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Sensitivity of thermal transport in thorium dioxide to defects

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ABSTRACT

In this research, the reverse non-equilibrium molecular dynamics is employed to investigate the effect of vacancy and substitutional defects on the thermal transport in thorium dioxide (ThO_2). Vacancy defects are shown to severely alter the thermal conductivity of ThO_2. The thermal conductivity of ThO_2 decreases significantly with increasing the defect concentration of oxygen vacancy; the thermal conductivity of ThO_2 decreases by 20% when 0.1% oxygen vacancy defects are introduced in the 100 unit cells of ThO_2. The effect of thorium vacancy defect on the thermal transport in ThO_2 is even more detrimental; ThO_2 with 0.1% thorium vacancy defect concentration exhibits a 38.2% reduction in its thermal conductivity and the thermal conductivity becomes only 8.2% of that of the pristine sample when the thorium vacancy defect concentration is increased to 5%. In addition, neutron activation of thorium produces uranium and this uranium substitutional defects in ThO_2 are observed to affect the thermal transport in ThO_2 marginally when compared to vacancy defects. This indicates that in the thorium fuel cycle, fissile products such as ^{233}U is not likely to alter the thermal transport in ThO_2 fuel.

1. Introduction

There are several reasons that thorium is considered as an alternative to the conventional uranium nuclear fuel. Thorium exists in nature as ^{232}Th and is three to four times more abundant than uranium. The difficulty in making nuclear weapons utilizing a thorium fuel cycle makes thorium a more attractive and safe energy source. However, it should be noted that researchers raised concerns recently that thorium can be converted to an isotope of uranium that could be used in nuclear weapons during chemical reprocessing of irradiated thorium [1]. Thorium is fertile and cannot be used to start a nuclear reactor by itself; thorium must be converted into fissile material that allows sustaining a chain reaction via a breeding process accomplished by neutron absorption in a nuclear reactor and subsequent nuclei conversions [2,3]. This is typically accomplished by combining thorium with uranium or plutonium in oxide forms, or by using fuel rods containing pure thorium in combination with separate fuel rods enclosing uranium or plutonium. The resulting fissile ^{233}U can be used in any of several kinds of national or international nuclear reactors [3–5].

Thorium oxide (ThO_2), also known as thoria, has a face-centered cubic crystal structure and one of the highest melting points among all oxides (3573.15 K) [6]. Consequently, ThO_2, a crystalline solid, is used in light bulbs, arc-light lamps, lamp mantles, glass manufacture, welding electrodes, and heat-resistant materials [7–9]. Particularly, the thermophysical properties of ThO_2 make it an attractive candidate for use as a fertile fuel matrix in present reactors and for consuming plutonium or transmuting transuranic nuclides when compared with the uranium dioxide. The high melting point of ThO_2 provides an extra margin for safety in the event of a transitional power surge or loss of coolant. Since ThO_2 is relatively inert, it significantly reduces the chance of the fuel pellet reacting chemically with cooling water or the metal cladding [10]. Fission gas release from ThO_2 nuclear fuel pellets is much lower than that from UO_2, resulting in reduced internal gas pressure that facilitates achieving higher burnup [11].

Efficient thermal transport in nuclear fuels is an important research topic that is directly related to the life-time of nuclear fuels. During the operation of a nuclear reactor, a large temperature gradient is induced in nuclear fuel pellets; the temperature at the center of fuel pellets becomes much higher when compared to the temperature at the outer shells of the pellets. This large temperature gradient generates thermal stresses that generally result in cracks in fuel pellets. Moreover, the hot spots in fuel pellets

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increases the rate of fission gas release and can cause fuel pellet swelling due to fission gas bubbles and thermal expansion. Fission gas release degrades the fuel's mechanical quality further by causing embrittlement in grain boundaries. Therefore, the relatively high thermal conductivity of ThO_2 provides an extra important advantage as a nuclear fuel. There are several types of reactors where ThO_2 can be considered to be a potential nuclear fuel: Heavy Water Reactors, High-Temperature Gas-Cooled Reactors, Boiling Water Reactors, Pressurized Water Reactors, Fast Neutron Reactors, and Molten Salt Reactors. India has been using ThO_2 fuel extensively in their several reactors; CIRUS reactor, Dhruva reactor, Kalpakkam Mini reactor, Kakrapar Atomic Power Station, Rajasthan Atomic Power Station, Fast Breeder Test Reactor. Lingen Nuclear Power Plant in Germany also used to use ThO_2 as a nuclear fuel but it is inactive currently.

The defects in ThO_2 is considered to have a detrimental effect on the thermal transport in ThO_2 since they alter the vibrational motions of the crystalline structure. Defects in ThO_2 is understood as the interruption in its fluorite crystal structure; defects exist as single to multi-point vacancies, interstitial species, and substitutional atoms. Although there have been research studies regarding the defects in ThO_2, they generally focus on the formation energy [12], oxygen diffusion, and uranium doping [13].

The present study provides a meaningful addition to current literature as it presents microscopic understanding on the effect of vacancy and substitutional defects on the thermal transport in ThO_2. Using classical molecular dynamics (MD) along with the potential field for actinide oxides developed by Cooper et al. [14–16], the thermal conductivities of ThO_2 with different defects of various concentrations were obtained in this study. By progressively increasing the sample length up to 200 unit cells, the effect of defects on the thermal conductivity of the bulk ThO_2 is explored. Additionally, in order to better understand the effects of different defect types, phonon density of states are plotted using velocity autocorrelation function.

2. Simulation method

In this research study, reverse non-equilibrium molecular dynamics (RNEMD) is utilized to measure the thermal conductivity of ThO_2 with defects (Fig. 1a). RNEMD is a cause and effect reversed algorithm that is introduced by Müller-Plathe [17] and has been constantly used to estimate thermal properties of materials [18–21]. In this study, the RNEMD algorithm implemented in LAMMPS [22] is used to create a heat flux by swapping energy between a hot bath and a cold bath in a simulation box. By the help of the periodic boundary condition (Fig. 1b), two cold baths are generated at the ends of the simulation box. It must be noted that phonons with wavelength larger than the size of the simulation unit cell cannot be studied even if a periodic boundary condition is imposed on the simulation box (Fig. 1b).

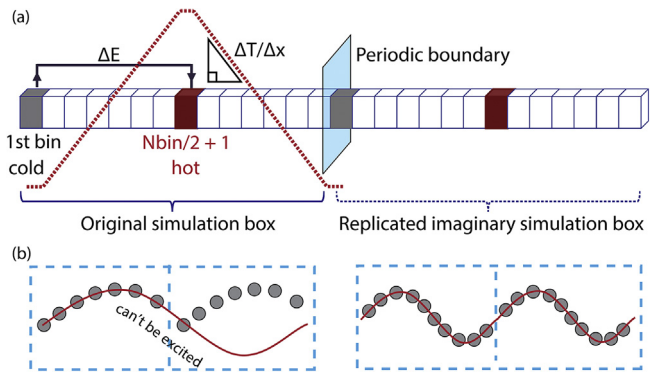

Fig. 1. (a) Schematic of RNEMD. (b) Illustration of a phonon mode that cannot be activated in MD.

In order to perform RNEMD, the simulation system needs to be well-equilibrated to forget its initial thermodynamic state. Once the simulation structure is properly equilibrated, the simulation box is divided into many imaginary bins along the direction in which the thermal conductivity is to be calculated using the simulation algorithm. During the simulation, energy is swapped at each specified time step by exchanging velocity vectors of the coldest atoms in the hot region and the hottest atoms in the cold region to create a temperature gradient in the simulation structure. Energy exchange between the cold bath and hot bath occurs until the heat flow reaches a steady state. Once the heat flow in the structure reaches a steady state, the thermal conductivity, k, is calculated using the Fourier's heat conduction law with averaged heat flux and temperature gradient dT/dx as the following.

$$k = -\frac{\langle q \rangle}{\langle dT/dx \rangle}, \tag{1}$$

where $\langle q \rangle$ is the heat flux and $\langle dT/dx \rangle$ is the temperature gradient in the sample averaged over time and space. The brackets $< >$, indicate the average of the quantities over time as well as over the particles in the simulation cell.

All simulation structures (Fig. 2) are constructed by using custom MATLAB programs. To investigate the effect of sample length on thermal conductivity, the sample length is increased progressively in the direction of thermal conductivity measurement (x direction in the present study). In the present study, the number of unit cells (N) is used to represent the side lengths of the simulation structures instead of the physical length for clarification; the physical length can vary depending on defect concentrations and simulation temperatures after equilibration even when the number of unit cells is the same. N_x, N_y, N_z denote the number of unit cells of a simulation structure in the direction of x, y, z, respectively. In all structures simulated, the number of unit cells in x and y directions, i.e. N_y and N_z, are fixed to be 6. In the authors' previous study [23], it was observed that the effect of side length on the thermal conductivity is minimal (comparable to the measurement errors during RNEMD) when compared to the effect of the sample length. This indicates that thermal transport in the x direction is not altered much by the boundary scatterings from x-y or x-z planes, and the effect of the cross-sectional area may be ignored during the thermal conductivity estimation using RNEMD. This is consistent with other thermal transport studies that utilized MD [24–26], where researchers identified a minimal effect of cross sectional area on thermal conductivity calculation; this justifies the fixed side length in the present study.

The number of unit cells, N_x, is defined as the half of the total number of unit cells in the x direction of the simulation structure since the characteristic length for thermal conductivity estimation in RNEMD is the distance between the hot bath located in the middle of the simulation structure and the cold bath located in the end of the simulation structure. Seven different number of unit cells ($N_x = 10$, 20, 30, 40, 50, 75, and 100) are selected for the present study.

Fig. 3 illustrates the defects that are studied in the present study. Oxygen vacancy defect, thorium vacancy defect, and uranium substation are selected for the present research study. For the case of oxygen vacancy defects (Fig. 3b) and thorium vacancy defects (Fig. 3c), simulation structures with five different defect concentrations, i.e. 0.1% 0.5%, 1%, 2%, 5% are simulated. The defect concentration for oxygen vacancy defects is defined by the expression