FIRST PRINCIPLES MOLECULAR DYNAMICS STUDIES OF OXYGEN SUB-LATTICE MELTING IN THORIA

B. Szpunar[1] and J.A. Szpunar [2]
[1] Department of Physics and Engineering Physics, University of Saskatchewan,
Saskatoon, SK S7N 5E2, Canada
[2] Department of Mechanical Engineering
Saskatoon, SK S7N 5A9, Canada
B.Szpunar@usask.ca, jerzy.szpunar@usask.ca

Abstract

We apply first principles molecular dynamics to investigate the order-disorder transition in the oxygen sub lattice, observed experimentally in thoria. The mean-square displacements were calculated at temperatures of 3000 K, 3300 K and 3600 K and we demonstrated that oxygen atoms become mobile, while they stay confined at 2700 K. The rate of diffusion of oxygen atoms was calculated while, for thorium, the mean-square amplitudes of vibrations were evaluated.

Keywords: Sub-lattice melting, Diffusion, Thermal expansion, *Ab initio* molecular dynamics, Thoria

1. Introduction

Although many metal oxides, for example thoria have been investigated for some time [1], their high temperature behaviour, is not well understood. Therefore in our recent work, we have presented an attempt at applying first-principles calculations to evaluate the high temperature thermo-mechanical properties of thoria [2]. We have demonstrated that the more recently proposed GGA: WC functional [3] leads to improved lattice constant values (a), with bulk modulus (B) in agreement with experiment.

Additionally we found previously [2] that the longitudinal optical mode gradually softens with the temperature and for lattice constants corresponding to temperature 2700 K or higher the negative frequency in the longitudinal optical mode appears at q-point X. The 2700 K temperature coincides with the reported premelting transition in thoria, which is attributed to order-disorder transition in the oxygen sub-lattice in thoria (between 2600 to 3300 K [4] and λ-type premelting transition around 3090 K [5]). It was also confirmed by neutron diffraction measurement [6] that a dramatic increase in the oxygen defect concentration in ThO_2 occurred at these temperatures. It is also noteworthy that this transition appears in urania near the temperature 2670 (30) K [7] when Frenkel defect concentration becomes saturated. We expect that this phenomenon occurs in other metal dioxides with fluorite type structure, therefore we propose here to use first principles calculations to confirm it.

2. Methodology

In order to examine the premelting in thoria, we repeated the first-principles molecular dynamics simulations [2] using an Andersen-Hoover barostat [8,9], but with a fixed centre of mass and only for the temperatures where premelting occurs (with selected temperatures: 3000, 3300 and 3600 K) and constant pressure (1 atm) [10]. We used a unit cell eight times larger than conventional (96 total number of atoms), with periodic boundary condition. We reduced the grid for k-points for this super-cell to 2x2x2 and electron energy tolerance to 2×10^{-6} eV. As with our previous calculations [2], we set-up the cutoff energy equal to 500 eV with implemented on-the-fly generated (OTFG) pseudopotentials [11], which were developed within the CASTEP code [12]. The scalar relativistic corrections were found to be important for core (non-valence) electrons, therefore scalar relativistic atomic calculations are used for generation of pseudopotentials. It has been shown previously that this level of theory allows one to achieve qualitative agreement with experiment for such a sensitive probe of electronic structure as the electron energy loss spectra, EELS, for a variety of cubic oxides including urania [13].

3. Results

We did the calculations for a longer time than previously [2]: up to 23.013 ps (for 3000 K) and the time-step of 0.001 ps. We observed that at 3000 K oxygen atoms already became mobile while thorium atoms only vibrated. In Fig. 1, we present the radial distribution function for temperatures from 2400 to 3300 K for both oxygen and thorium atoms, derived from our previous calculations.

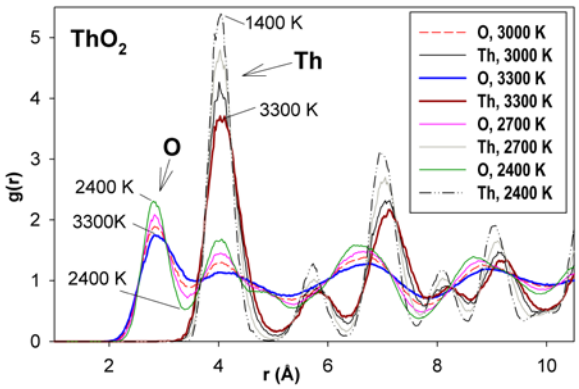

Figure 1 Calculated radial distribution function (RDF) of thorium and oxygen atoms in thoria at 2400, 2700, 3000 and 3300 K temperatures, as indicated.

The sharp maxima and minima can be seen in RDF for thorium atoms even at 3300 K (indicated by a thick brown solid line) while oxygen atoms become disordered between 3000 and 3300 K with the first minimum and second maximum almost disappearing (solid blue thick line indicates 3300 K). However, although the radial distribution function presented in Fig. 1 indicates shifts of oxygen atoms, we need to study mean square displacement as a function of time to confirm theirs mobility. In Fig. 2 we present the running averages of the lattice constants (a in Å), simulated by CASTEP (WC functional) molecular dynamics, as a function of temperature. We combined the previous calculations [2] for up to 3300 K (indicated by open black squares) with the new calculations for longer time and fixed mass centre and for higher temperatures of 3000 – 3600 K (indicated by solid black triangles). We see that the old and new predictions of the lattice constants agree well for 3000 K and 3300 K. There are no experimental results available at high temperatures but, as discussed before, the calculated lattice constants of thoria

agree with available experimental data [14], which are indicated by blue open diamonds in Fig. 2. We also include in Fig. 2 a parabolic fit to the previously simulated lattice constants [2] in the temperature range 273 K to 3300 K, indicated by the black dashed line, while the solid thick red line is the respective parabolic fit to the new calculated lattice constants at temperatures from 3000 K to 3600 K.

As discussed before, the linear thermal expansion coefficient, shown in the insert in Fig. 2, has a low temperature slope (~$3.99\times10^{-9}K^{-2}$) similar to the observed one [15] (indicated by blue triangles) ~$3.96\times10^{-9}K^{-2}$, but higher than that derived from the wider temperature range in the earlier experimental data [16]: ~$2.15\times10^{-9}K^{-2}$. The pseudopotentials and WC functional used here slightly overpredict the thermal expansion. The earlier quasi-harmonic approximation calculations (e.g. [17,18]) show better agreement with experiment but are limited to a low temperature range. Our recent tests (described elsewhere) for the same temperature range indicate that thermal expansion is sensitive to the quality of the pseudopotentials and some norm-conserved potentials lead to thermal expansion predictions that have very good agreement with experiment. However, these potentials cannot be used in our molecular dynamics calculations, which are already very demanding on computational resources. Although the linear thermal expansion is predicted to be larger than available experimental results [16], it should also be noted that the calculations are done for a bulk structure, while thoria samples used in experiments contain defects and often are not fully dense.

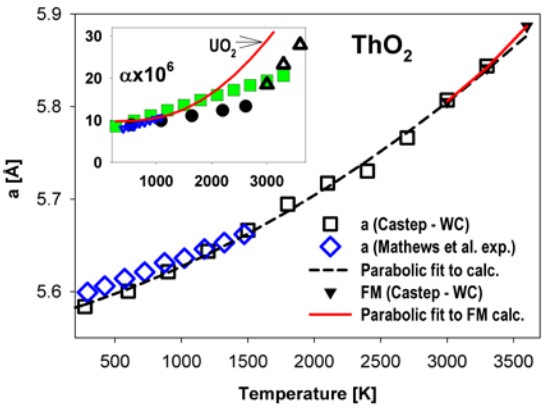

Figure 2 The calculated lattice constants of thoria as a function of temperature (open black squares indicate the previous results [2] and black solid triangles are new results) are shown versus experimental data (open diamonds) [14]. The black dashed and red thick solid lines show the parabolic fit to the previous [2] and present calculated data, respectively. In the insert, the derived linear thermal expansion coefficient (α in K^{-1}) is shown (filled green squares from Ref. [2] and black open triangles from present calculations) versus experimental points (filled black circles [16] and blue triangles [15]). Additionally, a red solid line shows the Fink correlation [7] for UO_2.

The new molecular dynamics calculation with the fixed centre of mass allows us to evaluate the mean-square displacements, which provide information on vibrational amplitudes for fixed atoms and diffusion constants for atoms that are mobile. In Fig. 3, we see clearly that mean-square displacements of oxygen atoms at temperatures from 3000 K to 3600 K are linearly dependent on time ($MSD = At + B$), indicating that oxygen atoms are mobile. In contrast, the respective mean-square displacements of thoria shown in the insert do not increase with time but increase with temperature and therefore represent only mean square amplitudes of vibrations of thoria, which is immobile at these temperatures.

This result also estimates that bulk thoria's melting point is higher than 3600 K as confirmed experimentally (3651 ± 17 K [4]). The higher slope of thermal expansion at high temperature predicted here shows similar behaviour to the correlation for urania [7] recommended by Fink in the region where premelting also occurs. Our calculations therefore support the theory, indirectly suggested by experimental observation [4-6], of a premelting due only to oxygen lattice melting.

Next, we evaluate the oxygen diffusion constant for the 3000 K – 3600 K temperature range, which is related to Einstein's mean-square displacement relation and can be evaluated from the respective slopes of presented mean square displacements equal to the A coefficient in fitting linear equations presented in Fig. 3 (note in Fig. 3 units: $Å^2s^{-1}$):

$$D = \lim_{t\to\infty} \frac{<R^2(t)>}{2dt} = \frac{A\times 10^{-8}}{6} [\mathrm{m^2 s^{-1}}] \quad (1)$$

where t indicates time, $<R^2(t)>$ is mean square displacement, and d is the dimensionality of space (d = 3 for bulk diffusion). The mean square displacement is calculated as the average over all initial times (t_0) such that t does not exceed 50% of the total time length (e.g. for 3000 K, t = 11.506 ps for 23.013 ps the total time length).

$$\left\langle R^2(t) \right\rangle = \left\langle | \, [R(t+t_0)-R(t_0)]^2 \, | \right\rangle_{t_0} \quad (2)$$

In Table 1 we show the oxygen diffusion constant (D) as calculated using Eq. 1.

Table 1
Oxygen's diffusion constant (D) as a function of temperature calculated from Eq. 1.

Property	3000 K	3300 K	3600 K
$D\times 10^8$ [$\mathrm{m^2 s^{-1}}$]	0.039	0.301	0.729

The estimated average activation energy for oxygen diffusion in thoria (~4.57 eV) is one order of magnitude larger than the evaluated activation energy for hydrogen diffusion in nickel (see e.g. 0.5 eV [19]) confirming, as expected, higher bonding of atoms in ceramics than in metals.

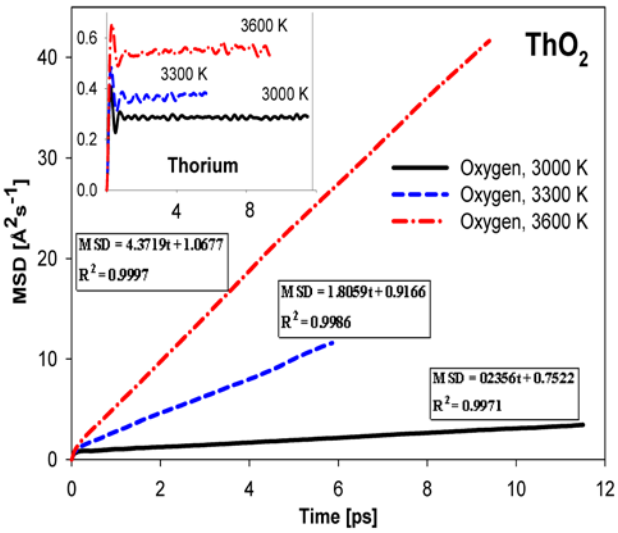

Figure 3 The calculated mean-square displacements of oxygen atoms in thoria as indicated a) by black solid line for temperature 3000 K, b) blue dashed line at 3300 K and c) red dot-dashed line for 3600 K. The fitted respective linear equations and R^2 are also shown respectively. In the insert, the respective mean-square amplitudes of vibration of thoria are presented for the indicated temperatures.

Additionally at ~2700 K we found that all atoms are confined and MSD is equal to ~0.23 $Å^2$ and ~0.57 $Å^2$ for thorium and oxygen atoms respectively.

4. Summary

In summary we have demonstrated, using first principles molecular dynamics, the melting of the oxygen sublattice in thoria in the temperature range 3000 K to 3600 K in contrast to the thoria sublattice, which does not melt at these temperatures. We have also evaluated oxygen diffusion for this temperature range. Thoria is predicted to exhibit a higher increase of thermal expansion with temperatures in the premelting region, similar to urania.

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