Models of thermophysical properties of uranium dioxide

Yu N Devyatko¹, V V Novikov², V I Kuznetsov², O V Khomyakov¹ and D A Chulkin²

¹National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe highway, 115409 Moscow, Russia
²Join Stock Company “A.A. Bochvar High-Technology Research Institute of Inorganic Materials”, 5a Rogova st., 123098 Moscow, Russia

E-mail: homaykov_o_v@rambler.ru

Abstract. Physical models of specific heat at constant volume and thermal conductivity of uranium dioxide are developed based on phonon spectrum data. It is explained an abnormal growth of thermal conductivity coefficient of oxide nuclear fuel in high temperature region. It is shown that the contribution from charge carrier’s degrees of freedom into observed thermal conductivity coefficient of uranium dioxide can be neglected up to melting point. Developed models of thermophysical properties do not contain fitting parameters.

1. Introduction

The thermal conductivity of uranium dioxide is measured in the wide range of temperatures [1-4]. An unalloyed (pure) uranium dioxide of stoichiometric composition upon its electrophysical properties represents the typical dielectric because its energy gap width is great and is equal to $\varepsilon_G = 2.7-3$ eV [5]. An electron concentration in the conduction band at such energy gap value in the temperature range $1000 < T < 3100$ K is $4 \cdot 10^{12} < n_e < 3 \cdot 10^{18}$ cm$^{-3}$ that significantly lower than in conductor ($n_e \sim 10^{22}$ cm$^{-3}$) or in intrinsic semiconductor ($n_e \sim 10^{19}$ cm$^{-3}$). Therefore the contribution of charge carriers to the process of heat transmission in the uranium dioxide is negligible compared with its lattice thermal conductivity in this temperature range.

It’s known that the processes of heat transmission are realized in the dielectrics by the quasiparticles - phonons. The thermal conductivity coefficient $\lambda(T)$ falls with increasing temperature according to the power law $\lambda(T \gg \theta_D) \sim 1/T^x$ ($x \sim 1-2$) for the most dielectrics at temperatures higher than Debye temperature $\theta_D$ [7]. However, on the graph (see Figure 1) of experimental temperature dependence of the uranium dioxide thermal conductivity there is temperature region $1800 < T < 3100$ K in which thermal conductivity coefficient increases with temperature. While the uranium dioxide thermal diffusivity falls monotonically in high-temperature region in according with Debye law (see Figure 2). Such abnormal growth of uranium dioxide thermal conductivity contradicts to the heat transmission theory in the dielectrics and therefore it is connected either with an inaccuracy of measurements or with the calculation error. Therefore for an explanation of high-temperature thermal conductivity is required a physical (uncorrelation) model applicable in temperature range inaccessible for the carrying out of experiment with required degree of accuracy.

The purpose of this work is to develop a model of thermal conductivity of unalloyed, stoichiometric uranium dioxide.
2. The abnormal growth of uranium dioxide thermal conductivity in high-temperature range

The thermal conductivity of dielectrics represents the quantity determined at constant volume because according to the Second law of thermodynamics exactly in this case the change of internal energy ($\Delta U$)$_V$ is equal to heat quantity ($\Delta Q$)$_V$ received or given by the sample. In the system at constant volume the thermal conductivity equation takes the canonical form:

$$\nabla \left( \frac{\partial Q}{\partial t} \right)_V = \nabla \left( \lambda(T) \nabla T \right) \Leftrightarrow C_v \rho \frac{\partial T}{\partial t} = \nabla \left( \lambda(T) \nabla T \right), \quad C_v = \frac{1}{\rho V} \left( \frac{\partial Q}{\partial T} \right)_V, \quad (1)$$

where $C_v(T)$ is specific heat at constant volume, $\rho=10.96$ g/cm$^3$ is density of uranium dioxide.

In practice it is impossible to provide the condition of volume constancy due to phenomenon of thermal expansion of solids therefore the measurement of thermophysical properties is carried out at constant pressure. In systems at constant pressure it is accomplished the work on thermal expansion ($\Delta Q$)$_P = (\Delta U)_P + A$ which necessary to take into consideration in the heat balance equation:

$$C_P \rho \frac{\partial T}{\partial t} = \nabla \left( \lambda(T) \nabla T \right) + \frac{1}{V} \left( \frac{\partial A}{\partial t} \right)_P, \quad C_p = \frac{1}{\rho V} \left( \frac{\partial Q}{\partial T} \right)_P, \quad (2)$$

where $C_p(T)$ is specific heat at constant pressure.

The last term in the thermal conductivity equation (2) is proportional to the heating rate of solid and can be rewritten using directly measured physical magnitudes:

$$\frac{1}{V} \left( \frac{\partial A}{\partial t} \right)_P = (3\alpha)^2 B_r T \frac{\partial T}{\partial t}. \quad (3)$$

Here $\alpha(T)$ is the coefficient of linear thermal expansion (CLTE), $B_r = \left[ -\frac{1}{V \left( \frac{\partial V}{\partial T} \right)_T} \right]^{-1}$ is the compression modulus at constant temperature.

Specific heat at constant volume is connected with specific heat at constant pressure by thermodynamic relation [7]:

$$C_p - C_v = \frac{(3\alpha)^2 B_r T}{\rho}. \quad (4)$$
Substitution of specific heat at constant pressure from Eq. (4) into thermal conductivity equation at constant pressure (2) leads to its canonical form (1).

Nowadays the laser flash method [9] is used for measurement of thermal conductivity of high-temperature ceramics. Within this method from the non-steady thermal conductivity equation (2) the thermal diffusivity coefficient \( \chi(T) \) of studied ceramic sample is being restored. Since thermal conductivity equations in the form (2) and in the form (1) are equal then thermal conductivity coefficient is being calculated as a product of thermal diffusivity and specific heat at constant volume of studied ceramic.

\[
\lambda(T) = C_v(T) \rho \chi(T). \tag{5}
\]

However the authors of experimental works usually do not take into consideration the anharmonic forces work in the equation (2) formally supposed that \( \lambda(T) = C_p(T) \rho \chi(T) \) what leads to systematic error in the thermal conductivity coefficient. The difference between specific heat at constant volume and specific heat at constant pressure increases with temperature faster than thermal diffusivity decreases. The admission of this systematic error leads to abnormal nonphysical growth of the uranium dioxide thermal conductivity coefficient at high temperatures.

For taking into consideration an anharmonic corrections the uranium dioxide thermal conductivity coefficient within laser flash method should be calculated using relation (5). Specific heat at constant volume is design value for which it is necessary to build the corresponding model.

3. A model of the uranium dioxide specific heat at constant volume

The uranium dioxide has the fluorite–type crystal lattice \( \text{CaF}_2 \) with the lattice constant \( a=547 \, \text{pm} \) at room temperature. Since unit cell contains \( g=3 \) atom types – uranium atom (U) and 2 oxygen atoms (O) then there is 9 branches in the spectrum of normal modes: 3 phonon branches are acoustic and 6 are optical.

By definition the specific heat of uranium dioxide at constant volume per unit volume [6,7] is given by:

\[
C_v(T) = 3gR \frac{\partial}{\partial (k_B T)} \int_0^{\omega_{\text{max}}} d\omega D(\omega) \hbar \omega \bar{n}(\omega, T). \tag{6}
\]

Here \( \omega_{\text{max}} \) is the maximum frequency in the spectrum of normal modes of uranium dioxide; \( R=8.31 \, \text{J/(mol-K)} \) is universal gas constant; \( \bar{n}(\omega, T) = \left[ \exp(\hbar \omega / k_B T) - 1 \right]^{-1} \) is Bose-Einstein distribution for phonons, \( D(\omega) \) is the phonon density of states (fig. 3) [10].

![Figure 3. Phonon density of states [10].](image1)

![Figure 4. The comparison of the calculated specific heat at constant volume with specific heat at constant pressure experimental data [12-16].](image2)
The uranium dioxide specific heat as analytical function of absolute temperature could be obtained introducing the model phonon density of states instead an experimental phonon density of states. This approach is founded because specific heat is an integral value over phonons spectrum. The introduced model phonon density of states should be normalized per unit and must have characteristic frequencies coinciding with characteristic frequencies of experimental phonon spectrum.

We will take into consideration acoustic phonon branches within Debye model and optical within Einstein model. Then the model density of states would be chosen in the following form:

$$D(\omega) = \frac{1}{g} \frac{3\omega_0^2}{\omega_D^2} \eta(\omega_D - \omega) + \frac{2}{3g} \delta(\omega - \omega_{E_1}) + \frac{2}{3g} \delta(\omega - \omega_{E_2}) + \frac{2}{3g} \delta(\omega - \omega_{E_3}),$$  \hspace{1cm} (7)

where $\eta(x)$ is the Heaviside function; $\delta(x)$ is the Dirac delta function; $\omega_0=22$ THz is the uranium dioxide Debye frequency [11]. The Einstein frequencies for optical branches of normal modes spectrum which determined using fig.3 are equal to $\omega_{E_1} = 2\pi\nu_{E_1} = 51.1$ THz, $\omega_{E_2} = 2\pi\nu_{E_2} = 82.3$ THz, $\omega_{E_3} = 2\pi\nu_{E_3} = 109$ THz, respectively.

Substituting density of phonon states (7) to the Eq. (6) we will get the formula for calculation of specific heat at constant volume within proposed model:

$$C_v(T) = 3gR \left[ \frac{4}{g} \left( \frac{T}{\theta_D} \right)^3 \right] I_3 \left( \frac{\theta_D}{T} \right) \frac{3}{g} \frac{\theta_D/T}{\exp(\theta_D/T) - 1} + \frac{2}{3g} \sum_{i=1}^{3} \left( \frac{\theta_{E_i}}{T} \right)^2 \frac{\exp(\theta_{E_i}/T)}{[\exp(\theta_{E_i}/T) - 1]^2} \right] .$$  \hspace{1cm} (8)

Here $I_3(z) = \int_0^\infty \frac{x^3}{\exp(x) - 1} dx$ is the Debye integral of third order. The characteristic temperatures in (8) are equal to $\theta_D = \hbar\omega_D/k_B = 168$ K, $\theta_{E_1} = \hbar\omega_{E_1}/k_B = 391$ K; $\theta_{E_2} = \hbar\omega_{E_2}/k_B = 629$ K; $\theta_{E_3} = \hbar\omega_{E_3}/k_B = 836$ K, respectively.

On the figure 4 it is shown the comparison of model specific heat at constant volume of uranium dioxide (8) with experimental temperature dependence of uranium dioxide specific heat at constant pressure [12-16]. It is seen that the calculated specific heat at constant volume $C_v$ in the temperature range $35<T<100$ K coincides with the low-temperature part of specific heat at constant pressure $C_p$ within marker thickness. It indicates a validity of choice of the phonon density of states in (7).

The formula (8) is not applicable for the calculation of specific heat at constant volume within proposed model:

$$C_v(T) = C_v(\theta_E) \left( \frac{\theta_E}{T} \right)^{0.89} ,$$  \hspace{1cm} (9)

where $C_v(\theta_E) = 1.3$ mm$^2$/s is the value of thermal diffusivity at $T = \theta_E$.

To calculate the thermal conductivity $\lambda$ let us apply developed in the present study a model of uranium dioxide specific heat at constant volume. Finally, substituting Eq. (8) into relation (5) we obtain:

$$\lambda(T) = \frac{9R}{M} \left[ 4 \left( \frac{T}{\theta_D} \right)^3 I_3 \left( \frac{\theta_D}{T} \right) - \frac{\theta_D/T}{\theta_0/T} \frac{e^{\theta_0/T}}{e^{T/\theta_0} - 1} + \frac{2}{g} \sum_{i=1}^{3} \left( \frac{\theta_{E_i}}{T} \right)^2 \frac{e^{\theta_{E_i}/T}}{e^{\theta_{E_i}/T} - 1} \right] \chi(\theta_{E_3}) \left( \frac{\theta_{E_3}}{T} \right)^{0.89} \cdot \rho ,$$  \hspace{1cm} (10)

where $M = 270$ g/mol is molar mass of uranium dioxide.
On the figure 1 it is shown the results of comparison of calculated (equation (10)) and experimental [1-4] thermal conductivity of UO$_2$ as functions of temperature. It is obvious that in whole temperature range the calculated coefficient of thermal conductivity $\lambda(T)$ is closed to the experimental points. Therefore, for calculation of the thermal conductivity of oxide nuclear fuel in the temperature range 400 < T < 2800 K is recommended to use semi-empirical formula (10).

5. Conclusion
Unalloyed stoichiometric uranium dioxide shows dielectric properties up to melting temperature since the charge carrier concentration in its conduction band and valence band is negligibly small compared with the typical intrinsic semiconductor. It is shown that the abnormal growth of the thermal conductivity of uranium dioxide at high temperatures (T > 1800 K) is the systematic error. This growth is a consequence of neglecting of the anharmonic forces work on the thermal expansion of solids during process of measurement of UO$_2$ thermal conductivity by laser flash method. Based on the experimental phonon spectrum a model of specific heat at constant volume of uranium dioxide is constructed which describes the experimental data on specific heat of UO$_2$ at constant pressure $C_p$ in the low temperature range as well as Dulong and Petit limit $C_v = 9R$ in high-temperature range. The calculated thermal conductivity of uranium dioxide obeys the Debye law $\sim 1/ T^{3.9}$ at higher temperatures.

Acknowledgements
This work was performed within the framework of the Center of Nuclear Systems and Materials supported by MEPhI Academic Excellence Project (contract № 02.a03.21.0005, 27.08.2013).

References
[1] Scientific report 1976 № 74-3-10A
[2] Moore J P and McElroy D L 1971 J. Am. Ceram. Soc. 51 (1) 40
[3] Ronchi C, Sheindlin M, Musella M, Hyland G J 1999 J. Appl. Phys. 85 776
[4] Godfey T G, Fulkerson W, Kollie T G, Moore J P and McElroy D L 1965 J. Am. Ceram. Soc. 48 (6) 297
[5] Willardson R K, Moody J W and Goering H L 1958 J. Inorg. Nucl. Chem. 6 19
[6] Ziman J M 2001 Electrons and Phonons: The Theory of Transport Phenomena in Solids (Oxford University Press)
[7] Ashcroft N W and Mermin N D 1976 Solid State Physics (Harcourt College Publisher)
[8] Hobson I C, Taylor R and Ainscough J B 1974 J. Phys. D: Appl. Phys. 7 1003
[9] Parker W J, Jenkins R J, Butler C P and Abott G L 1961 J. Appl. Phys. 32 (9) 1679
[10] Dolling G, Cowley R A and Woods A 1965 Canadian Journal of Physics 43 (8) 1397
[11] Devyatko Yu N, Khomyakov O V, Kuznetsov V I, Chulkin D A 2015 Atomic Energy 118 (3) 179
[12] Engel T K 1969 J. Nucl. Mater. 31 211
[13] Gronvold F, Kveseth N J, Sven A et al. 1970 J. Chem. Therm. 2 665
[14] Huntzicker J J and Westrum E F 1971 J. Chem. Thermodyn. 3 61
[15] Inaba H, Naito K and Oguma M 1987 J. Nucl. Mater. 149 341
[16] Takahashi Y and Asou M 1993 J. Nucl. Mater. 201 108