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Thermophysical properties of hafnium titanate

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Abstract

Heat capacity and lattice thermal expansion of hafnium titanate ($HfTiO_4$) have been studied by differential scanning calorimeter (DSC) and high temperature X-ray diffraction technique (HT-XRD) in the temperature range 298–800 K and 298–1973 K respectively. From the heat capacity data, other thermodynamic functions such as enthalpy, entropy and Gibbs energy functions were computed. Percentage linear thermal expansion and mean linear thermal expansion coefficients were computed from the lattice parameter data. The thermal expansion of $HfTiO_4$ was found to be anisotropic. The lattice parameters at 298 K viz., *a*, *b* and *c* axes are 0.5042, 0.5579 and 0.4732 nm respectively. The expansivity along the '*a*' axis was found to be larger than the expansivity along '*b*' and '*c*' axes. The lattice was found to contract along *b*-axis below 1073 K. The heat capacity of $HfTiO_4$ at 298 K was found to be121.4 J K^{-1} mol^{-1}. The percentage linear thermal expansion in the temperature range 298–1973 K along *a*, *b* and *c* axes are 2.74, 0.91 and 1.817 respectively.

Keywords: C. Thermal expansion; Hafnium titanate; Heat capacity; Negative thermal expansion; Control rod

1. Introduction

Owing to its desirable nuclear and mechanical properties such as good absorption cross-section for thermal neutrons (105 barns) [1–8] and low thermal expansion, hafnium titanate ($HfTiO_4$) finds application as control rods for nuclear reactors. In view of this, reliable data on heat capacity and thermal expansion of $HfTiO_4$ is of relevance in nuclear technology. The lattice thermal expansion of this compound was reported by Lynch and Morosin [6] in the temperature range 298 to 1173 K, Bayer et al. [7] up to 773 K and Ikawa et al. [8] up to 1673 K. However, measurements on the thermal expansion of this compound beyond 1673 K have not been reported so far. Further, the heat capacity of this compounds have not been experimentally determined. Hence, in the present study heat capacity measurements in the temperature range 298–800 K and thermal expansion characteristics in the temperature range 298–1973 K were carried out by using DSC and HTXRD respectively.

2. Experimental

2.1. Equipments

Heat capacity measurements were carried out by using a heat flux type differential scanning calorimeter (model number DSC 821e/700 of M/s. Mettler Toledo GmbH, Switzerland). In a typical experiment a pellet of $HfTiO_4$ was sealed in a 40 μl Al-pans (with pin hole on the lid), loaded into the calorimeter and was heated at a heating rate of 10 K min^{-1} in the temperature range 298–800 K. High purity argon was used as the purge gas at a flow rate of 50 mL min^{-1}. Details pertaining to calibration of this equipment and procedure with respect to the measurement of heat capacity are described elsewhere [9]. The XRD experiments were performed in a Philips X'Pert MPD® system with Cu-Kα radiation in Bragg–Brentano geometry. The X-ray diffraction patterns were recorded in the two-theta range, $10^\circ < 2\theta < 80^\circ$. The peak positions and the relative intensities were estimated by using a peak-fit program incorporated in the Philips X'pert Plus software. The calibration of this diffractometer was carried out by using

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silicon and α-alumina standards obtained from the National Institute of Standards and Technology (NIST), USA. The thermal expansion behavior was studied from 298 to 1973 K under vacuum (10^{-4} Pa) by using the XRD-HDK 2.4 high temperature attachment of this diffractometer. A detailed description of the HTXRD procedure has already been described elsewhere [10].

2.2. Sample preparation and characterization

Hafnium titanate ($HfTiO_4$) was prepared by a wet chemical method. In this procedure stoichiometric amounts of hafnium oxide and titanium oxide were dissolved in concentrated HNO_3. This solution was then evaporated to dryness. The residue thus obtained was calcined at 1073 K for 8 h. This product was ground in an agate mortar, compacted and sintered at 1573 K for 12 h in air. The phase characterization and lattice parameter measurements were then carried out. The diffraction pattern shown in Fig. 1 indicated that these samples were single-phase orthorhombic α-PbO_2 structure (space group is Pcnb) and is in good agreement with the pattern cited in Ref. [11]. The detailed structural information of α-PbO_2 is explained elsewhere [12].

2.3. Lattice parameter computation

In an orthorhombic unit cell, the lattice parameters a, b, c could be related to the d-spacing by the following equation

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

$d_{(hkl)}$ – values corresponding to three principal reflections between 20° and 80° were calculated at each temperature. Three linear equations pertaining to these three reflections were set up by using Eq. (1). These lattice parameters a, b and c were computed by solving these three linear equations simultaneously. This procedure was repeated for the computation of lattice parameters at each temperature. The room temperature lattice parameter along a, b and c-axes are 0.5042(4), 0.5579(4) and 0.4732(4) nm respectively.

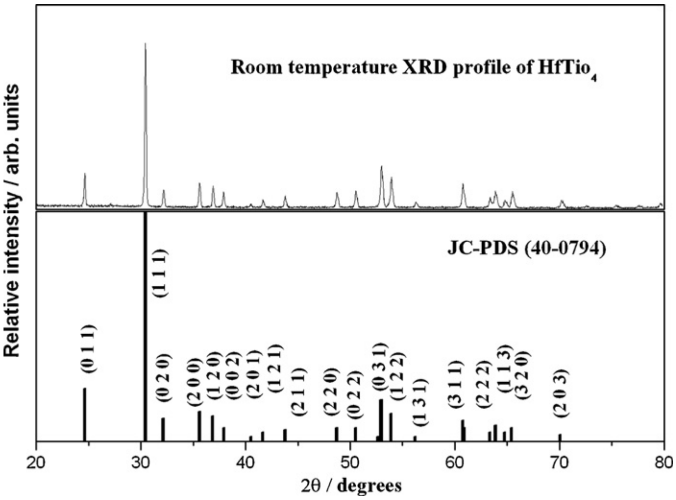

Fig. 1. Room temperature XRD pattern of $HfTiO_4$.

3. Results and discussion

3.1. Heat capacity measurements

Measured values of the heat capacity of $HfTiO_4$ in the temperature range 298–800 K are given in Table 1. Each value reported is the mean of ten measurements. The uncertainty in this heat capacity had been determined earlier to be ±3% (by measurements on ThO_2 samples) [13]. The relative standard deviations of the values reported here are in the range of 1–3%. Therefore, it is reasonable to estimate that the uncertainty in the values to be ±3%. The temperature dependence of these heat capacity values were fit to a polynomial by least squares regression analysis (Eq. (2))

$$C_{p,m}\,(\mathrm{J\ K^{-1}mol^{-1}}) = 132.044 + 2.861\times10^{-2}\,T - 1.710464\times10^{6}\,T^{-2} \tag{2}$$

The standard error of this fit was found to be 0.59 J K^{-1} mol^{-1}. The measured values of heat capacity along with this fit are shown in Fig. 2. The heat capacity of $HfTiO_4$ computed by the Neumann–Kopp's approximation by using the auxiliary data on the heat capacities of HfO_2 ([14], Eq. (3)) and TiO_2 ([14], Eq. (4)) are also shown in Fig. 2.

$$C_{p,m}\,(\mathrm{HfO_2})\,(\mathrm{JK^{-1}\ mol^{-1}}) = 128.997 + 20.255\times10^{-3}\,T - 1.707\times10^{6}\,T^{2} \tag{3}$$

$$C_{p,m}(\mathrm{TiO_2})\,(\mathrm{JK^{-1}\ mol^{-1}}) = 73.346 + 3.054\times10^{-3}\,T - 1.703\times10^{6}\,T^{2} \tag{4}$$

As seen from Fig. 2 the measured heat capacity values are in good agreement within ±2% than that computed from Neumann–Kopp's approximation using the heat capacity data of its component oxides [14]. However, the measured heat capacity values are around 3% higher than the estimated values in the temperature range 300–400 K and 700–800 K. This may due to the difference in the dilation contribution to heat capacity (thermal expansion and isothermal compressibility contribution) between $HfTiO_4$ and its component binary oxides HfO_2 and TiO_2 [15].

From the heat capacity data other thermodynamic functions viz., enthalpy, entropy and Gibbs energy functions were computed and these are listed in Table 1. The S_0^{298} values of $HfTiO_4$ required for the computation of entropies were estimated by using Neumann–Kopp's approximation from the literature data [14] of their respective component oxides is 110.04 J K^{-1} mol^{-1}.

3.2. Thermal expansion measurements

The lattice parameters of $HfTiO_4$ at room temperature are a = 0.5042 nm; b = 0.5579 nm; and c = 0.4732 nm. The room

Table 1
Thermodynamic functions of $HfTiO_4$.

T/K	$C_{p,m}$/J K^{-1} mol^{-1}		$H_T^0 - H_{298}^0$/J mol^{-1}	S_T^0/J K^{-1} mol^{-1}	$G_T^0 - H_{298}^0 T$//J K^{-1} mol^{-1}
	Measured	Fit			
298	121.4	121.3	0	110.0	−110.0
300	121.7	121.6	243	110.9	−110.0
400	133.2	132.8	13,023	147.5	−115.0
500	139.5	139.5	26,660	177.9	−124.6
600	144.4	144.5	40,868	203.8	−135.7
700	147.8	148.6	55,524	226.4	−147.1
800	153.8	152.3	70,569	246.5	−158.3

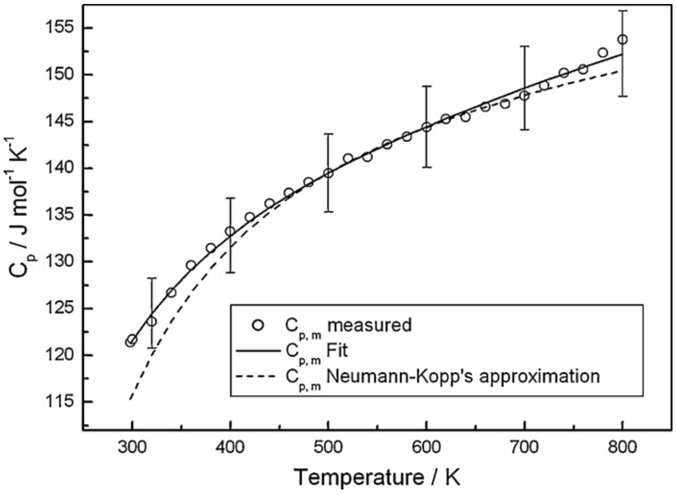

Fig. 2. Temperature dependence of the heat capacity of $HfTiO_4$.

temperature diffraction pattern and the lattice parameter values are in good agreement with those reported in the literature [11]. The temperature dependent variation of these values are listed in Table 2. Also, their temperature dependence was fitted into the following polynomials (Eqs. (5)–(7)) by least squares regression analysis.

$$a\,(\text{nm}) = 0.50415 + 1.9399 \times 10^{-6}(T - 298) + 2.8363 \times 10^{-9}\,(T - 298)^2 \quad (5)$$

$$b\,(\text{nm}) = 0.55795 - 4.7910 \times 10^{-6}\,(T - 298) + 3.4349 \times 10^{-9}\,(T - 298)^2 \quad (6)$$

$$c\,(\text{nm}) = 0.47319 + 1.1586 \times 10^{-6}\,(T - 298) + 1.8107 \times 10^{-9}\,(T - 298)^2 \quad (7)$$

Table 2
The lattice parameter as a function of temperature, thermal expansion (%) and mean linear thermal expansivity.

T/K	Lattice parameter/nm			Thermal expansion/%			Mean thermal expansion coefficients/ 10^6 K^{-1}		
	a-axis	b-axis	c-axis	a-axis	b-axis	c-axis	a-axis	b-axis	c-axis
298	0.5042	0.5579	0.4732						
383	0.5043	0.5565	0.4739	0.03	−0.037	0.05	3.01	−7.84	1.05
448	0.5045	0.5562	0.4740	0.08	−0.060	0.08	5.40	−5.95	3.09
493	0.5048	0.5561	0.4744	0.12	−0.073	0.11	6.26	−5.22	3.77
548	0.5048	0.5565	0.4743	0.18	−0.085	0.15	7.02	−4.55	4.31
638	0.5053	0.5565	0.4747	0.27	−0.096	0.20	7.95	−3.69	4.90
743	0.5059	0.5563	0.4749	0.39	−0.097	0.28	8.81	−2.84	5.38
823	0.5067	0.5567	0.4754	0.49	−0.089	0.34	9.40	−2.24	5.68
873	0.5071	0.5567	0.4757	0.56	−0.079	0.37	9.75	−1.89	5.85
973	0.5074	0.5565	0.4756	0.70	−0.051	0.45	10.41	−1.20	6.16
1023	0.5085	0.5566	0.4765	0.78	−0.033	0.49	10.73	−0.86	6.31
1073	0.5088	0.5568	0.4765	0.86	−0.011	0.54	11.05	−0.52	6.45
1173	0.5087	0.5572	0.4764	1.02	0.041	0.63	11.67	0.14	6.72
1223	0.5104	0.5573	0.4773	1.11	0.072	0.67	11.98	0.46	6.85
1273	0.5103	0.5572	0.4773	1.20	0.106	0.72	12.28	0.79	6.98
1373	0.5109	0.5573	0.4774	1.38	0.183	0.82	12.88	1.43	7.23
1473	0.5118	0.5580	0.4778	1.58	0.273	0.92	13.47	2.07	7.48
1573	0.5131	0.5589	0.4786	1.79	0.375	1.02	14.06	2.71	7.72
1673	0.5147	0.5601	0.4793	2.01	0.489	1.13	14.65	3.34	7.95
1773	0.5153	0.5602	0.4794	2.25	0.615	1.25	15.23	3.97	8.19
1873	0.5165	0.5610	0.4802	2.49	0.754	1.36	15.81	4.60	8.42
1973	0.5182	0.5619	0.4810	2.74	0.905	1.49	16.39	5.23	8.65

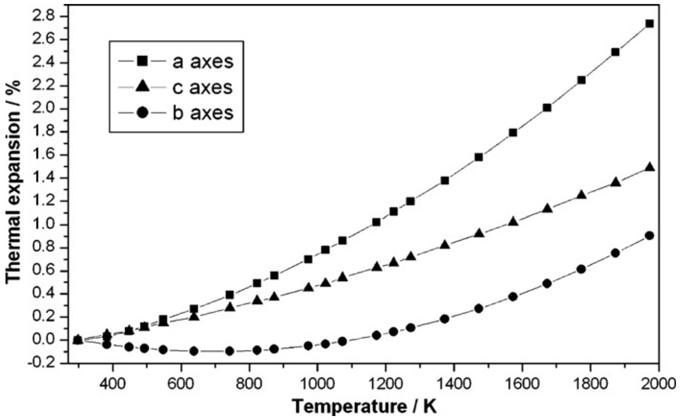

Fig. 3. Percentage thermal expansion of $HfTiO_4$.

The thermal expansion (%) and the average coefficient of thermal expansion were obtained by using the above expressions. The temperature dependence of percentage thermal expansion along the axis *a*, *b* and *c* are shown in Fig. 3. The percentage thermal expansion and co efficient of average linear thermal expansion as a function of temperature are also listed in Table 2.

The average linear thermal expansion (%) values obtained in the present study up to 1673 K is 1.27; which is higher compared to the value of 0.97, reported by Ikawa et al. [8]. and the coefficient of thermal expansion values obtained in the present study up to 743 K along *a*, *b* and *c* axes are $8.81 \times 10^{-6}\,K^{-1}$, $-2.84 \times 10^{-6}\,K^{-1}$ and $5.24 \times 10^{-6}\,K^{-1}$; are in good agreement with the values reported by Bayer et al. [7]. Contraction was observed along the *b*-axis at temperatures below 1073 K. This phenomenon was also reported by other researchers [7,16]. The large increase in the lattice parameter "*a*" in the high temperature region ($T > 1273$ K) is due to the order-disorder transition. At high temperatures, $HfTiO_4$ exists in the same α-PbO_2 structure and same space group (Pcnb). However, complete disordering of Hf^{4+} and Ti^{4+} cations on equivalent octahedral sites occurs. The large expansion at $T > 1273$ K is due to overlap of thermal expansion and enlargement of the high-temperature form [8].

4. Conclusion

Hafnium titanate was prepared by the wet chemical method. Thermal expansion characteristics were computed from the measured lattice parameters along *a*, *b* and *c*-axes as a function of temperature in the temperature range 298–1973 K using HT-XRD. The mean linear thermal expansion coefficients in this temperature range, for *a*, *b* and *c* axes were found to be $16.39 \times 10^{-6}\,K^{-1}$, $5.23 \times 10^{-6}\,K^{-1}$ and $8.65 \times 10^{-6}\,K^{-1}$, respectively. Negative thermal expansion was observed along *b*-axis at temperatures below 1073 K. For the first time experimentally present measured values of the heat capacity data of $HfTiO_4$ are being reported. Also, thermal expansion characteristics of this compound at temperatures above 1673 K are being reported for the first time.

References

[1] J.G. Goodwin, W.J. Hurford, Iodide process produces ductile hafnium for fabrication, J. Metals 7 (1955) 1162–1165.
[2] J.G. Goodwin, F.R. Lorenz, The study of some mechanical, physical and corrosion properties of iodine hafnium, Nucl. Sci. Eng. 6 (1959) 49–56.
[3] R. Kuwae, T. Hatanko, J. Kawashima, Hafnium corrosion behavior in high temperature steam, J. Nucl. Mater. 139 (1986) 42–47.
[4] J.H. Scheme, ASTM Manual on Zirconium and Hafnium STP639, ASTM, Philadelphia, 1977.
[5] H.W. Keller, J.M. Shallenberger, D.A. Hollein, A.C. Hott, Development of hafnium and comparison with other pressurized water reactor control rod materials, Nucl. Technol. 59 (1982) 476–479.
[6] R.H. Lynch, B. Morosin, Thermal expansion, compressibility and polymorphism in hafnium and zirconium titanates, J. Am. Ceram. Soc. 55 (1972) 409–413.
[7] G. Bayer, M. Hofmann, L.J. Gauckler, Effect of ionic substitution on thermal expansion of $ZrTiO_4$, J. Am. Ceram. Soc. 74 (1991) 2205–2208.
[8] H. Ikawa, A. Iwai, K. Hiruta, H. Shimojima, K. Urabe, S. Udagawa, Phase transformation and thermal expansion of zirconium and hafnium titanates and their solid solutions, J. Am. Ceram. Soc. 71 (1988) 120–127.
[9] R. Venkata Krishnan, K. Nagarajan, Heat capacity measurements on uranium–cerium mixed oxides by differential scanning calorimetry, Thermochim. Acta 440 (2006) 141–145.
[10] G. Panneerselvam, M.P. Antony, T. Vasudevan, Studies on lattice thermal expansion and XPS of ThO_2–$NdO_{1.5}$ solid solutions, Thermochim. Acta 443 (2006) 109–115.
[11] Powder diffraction files (Inorganic Phases), Joint Committee on Powder Diffraction Data (JCPDS), International Centre for Diffraction Data (1999) (ICDD card number: 40-0794).
[12] G. Bayer, M. Hofmann, L.J. Gauckler, Effect of ionic substitution on the thermal expansion of $ZrTiO_4$, J. Am. Ceram. Soc. 74 (1991) 2205–2208.
[13] R. Venkata Krishnan, K. Nagarajan, P.R. Vasudeva Rao, Heat capacity measurements on $BaThO_3$, $BaCeO_3$, J. Nucl. Mater. 299 (2001) 28–31.
[14] L.B. Pankratz, Thermodynamic properties of element and oxides, Bull. US. Bur. Mines (1984).
[15] J. Leitner, P. Vonka, D. Sedmidubsky, P. Svoboda, Application of Neumann–Kopp rule for the estimation of heat capacity of mixed oxides, Thermochim. Acta 497 (2010) 7–13.
[16] R.G. Hoagland, C.W. Marchall, A.R. Rosenfied, Microstructural factors influencing fracture toughness of hafnium titanate, Mater. Sci. Eng. 15 (1974) 51–62.