ELSEVIER

Journal of Alloys and Compounds 381 (2004) 37–40

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The bulk modulus of ThO_2—an experimental and theoretical study

J. Staun Olsen [a], L. Gerward [b,*], V. Kanchana [c], G. Vaitheeswaran [c]

[a] *Oersted Laboratory, Niels Bohr Institute, University of Copenhagen, 2100 Copenhagen, Denmark*
[b] *Department of Physics, Technical University of Denmark, 2800 Kongens Lyngby, Denmark*
[c] *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

Received 31 March 2004; received in revised form 16 April 2004; accepted 16 April 2004

Abstract

In view of the large scatter in the literature, we have re-evaluated the high-pressure behaviour and the bulk modulus of thorium dioxide, experimentally using high-pressure X-ray diffraction (XRD) in conjunction with synchrotron radiation. To compare with the experimental measurements, theoretical calculations were performed using the full-potential linear muffin-tin orbital method (FP-LMTO) together with the local density approximation (LDA) as well as the generalised gradient approximation (GGA). The experimental value for the bulk modulus is found to be 195.3 ± 2.0 GPa, which compares well with the calculated value of 198 GPa obtained by using the generalised gradient approximation to the exchange correlation potential.

Keywords: X-ray diffraction; Crystal binding and equation of state, electron band calculation; Synchrotron radiation, high pressure

1. Introduction

During the last two decades, actinide dioxides have attracted a great deal of interest from experimentalists as well as theoreticians. The chemistry of actinide oxides is a complex field, with complications stemming from non-stoichiometry and often from self-damage resulting from decay of radioactive isotopes [1]. Careful experimental procedures have overcome most of these difficulties to produce an overall picture in which only ThO_2 is a stable diamagnetic transparent insulating solid and the other actinide dioxides are all darkly opaque and poorly conducting. Interest in thorium dioxide is not confined to its use as a nuclear material, but also as a solid-state electrolyte and it is traditionally used in fluorescent tubes.

At ambient conditions, the actinide dioxides have the predominantly ionic fluorite (CaF_2) type structure with space group $Fm\bar{3}m$ (No. 225). The fluorite crystal structure yields cubic site symmetry for the actinide atoms and tetrahedral site symmetry for the oxygen atoms. The most profound differences (notably with respect to the conductivities, color and magnetism) in the two dioxides ThO_2 and UO_2 is directly related to the 5f electrons present in UO_2 and missing in ThO_2 [2]. Like other fluorite-type compounds, ThO_2 undergoes a pressure-induced structural phase transformation to the orthorhombic α-$PbCl_2$ type structure with space group *Pnma* (No. 62). The transition pressure for ThO_2 is stated as 40 GPa, although weak lines of the high-pressure phase begins to appear above 30 GPa [3,4].

In 1964, Macedo et al. [5] determined the elastic constants c_{11}, c_{12} and c_{44} of ThO_2 by measuring the velocity of sound waves in single-crystal samples. The zero-pressure adiabatic bulk modulus, B_0, is given by

$$B_0 = \frac{1}{3}(c_{11} + 2c_{12}). \quad (1)$$

Macedo et al. got $B_0 = 193 \pm 2$ GPa. The same result was obtained by Wawra [6] 9 years later, also by a sonic-ultrasonic method. Experimental work using high-pressure X-ray diffraction (XRD) and theoretical calculations in the 1980s, however, tended to give much higher values for the bulk modulus of ThO_2 (Table 1). Thus, Benedict et al. [7] measured $B_0 = 278$ GPa. Later, the same group [4] reported the revised experimental value $B_0 = 262 \pm 4$ GPa together with $B_0' = 6.7 \pm 0.5$, the latter parameter being the pressure derivative of the bulk modulus at zero pressure. The B_0 values above seemed to be supported by theoretical calculations of Kelly and Brooks [8] who,

* Corresponding author. Tel.: +45-45-25-31-46; fax: +45-45-93-2399.
E-mail address: gerward@fysik.dtu.dk (L. Gerward).

0925-8388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.04.099

Table 1
Lattice constant, a, and relative volume, V/V_0, of ThO_2 as functions of pressure

P (GPa)	a (Å)		V/V_0	
	Experiment	Theory	Experiment	Theory
0.00	5.5969(15)	5.6113	1.0000(8)	1.0070
1.05	5.5875	5.6014	0.9950	1.0020
2.51	5.5737	5.5880	0.9876	0.9948
3.71	5.5616	5.5775	0.9812	0.9892
8.72	5.5228	5.5359	0.9608	0.9670
10.56	5.5099	5.5350	0.9541	0.9600
16.20	5.4700	5.4811	0.9335	0.9388
21.66	5.4368	5.4443	0.9166	0.9220
31.39	5.3849	5.3868	0.8906	0.8942

The number within parenthesis is the estimated experimental error in units of the last decimal place. Theoretical V/V_0 corresponding to the experimental pressure values are obtained by interpolating the calculated pressure–volume points. Here V_0 is the experimental equilibrium volume. Theoretical values given here are obtained using GGA.

using density-functional theory, arrived at $B_0 = 290$ GPa. The method used to solve the Schrödinger equation was the linear muffin-tin orbital (LMTO) method, together with the so-called atomic-sphere approximation (ASA). Clausen et al. [9], using inelastic neutron scattering, got a somewhat lower experimental value of 223 GPa. Harding et al. [10], using the relativistic Dirac-Fock approximation and density functional theory, arrived at the calculated value of 175 GPa for the bulk modulus. Recent calculations by Li et al. [11], using the full-potential linear muffin-tin orbital (FP-LMTO) method, together with the generalized gradient approximation (GGA) resulted in the theoretical values $B_0 = 221$ GPa and $B_0' = 3.2$.

In view of the large scatter of the B_0 values for ThO_2, mentioned above, and the fact that previous XRD measurements have been performed with laboratory X-ray sources, it was thought worthwhile to undertake a remeasurement of the bulk modulus using high-pressure X-ray diffraction in conjunction with synchrotron radiation. In possible support of these measurements, renewed calculations have been undertaken, using the full-potential linear muffin-tin orbital method together with the local density approximation (LDA) as well as the generalized gradient approximation.

2. Experimental procedure

High-pressure powder X-ray diffraction patterns were recorded at room temperature using the white-beam method and synchrotron radiation at Station F3 of HASYLAB-DESY in Hamburg, Germany. The diffractometer, working in the energy-dispersive mode, has been described elsewhere [12]. High pressures up to 70 GPa were obtained in a Syassen–Holzapfel type diamond-anvil cell. A finely ground powder sample and a ruby chip were placed in a 200 μm diameter hole of the inconel gasket, preindented to a thickness of 60 μm. A 16:3:1 methanol:ethanol:water mixture was used as the pressure-transmitting medium. The pressure was determined by measuring the wavelength shift of the ruby R_1 luminescence line and applying the non-linear pressure scale of Mao et al. [13]. The Bragg angle was calculated from a zero-pressure diffraction spectrum of NaCl in the diamond-anvil cell.

From the observed diffraction spectra, the lattice parameters and the unit-cell volume can be derived and refined by a least-squares method. The experimental pressure–volume data can then be described by the Birch [14] or the Murnaghan [15] equations of state:

$$\frac{P}{B_0} = \frac{3}{2}(x^{-7/3} - x^{-5/3})\left[1 + \frac{3}{4}(B_0' - 4)(x^{-2/3} - 1)\right], \tag{2a}$$

$$\frac{P}{B_0} = \frac{(x^{-B_0'} - 1)}{B_0'}. \tag{2b}$$

Here $x = V/V_0$, V is the volume at pressure P, V_0 is the volume at zero pressure, and B_0 and B_0' are the isothermal bulk modulus and its pressure derivative, both parameters evaluated at zero pressure. Values of B_0 and B_0' are obtained from a least-squares fit of Eq. (2a) or (2b) to the experimental pressure–volume points.

3. Computational aspects

In this work, the all-electron full-potential linear muffin-tin orbital method [16] is used for calculating the total energies as well as the basic ground state properties, such as equilibrium lattice constant, bulk modulus and its pressure derivative. This method treats the muffin tin spheres and the interstitial regions on the same footing leading to improvements in the precision of the eigen values. Here the crystal is divided into two regions: non-overlapping muffin-tin spheres surrounding every atom and the interstitial region between the spheres. Within the spheres, the potential is expanded in spherical harmonics, while in the interstitial region it is expanded in terms of plane waves. The exchange correlation energy of the electrons is described in the local density approximation using the parameterisation of Vosks et al. [17] and the generalised gradient approximation using the formalism of Perdew et al. [18]. The charge density and the potential are represented inside the muffin tin spheres (MTS) by spherical harmonics up to $l_{max} = 6$, while in the interstitial region, 12050 plane waves with energies up to 180 Ry were included in the calculation. The basis orbitals used in the present calculation are 7s, 6p, 6d, 5f for Thorium and 2s, 2p orbitals for Oxygen, respectively. Total energies were calculated as a function of reduced volumes ranging from $1.05V_0$ to $0.75V_0$, where V_0 is the experimental equilibrium volume and fitted to the Birch equation of state [14] to obtain the ground state properties.

4. Results and discussions

Fig. 1a shows a diffraction spectrum recorded at ambient pressure. The lattice parameter of the cubic phase (space group $Fm\bar{3}m$) is $a_0 = 5.598(4)$ Å. This value agrees, within the estimated error, with the value $a_0 = 5.596$ Å compiled from literature data [19]. Fig. 1b has been recorded at the pressure 43.5 GPa. The sample is partly transformed, and the spectrum is a mixture of diffraction lines from the low- and high-pressure phases. Fig. 1c shows the fully transformed sample at 55 GPa. Only diffraction lines from the orthorhombic high-pressure phase (space group *Pnma*) are now seen.

Table 1 gives the experimental and theoretically calculated values of the lattice constant, a, and the relative volume, V/V_0, as functions of pressure. The Birch and the Murnaghan equations of state give almost identical results when fitted to the present experimental pressure–volume data. As a final result we quote $B_0 = 195.3 \pm 2.0$ GPa and $B_0' = 5.4 \pm 0.2$, where the uncertainties are the standard errors of the least-squares fit.

The FP-LTMO-LDA calculation slightly underestimates the lattice constant, giving $a_0 = 5.5227$ Å, and consequently overestimates the bulk modulus, giving $B_0 = 224.63$ GPa and $B_0' = 4.2$. In contrast, the data obtained by the FP-LTMO-GGA calculation are in very good agreement with experiment, both for the lattice constant ($a_0 = 5.6113$ Å) and the bulk modulus ($B_0 = 198.44$ GPa and $B_0' = 4.2$) as seen in Table 2. The calculations also show that ThO_2 is a direct bandgap insulator. The band gap is 4.485 eV according to the LDA calculations, and 4.522 eV according to the GGA calculations. This theoretical value of the energy gap underestimates the reported experimental gap value of 6 eV, because of the inherent limitations of the LDA and GGA schemes (Fig. 2).

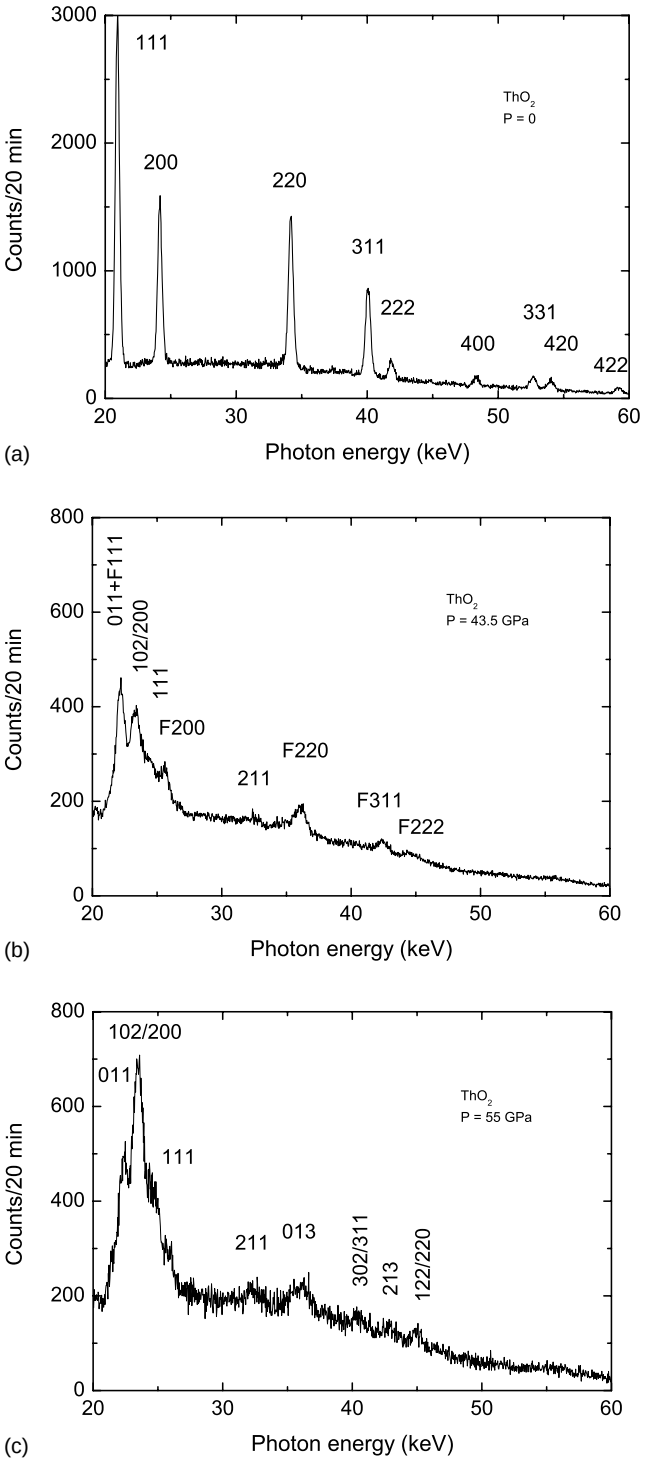

Fig. 1. (a) Indexed diffraction diagram of ThO_2 at ambient pressure. (b) Indexed diffraction diagram at 43.5 GPa showing partly transformed ThO_2. The diffraction peaks due to the fluorite-type low-pressure phase are denoted by F. (c) Indexed diffraction diagram at 55 GPa showing fully transformed ThO_2.

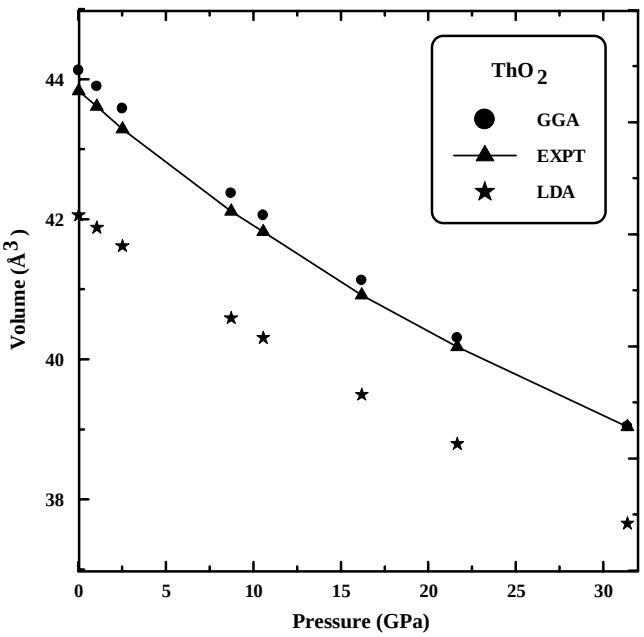

Fig. 2. Compression curve of ThO_2. The full curve has been calculated from the fitted equation of state. Theoretical LDA and GGA values are also shown for comparison.

Table 2
Comparison of experimental and calculated values of the lattice constant, a_0, the zero-pressure bulk modulus, B_0, and its pressure derivative, B_0', of ThO_2

a_0 (Å)	B_0 (GPa)	B_0'	Method	Reference
5.5957			Compiled from literature	Benedict [19]
	193(2)		Ultrasound	Macedo et al. [5]
	193		Ultrasound	Wawra [6]
5.597	278		XRD	Benedict et al. [7]
5.535	290		LTMO-ASA	Kelly and Brooks [8]
	223		Inelastic neutron scattering	Clausen et al. [9]
	175		Dirac-Fock approximation	Harding et al. [10]
5.595(1)	262(4)	6.7(5)	XRD	Dancausse et al. [4]
	221	3.2	FP-LTMO-GGA	Li et al. [11]
	198(1)	4.6(1)	XRD	Idiri et al. [20]
5.598(3)	195(2)	5.4(2)	XRD	Present work
5.523	225	4.2	FP-LTMO-LDA	Present work
5.611	198	4.2	FP-LTMO-GGA	Present work

The number in parenthesis is the estimated error, or the standard deviation of the least-squares fit, in units of the last decimal place. XRD = X-ray diffraction.

During the course of the present work it has been brought to our attention that Idiri et al. [20] have also undertaken a remeasurement of the bulk modulus of ThO_2 using X-ray diffraction and synchrotron radiation. They arrive at $B_0 = 198 \pm 2$ GPa, and $B_0' = 4.6 \pm 0.3$. The value of the bulk modulus is in very good agreement with our result. Thus, it now seems to be well established, experimentally as well as theoretically, that the value of the zero-pressure bulk modulus of ThO_2 is close to 195 GPa.

In conclusion, experiment and theory, after a détour in the 1980s and 1990s, now have settled the value of the zero-pressure bulk modulus of ThO_2 at about 195 GPa.

Acknowledgements

We thank HASYLAB-DESY for permission to use the synchrotron radiation facility. Part of this work was supported by the IHP Contract HPRI-CT-2001-00140 of the European Commission. Financial support from the Danish Natural Science Research Council through DANSYNC is gratefully acknowledged by L.G. and J.S.O. The authors V.K. and G.V. acknowledge the Max-Planck Society for financial support. We are grateful to S. Heathman for communicating his results prior to publication.

References

[1] L. Eyring, Fluorite-related oxide phases of rare earth and actinide elements, in: P.R. Fields, T. Moeller (Eds.), Lanthanide/Actinide Chemistry, American Chemical Society, Washington, DC, 1967.
[2] B.W. Veal, D.J. Lam, Phys. Rev. B 10 (1974) 4902.
[3] A. Jayaraman, G.A. Kourouklis, L.G. Van Uitert, Praman-J. Phys. 30 (1988) 225.
[4] J.-P. Dancausse, E. Gering, S. Heathman, U. Benedict, High Pressure Res. 2 (1990) 381.
[5] P.M. Macedo, W. Capps, J.B. Wachtman, J. Am. Ceram. Soc. 47 (1964) 651.
[6] H.H. Wawra, Radex-Rundschau (1973) 602.
[7] U. Benedict, C. Dufour, J.C. Spirlet, J.S. Olsen, L. Gerward, Proceedings of the 13th Journées des Actinides, Eilat, Israel, 1983.
[8] P.J. Kelly, M.S.S. Brooks, J. Chem. Soc., Faraday Trans. II 83 (1987) 1189.
[9] K. Clausen, W. Hayes, J.E. Macdonald, R. Osborn, P.G. Schnabel, M.T. Hutchings, A. Magerl, Faraday Trans. II 83 (1987) 1109.
[10] J.H. Harding, P.J.D. Lindan, N.C. Pyper, J. Phys. C 6 (1994) 6485.
[11] S. Li, R. Ahuja, B. Johansson, High Pressure Res. 22 (2002) 471.
[12] J.S. Olsen, Rev. Sci. Instrum. 83 (1992) 1058.
[13] H.K. Mao, J. Xu, P.M. Bell, J. Geophys. Res. 91 (1986) 4673.
[14] F.J. Birch, J. Appl. Phys. 9 (1938) 279;
F.J. Birch, Phys. Rev. 71 (1947) 809.
[15] F.D. Murnaghan, Finite Deformation of an Elastic Solid, Wiley, New York, 1951.
[16] S.Y. Savrasov, Phys. Rev. B 54 (1996) 16470.
[17] S.H. Vosks, L. Wilk, M. Nussiar, Can. J. Phys. 58 (1980) 1200.
[18] J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1996) 16533.
[19] U. Benedict, J. Less-Common Metals 128 (1987) 7.
[20] M. Idiri, T. LeBihan, S. Heathman, J. Rebizant, Phys. Rev. B, in press.