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Letter to the Editors

Bulk thermal expansion studies of $Th_{1-x}Ce_xO_2$ in the complete solid solution range

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Abstract

ThO_2 and CeO_2 are shown to form an almost ideal solid solution throughout the homogeneity range. Bulk thermal expansion studies on $Th_{1-x}Ce_xO_2$ ($0.0 \leqslant x \leqslant 1.0$) were carried out by dilatometry from 293 to 1123 K in air. The average linear thermal expansion coefficients, $\bar{\alpha}$, of ThO_2 and CeO_2 were found to be 9.04×10^{-6} and 11.58×10^{-6} K^{-1}, respectively, between 293 and 1123 K. The substitution of Ce^{4+} at Th^{4+} sites in ThO_2 induced a systematic upward trend in the thermal expansion behavior throughout this series of solid solution on going from ThO_2 to CeO_2.

1. Introduction

A research program on the investigation of thermophysical properties of thorium-based systems has been initiated in our laboratory. As part of this program, the lattice thermal expansion behavior of ThO_2 containing 2 wt% UO_2 by high-temperature XRD has been investigated [1]. The preparation and bulk thermal expansion studies on pseudo-binary products of ThO_2 with oxides of some of the fission products were also communicated [2]. The lattice thermal expansion of PuO_2 has been reported by several groups [3–5]. Recently, we successfully used [6] CeO_2 as a surrogate material in place of PuO_2 to simulate the thermal expansion behavior of $Th_{1-x}Pu_xO_2$ ($x = 0.04$ and 0.08). It was shown that CeO_2 can indeed be used to simulate the thermal expansion behavior of plutonia bearing ThO_2 fuel pins. In this paper the bulk thermal expansion data of $Th_{1-x}Ce_xO_2$ in the complete solid solution range will be discussed.

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 sintering was done at 1573 K for 48 h to get dense pellets (≈85% th.d.) with about 12 mm diameter and 10 mm height. The dilatometric data were collected in static air, during heating, as described earlier [2,3]. The unit-cell parameters were determined using a least-squares refinement program.

3. Results and discussion

The XRD patterns showed a systematic shift in peak positions towards lower d-values throughout the range on going from ThO_2 to CeO_2. In order to ascertain the incorporation of Ce^{4+} into the lattice of ThO_2, the room temperature XRD patterns of ThO_2, CeO_2 and all other mixed oxides were refined (Fig. 1 and Table 1). It can be seen that there is a well-defined decrease in lattice parameter on going from ThO_2 to CeO_2 without causing any distortion of the unit cell or phase separation. It is evident from the XRD data that ThO_2–CeO_2 form a substitutional solid solution in the complete homogeneity range. The observed decrease in lattice parameter as a function of the Ce^{4+} concentration can be attributed

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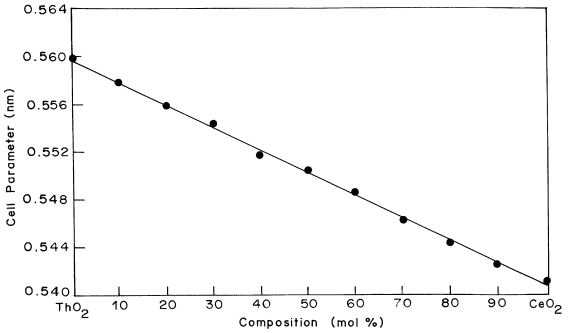

Fig. 1. Room temperature lattice parameter of $Th_{1-x}Ce_xO_2$ as a function of composition.

Table 1
Average linear thermal expansion coefficient $\bar{\alpha}$ of $Th_{1-x}Ce_xO_2$ between 293 and 1123 K measured by dilatometry

x	a (nm)	$\bar{\alpha} \times 10^6$ (K^{-1})
0.0	0.5599(7)	9.04
0.1	0.5578(1)	9.50
0.2	0.5559(1)	9.64
0.3	0.5543(2)	9.86
0.4	0.5517(4)	9.98
0.5	0.5505(1)	10.17
0.6	0.5486(1)	10.38
0.7	0.5464(2)	10.89
0.8	0.5445(1)	11.13
0.9	0.5427(1)	11.45
1.0	0.5411(1)	11.58

to the different ionic radii of Th^{4+} and Ce^{4+}, which are 0.105 and 0.0902 nm, respectively, in eight-fold coordination [6].

Hereafter, the average linear thermal expansion coefficient obtained by dilatometry will be denoted as $\bar{\alpha}$. The typical variation of the linear thermal expansion (%) as a function of the temperature (293–1123 K) for $Th_{0.5}Ce_{0.5}O_2$ is shown in Fig. 2. The average linear thermal expansion coefficients ($\bar{\alpha}$) of all the samples are also included in Table 1. The percentage linear thermal expansion, $100\Delta l/l_o$, in the temperature range 323–1123 K, of each sample was fitted, using a polynomial regression, as given below (T in K).

ThO_2:

$$100\Delta l/l_o = +0.12319 - (0.00193)T + (7.03017 \times 10^{-6})T^2 - (7.17758 \times 10^{-9})T^3 + (2.57736 \times 10^{-12})T^4 \quad (1)$$

$Th_{0.90}Ce_{0.10}O_2$:

$$100\Delta l/l_o = +0.16692 - (0.00196)T + (6.02470 \times 10^{-6})T^2 - (4.90122 \times 10^{-9})T^3 + (1.36113 \times 10^{-12})T^4 \quad (2)$$

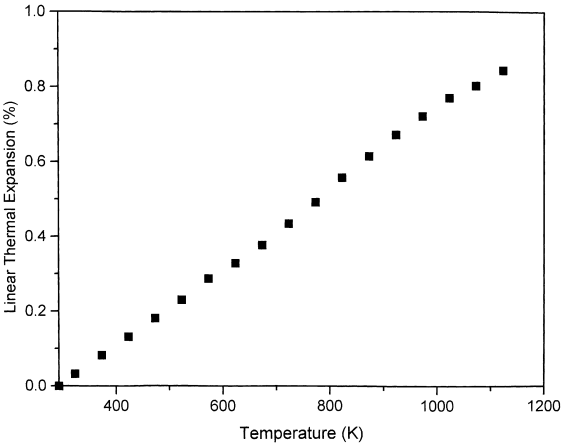

Fig. 2. Linear thermal expansion of $Th_{0.5}$ $Ce_{0.5}O_2$ as a function of temperature.

$Th_{0.80}Ce_{0.20}O_2$:

$$100\Delta l/l_o = +0.19192 - (0.00202)T + (5.93926 \times 10^{-6})T^2 - (4.71970 \times 10^{-9})T^3 + (1.30062 \times 10^{-12})T^4 \quad (3)$$

$Th_{0.70}Ce_{0.30}O_2$:

$$100\Delta l/l_o = +0.18456 - (0.00252)T + (8.45934 \times 10^{-6})T^2 - (8.23317 \times 10^{-9})T^3 + (2.80391 \times 10^{-12})T^4 \quad (4)$$

$Th_{0.60}Ce_{0.40}O_2$:

$$100\Delta l/l_o = -0.23857 + (9.51322 \times 10^{-4})T - (1.33495 \times 10^{-6})T^2 + (2.94449 \times 10^{-9})T^3 - (1.56528 \times 10^{-12})T^4 \quad (5)$$

$Th_{0.50}Ce_{0.50}O_2$:

$$100\Delta l/l_o = -0.53301 + (0.00289)T - (5.16312 \times 10^{-6})T^2 + (5.83681 \times 10^{-9})\mathrm{T}^3 - (2.27770 \times 10^{-12})T^4 \quad (6)$$

$Th_{0.40}Ce_{0.60}O_2$:

$$100\Delta l/l_o = -0.42965 + (0.00171)T - (1.19222 \times 10^{-6})T^2 + (1.11490 \times 10^{-9})T^3 - (4.39656 \times 10^{-13})T^4 \quad (7)$$

$Th_{0.30}Ce_{0.70}O_2$:

$$100\Delta l/l_o = -0.47243 + (0.00218)T - (2.60000 \times 10^{-6})T^2 + (2.65162 \times 10^{-9})T^3 - (9.72281 \times 10^{-13})T^4 \quad (8)$$

$Th_{0.20}Ce_{0.80}O_2$:

$$100\,\Delta l/l_o = -0.46172 + (0.00203)T - (2.10882 \times 10^{-6})T^2 + (1.99383 \times 10^{-9})T^3 - (6.64361 \times 10^{-13})T^4 \quad (9)$$

$Th_{0.10}Ce_{0.90}O_2$:

$$100\,\Delta l/l_o = -0.47507 + (0.00188)T - (1.16966 \times 10^{-6})T^2 + (9.60247 \times 10^{-10})T^3 - (3.52956 \times 10^{-13})T^4 \quad (10)$$

CeO_2:

$$100\,\Delta l/l_o = +0.03863 - (0.00138)T + (5.40097 \times 10^{-6})T^2 - (4.40988 \times 10^{-9})T^3 + (1.20104 \times 10^{-12})T^4 \quad (11)$$

It can be clearly seen from Table 1 that the substitution of Ce^{4+} into ThO_2 has got a very well-defined effect on its thermal expansion behavior. The increase in the average thermal expansion coefficients on going from ThO_2 to CeO_2 can be attributed to a 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. In general the coefficient of average thermal expansion is inversely proportional to the melting point of a solid [7].

4. Conclusions

ThO_2 and CeO_2 form almost an ideal solid solution in the complete homogeneity range. The bulk thermal expansion behavior undergoes systematic changes on going from ThO_2 to CeO_2 in $Th_{1-x}Ce_xO_2$ series. This observation could be attributed to the individual thermal expansion behavior of ThO_2 and CeO_2. This study will be useful in simulating the thermal expansion behavior of mixed oxides in the entire range of the ThO_2–PuO_2 systems.

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