ThO_2–PuO_2 system are very scantily reported in the literature. The main difficulties while investigating the PuO_2 based systems are its high radioactivity and toxicity which require extensive and expensive safety precautions. One way to overcome this problem is to use CeO_2 in place of PuO_2 as they both have quite similar physico-chemical properties, viz., ionic size in octahedral and cubic coordination, melting points, standard enthalpy of formation and specific heat, etc. Thus the plutonium chemistry can be well simulated using CeO_2 in place of highly active PuO_2 [6,7]. However, to the best of our knowledge, there are not many reports on thermo-physical and thermodynamic properties of mixed oxides in the ThO_2–CeO_2 system also. Whitfield et al. [8] reported X-ray studies of the mixed oxides in the ThO_2–CeO_2–Ce_2O_3 system at ambient temperature. They prepared two series of mixed oxides of $(ThCe)O_2$, and $(ThCe)O_{2-x}$ by hydrogen reduction in the temperature range 973–1673 K. Santos et al. [9] reported the preparation of thorium–cerium ceramic alloys in which ThO_2 powder was blended with $(Th_{0.87}Ce_{0.13})O_2$ coprecipitated powder to get the sintered pellets with the mean composition $(Th_{0.94}Ce_{0.06})O_2$. The results were supported by sintering dilatometric tests on ThO_2 and $(Th_{0.87}Ce_{0.13})O_2$ pellets. The lattice thermal expansion behavior of CeO_2 from ambient temperature to 1300 K was reported by Mahanta et al. [10].

2. Experimental

ThO_2 and CeO_2 were mechanically mixed in an appropriate molar ratio, pelletized and heated at 1473 K for 48 h with three intermittent grindings. The final

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Table 1
Summary of the linear thermal expansion coefficient data obtained from dilatometry and HT-XRD

S. no.	Compound	Bulk density (Mg m^{-3})	% Theoretical density	$\bar{\alpha} \times 10^6$ (K^{-1}) (293–1123 K)	$\bar{\alpha}_a \times 10^6$ (K^{-1}) (293–1173 K)[a]	m.p. (K)
1.	ThO_2	9.60	96	9.04	9.54	3650
2.	$Th_{0.96}Ce_{0.04}O_2$	8.22	83	9.35	9.76	–
3.	$Th_{0.92}Ce_{0.08}O_2$	8.10	83	9.49	9.96	–
4.	CeO_2	6.12	85	11.58	11.76	2873

[a] From HT-XRD data, see Table 2 for α_a (293–1473 K).

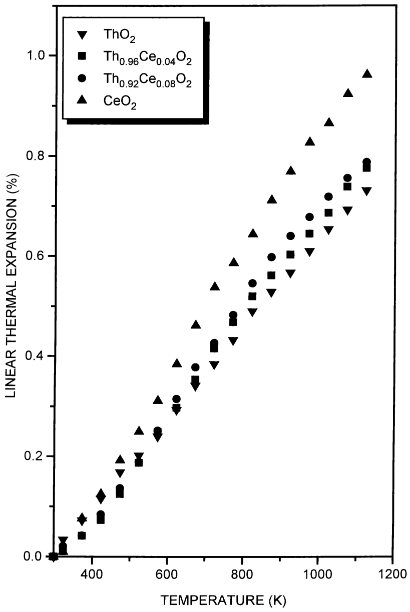

Fig. 1. Variation of linear thermal expansion (%) of $Th_{1-x}Ce_xO_2$ as a function of temperature.

sintering was done at 1573 K for 48 h to get dense pellets with diameter and height about 12 and 10 mm, respectively. The dilatometric and HT-XRD measurements were performed in static air, during heating, as described earlier [1,2]. The unit-cell parameters were determined using a least-squares refinement program. The coefficients of average quasi-isotropic lattice thermal expansion were also computed for each sample (studies were performed on polycrystalline samples).

3. Results and discussion

In order to ascertain the incorporation of Ce^{4+} into the lattice of ThO_2, the room temperature XRD patterns of ThO_2 and mixed oxides were refined. The cubic lattice parameters of ThO_2, $Th_{0.96}Ce_{0.04}O_2$ and $Th_{0.92}Ce_{0.08}O_2$ were obtained as $a = 0.5599(1)$, 0.5591(1) and 0.5588(1) nm, respectively. The observed decrease in lattice parameter as a function of Ce^{4+} concentration can be attributed to the different ionic radii of Th^{4+} and Ce^{4+}, which are 0.105 and 0.0902 nm, respectively, in eightfold coordination. [1] It may be noted that the lattice parameter of CeO_2 is 0.5411 nm. [2]

Hereafter, the average linear thermal expansion coefficient obtained by dilatometry and the average lattice thermal expansion coefficient obtained by HT-XRD will be denoted as $\bar{\alpha}$ and $\bar{\alpha}_a$, respectively. The variation of the linear thermal expansion (%) as a function of temperature (293–1123 K) for all the four samples is shown in Fig. 1. The bulk densities and average linear thermal expansion coefficients ($\bar{\alpha}$) of all the four samples are given in Table 1. The percentage linear thermal expansion, $100 \cdot \Delta l/l_0$, of each sample was fitted using a polynomial regression and the fits are given below (T in K, $\Delta l = 0$ at 293 K).

For ThO_2:

$$\begin{aligned}100 \cdot \Delta l/l_0 = {} & +0.00057(T-293) \\ & +2.1614 \times 10^{-6}(T-293)^2 \\ & -4.3369 \times 10^{-9}(T-293)^3 \\ & +2.6737 \times 10^{-12}(T-293)^4. \end{aligned} \tag{1}$$

For $Th_{0.96}Ce_{0.04}O_2$:

$$\begin{aligned}100 \cdot \Delta l/l_0 = {} & +0.0002(T-293) \\ & +3.8477 \times 10^{-6}(T-293)^2 \\ & -6.1753 \times 10^{-9}(T-293)^3 \\ & +3.1435 \times 10^{-12}(T-293)^4. \end{aligned} \tag{2}$$

For $Th_{0.92}Ce_{0.08}O_2$:

$$\begin{aligned}100 \cdot \Delta l/l_0 = {} & +0.00033(T-293) \\ & +3.1044 \times 10^{-6}(T-293)^2 \\ & -4.3164 \times 10^{-9}(T-293)^3 \\ & +1.7818 \times 10^{-12}(T-293)^4. \end{aligned} \tag{3}$$

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[1] VCH Periodic Table of Elements, 1995, compiled by Fluck and Heumann.

[2] PC-PDF No. 4-593.

Table 2
Lattice parameters a and coefficients of average linear thermal expansion $\bar{\alpha}_a$ of $Th_{1-x}Ce_xO_2$ ($x = 0.0$, 0.04, 0.08 and 1.0) between 293 and 1473 K obtained by HT-XRD data

Temp. (K)	ThO_2 a (nm)	$Th_{0.96}Ce_{0.04}O_2$ a (nm)	$Th_{0.92}Ce_{0.08}O_2$ a (nm)	CeO_2 a (nm)
293	0.5599(1)	0.5591(1)	0.5588(1)	0.5411(2)
423	0.5606(2)	0.5600(1)	0.5597(2)	0.5419(2)
573	0.5614(2)	0.5606(2)	0.5602(2)	0.5430(2)
723	0.5621(2)	0.5612(2)	0.5610(3)	0.5445(3)
873	0.5631(2)	0.5620(6)	0.5617(3)	0.5452(1)
1023	0.5636(2)	0.5631(4)	0.5626(2)	0.5462(3)
1173	0.5646(2)	0.5639(4)	0.5637(2)	0.5467(3)
1323	0.5653(3)	0.5648(3)	0.5640(2)	0.5478(2)
1473	0.5662(1)	0.5656(3)	0.5654(2)	0.5488(1)
$\bar{\alpha}_a$ (K^{-1})	9.54×10^{-6}	9.85×10^{-6}	10.01×10^{-6}	12.06×10^{-6}

For CeO_2:

$$\begin{aligned} 100 \cdot \Delta l/l_0 = {} & +0.0007(T-293) \\ & +2.427 \times 10^{-6}(T-293)^2 \\ & -3.4516 \times 10^{-9}(T-293)^3 \\ & +1.4404 \times 10^{-12}(T-293)^4. \end{aligned} \tag{4}$$

In order to study further the thermal expansion behavior of these materials, their lattice thermal expansion was also investigated using a high-temperature X-ray diffractometer. The lattice parameters of all the four samples at each temperature are given in Table 2. The coefficients of average lattice thermal expansion ($\bar{\alpha}_a$) in the temperature range from 293 to 1473 K are also included in Table 2. The $\bar{\alpha}_a$ value for CeO_2 in the present investigation compares well with that reported by Mahanta et al. [10]. The observed percentage lattice thermal expansion, $100 \cdot \Delta a/a_0$, at each temperature was polynomially fitted as follows (T in K, $a = 0$ at 293 K).

For ThO_2:

$$\begin{aligned} 100 \cdot \Delta a/a_0 = {} & +0.00094(T-293) \\ & +7.3263 \times 10^{-8}(T-293)^2 \\ & -1.8815 \times 10^{-10}(T-293)^3 \\ & +1.1415 \times 10^{-13}(T-293)^4. \end{aligned} \tag{5}$$

For $Th_{0.96}Ce_{0.04}O_2$:

$$\begin{aligned} 100 \cdot \Delta a/a_0 = {} & 0.00132(T-293) \\ & -1.9605 \times 10^{-6}(T-293)^2 \\ & +2.8934 \times 10^{-9}(T-293)^3 \\ & -1.2482 \times 10^{-12}(T-293)^4. \end{aligned} \tag{6}$$

For $Th_{0.92}Ce_{0.08}O_2$:

$$\begin{aligned} 100 \cdot \Delta a/a_0 = {} & +0.00104(T-293) \\ & -4.0670 \times 10^{-7}(T-293)^2 \\ & +4.0865 \times 10^{-10}(T-293)^3 \\ & -8.4184 \times 10^{-14}(T-293)^4. \end{aligned} \tag{7}$$

For CeO_2:

$$\begin{aligned} 100 \cdot \Delta a/a_0 = {} & +0.00091(T-293) \\ & +2.4477 \times 10^{-6}(T-293)^2 \\ & -3.9797 \times 10^{-9}(T-293)^3 \\ & +1.7985 \times 10^{-12}(T-293)^4. \end{aligned} \tag{8}$$

In order to compare the bulk and lattice thermal expansion behavior of these samples, the $\bar{\alpha}_a$ values, calculated in the temperature range 293–1173 K, are also included, along with the $\bar{\alpha}$ (293–1123 K) values, in Table 1. It was found that $\bar{\alpha}$ is slightly smaller than the $\bar{\alpha}_a$. This difference can probably be attributed to the porosity which decreases the bulk thermal expansion. Another reason could be the relaxation effect sometimes encountered in dilatometric experiments. It may be noted that the temperature ranges in which $\bar{\alpha}$ and $\bar{\alpha}_a$ are compared differ slightly due to the experimental limitations.

Yamashita et al. [3] reported the coefficient of the average lattice thermal expansion ($\bar{\alpha}_a$) of PuO_2 from 293 to 1200 K as 11.61×10^{-6} K^{-1} which compares quite well with the $\bar{\alpha}_a$ of CeO_2 i.e., 11.76×10^{-6} K^{-1} between 293 and 1173 K obtained in the present investigation. However, it may be noted that the coefficient of the average lattice thermal expansion of PuO_2, in the temperature range 293–1200 K, given in the TPRC data base [11] and reported by Fahey et al. [12] and Taylor [13] are: $\bar{\alpha}_a = 12.00 \times 10^{-6}$, 12.14×10^{-6} and 12.27×10^{-6} K^{-1}, respectively, which are slightly higher than the $\bar{\alpha}_a$ of PuO_2 reported by Yamashita et al. [3] and of CeO_2 (293–1173 K) in the present investigation. The slight difference in various temperature ranges will make a negligible difference in the above comparison. It is apparent, based on the present investigation on CeO_2 and literature on PuO_2 [3,11–13], that CeO_2 can indeed be nicely used to simulate the thermal expansion behavior of PuO_2.

It can be clearly seen that the doping of 4 and 8 mol% CeO_2 (i.e., 2.644 and 5.365 wt%) into ThO_2 has got a noticeable effect on its thermal expansion behavior. The increase in the average thermal expansion coefficients on going from ThO_2 to $Th_{0.92}Ce_{0.08}O_2$ can be attributed to the relatively higher thermal expansion coefficient of CeO_2 which in turn can be correlated to its lower melting point as compared to that of ThO_2. It is generally observed that the coefficient of average thermal expansion is inversely proportional to the melting point of a solid [14].

4. Conclusion

Doping of 4 and 8 mol% CeO_2 in ThO_2 changes its linear thermal expansion behavior. This observation is explained on the basis of the individual thermal expansion behavior of ThO_2 and CeO_2. This study will be useful in designing the plutonium bearing ThO_2 fuel pin assembly.

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References

[1] A.K. Tyagi, M.D. Mathews, J. Nucl. Mater. 278 (2000) 123.
[2] R.D. Purohit, A.K. Tyagi, M.D. Mathews, S. Saha, J. Nucl. Mater. 280 (2000) 51.
[3] T. Yamashita, N. Nitani, T. Tsuji, H. Inagaki, J. Nucl. Mater. 245 (1997) 72.
[4] M.D. Freshley, H.M. Mattys, General Electric Report HW-76559, 1962, p. 11.6.
[5] K. Bakker, E.H.P. Cordfunke, R.J.M. Konings, R.P.C. Schram, J. Nucl. Mater. 250 (1997) 1.
[6] Y.W. Lee, H.S. Kim, S.H. Kim, C.Y. Young, S.H. Na, G. Ledergerber, P. Heimgarbner, M. Pouchon, M. Burghartz, J. Nucl. Mater. 274 (1999) 7.
[7] C. Ganguly, in: I.J. Hasting (Ed.), Second International Conference on CANDU Fuel, Pembroke, Ont., Canada, 1989, p. 398.
[8] H.J. Whitfield, D. Roman, A.R. Palmer, J. Inorg. Nucl. Chem. 28 (1966) 2817.
[9] A.M. Santos, F. Neto, A. Ricardo, F.S. Lameiras, P.E. Cardoso, An. Congr. Bras. Ceram. 34 (1990) 296; Pub. Assoc. Bras. Ceram., Sao Paulo, Brazil.
[10] P.C. Mahanta, J. Hatibarua, R.K. Das, J. Sci. Ind. Res. B 21 (1962) 596.
[11] Y.S. Touloukian (Ed.), Thermophysical Properties of Materials, vol. 13, IFI/Plenum, New York, 1977; Thermochemical Properties Research Center (TPRC), Purdue University.
[12] J.A. Fahey, R.P. Turcotte, T.D. Chikalla, Inorg. Nucl. Chem. Lett. 10 (1974) 549.
[13] D. Taylor, Br. Ceram. Trans. J. 83 (1984) 32.
[14] L.G.V. Uitert, H.M. O'Bryan, M.E. Lines, H.J. Guggenheim, G. Zydig, Mater. Res. Bull. 12 (1977) 261.