ELSEVIER

Journal of Nuclear Materials 294 (2001) 198–201

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Solubility limits and bulk thermal expansion of ThO_2:M^{n+} ($M = Y^{3+}$, Sr^{2+} and Ba^{2+})

A.K. Tyagi [a,*], M.D. Mathews [a], R. Ramachandran [b]

[a] *Applied Chemistry Division, Bhabha Atomic Research Center, Mumbai 400 085, India*
[b] *Radiometallurgy Division, Bhabha Atomic Research Center, Mumbai 400 085, India*

Abstract

In order to simulate the bulk thermal expansion behaviour of ThO_2 containing different amounts of fission products, a series of mixed oxides of ThO_2 and oxides of some major fission products (Ba^{2+}, Sr^{2+} and Y^{3+}) were prepared and characterized by powder XRD. The upper solubility limit of these dopants was determined by following the change in lattice parameters as a function of their content. The bulk thermal expansion of the each product was investigated from ambient temperature to 1123 K using a dilatometer. The substitution of alkaline-earth ions and Y^{3+} was shown to have the opposite effects on thermal expansion behaviour of ThO_2; e.g., in the presence of 12.5 mol% of Y^{3+}, the average linear thermal expansion coefficient $\bar{\alpha}$ (293–1123 K) of ThO_2 decreased from 9.04×10^{-6} to 8.27×10^{-6} K^{-1}. On the other hand, in the presence of 10.0 mol% of Ba^{2+}, the $\bar{\alpha}$ (293–1123 K) of ThO_2 increased to 9.65×10^{-6} K^{-1}. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thorium has attracted considerable attention in the recent past as it is expected to play an important role in the third stage of the Indian nuclear power generation program [1]. Since thorium itself is not a fissile material in the thermal region of neutrons, it is proposed to use about 2–6 wt% of uranium and plutonium dioxides in the ThO_2 matrix. Thermal expansion and thermal conductivity are two important thermo-physical properties which directly govern the design and performance of a fuel pin assembly. There are few data on the thermodynamic and thermo-physical properties of mixed oxides based on thoria, compared to urania. We have measured the bulk and lattice thermal expansion of thoria-based fuels and other related mixed oxides [2–5]. Thermal expansion of ThO_2 containing 2 wt% UO_2 was about 1.7% higher than that of pure ThO_2 (ambient temperature to 1473 K) [2]. $BaThO_3$ and $SrThO_3$ powders were synthesized [3] by a gel combustion technique using citric acid as fuel and the nitrate as an oxidizer. These powders resulted in highly dense pellets on sintering at 1923 K. It was observed that the average linear thermal expansion coefficients, $\bar{\alpha}$, of $BaThO_3$ and $SrThO_3$ are higher than that of pure ThO_2 by about 21.9% and 15.3%, respectively. Recently, it was demonstrated [4] that $Th_{1-x}Ce_xO_2$ can be used to simulate the thermal expansion behaviour of $Th_{1-x}Pu_xO_2$. The preparation of nano-crystalline thoria powders by a glycine–nitrate combustion route, which could be sintered to high-density pellets at a relatively low temperature [5]. There are few reports [6,7] on thermodynamic properties of several thorates. In this manuscript, we report the bulk thermal expansion behaviour of ThO_2 in the presence of various amounts of fission products; viz. Y^{3+}, Ba^{2+}, Sr^{2+} in the temperature range 293–1123 K using a thermo-dilatometer.

2. Experimental

ThO_2 and MCO_3 (M = Ba, Sr) or Y_2O_3 were mechanically mixed in the appropriate molar ratio and pressed into pellets of diameter and height about 12 and 10 mm, respectively. Each pellet was heated at 1923 K for 4 h in flowing N_2–8% H_2 atmosphere and slowly

---

[*] Corresponding author. Tel.: +91-22 550 5146; fax: +91-22 550 5151.

E-mail address: aktyagi@magnum.barc.ernet.in (A.K. Tyagi).

PII: S0022-3115(01)00466-4

cooled back to room temperature. This heat treatment resulted in high-density pellets (~95% of theoretical density) with diameter about 11 mm and height about 10 mm. The final products were analysed by powder XRD. The XRD patterns were recorded using monochromatic Cu-Kα radiation on a Philips X-ray diffractometer. Silicon powder was used to calibrate the instrument. The unit-cell parameters were determined using a least-squares refinement program. The bulk thermal expansion was measured in air from ambient temperature to 1123 K as a function of temperature using an LKB 3185 fused quartz vertical thermo-dilatometer.

3. Results and discussions

There was no change in room temperature XRD patterns after incorporating 2%, 5% and 10% of Y^{3+} and Sr^{2+} into ThO_2 and all the reflections remain unsplit. However, a few new lines appeared in the case of Ba^{2+} even at 5 mol% doping, indicating that Ba^{2+} was not getting incorporated into the lattice of ThO_2. Instead, an additional phase formed, which was identified as $BaThO_3$ by XRD in the ThO_2–10 mol% Ba^{2+} sample. (In the ThO_2–2 mol% Ba^{2+} sample, the lines were not strong enough to identify the emerging phase.) Typical XRD patterns of ThO_2, ThO_2–10 mol% Y^{3+} and ThO_2–10 mol% Ba^{2+} are shown in Fig. 1. The lattice parameters of all the compositions are given in Table 1. The cubic lattice parameter of ThO_2 decreased progressively on increasing the content of Y^{3+} up to 10 mol% and subsequently saturated. This trend can be attributed to only a slight difference between the ionic radii of Th^{4+} and Y^{3+}, in cubic coordination, which are 0.105 and 0.102 nm, respectively. [1] Hence, it can be inferred that about 10 mol% of Y^{3+} can be incorporated into the lattice of ThO_2 under the present experimental conditions. In the case of Sr^{2+}, the lattice parameter increased up to 5 mol% Sr^{2+} doping and subsequently saturated, indicating that only about 5 mol% of Sr^{2+} can be incorporated into ThO_2 lattice. This is attributed to a rather large difference between the ionic radii of Th^{4+} and Sr^{2+} (0.126 nm) in a cubic coordination.[1] However, the lattice parameter of ThO_2 remained unaltered, within the experimental limits, even after doping of just 2 mol% Ba^{2+}. The compositions with 5 and 10 mol% of Ba^{2+}, and possibly 2%, were not single phase, but showed evidence of $BaThO_3$. This observation is not surprising since the ionic radius of Ba^{2+} (0.142 nm), in eight-fold coordination[1], is very large compared to that of Th^{4+}. It can be inferred that even 2 mol% Ba^{2+} cannot be incorporated into the lattice of ThO_2, to yield a solid solution, under the heat treatment employed in the present investigations.

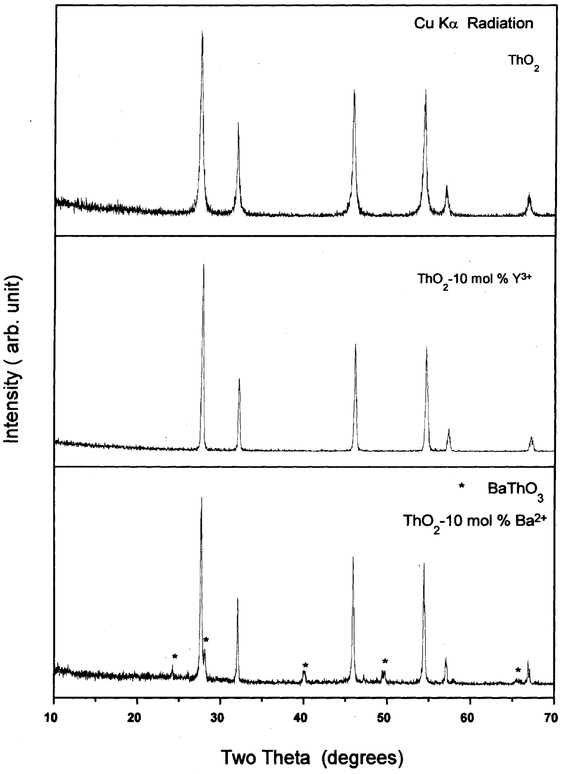

Fig. 1. Powder XRD patterns of a few samples.

Table 1
Lattice parameters (in nm) of ThO_2:M^{n+}

Mol%	Y^{3+}	Sr^{2+}	Ba^{2+}
0	0.5593 (1)	0.5593 (1)	0.5593 (1)
2	0.5589 (2)	0.5592 (1)	0.5590 (1)
5	0.5581 (1)	0.5598 (1)	0.5590 (1)
7.5	0.5579 (1)	0.5596 (2)	[a]
10	0.5570 (2)	0.5597 (1)	0.5590 (1)
12.5	0.5572 (1)	[a]	[a]

[a] Not prepared as these compositions would yield two phases and hence would not reveal any additional information on solubility or thermal expansion.

The bulk thermal expansion of all the products was investigated in the temperature range 293–1123 K on these dense pellets using a thermo-dilatometer. A typical linear thermal expansion as a function of temperature for ThO_2–5 mol% Y^{3+} is shown in Fig. 2. The linear thermal expansion data of all the samples was fitted using a polynomial regression, as shown below, and the fitting parameters, a, b, c and d, are given in Table 2 (T in K and $\Delta l = 0$ at 293 K).

---

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

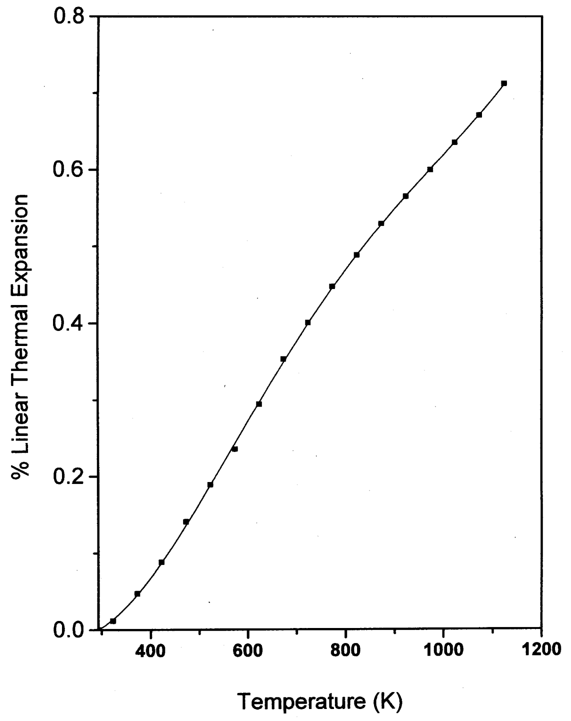

Fig. 2. Linear thermal expansion as a function of temperature for ThO_2–5 mol% Y^{3+}.

$$100\Delta l/l_0 = a(T-293) + b(T-293)^2 + c(T-293)^3 + d(T-293)^4. \quad (1)$$

The average linear thermal expansion coefficients, $\bar{\alpha}$ (293–1123 K), of all the samples are given in Table 3. It can be seen clearly that the average linear thermal expansion coefficient exhibits a definite trend as a function of dopant's nature and content; e.g., the $\bar{\alpha}$ ($\times 10^6$) of ThO_2 in the same temperature range was found to be 9.04 K^{-1}, systematically decreasing to 8.27 K^{-1} on increasing the content of Y^{3+} up to 12.5 mol%. However, the $\bar{\alpha}$ values show the reverse effect for alkaline-earth dopants, i.e., it showed an upward trend as a function of M^{2+} content in the matrix. The observed trend in thermal expansion of thoria as a function of the dopant's nature and content was seen even in two-phase samples. These observations can be explained based on the relative ionic character of bonds. The Y–O bond has a higher covalent character compared to Ba–O or Sr–O bonds. In general, the higher the ionic character, the higher the thermal expansion coefficient.

Table 3
Coefficient of average linear thermal expansion $\bar{\alpha} \times 10^6$ (293–1123 K) of ThO_2:M^{n+} $[K^{-1}]^a$

Mol%	Y^{3+}	Sr^{2+}	Ba^{2+}
2	8.85	9.08	9.10
5	8.58	9.19	9.34
7.5	8.50	9.33	[b]
10	8.35	9.43	9.65
12.5	8.27	[b]	[b]

[a] $\bar{\alpha} \times 10^6$ (293–1123 K) of pure ThO_2: 9.04 K^{-1}.
[b] Not prepared.

4. Conclusions

The present study reveals the part of the phase equilibria in Th–M–O (M = Ba, Sr, Y) system under the present heat treatment. The solubility limits of Ba^{2+}, Sr^{2+} and Y^{3+} into ThO_2, under the equilibrium conditions, were determined by XRD. The effect and nature of the dopants were the important parameters influencing the thermal expansion of ThO_2. This work is also likely to find an application in thoria-based ionic conductors.

Table 2
Fitting parameters of Eq. (1) for linear thermal expansion for various ThO_2:M^{n+} samples

Compound	*a*	*b*	*c*	*d*
ThO_2	0.00057	2.1614×10^{-6}	-4.3369×10^{-9}	2.6737×10^{-12}
ThO_2:2% Y^{3+}	0.00034	3.0216×10^{-6}	-4.8373×10^{-9}	2.4119×10^{-12}
ThO_2:5% Y^{3+}	0.00036	3.0176×10^{-6}	-5.0997×10^{-9}	2.6246×10^{-12}
ThO_2:7.5% Y^{3+}	0.00032	2.7630×10^{-6}	-4.4329×10^{-9}	2.3345×10^{-12}
ThO_2:10% Y^{3}	0.00085	-5.7035×10^{-9}	6.2320×10^{-10}	-7.6676×10^{-13}
ThO_2:12.5% Y^{3+}	0.00078	3.4970×10^{-7}	-3.4344×10^{-10}	-2.8149×10^{-14}
ThO_2:2% Sr^{2+}	0.00053	2.0814×10^{-6}	-3.4423×10^{-9}	1.8030×10^{-12}
ThO_2:5% Sr^{2+}	0.00006	5.0653×10^{-6}	-8.4500×10^{-9}	4.3461×10^{-12}
ThO_2:7.5% Sr^{2+}	0.00106	-6.5313×10^{-7}	7.8181×10^{-10}	-2.0771×10^{-13}
ThO_2:10% Sr^{2+}	0.0001	3.6246×10^{-6}	-5.4510×10^{-9}	2.7857×10^{-12}
ThO_2:2% Ba^{2+}	0.00042	1.7189×10^{-6}	-2.0607×10^{-9}	8.5722×10^{-13}
ThO_2:5% Ba^{2+}	0.00044	2.0023×10^{-6}	-2.9746×10^{-9}	1.5376×10^{-12}
ThO_2:10% Ba^{2+}	0.00046	1.9573×10^{-6}	-2.8838×10^{-9}	1.5240×10^{-12}

Acknowledgements

The authors acknowledge N.M. Gupta, Head, Applied Chemistry Division, BARC and S. Majumdar, Head, Radiometallurgy Division, BARC, for their keen interest in this work.

References

[1] R. Chidambaram, in: M. Srinivasan, I. Kimura (Eds.), Proceedings of the Indo-Japan Seminar of Thorium Utilization, 10–13 December 1990, Bombay, India, Indian Nuclear Society, and Atomic Energy Society of Japan, p. 7.

[2] A.K. Tyagi, M.D. Mathews, J. Nucl. Mater. 278 (2000) 123.

[3] R.D. Purohit, A.K. Tyagi, M.D. Mathews, S. Saha, J. Nucl. Mater. 280 (2000) 51.

[4] M.D. Mathews, B.R. Ambekar, A.K. Tyagi, J. Nucl. Mater. 280 (2000) 246.

[5] R.D. Purohit, S. Saha, A.K. Tyagi, J. Nucl. Mater. 288 (2001) 7.

[6] S.R. Bharadwaj, R. Mishra, M. Ali, D. Das, A.S. Kerkar, S.R. Dharwadkar, J. Nucl. Mater. 275 (1999) 201.

[7] R. Mishra, M. Ali, S.R. Bharadwaj, A.S. Kerkar, D. Das, S.R. Dharwadkar, J. Alloys Compounds 290 (1999) 97.