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Theoretical investigation of structural and thermo-mechanical properties of thoria

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ABSTRACT

We investigated the thermo-mechanical properties of thoria. Thoria is considered to be a candidate for a new safer nuclear fuel due to its higher thermal conductivity and because, unlike urania, it does not degrade in an oxidizing atmosphere. Thoria is also of interest since, like other metal oxides, it has high dielectric constant. Here we analyze thoria's thermo-mechanical properties using the *ab initio* method. We demonstrate that first principles calculations are valuable in complementing the limited experimental data available for thoria. The lambda phase transition is determined to be at higher temperature than in urania, where transition is observed at 2670 K, and therefore, in contrast to urania, we found that in thoria both atoms (Th and O) are confined at 2700 K.

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1. Introduction

The semiconductive properties of metal oxides are of interest since they have dielectric constants ($\varepsilon \sim 20$ for thoria [1]) much higher than, for example, the traditionally used in electronics SiO_2 (3.5). Although many metal oxides, for example thoria, have been investigated for some time [2], their high temperature behaviour is not well understood. Thoria is also regarded as a fuel for safer reactors as it has a higher thermal conductivity (for most temperatures of interest) and melting point [2] than urania, which helps to prevent reactor melt down. Additionally, as discussed previously [3], thoria does not oxidize to the higher oxidation states like urania and even inhibits oxidation of urania when mixed. Therefore it has the further benefit that cracking and fragmentation would not occur as happens in urania when oxidizing to U_3O_8 [4]. Additionally its thermal conductivity does not deteriorate due to oxidation as with urania [5,6] and its negative implications have been previously explored [5,7]. The recent tragic accident in Fukushima clearly illustrates the risks associated with the present design of reactors based on uranium dioxide (UO_2) fuel and justifies the research towards a safer fuel.

In contrast to urania, which has been studied extensively because it has long been used in nuclear reactors as a fuel, there are only limited experimental data available for thoria as reviewed in Ref. [2] and especially its high temperature thermo-mechanical properties, needed for nuclear safety analysis, are not available. Therefore in our previous work, we presented an attempt at applying first-principles calculations to evaluate the high temperature thermo-mechanical properties of thoria [8]. Here we expand our simulations to even higher temperatures (3660 K) and perform sensitivity studies of the derived thermomechanical properties on thermal expansion. The molecular dynamics (MD) approach used here has an advantage over the previously used quasi-harmonic method [9,10], because it can be applied even at temperatures (above 2700 K) where the longitudinal optical mode breaks in thoria, as our analysis of phonon dispersions implies [8]. At higher temperatures, the MD method predicts slightly larger linear thermal expansion than extrapolated experimental values [11]. However as we will show here, the effect of this discrepancy on the calculated thermo-mechanical properties is not significant. In the Appendix in Table A1 we also provide fits to our calculations for both thermal expansions (predicted by molecular dynamics calculation and experiment [11]).

It has been shown recently, [12] within the quasi-harmonic approximation (QHA) [13] and for temperatures up to 1000 K, that thermal expansion may vary a lot for different pseudopotentials and functionals. Using double the value of the cutoff energy ($\sim$2000 eV) of that necessary for very accurate calculation of structural and mechanical properties of thoria at 0 K (1090 eV), we were able to reproduce experimental thermal expansion, but only for some norm-conserved pseudopotentials [12]. However both

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experimental data and QHA calculations [12] for thermal expansion are not available at very high temperatures; therefore we use here an extrapolation of available experimental data [11] to evaluate the effect on thermomechanical properties of slightly higher thermal expansion derived by molecular dynamics calculation.

2. Methodology

Here we present the methodology we used to calculate the thermo-mechanical properties of thoria. In Ref. [8] we demonstrate that lately proposed version of the generalized-gradient approximation (GGA) to density functional theory (WC: Wu–Cohen) [14] leads to improved lattice constant values, with bulk (B) modulus in agreement with experiment. We implemented the same functional in molecular dynamics calculations. The scalar relativistic corrections were found to be important for core (non-valence) electrons, and therefore scalar relativistic atomic calculations were 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 [15].

2.1. Structure

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 2 × 2 × 2 and electron energy tolerance to 2×10^{-6} eV. As with our previous calculations [8], we set up the cutoff energy equal to 500 eV with implemented on-the-fly generated (OTFG) pseudopotentials [16], which were developed within the CASTEP code [17]. The *first-principles* molecular dynamics simulations were performed using an Andersen–Hoover barostat [18,19], and constant pressure (1 atm) [20]. The lattice constants (a) were calculated as the running averages from the molecular dynamics values as a function of temperature simulated by CASTEP (WC functional). These values were next fitted by two parabolic fits respectively at low and high temperatures (between 3000 K and 3660 K). The thermal expansion coefficient $\alpha(T)_\mathrm{P}$ was calculated by taking a respective derivative over a temperature:

$$\alpha(T)_P = \frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_P \tag{1}$$

2.2. Mechanical properties

Knowledge of the lattice constants as a function of temperature allows the derivation of the adiabatic elastic moduli (c_{ij}) defined as [21]:

$$c_{ijS} = (\partial^2 U/\partial\varepsilon_i\partial\varepsilon_j)_{S,\varepsilon} \tag{2}$$

where U is internal energy, S is entropy and $\varepsilon_{i(j)}$ is strain. Only one strain pattern (with only xx and yz non-zero) is sufficient since thoria has a cubic structure ($Fm\bar{3}m$ symmetry) [22]. Four values for the amplitude of the strain were applied: ±0.3%, ±0.1%. We calculated the values of bulk (B) and shear (G) moduli as the Hill averages of the values obtained by Voigt [23] and Reuss [24] methods. Having calculated the bulk and shear moduli, Young's modulus (Y) could be evaluated for an isotropic material or an isotropic aggregate of grains with non-isotropic elastic properties as:

$$Y = \frac{9BG}{3B+G} \tag{3}$$

Additionally, Young's modulus was calculated in ⟨100⟩ cubic symmetry directions from a reciprocal of the respective (s_{11}) compliance ($Y_{[100]}={s_{11}}^{-1}$).

The Poisson's ratio was calculated as:

$$\eta = \frac{3B-2G}{2(3B+G)} \tag{4}$$

2.3. Heat capacity and enthalpy

Peng and Grimvall have shown previously [25] that anharmonicity in thoria, at temperatures up to 2500 K, can be well accounted for by simply including the thermal expansion effect. Therefore this justifies using quasi-harmonic approximation within density functional perturbation theory (DFPT) [26]. We have also demonstrated [8] that this implementation within CASTEP code [17] predicts phonon spectra in good agreement with experiment and phonon density of states are easily obtained. The norm-conserving pseudopotentials in the Kleinman Bylander form [27] were used. They were generated using the Opium package [28] and tested against a wide range of experimental data on the structure of inorganic compounds. These potentials require a larger cut off energy (1090 eV) than we used above for ultrasoft pseudopotentials (500 eV). To calculate the phonon density of states we used a Monkhorst-Pack grid of 13 × 13 × 13 k points (84 irreducible k points) and a 7 × 7 × 7 grid for q points (20 irreducible q points). The fixed volume heat capacity per mole was calculated from [26]:

$$C_v(T) = N_A k_B \int_{\omega_\mathrm{min}}^{\omega_\mathrm{max}} \frac{\left(\frac{\hbar\omega}{2k_BT}\right)^2}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)}\rho(\omega)d\omega \tag{5}$$

where T is temperature, N_A is Avogradro's number, k_B is the Boltzman constant and $\rho(\omega)$ is the density of states of phonons (with $\hbar\omega$ energy) per primitive unit cell. The calculated heat capacities at fixed volume (dependent on temperature) of thoria remain constant at higher temperatures (at the temperature region where there is no phase transition). However, what is usually measured is a heat capacity at constant pressure ($C_p(T)$), which can be evaluated from:

$$C_P(T) = C_V(T) + 9(\alpha(T))^2 B(T)V(T)T \tag{6}$$

where $\alpha(T)$ is linear thermal expansion, $B(T)$ is bulk modulus, and $V(T)$ is molar volume.

Heat capacity at constant pressure can also be derived from enthalpy (H), which can be extracted from our constant pressure molecular dynamics calculations:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{7}$$

2.4. Thermal conductivity

It was noted previously [9,10] and we also confirmed in our paper [8] that the phonon contribution to the thermal conductivity of thoria can be well reproduced using a simplified Slack model [29]. Therefore we will explore its application even further using the thermal expansion ($\alpha(T)$, $a(T)$), heat capacity and the adiabatic elastic moduli evaluated as described above.

Next we calculated the Grüneisen parameter from:

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