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Considerations for ab-initio based thermal conductivity prediction of ThO_2

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ABSTRACT

Actinide oxides like uranium dioxide and mixed oxides are the primary fuel materials used in nuclear reactors around the globe. Thorium dioxide (ThO_2) is a promising material from the actinide oxide family, that can be considered as an alternative to replace the aforementioned nuclear fuels. Understanding the thermal energy transport in nuclear fuel materials is crucial, as it directly impacts the safety and efficiency of nuclear reactors. In this work, ab-initio calculations are used to determine the lattice thermal conductivity of ThO_2 at different temperatures. Density functional perturbation theory (DFPT) and density functional theory (DFT), along with lattice dynamics calculations are used to predict the harmonic and anharmonic phonon properties of ThO_2, which are then used to calculate the lattice thermal conductivity of the material. The results from ab-initio calculations are compared with experimentally reported values and are in good agreement. The effect of temperature-dependent inter-atomic force constants (IFC) on the predicted thermal conductivity is investigated. It is found that these temperature-dependent IFCs affect the accuracy of predicted thermal conductivity for ThO_2 crystals.

Keywords: thermal conductivity, nuclear fuels, ab-initio calculations, density functional theory, lattice dynamics

1. INTRODUCTION

Nuclear energy has a significant role in a world that is steadily transitioning to clean energy sources to meet its energy needs. Nuclear reactors produce energy by making use of the heat released during the fission reaction of nuclear fuel materials. Actinide oxides are the primary nuclear fuel materials used in most reactors. Among them, uranium dioxide (UO_2) and mixed oxides (a combination of UO_2 and plutonium dioxide) are the most commonly used fuel materials. The high amount of heat energy released during the fission reaction of these materials has to be tapped and transferred effectively for the safe and efficient operation of the nuclear reactors. A good understanding of the thermal energy transport phenomenon in these fuel materials is necessary to ensure the safe and effective functioning of the reactors.

Anticipating a future shortage of uranium, and also taking into account the bulk deposits of other actinide fuel materials, it is crucial to have replacement nuclear fuels other than UO_2 and MOX fuels. Thorium dioxide (ThO_2) is a promising nuclear fuel material in this regard [8]. As a nuclear fuel material candidate, it is important to study the thermal transport phenomenon in this material. The rest of this paper will focus on the thermal energy transport phenomenon in ThO_2.

Thermal conductivity is a measure to indicate the heat transfer rate in any material. The thermal conductivity of materials can be experimentally measured, or calculated from ab-initio methods. In this work, we aim to predict the thermal conductivity of ThO_2 from ab-initio calculations for different temperature levels. The thermal energy generated in ThO_2 is carried and transported primarily by the lattice vibrations, also called phonons. In this work, we do phonon calculations to predict the lattice thermal conductivity of single crystal ThO_2. Researchers over the years have made significant advancements in predicting lattice thermal conductivity of ThO_2 from using ab-initio methods [12, 14, 15, 19, 20], including thermal transport under the presence of defects [2, 3, 11, 13, 21]. Although a significant amount of work has been carried out, there is much more left to understand about the thermal transport phenomenon in ThO_2 crystals, which would include calculations involving higher levels of thermal transport theory [9]. One such study would be to understand the effect of temperature-dependent IFCs on the accuracy of the predicted lattice thermal conductivity of ThO_2.

In this work, we employ DFPT and DFT, in conjunction with anharmonic lattice dynamics calculations to predict the lattice thermal conductivity of pure, bulk, single crystal ThO_2. We compute fixed-temperature IFCs and temperature-dependent IFCs to investigate their effect on the predicted thermal conductivity. Lattice thermal conductivity is calculated using both approaches and is compared at different temperature levels to study the significance of temperature-dependent IFCs.

The subsequent sections of this paper are organized as follows. Section 2 discusses the methods we employed for predicting lattice thermal conductivity from phonon calculations. The results are discussed in section 3, and the concluding remarks are given in section 4.

2. THEORY AND METHODS

The following sub-sections will give a step-by-step overview of the methods employed in current work to obtain lattice thermal conductivity of ThO_2 crystals. The readers are requested to refer to [7, 10, 18] for a detailed description of the methodology for thermal conductivity prediction using phonon calculations.

2.1 Structure relaxation

Figure 1 shows a schematic of the conventional unit cell of ThO_2 crystal. ThO_2 is fluorite structured and crystallizes in the cubic $Fm\bar{3}m$ space group, with 4 thorium atoms and 8 oxygen atoms in the conventional unit cell. A structural relaxation was carried out for the unit cell to find the lattice parameters corresponding to the minimum energy configuration. The electronic structure calculations

are performed using the density functional theory (DFT) method, and Quantum ESPRESSO [5, 6] (version: qe 6.2.0) is used for all the DFT calculations. PAW pseudo-potentials with LDA exchange-correlational functionals are used for the current study. A comparison of different exchange-correlational functions for predicting phonon dispersion for ThO_2 can be found in [2], from which the choice of LDA over GGA is justified. Converged values of plane wave energy cut-off of 90 Ry and electronic wave vector grid of 8×8×8 are used for all calculations. We obtained a relaxed lattice constant of 5.52 Å for the ThO_2 conventional unit cell.

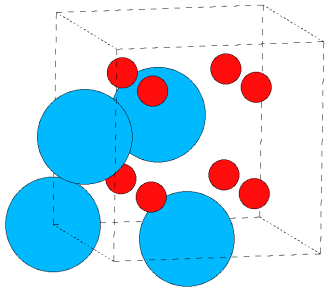

Figure 1: **Conventional unit cell of ThO_2 with fluorite structure. Th and O atoms are represented by the 4 blue and 8 red spheres respectively.**

2.2.Phonon calculations

The harmonic properties of the phonon can be obtained from second-order IFCs. In this work, DFPT is used to calculate the second-order IFCs. The phonon frequencies are obtained by solving the eigenvalue problem involving the dynamical matrix (comprising second-order IFCs) for the system. The Born effective charges and dielectric constant were calculated using DFPT, to account for the non-analytical contribution emerging from long-range ionic interactions. The Born effective charges for ThO_2 were obtained to be (in units of elementary charge e) $Z^*_{Th} = 5.412$ and $Z^*_O = -2.706$, and the dielectric constant was $\epsilon = 4.887$.

Phonons can also undergo scattering which would inhibit the thermal conductivity of the material. These scatterings could be intrinsic (phonon-phonon scattering) or extrinsic (phonon-defect, phonon-boundary scattering, etc.). In this work, we are considering pure single crystal ThO_2 for our study, so our focus would be on the intrinsic phonon-phonon scattering. These anharmonic phonon properties can be found by solving the Boltzmann transport equation (BTE). In this work, we focus only on the 3-phonon scattering phenomenon. We need third-order IFCs for performing these calculations. We made use of DFT calculations on a 4×4×4 supercell of the ThO_2 primitive unit cell and enforced a force cutoff of 7.5 Å for the third-order IFC calculations [18].

2.3.Thermal conductivity calculation

The lattice thermal conductivity of the material is calculated from the harmonic and anharmonic properties of the crystal system, and is given by [4, 17],

$$\kappa_\alpha = \sum_{q,v} c(q,v) v^2_{g,\alpha}(q,v) \tau_\alpha(q,v) \quad (1)$$

where, κ_α is the thermal conductivity in the α direction, (q,v) are the phonon wave vectors and polarization respectively, c is the volumetric specific heat, $v_{g,\alpha}$ is the phonon mode's group velocity in the α direction and τ_α is the phonon lifetime when heat flux is applied in the α direction. Here, volumetric specific heat and phonon group velocities are harmonic properties that can be obtained directly from the phonon dispersion relation. The phonon group velocity can be obtained as the slope of the phonon dispersion curve and is a significant contributor to the lattice thermal conductivity of the crystal. Phonon lifetime is an anharmonic property, which is a measure of the time until a phonon undergoes scattering. Increased phonon scatterings would reduce the phonon lifetime and would thus inhibit thermal transport. Phonon lifetimes are obtained by solving the BTE. In this work, the relaxation time approximation (RTA) method is used for solving the BTE. A converged phonon grid resolution of 20×20×20 is used for these calculations.

3. RESULTS AND DISCUSSIONS

The results obtained from the harmonic and anharmonic calculations are presented and discussed in the following sub-sections.

3.1.Phonon bandstructure

The phonon bandstructure for ThO_2 obtained from DFPT calculations is shown in Fig. 2. The corresponding projected density of states (PDOS) is also shown in the same figure. The bandstructure is plotted along the high symmetry directions Γ-X-U, K-Γ-L in the crystal reciprocal space. It is observed that the predicted phonon bandstructure agrees well with experimentally measured values by Bryan *et al* [1].

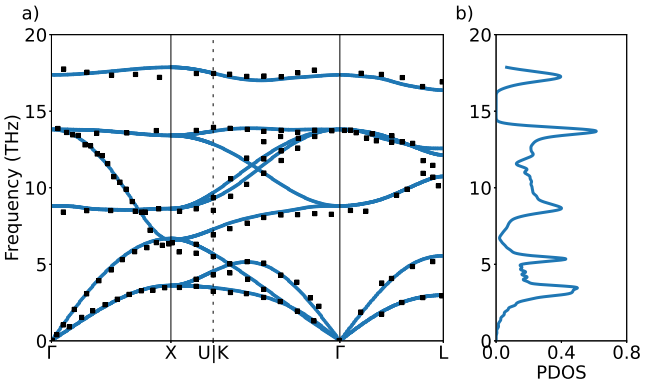

Figure 2: **a) Calculated phonon bandstructure along high symmetry directions and b) projected density of states (PDOS). The solid black squares are experimental measurements taken from [1].**

The primitive cell of ThO_2 is a three-atom basis FCC lattice, with Th atoms at 000 and O atoms at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ and $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ positions in reduced coordinates. Corresponding to the 3

atoms in the primitive unit cell, we obtain 9 different phonon modes, out of which 3 are acoustic and the rest are optical modes. The heavy Th atoms give rise to the acoustic modes and the light O atoms give rise to optical modes. The long-range interactions in the ThO_2 ionic crystal give rise to LO-TO splitting and are well captured by our calculations. All the required harmonic properties for thermal conductivity calculations (volumetric heat capacity and phonon group velocity) can be obtained from these phonon dispersion relations.

3.2.Cumulative thermal conductivity with frequency

Phonon lifetimes needed to calculate the thermal conductivity are obtained by solving the BTE as mentioned in the previous section. Substituting necessary harmonic and anharmonic properties in Eq. 1 gives us the lattice thermal conductivity of the material. Figure 3 shows the cumulative thermal conductivity with phonon frequency for two different temperature levels (100 K and 300 K).

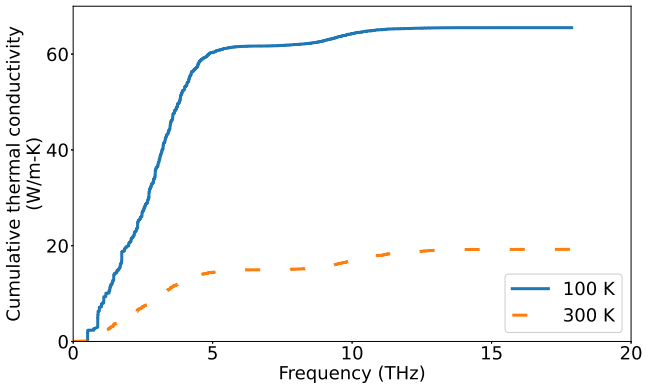

Figure 3: **Variation of cumulative thermal conductivity with phonon frequency for 100 K and 300 K. The blue solid line represents 100 K and the orange broken line represents 300 K.**

This plot tells us how different phonon frequencies contribute to the thermal conductivity of the material. For both temperatures, it can be observed that acoustic modes (below 5 THz) are the major contributors to lattice thermal conductivity in ThO_2 crystal. This result is expected given the higher group velocity of acoustic modes that can be confirmed from Fig. 2. Another observation to be made is the comparison of thermal conductivity at two different temperatures. Temperature-dependent IFCs were used to calculate the thermal conductivity at these two temperatures, which will be discussed later in this section. We obtained a lattice thermal conductivity of 65.5 W/m-K at 100 K and 19.2 W/m-K at 300 K. We can observe that the thermal conductivity decreases as we move from 100 K to 300 K. This reduction in thermal conductivity can be attributed to the increased phonon population at higher temperatures, which leads to an increased scattering rate and thus lower phonon lifetimes.

3.3.Effect of temperature dependent IFCs

Materials in their lifetime would be operating at different temperature levels, and it is important to study how the thermal conductivity of a material varies with these temperatures. In this work, we calculated the lattice thermal conductivity of ThO_2 at different temperatures, ranging from 100 K to 320 K. This temperature range was chosen so as to minimize the effect of four-phonon scatterings, which is expected to be noticeable at much higher temperatures. Another reason for limiting the calculations to 320 K is the lack of availability of experimental results for pure (defect-free), single crystal, bulk ThO_2 beyond this temperature, with which we can compare our results [8, 16].

In this work, we investigated the effect of including temperature-dependent IFCs in the thermal conductivity prediction for ThO_2. Temperature-dependent IFCs are obtained using Taylor series fitting on force-displacement datasets obtained by evaluation of DFT forces on 200 perturbed/thermally populated supercells. The third-order and fourth-order IFCs are evaluated simultaneously with enforced force cutoff values of 7.5 Å and 4.0 Å respectively. The atoms in these thermally populated supercells (each of size 192 atoms) are displaced according to their thermal mean square displacement (temperature-dependent) based on phonon eigenmodes as discussed in [22]. For the whole temperature range, we calculated thermal conductivity in two ways: 1) using IFCs calculated using fixed temperatures of 0 K (0K-FC) and 300 K (300K-FC) and 2) using temperature-dependent IFCs (TD-FC) corresponding to each temperature. A comparison of these three results with the experimental results from Mann *et al* [16] is shown in Fig. 4.

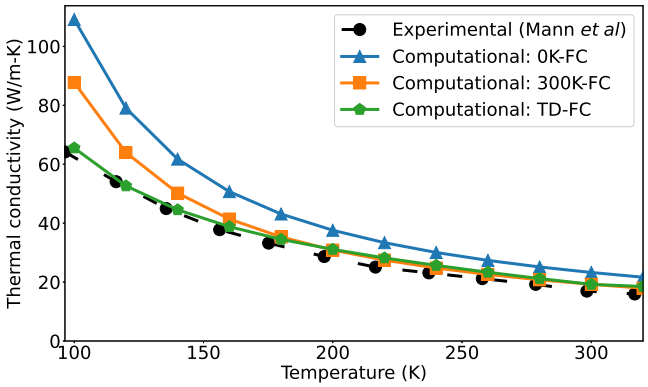

Figure 4: **Variation of lattice thermal conductivity with temperature. A comparison of computed lattice thermal conductivity using fixed-temperature IFCs and temperature-dependent IFCs with the experimental results from [16] is shown.**

It is observed that the thermal conductivity predicted using fixed-temperature IFCs (0K-FC and 300K-FC) agrees with experimental results only at higher temperatures, and the deviation from experimentally measured values grows larger as we move towards lower temperatures. A noticeable difference between these two results suggests that consid-

eration of temperature effect during IFC calculations is crucial in accurately predicting the temperature-dependent thermal conductivities for ThO_2. We can observe from Fig. 4 that the inclusion of temperature-dependent IFCs (TD-FC) in thermal conductivity prediction is able to address this discrepancy, and the computed results now agree well with the experimentally measured values throughout the considered temperature range. These results indicate that there is a noticeable temperature dependency in IFCs for ThO_2 that should be taken into account while performing lattice thermal conductivity calculations at lower temperatures.

4. CONCLUDING REMARKS

Lattice thermal conductivity of ThO_2 is calculated from ab-initio calculations, and the results are in good agreement with experimentally measured values. The acoustic phonons in ThO_2 crystal predominantly contribute to the heat transport in this material. The effect of temperature-dependent IFCs is explored, and it is observed that they have a noticeable effect on the predicted thermal conductivity for ThO_2. It is concluded that temperature-dependent IFCs need to be considered while doing thermal transport calculations for ThO_2 crystals at lower temperatures.

The current study focuses on thermal transport in single crystal ThO_2 with intrinsic three-phonon scattering, for a temperature range of 100 K to 320 K only. Further studies have to be carried out including phonon renormalization calculations and additional scattering channels [9] (four-phonon, defect, grain boundary, etc.), and the study has to be extended for higher temperature levels to derive a complete picture of the thermal transport phenomenon in ThO_2 crystals.

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