Thermal Conductivity of Thorium Dioxide with Defects

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INTRODUCTION

Efficient thermal transport in nuclear fuels is an important research topic that is 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 increases the rate of fission gas release and can cause fuel pellet swelling due to fission gas bubbles and thermal expansion.

Defects are considered to have a detrimental effect on the thermal transport in ThO_2 since they alter the vibrational motions of the crystalline 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 [1], oxygen diffusion, and uranium doping [2]. Here, we utilize reverse non-equilibrium molecular dynamics (RNEMD) to measure the thermal conductivity of ThO_2 with various types of defects and defect concentrations.

SIMULATION METHOD

The schematic of the RNEMD simulation is shown in Fig. 1. RNEMD is a cause and effect reversed algorithm that is introduced by Müller-Plathe [3] and has been constantly used to estimate thermal properties of materials [4]. RNEMD calculates thermal conductivity by imposing a heat flux and measuring the induced temperature gradient. In this study, the RNEMD algorithm implemented in LAMMPS [5] is used together with the force field developed by Cooper and Rushton [6]. During the simulation, energy is swapped at each specified time step by exchanging energies between the hot bath and the cold bath to generate 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. The thermal conductivity, k, is calculated using the Fourier's law with averaged heat flux and temperature gradient, dT/dx, as the following.

$$k = -\frac{\langle q \rangle}{\langle dT/dx \rangle}. \quad (1)$$

All simulation structures are constructed by using custom MATLAB programs. In all structures simulated, the two side lengths, i.e. L_y and L_z, are fixed to be 3.36 nm. 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). The sample length, L_x, is defined as the half length of the x-direction length 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 ends of the simulation structure. Seven different sample lengths (L_x = 5.6 nm, 11.2 nm, 16.8 nm, 22.4 nm, 28 nm, 42 nm, and 56 nm) are selected for the present study; these seven different lengths are equivalent to 10, 20, 30, 40, 50, 75, and 100 unit cells, respectively.

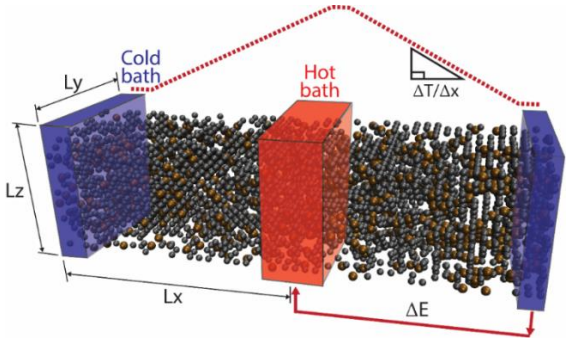

Fig. 1. Schematic of RNEMD simulation.

Fig. 2 illustrates the defects studied in the present study. For the case of oxygen vacancy defects (Fig. 2b) and thorium vacancy defects (Fig. 2c), simulation structures with five different defect concentrations, i.e. 0.1% 0.5%, 1%, 2%, 5% are simulated. The number of thorium atoms defect concentration for oxygen vacancy defects is determined by dividing the number of oxygen defect sites by the total number of atoms in the original structure without a defect, not by the number of oxygen atoms. For example, the pristine ThO_2 of 56 nm length contains 86,400 atoms that are consisted of 28,800 thorium atoms and 57,600 oxygen atoms. Therefore, ThO_2 of 56 nm length with 1% oxygen vacancy defects contains 864 (1% of 86,400) oxygen vacancy sites. The defect concentration for thorium vacancy defects or uranium substitutional defects is defined in the same way.

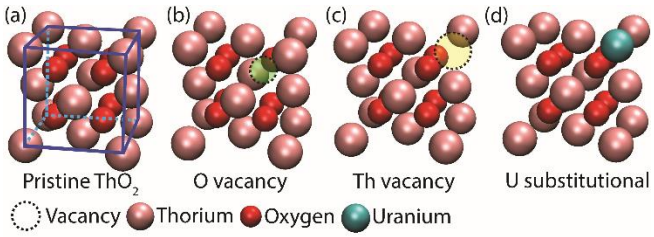

Fig. 2. Various defects in ThO_2 simulated in this study.

RESULTS

A significant finding of this study is that the oxygen vacancy has a detrimental effect on the thermal conductivity of ThO_2 in spite of its small atomic mass; 0.1% oxygen vacancy decreases the thermal conductivity of ThO_2 by 20% when compared to that of the pristine ThO_2 when the sample length is 56 nm (Fig 3a). Thorium vacancy is shown to have more negative effect on the thermal transport in ThO_2; 0.1% thorium vacancy results in the thermal conductivity sitting at 61.8% of that of the pristine ThO_2 (Fig. 3b). From this, it can be concluded that the missing of larger atoms alters vibrational motions of ThO_2 lattice structures more severely when compared to the missing of smaller atoms. The dependency of thermal conductivity reduction on the vacancy defect size has been repeatedly observed in other nanomaterials. Li and Zhang [7] reported that the thermal conductivity of silicone decreases when the size of vacancy cluster increases. Wei *et al*. [8] also observed that the thermal conductivity of graphene decreases with an increase in the size of vacancy. Considering the difference in the atomic masses of thorium (232 u) and oxygen (16 u), however, oxygen vacancy degrades the thermal transport property of ThO_2 significantly although it alters the lattice structure of ThO_2 very small when compared to thorium vacancy defect.

Another important finding is that uranium substitutional defect has a minimal effect on the thermal transport in ThO_2; the thermal conductivity (15.9 W/m-K) of ThO_2 with 0.1% uranium substitutional defect is still very close to that (15.9 W/m-K) of the pristine ThO_2 for the sample length of 56nm (Fig. 3b). The negligible effect of uranium substitution on the thermal conductivity of ThO_2 can be explained by their small alteration to the phonon spectrum of ThO_2. Provided that the uranium substation simulated in this study is ^{238}U, the actual uranium substitution (^{233}U) that is bred from ^{232}Th as part of the thorium fuel cycle is not likely to affect the thermal transport in ThO_2 due to its similar atomic mass to thorium.

CONCLUSION

In summary, the detrimental effect of vacancy defects on the thermal conductivity of ThO_2 has been identified in this research. In addition, it was observed that uranium substitution does not alter the thermal transport in ThO_2 much. These results will be utilized to develop novel nanostructured nuclear fuel materials that can increase the efficiency of nuclear fuel cycle significantly. The authors will continue to present optimized structures of nanostructured nuclear fuels by using atomistic simulations.

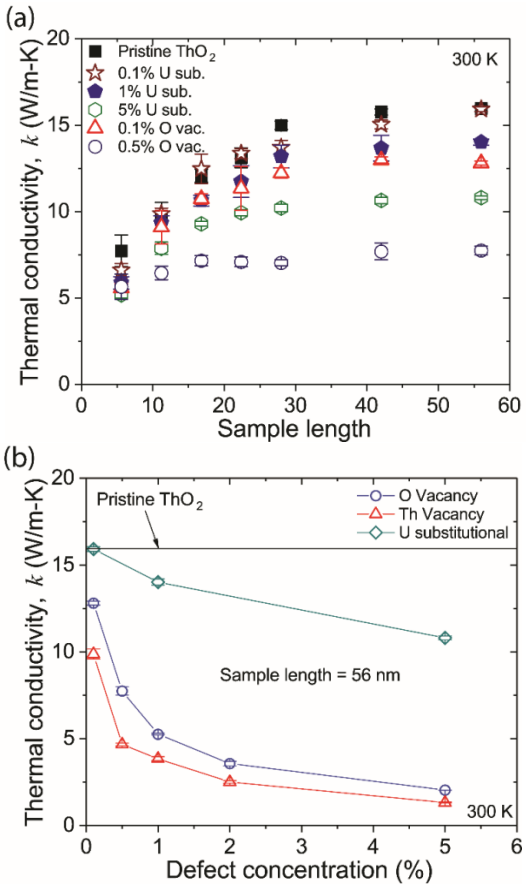

Fig. 3. Thermal conductivity of ThO_2 with O vacancy, Th vacancy, and U substitutional.

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