ELSEVIER

Journal of Nuclear Materials 277 (2000) 116–119

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Letter to the Editors

Thermal conductivity of ThO_2 and $Th_{0.98}U_{0.02}O_2$

C.G.S. Pillai, P. Raj*

Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Received 27 July 1999; accepted 14 September 1999

Abstract

The thermal conductivity of ThO_2 and $Th_{0.98}U_{0.02}O_2$ was measured from 300–1200 K. Calculations using a simple theoretical model show that the decrease in thermal conductivity of $Th_{0.98}U_{0.02}O_2$ over that of ThO_2 is due to the enhanced phonon–lattice strain interaction in the oxide. It is shown that the intrinsic thermal resistivity arising due to phonon–phonon interaction in these oxides can be quantitatively explained in terms of the modified Leibfried–Schlomann equation of Slack. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The thermal conductivity of fuel elements is one of the most important parameters which determine the fuel temperature. The oxide materials are widely used as nuclear fuel, notwithstanding their low value of thermal conductivity. The mixed oxides exhibit even lower thermal conductivity in comparison with the individual oxides. While several investigations of an extensive nature have been reported on the thermal conductivity of uranium and plutonium oxides and their solid solution with fission products, much less attention has been paid to the thorium and thorium-based oxide systems. The thermal conductivity values reported in literature on $Th_{1-x}U_xO_2$ oxides show a wide spread in the data [1–5]. Much of this variation, most probably, arises due to the impurities and the inhomogeneity present in the samples used for the measurements. Complete characterization of materials investigated is seldom reported for judicious intercomparison. Further, appropriate theoretical expressions have not been identified to account for the observed thermal conductivity arising due to the different modes of heat conduction [6–8]. In the present study, the thermal conductivity of pure ThO_2 and $Th_{0.98}U_{0.02}O_2$ solid solution has been measured in the temperature range 300–1200 K. The phonon-defect and the phonon–phonon interaction modes of heat conduction are delineated. The latter mode of heat conduction is quantitatively accounted for by the modified Leibfried–Schlomann equation of Slack [8].

2. Experimental

Samples for the measurements were prepared from nuclear pure ThO_2/UO_2 powder. Cylindrical samples of 2.5 cm in diameter and ≃2 cm in height required for the thermal conductivity measurements were prepared by uniaxial cold compaction of the powder at 300 MPa pressure followed by sintering at 1925 K in N_2/8% H_2 for 4 h. Their bulk densities were found to be 94% of the theoretical value. The oxides were characterised by X-ray diffraction analysis, using a powder diffractometric technique. The patterns were obtained by Ni filtered CuKα radiation and a computer controlled X-ray diffractometer PW 1820 with PW 1710 microprocessor.

The thermal conductivity of the samples was measured in air in the temperature range 300–1200 K by a steady state axial heat flow comparative apparatus. In this, the sample is inserted between two identical reference materials (pyroceram 9606 certified against NBS, USA) having the same diameter as that of the sample. An axial heat flow is established through this three-element stack by sandwiching it between a heat source and

---

[*] Corresponding author. Tel.: +91-22 550 5148; fax: +91-22 550 5151.

E-mail address: praj@apsara.barc.ernet.in (P. Raj).

PII: S0022-3115(99)00237-8

a heat sink. The conductivity of the sample is determined from the thermal conductivities of the references and the measured temperature gradients of the sample and the references. The temperature gradients were measured with thermocouples inserted into the axially displaced radial holes. The thermal resistance at the interfaces of the sample and the reference was minimized by introducing a thin platinum foil of 0.01 mm thickness between two finely polished interfaces of each cylinder. This also helps to avoid any reaction between the contacting faces of the sample and the reference. The radial heat loss from the sample stack is minimized by inserting it into a guard furnace consisting of four separate heaters. The accuracy of the measurements is within ±3%. More details of the experimental apparatus have been described elsewhere [9].

3. Results

The measured thermal conductivity values of ThO_2 and $Th_{0.98}U_{0.02}O_2$ were corrected for porosity employing the simplified equation of Leob [10]. The corrected thermal conductivity is plotted as function of temperature in Fig. 1. From the figure, it is clear that the thermal conductivity of these oxides decreases with increase in temperature. The observed conductivity of ThO_2 is found to be higher than that of UO_2 [11] and is in good agreement with that reported in the literature [12] in the entire temperature range. It is also noted that the addition of uranium in thorium oxide decreases the conductivity and this decrease is predominant at low temperatures.

As in the case of typical ceramic oxide systems, the temperature dependence of the thermal resistivity (R), which is the reciprocal of the thermal conductivity (λ), of these oxides can be described by the following equation:

$$R = \frac{1}{\lambda} = A + BT, \tag{1}$$

where T is the absolute temperature and A and B are constants which can be obtained from the least squares fitting of the experimental data. The linear variation of resistivity with temperature and the fitted values of the constants A and B are shown in Fig. 2. The value of A is found to be higher for $Th_{0.98}U_{0.02}O_2$ than that of pure ThO_2, whereas B is nearly the same for both these oxides within the limits of experimental error.

4. Discussion

The observed linear variation of the thermal resistivity with temperature (Fig. 2) reveals that, in the temperature range under investigation, the heat conduction is predominantly due to phonon scattering interactions [13]. Accordingly, A, the first term in Eq. (1), represents the defect thermal resistivity. This results from the phonon interactions with lattice imperfections, impurities, isotopic or other mass differences as well as bulk defects such as grain boundaries in the sample. As these factors depend on the sample purity as well as on exact preparation conditions, the values reported for A by different authors show large variations and cannot be easily quantified. However, contributions from these factors remain fairly constant when the purity of the starting oxide materials and the preparation conditions are identical. The second term in Eq. (1), namely BT, represents the intrinsic lattice thermal resistivity caused by phonon–phonon scattering interactions. As the temperature increases, this term becomes predominant. Various contributions which add up to account for the A and B terms and their relationship with thermophysical and structural parameters are as follows.

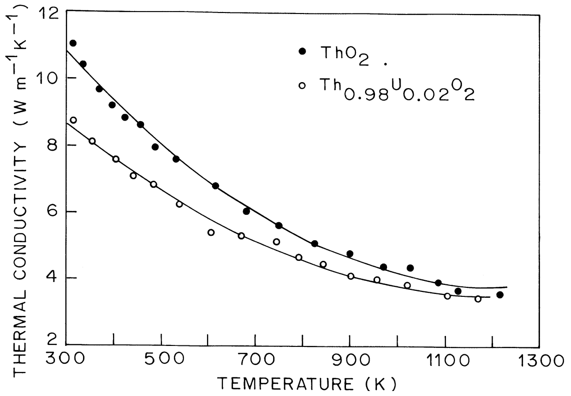

Fig. 1. Thermal conductivity of ThO_2 and $Th_{0.98}U_{0.02}O_2$ as a function of temperature.

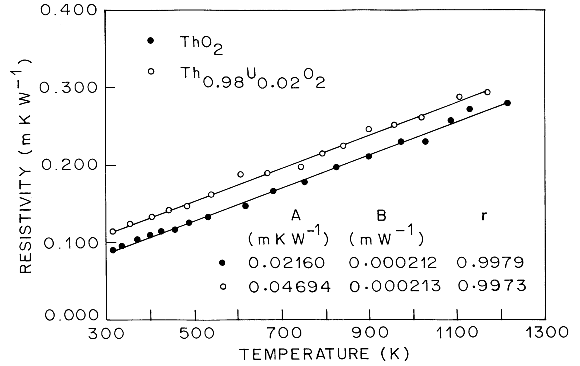

Fig. 2. Thermal resistivity of ThO_2 and $Th_{0.98}U_{0.02}O_2$ as a function of temperature. Solid lines are determined by fitting the thermal conductivity data to a relation $R = 1/\lambda = A + BT$, using the least squares method.

4.1. Defect thermal resistivity

The analysis of the lattice defect thermal resistivity and the evaluation of phonon scattering by the various defect scattering centres in pure and mixed actinide oxides have been carried out by several authors [14–17]. They have adopted the theoretical treatment of the problem as given by Ambegaokar [18]. Accordingly, A of Eq. (1) can be given as

$$A = [(\pi^2 V\theta)/(3hv^2)]\Sigma_i \Gamma_i, \tag{2}$$

where V, θ, h and v denote the average atomic volume, Debye temperature, Planck's constant and phonon velocity, respectively. The term $\Sigma_i \Gamma_i$ is the sum of the cross sections of all the phonon-defect scattering centres. The U atoms substituted for Th in the lattice introduce additional scattering centres for phonons because of their mass and ionic size difference leading to an increase in the defect thermal resistivity in $Th_{0.98}U_{0.02}O_2$. Hence, the summation of the scattering cross section in this case can be expressed as

$$\Sigma_i \Gamma_i = \Gamma_u + \Gamma_o, \tag{3}$$

where Γ_u is the scattering cross section arising from U atom substitution and Γ_o is that from all other native defects present in the sample, assumed to be equal to that of pure ThO_2. Thus, Eq. (2) can be written as

$$A = C(\Gamma_u + \Gamma_o), \tag{4}$$

where $C = (\pi^2 V\theta)/(3hv^2)$ and $C\Gamma_o$ equals the experimentally observed A value of pure ThO_2. The calculated value of C for ThO_2 is found to be 2.75 m K W^{-1} using the cell volume of 26.8 cm^3 mol^{-1}, $\theta = 393$ K [19] and the average phonon velocity v computed from the Debye approximation [18]:

$$v = (2\pi k\theta/h)(V/6\pi^2)^{1/3}, \tag{5}$$

where k is Boltzmann's constant.

The scattering cross section Γ_u can be expressed in terms of the mass and size difference of the substituted atom over that of the host [14,20]:

$$\Gamma_u = (1-x)x\left[\left(\frac{\Delta M}{\overline{M}}\right)^2 + \epsilon\left(\frac{\Delta r}{\overline{r}}\right)^2\right], \tag{6}$$

where x is the atomic fraction of the substituted U in place of Th, ΔM and Δr are the mass and radius difference between U and Th atoms, respectively. $\overline{M}$ and $\overline{r}$ are the average mass and radius, respectively, of the substituted oxide and ϵ is an adjustable parameter.

Assuming that the C value for $Th_{0.98}U_{0.02}O_2$ is the same as that estimated for pure ThO_2, the contribution of the mass difference to the thermal resistivity for the mixed oxide is calculated using Eqs. (4) and (6). It is found to be much less than the additional defect resistivity observed for this oxide. In view of a rather large range of values assumed for ϵ in U/Th oxide systems [14–17], it is not possible to quantify the contribution due to the size difference to the observed thermal resistivity. Thus, it can only be inferred that the observed difference in thermal resistivity is mostly due to the phonon lattice–strains interaction resulting from the size difference between the Th and U atoms.

4.2. Intrinsic thermal resistivity

Different theoretical expressions have been derived for the estimation of the intrinsic thermal resistivity arising due to phonon–phonon interaction processes in dielectric solids (BT term in Eq. (1)) [6–8]. Because of the high divergence found between values obtained from theoretical calculations and experimental data, its relation to the structural and thermodynamic parameters has not been satisfactorily delineated. Due to the uncertainty in the evaluated values, Gibby [14] and Fukushima et al. [15] calculated the variation of the intrinsic thermal resistivity of the mixed oxide by taking the ratio of the substituted oxide with that of the pure oxide based on the Leibfried–Schlomann relation [6]. In an earlier work on the thermal conductivity of UO_2 [11], we have calculated the intrinsic thermal conductivity of UO_2 using the Slack expression [8] obtained by modifying the Leibfried–Schlomann relation.

The Slack expression for B is given as [8]

$$1/B = (3.04 \times 10^{-6}\overline{M}d\theta^3)/(n^{2/3}\gamma^2), \tag{7}$$

where $d = V^{1/3}$ (in Å), γ is the Grüneisen parameter, n is the number of atoms per molecule and the other terms are as defined previously. Using $\gamma = 2$ [8], $n = 3$ and other parameter as defined earlier, the calculated value of

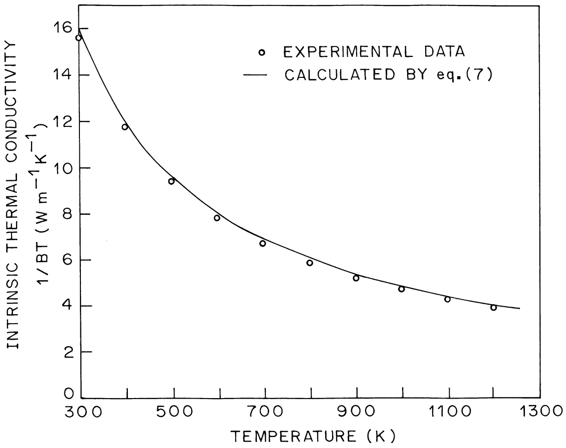

Fig. 3. Intrinsic phonon thermal conductivity of thorium dioxide obtained from experimental data and computed using the Slack's equation (7), given as a function of temperature.

B is found to be (2.091×10^{-4} m W^{-1}) for ThO_2. This value is in good agreement with that obtained from the experimental data of 2.12×10^{-4} m W^{-1} (Fig. 2). The phononic intrinsic conductivity calculated using the theoretical and experimental values of *B* are plotted in Fig. 3 in the temperature range 300–1200 K. The deviation observed is insignificant. Thus, Slack's expression provides a highly acceptable theoretical solution for the calculation of the intrinsic phonon conductivity of thorium oxide as well as that of uranium oxide reported earlier [11]. It is also interesting to note that the intrinsic thermal conductivity is found to be the same for both the pure ThO_2 and the substituted oxide, $Th_{0.98}U_{0.02}O_2$. This can be justified from Eq. (7) where the parameters involved are not significantly affected by the small amount of substitution of uranium for thorium in the oxide.

5. Conclusions

The addition of uranium atoms in ThO_2 decreases its thermal conductivity and this variation is ascribed to the phonon–defect interaction processes arising due to the mass and size difference between the Th and the U atoms. The theoretical treatment shows that the phonon-mass difference scattering contribution is insignificant compared to that due to the observed defect resistivity. It is also shown that the theoretical expression of Slack obtained by the modified LS equation is able to account quantitatively for the observed intrinsic phonon conductivity in these oxides.

Acknowledgements

The authors are grateful to Dr J.P. Mittal, Director, Chemistry and Isotope Group, BARC for the encouragement. Thanks are also due to Mr R. Ramachandran and Mr M.R. Nair of Radio Metallurgy Division, BARC, Mr V.G. Date and Mr P. Sundararajan of Atomic Fuels Division, BARC, for the sample preparation.

References

[1] W.D. Kingery, J. Am. Ceram. Soc. 42 (1959) 617.
[2] M. Murabayashi, S. Namba, Y. Takahashi, J. Nucl. Sci. Technol. 6 (1969) 128.
[3] J. Belle, R.M. Berman, W.F. Bourgeois, I. Cohen, R.C. Daniel, Westinghouse Report WAPD-TM 586, 1967.
[4] J.P. Moore, B.S. Graves, T.G. Kollic, D.L. McElroy, Oak Ridge National Laboratory Report ORNL-4121, 1967.
[5] C. Ferro, C. Patirno, C. Piconi, J. Nucl. Mater. 43 (1972) 273.
[6] G. Leibfried, E. Schlomann, Nachr. Akad. Wiss. Göttingen Math. Phys. Kl 4 (1954) 71.
[7] M. Roufosse, P.G. Kelmen, Phys. Rev. B 7 (1973) 5379.
[8] G.A. Slack, in: H. Ehrenreich, F. Seitz, D. Turnbull (Eds.), Solid State Physics, vol. 34, Academic Press, New York, 1979, p. 1.
[9] C.G.S. Pillaim, A.M. George, Int. J. Thermophys. 12 (1991) 563.
[10] A.L. Loeb, J. Am. Ceram. Soc. 37 (1954) 96.
[11] C.G.S. Pillai, A.M. George, J. Nucl. Mater. 200 (1993) 78.
[12] K. Bakker, E.H.P. Cordfunke, R.J.M. Konings, R.P.C. Schram, J. Nucl. Mater. 250 (1997) 1.
[13] P.G. Klemens, in: F. Seitz, D. Turnbull (Eds.), Solid State Physics, vol. 7, Academic Press, New York, 1958, p. 1.
[14] R.L. Gibby, J. Nucl. Mater. 38 (1971) 163.
[15] S. Fukushima, T. Ohmichi, A. Maeda, H. Watanabe, J. Nucl. Mater. 105 (1982) 201.
[16] S. Fukushima, T. Ohmichi, A. Maeda, M. Handa, J. Nucl. Mater. 115 (1983) 118.
[17] P. Srirama Murti, C.K. Mathews, J. Phys. D 24 (1991) 2202.
[18] V. Ambegaokar, Phys. Rev. 114 (1959) 488.
[19] B.T.M. Willis, Proc. Royal. Soc. London A 274 (1963) 134.
[20] B. Abeles, Phys. Rev. 131 (1963) 1906.