Thermodynamic properties and structural stability of thorium dioxide

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Abstract

Using density functional theory (DFT) calculations, we have systematically investigated the thermodynamic properties and structural stabilities of thorium dioxide (ThO\(_2\)). Based on the calculated phonon dispersion curves, we have calculated the thermal expansion coefficient, bulk modulus, and heat capacities at different temperatures for ThO\(_2\) under the quasi-harmonic approximation. All the results are in good agreement with corresponding experiments proving the validity of our methods. Our theoretical studies can aid a clearer understanding of the thermodynamic behaviors of ThO\(_2\) at different temperatures. In addition, we have also studied possible defect formations and diffusion behaviors of helium in ThO\(_2\), to discuss its structural stability. It is found that in intrinsic ThO\(_2\) without any Fermi energy shifts, the interstitial Th\(^{4+}\) defect rather than oxygen or thorium vacancies, interstitial oxygen, or any kinds of Frenkel pairs, is the most probable to form with an energy release of 1.74 eV. However, after upshifting the Fermi energy, the formation of the other defects also becomes possible. Regarding helium diffusion, we find that only through the thorium vacancy can it occur with the small energy barrier of 0.52 eV. Otherwise, helium atoms can hardly incorporate or diffuse in ThO\(_2\). Our results indicate that upward shifting of the Fermi energy of ThO\(_2\) should be prevented to avoid the formation of thorium vacancies so as to avert helium caused damage.

1. Introduction

As the world’s demands for energy keep growing, corresponding researches on developing new energy sources or enhancing the energy-consumption efficiency are attracting more and more attention. Currently, the fissile nuclear reactor is still a very important energy source, in which uranium dioxide (UO\(_2\)) has been the main fuel component for many years [1–5]. However, during the burning cycle of UO\(_2\), considerable amounts of radioactive elements emerge in the reaction waste [6], and such radioactive waste results in very troublesome long-term storage requirements. Based on these facts, many efforts have been made to look for possible substitutions for UO\(_2\). Thorium-based materials, which are naturally abundant, are identified as good candidates for replacing UO\(_2\) in fissile nuclear reactors because they are able to produce fewer transuranics (TRUs) compared to uranium- and plutonium-based fuels. And although \(^{233}\)Th is not fissile, it can absorb a slow neutron and then form fissile \(^{233}\)U just undergoing multiple beta-decays [7]. Moreover, because of the good solubility between thorium dioxide (ThO\(_2\)) and other transuranic dioxides, using the mix oxides (MOXs) of thorium and plutonium in nuclear reactors can also help in reducing the large plutonium stockpile while maintaining acceptable safety and control characteristics of the reactor system [8]. In comparison with previous uranium-based fuels, thorium-based fuels also have many additional physical advantages, such as higher melting points, higher corrosion resistivity, lower thermal expansion coefficients, and higher thermal conductivity [9]. In recent years, thorium-based fuels have already been tested in various reactors [7, 10–12].
As it is the first in the series of actinide elements, thorium and its compounds have been studied ever since 1950. At the earliest stage, a series of experimental measurements were carried out on the thermal properties of ThO$_2$ such as the thermal expansion coefficient, heat capacity, and thermal conductivity [13–22]. In 1997, Bakker et al [23] presented a conclusion and comparison for the measured values. On the other hand, Chadwick and Graham [24], Allen and Tucker [25], and Veal et al [26] investigated the valence-band structures of thorium and its oxides by means of x-ray photoemission spectroscopy. The pressure-induced phase transition of ThO$_2$ has been studied by Jayaraman [27], Dancausse [28], and Idiri et al [29] experimentally. Recently, in 2006, researchers from the International Atomic Energy Agency (IAEA) built a thermal–physical database of materials for light water reactors and heavy water reactors [30], and the earlier experimental measurements were re-addressed.

Despite the vast quantity of experimental measurements, it is to our surprise that no one has ever theoretically investigated the thermodynamic properties and defect behaviors of ThO$_2$, which are critically important for its use in thermonuclear reactors. Only recently, several theoretical studies have been carried out on the mechanical and electronic properties [31–33], phase transition behaviors [34, 35], and elastic and optical properties [36] for ThO$_2$. Our previous study has already proven that the thorium 5f states are no longer localized after electronic hybridizations, and density functional theory calculations are sufficient to produce correct descriptions for the ground-state properties of ThO$_2$ [35]. So in our present paper, we decide to systematically investigate the thermodynamic properties and structural stabilities of ThO$_2$ using density functional theory calculations. The thermodynamic stability will be discussed based on the calculated thermal parameters, while the structural stability will be discussed by calculating the formation energies of different kinds of defects, and diffusion energy barriers of helium in ThO$_2$. The rest of the paper is organized as follows. The computation methods are introduced in section 2. The discussion about the thermodynamic properties and structural stabilities of ThO$_2$ is presented in section 3. Finally, we give our conclusions in section 4.

2. Calculation methods

The density functional theory (DFT) calculations are carried out using the Vienna *ab initio* simulation package (VASP) [37, 38] with the projector-augmented-wave (PAW) potential method [39]. The cutoff energy for the plane-wave basis set is 500 eV. The exchange and correlation effects are described by the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form [40]. A $2 \times 2 \times 2$ supercell is employed to study defect formation and helium diffusion inside ThO$_2$. For calculations of the unit cell (12 total atoms) and $2 \times 2 \times 2$ supercell (96 total atoms), the integration over the Brillouin zone is carried out on $13 \times 13 \times 13$ and $5 \times 5 \times 5$ $k$-point meshes generated using the Monkhorst–Pack [41] method, which are both proven to be sufficient for energy convergence of less than 1.0 x 10$^{-4}$ eV per atom. During the supercell calculations, the shape and size of the supercell are fixed while all the atoms are free to relax until the forces on them are less than 0.01 eV Å$^{-1}$.

The Helmholtz free energy $F(V, T)$ of a semiconductor can be divided into two parts as

$$F(V, T) = E(V) + F_{\text{vib}}(V, T),$$

where $E(V)$ stands for the ground-state electronic energy, $F_{\text{vib}}(V, T)$ is the phonon free energy at a given unit cell volume $V$. Within the quasi-harmonic approximation (QHA), $F_{\text{vib}}(V, T)$ can be evaluated by

$$F_{\text{vib}}(V, T) = k_B T \sum_{j, q} \ln \left[ 2 \sinh \left( \frac{\hbar \omega_j(q, V)}{2 k_B T} \right) \right],$$

where $\omega_j(q, V)$ is the phonon frequency of the $j$th phonon mode with wavevector $q$ at fixed $V$, and $k_B$ is the Boltzmann constant. The total specific heat of the crystal is the sum of all phonon modes over the Brillouin zone (BZ),

$$C_v(T) = \sum_{j, q} c_{v,j}(q, T).$$

$c_{v,j}(q, T)$ is the mode contribution to the specific heat defined as

$$c_{v,j}(q, T) = k_B \sum_{j, q} \left( \frac{\hbar \omega_j(q, V)}{2 k_B T} \right)^{2} \frac{1}{\sinh^{2}(\hbar \omega_j(q, V)/2 k_B T)}.$$

(4)

The mode Grüneisen parameter $\gamma_j(q)$ describing the phonon frequency shift with respect to the volume can be calculated by

$$\gamma_j(q) = -\frac{d[\ln \omega_j(q, V)]}{d[\ln V]}.$$

The acoustic Grüneisen parameter $\gamma(T)$ defined as the weighted average of the mode Grüneisen parameters for all acoustic phonon branches is calculated to be

$$\gamma(T) = \frac{\alpha_v(T) B(T) V_m(T)}{C_v(T)},$$

where $\alpha_v(T)$ is the thermal expansion coefficient and equals $\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$, $V_m(T)$ is the volume per mole of material, and $B(T)$ and $C_v(T)$ are the bulk modulus and specific heat respectively.

3. Results and discussion

3.1. Structure and elastic constants of ThO$_2$

Our previous studies have shown that DFT calculations with GGA exchange–correlation functionals are good enough for obtaining the ground-state properties of ThO$_2$ [35, 42], and the addition of additional $U$ or $J$ modifications for localization effects might lead to incorrect results. We believe that this is because the 5f electronic states of Th become delocalized after electronic hybridizations in ThO$_2$. Here, based on our previous studies, we further investigate the thermodynamic properties of ThO$_2$. 

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From the mechanical point of view, the theoretical equilibrium volume \( V_0 \), bulk modulus \( B_0 \), and the pressure derivative of the bulk modulus \( B' \) can be obtained by fitting the third-order Birch–Murnaghan equation of state [43]. In this way, our calculated lattice parameter \( a_0 \) for ThO\(_2\) is 5.619 Å, which is in accordance with the experimental data of 5.60 Å [29, 44]. The bulk modulus \( B_0 \) and its pressure derivative \( B' \) are calculated to be 190 GPa and 4.3, also in agreement with corresponding experimental values of 195–198 GPa and 4.6–5.4 [29, 44], respectively. In comparison with other actinide dioxides, we can see that ThO\(_2\) has a slightly smaller bulk modulus than UO\(_2\) and PuO\(_2\) [42].

In order to evaluate the Poisson ratio \( \nu \), we calculated the three independent elastic constants \( C_{11}, C_{12} \) and \( C_{44} \) of ThO\(_2\). The calculation methods are the same as in our previous studies [35, 42, 45]. The obtained elastic constants for ThO\(_2\) are \( C_{11} = 351.2 \) GPa, \( C_{12} = 106.9 \) GPa, and \( C_{44} = 74.1 \) GPa, which are in accordance with experimentally measured values of \( C_{11} = 367 \) GPa, \( C_{12} = 106 \) GPa, and \( C_{44} = 79 \) GPa [46]. We have also examined the spin–orbit coupling (SOC) effects on the elastic constants of ThO\(_2\), since Shein \textit{et al.} found that SOC can lead to 10%–35% deviations from conventional DFT for ThC [47].

Our calculated results for SOC are as follows: \( C_{11} = 348.4 \) GPa, \( C_{12} = 107.3 \) GPa, and \( C_{44} = 72.1 \) GPa. These values are in consistency with the pure DFT results. Unlike ThC, the effects of SOC on the elastic constants are not obvious for ThO\(_2\). This may be attributed to the fact that the SOC effects on the bond distances and molecular frequencies of ThO\(_2\) are very small [48]. Furthermore, the Poisson ratio \( \nu \) is calculated to be 0.293, in excellent accordance with the experimental data of 0.285 [46]. All the good agreement between our calculated values and corresponding experimental measurements indicates that our calculation methods are effective and reliable.

3.2. Phonon dispersions, thermal expansion, and heat capacity of ThO\(_2\)

The thermodynamic properties of a material are connected with its phonon dispersion curves. In order to get accurate splittings between longitudinal optical (LO) and transverse optical (TO) phonon branches, the Born effective charge is firstly calculated. Because of the high symmetry of ThO\(_2\), the Born transverse effective charge tensor \( Z^T \) is the same along the [100], [010], and [001] directions, and the effective charge can be averaged by \( Z^T = \frac{1}{3} Tr Z^T \). For ThO\(_2\), we obtain that \( Z^T_{Th} = +5.41 \), and \( Z^T_{O} = -2.71 \). The static dielectric constant \( \epsilon = \frac{1}{3} Tr \epsilon \) is 4.83. The dielectric constant might be smaller than experimental measurements because of the underestimation of the electronic energy bandgap due to the drawbacks of the exchange–correlation approximation (GGA). The calculated phonon dispersion curves along the high-symmetry k-point lines using the above Born effective charges are shown in figure 1. As clearly shown, there is an obvious splitting between the LO and TO branches due to the Born effective charge. Moreover, we find that there is no evident gap between the acoustic and optical branches of the phonon for ThO\(_2\), with an observable overlap between the longitudinal acoustic (LA) and TO branches around the X point. Detailed vibrational modes analysis tells us that the vibrations of the Th and O atoms dominate the low- (0–6 THz) and high-frequency (6–18 THz) modes, respectively.

From the obtained phonon dispersion curves and equations (1) and (2), we then calculate the energy curves for ThO\(_2\), and find the lowest-energy lattice constants at different temperatures. The lattice expansion curve is thus obtained and is shown in figure 2. The experimental data by Touloukian \textit{et al.} [49] and Kim \textit{et al.} [30] are also shown in figure 2 for comparison with our calculation results. One can see that in the temperature range from 300 to 600 K, our result is in excellent agreement with the experimental data. In a higher temperature range from 600 to 1500 K, our obtained theoretical values are in the middle of the two different experimental measurements. And at 1500 K, the relative differences between our result and the two experimental values are 0.15% and 0.05%, respectively. The small relative differences indicate that the QHA method can give reasonable lattice parameters for ThO\(_2\) up to 1500 K. The thermal expansion coefficient \( \alpha(T) \) is calculated and shown in the inset of figure 2. The experimental values for the thermal expansion coefficient in the temperature range from 298 to 1500 K can be calculated from the corresponding thermal expansion curves, and are \( 3.318 \times 10^{-5} \) K\(^{-1}\) for Touloukian’s data and \( 3.630 \times 10^{-5} \) K\(^{-1}\) for Kim’s data. Our theoretical result of \( 3.509 \times 10^{-5} \) K\(^{-1}\) is consistent with the experimental values.

The bulk modulus \( B \) is also analyzed as a function of temperature according to the formula \( B = \frac{\partial^2 F}{\partial V^2} |_{V_0} \), and the result is displayed in figure 3. We can see that the value of the bulk modulus decreases with increasing temperature, and at 1500 K the ratio of the bulk modulus \( B/B_0 \) is 0.898, as depicted in the inset of figure 3.

Under the QHA, the considered vibration modes are harmonic but volume-dependent. The calculated heat capacity at constant volume using equations (3) and (4) is shown in figure 4, together with the heat capacity at constant pressure, \( C_p \), which is calculated according to the relationship

\[
C_p - C_v = \alpha^2(T)B(T)V(T)T.
\]
Figure 2. Temperature dependence of the linear thermal expansion for ThO$_2$. The inset is the volume thermal expansion coefficient as a function of temperature.

Figure 3. Temperature dependence of the bulk modulus B for ThO$_2$. The inset is the ratio of $B/B_0$.

The available experimental data from Bakker et al [23] and Kim et al [30] are also shown in figure 4 for comparison. It is evident that our theoretical result is in excellent agreement with the measured values for the whole experimentally considered temperature range. As temperature increases, the value of $C_p$ increases continuously, while the value of $C_v$ approaches a constant of 3R (R is the gas constant). At 1500 K, the value of $C_p$ becomes 81 J mol$^{-1}$ K$^{-1}$. In general, the QHA method is valid when the temperature is much lower than the material's melting point (around 3600 K for ThO$_2$ [23]) when the anharmonic effect is small.

3.3. Grüneisen parameters and the thermal conductivity of ThO$_2$

The lattice thermal conductivity $\kappa_L$ for a material can be calculated in different ways, depending on the specific mechanisms for phonon scattering. At relatively high temperatures, the dominant mechanism for phonon scattering is the Umklapp process, in which the acoustic phonon branches interact with each other and transport heat. With this mechanism, the lattice thermal conductivity of a crystal-like material can be expressed as [50–52]

$$\kappa_L = A \frac{\bar{M} \delta(T) n^{2/3}}{\gamma^2(T) \times T},$$ \hspace{1cm} (8)

where $A$ is a physical constant with the value of $3.1 \times 10^{-6}$, $\bar{M}$ is the average mass per atom in the crystal, $\gamma(T)$ is the Debye temperature of ThO$_2$, $n$ is the number of atoms in the primitive unit cell, and $\delta(T)$ is the cube root of the average volume per atom, i.e., the averaged radius per atom. The $\kappa_L$ and $\delta$ in equation (8) are in units of W m$^{-1}$ K$^{-1}$ and ˚Å respectively. With reasonable expressions for the Debye temperature and acoustic Grüneisen parameter to describe the harmonic phonon branches and the anharmonic interactions between different phonon branches, equation (8) can provide accurate predictions for a material’s thermal conductivity [51].

Firstly the Debye temperature $\Theta$ can be determined from the elastic constants within the Debye theory, in which the vibrations of the solid are considered as elastic waves, and the Debye temperature of the solid is related to an averaged sound velocity [53]. Within the isotropic approximation, the Debye temperature $\Theta$ can be expressed as [53]

$$\Theta(T) = \frac{\hbar}{k_B} \left[ 6\pi^2 V^{1/2}(T)n^{1/3}f(\nu) \right]^{1/2} \sqrt{\frac{B(T)}{M}},$$ \hspace{1cm} (9)

where $M$ is the molecular mass per formula unit, $B(T)$ is the bulk modulus, $\nu$ is the material’s Poisson ratio, and $f(\nu)$ is given by [54, 55]

$$f(\nu) = 3^{1/3} \left[ 2 \left( \frac{2}{3} \frac{1+\nu}{1-2\nu} \right)^{3/2} + \left( \frac{1+\nu}{3(1-\nu)} \right)^{3/2} \right]^{-1/3}. \hspace{1cm} (10)$$

Our calculations find that the Debye temperature monotonically decreases, while the acoustic Grüneisen parameter monotonically increases with increasing temperature.

Based on equation (8) and the obtained Debye temperature, we calculate the thermal conductivity for
The thermal conductivity of ThO$_2$. Figure 5 shows our thermal conductivity result, in comparison with the previous experimental results, in the temperature range from 300 to 1500 K. We can see that in the considered temperature range, our calculated values are in agreement with the experimental results, which proves the validity of our methods and model. In particular, in the high temperature range from 600 to 1200 K, our results accord very well with the experimental measurements by Murabayashi et al. [18], and by Pillai and Raj [19]. In the low temperature range around the Debye temperature of 402 K, our results are slightly different from some experimental results. This difference comes from our presumption that the dominant mechanism for phonon scattering is the Umklapp process. The accordance between our calculations and corresponding experiments in the temperature range from 600 to 1200 K proves that within this temperature area the contributions from other phonon scattering mechanisms are so small that they can be neglected.

The mode Grüneisen parameter describing the phonon frequency shift with respect to the volume can be used to discuss the anharmonic effects. By expanding or compressing the equilibrium volume by 1%, we calculate the mode Grüneisen parameter $\gamma_j(q)$ for all nine phonon branches according to equation (5). The corresponding results are shown in figure 6. It can be seen that all the mode Grüneisen parameter values are positive, indicating that all phonon frequencies increase with decreasing volume. Besides, the acoustic phonon mode Grüneisen parameters are relatively larger reflecting the fact that changes in volume have more influence on the collective vibration modes of ThO$_2$. We can also see from figure 6 that the LA and TO phonon branches have larger mode Grüneisen parameters, indicating that the anharmonic interactions between the LA and TO branches should be more intensive with respect to the volume change.

3.4. Defect formation in ThO$_2$

In this subsection and the next, we will investigate the structural stability of ThO$_2$ by systematically calculating the formation energy of different kinds of defects and investigating the diffusion behaviors of helium. A $2 \times 2 \times 2$ supercell with 96 Th and O atoms is employed in these two subsections to model defect formation and helium diffusion in ThO$_2$. Different charge states are considered for all the defects. To calculate the formation energies, the positions of all ions are fully relaxed before we calculate the electronic free energies of the system with different defects.

The formation energy of a point defect X with charge $q$ can be calculated by introducing the chemical potential concept as

$$E_{\text{for}}(X^q) = E_{\text{tot}} + n_X \mu - E_{\text{ThO}_2} + q(E_v + E_f + AV), \quad (11)$$

where $E_{\text{tot}}$ is the total energy of the supercell with defect X, $n_X$ represents the number of X defects, $\mu$ is the chemical potential of X with a positive sign for a vacancy and a negative sign for an interstitial defect, $E_{\text{ThO}_2}$ is the energy of the ThO$_2$ supercell without defects, $E_v$ and $E_f$ are the valence-band maximum (VBM) and the Fermi level of ThO$_2$ respectively. With these notations, $E_{\text{for}}(V^0)$, $E_{\text{for}}(O^0)$, $E_{\text{for}}(V^0_{\text{Th}})$, and $E_{\text{for}}(\text{Th}^0)$ represent the formation energies of a neutral oxygen vacancy, a neutral interstitial oxygen, a neutral thorium vacancy, and a neutral interstitial thorium respectively. The shift of the VBM in a defect supercell $AV$ takes the change of the valence-band maximum caused by the defect into account. Its value can be obtained by a macroscopic average technique [56, 57] through calculating the difference between the average electrostatic potential in a bulk-like environment of the defect supercell and the average electrostatic potential in the defect-free supercell.

The formation energy of a Frenkel pair can be calculated by summing up the formation energies of a vacancy and a corresponding interstitial add-in, i.e.,

$$E_{\text{for}}(FP_X) = E_{\text{for}}(V_X) + E_{\text{for}}(X_i). \quad (12)$$

For the Schottky defect, the formation energy can be calculated by

$$E_{\text{for}}(S) = E_{\text{for}}(V_{\text{Th}}) + 2E_{\text{for}}(V_O) - \frac{3(N - 1)}{N}E_{\text{ThO}_2}, \quad (13)$$

where $N$ is the number of atoms in the considered supercell. In this expression, the defect consists of a thorium vacancy.
and two oxygen vacancies, which are again supposed to be non-interacting.

The formation energies for oxygen (thorium) vacancies, interstitial oxygen (thorium) ions, oxygen (thorium) Frenkel pairs, and the Schottky defect of a ThO$_2$ unit in the $2 \times 2 \times 2$ supercell are obtained and are listed in table 1. One can see that the charged Th$_{4}^{4+}$ add-in defect is the only one with a negative formation energy. This means that once Th$_{4}^{4+}$ ions are available, an interstitial Th$_{4}^{4+}$ defect can form in ThO$_2$ with an energy release of 1.74 eV. Comparatively, for oxygen defects, the O$^{2-}$ vacancy is the most possible one because of its smallest formation energy among oxygen defects. These two results reflect the ionic character of the Th-O bonds in that each thorium atom almost loses four electrons to two oxygen atoms in ThO$_2$. From table 1, we can also see that all thorium vacancies and thorium Frenkel pairs have huge formation energies and thus can hardly form in intrinsic ThO$_2$. Comparatively, the formation of an oxygen Frenkel pair, containing an O$^{2-}$ vacancy and an interstitial O$^{2-}$ ion has a relatively smaller formation energy.

Table 1. Formation energies of different defects at different charge states in ThO$_2$. The defects include oxygen vacancies (V$_O$), interstitial oxygen ions (O$_i$), thorium vacancies (V$_{Th}$), interstitial thorium ions (Th$_i$), oxygen (FP$_O$) and thorium Frenkel pairs (FP$_{Th}$), and Schottky defects (S). The formation energies are in units of eV.

| Defect | Charge on defect | Kröger–Vink notation | $E_{tot}$  |
|--------|-----------------|-----------------------|-----------|
| V$_O$  | 0               | $V_X^-$               | 7.415     |
| V$_O$  | +1              | $V_X^+$               | 3.922     |
| V$_O$  | +2              | $V_{X^{*}}$            | 1.338     |
| O$_i$  | 0               | $O_i^-               | 1.901     |
| O$_i$  | -1              | $O_i^+               | 4.026     |
| O$_i$  | -2              | $O_{i^{*}}^-           | 5.487     |
| V$_{Th}$ | 0            | $V_{Th}^-               | 18.349     |
| V$_{Th}$ | -1          | $V_{Th}^+               | 18.600     |
| V$_{Th}$ | -2          | $V_{Th}^+               | 18.314     |
| V$_{Th}$ | -3          | $V_{Th}^+               | 18.327     |
| V$_{Th}$ | -4          | $V_{Th}^{***}^-           | 18.462     |
| Th$_i$ | 0              | $Th_i^+              | 6.094     |
| Th$_i$ | +1              | $Th_i^+              | 5.897     |
| Th$_i$ | +2              | $Th_{i^{*}}^+           | 2.869     |
| Th$_i$ | +3              | $Th_{i^{***}}^+           | 0.488     |
| Th$_i$ | +4              | $Th_{i^{****}}^+           | -1.741     |
| FP$_O$ | 0              | $V_{X}^- + O_i^+           | 9.316     |
| FP$_O$ | 0              | $V_{X}^- + O_i^+           | 7.948     |
| FP$_O$ | 0              | $V_{X}^- + O_i^+           | 6.825     |
| FP$_{Th}$ | 0        | $V_{Th}^- + Th_i^{*+}      | 24.443     |
| FP$_{Th}$ | 0        | $V_{Th}^- + Th_i^{*+}      | 24.497     |
| FP$_{Th}$ | 0        | $V_{Th}^- + Th_{i^{*}}^{*+} | 21.183     |
| FP$_{Th}$ | 0        | $V_{Th}^- + Th_{i^{***}}^{*+} | 18.815     |
| FP$_{Th}$ | 0        | $V_{Th}^- + Th_{i^{****}}^{*+} | 16.721     |
| S      | 0              | $V_{Th}^- + 2V_{O}^+         | 19.472     |
| S      | 0              | $V_{Th}^- + 2V_{O}^+         | 12.651     |
| S      | 0              | $V_{Th}^- + 2V_{O}^+         | 8.231     |

and charged defects can change due to the changes in the difficulty of electron transfer. Using equations (11)–(13) under different Fermi energies, we can calculate the formation energy as a function of the Fermi energy for different kinds of defects. The corresponding results for oxygen (thorium) vacancies and interstitial oxygen (thorium) ions in different charge states are shown in figures 7(a) and (b) respectively. The experimentally measured bandgap of 6.0 eV, instead of the 4.1 eV value obtained by first-principles calculations is chosen as the reference bandgap in discussions on defect formation.

As can be seen from figure 7(a), when comparing the energies associated with forming V$_O^0$, V$_O^{-}$, and V$_O^{2+}$ oxygen vacancies, a transition can be observed with the Fermi level increasing from the valence band to the conduction band. The +2 charged oxygen vacancy is favored near the valence band, indicating that oxygen vacancies have a tendency to donate electrons or behave as $n$-type defects. When the Fermi level increases to around 2.6 eV, the V$_O^+$ becomes energetically favorable. With further increase of the Fermi level, the neutral charge state is most probable for oxygen vacancies, and the tendency of oxygen vacancies to donate electrons diminishes.

We can also see from figure 7(a) that it can become very possible for the interstitial O$^{2-}$ defect to form when the Fermi energy is shifted to be near the conduction band of ThO$_2$.

From figure 7(b) we see that when the Fermi energy is near the valence band, it is difficult for all charged states of thorium vacancies to form because of the huge formation energies, and the interstitial Th$_{4}^{4+}$ ions can easily form in ThO$_2$ with a negative formation energy. With upshift of the Fermi energy, the interstitial thorium defect in the neutral state and the V$_{Th}^-$ vacancy can both become the most possible kinds of thorium defect. When considering only the vacancy defects, V$_O^{2+}$ is the most stable defect near the valence band, while near the conduction band V$_{Th}^{4-}$ is the most favorable one. Comparatively, for interstitial states, the Th$_{4}^{4+}$ and O$^{2-}$ defects are the most probable ones when the Fermi energy is near the valence band and conduction band respectively.

In addition, the electronic densities of states (DOSs) for both defect-free and defective ThO$_2$ are calculated and shown in figures 8 and 9, to further analyze the influence of the considered defects on the electronic structures of ThO$_2$. As clearly shown in both figures 8 and 9, the introduction of vacancies or interstitial ions does not change the DOS distribution of ThO$_2$ very much. The most prominent feature in both figures 8 and 9 is that a new defect energy level emerges in the bandgap for defective ThO$_2$. For the electronic structure of ThO$_2$ with oxygen vacancies, we see from figure 8(a) that the Fermi energy shifts from the valence-band maximum (VBM) in defect-free ThO$_2$ to above the defect energy level for the V$_{O}^{+}$ defect, and from above the defect energy level for the V$_{O}^{-}$ defect back to the VBM for the V$_{O}^{2+}$ defect. For the system with interstitial oxygen ions, we can see from figure 8(b) that the Fermi energy shifts respectively from the VBM for the O$_i^{+}$ defect to the defect energy level for the O$_i^{-}$ defect, and from the defect energy level for the O$_i^{2-}$ defect to above the defect energy level for the O$_i^{2-}$ defect. Similarly for the ThO$_2$ supercell with interstitial thorium ions,
Figure 7. Formation energies of oxygen related defects, i.e., oxygen vacancies or interstitial oxygen ions (a), and thorium related defects, i.e., thorium vacancies or interstitial thorium ions (b), as functions of the Fermi energy.

Figure 8. Electronic densities of states (DOSs) for ThO$_2$ with oxygen vacancies (a), and with interstitial oxygen defects (b) in different charge states. The Fermi energies are set to zero.

the Fermi energy shifts from the VBM to the defect energy level for the Th$^{+}$, Th$^{2+}$, and Th$^{3+}$ defects, and then shifts to above the defect energy level for the Th$^{4+}$ defect, as shown in figure 9(b). From figure 9(a), one can see that the defect energy levels for thorium vacancies in ThO$_2$ are very close to the VBM.

3.5. Diffusion of helium in ThO$_2$

In order to determine the structural influence of helium impurity on ThO$_2$, we systematically calculate the incorporation energy and diffusion energy barriers for helium in both defect-free and defective ThO$_2$. The incorporation energy is defined to be the energy required to incorporate one helium atom at a pre-existing vacancy or at an interstitial site. In this way, $E_{\text{inc}}$ can be expressed as follows:

$$E_{\text{inc}} = E_{\text{tot}} - E_{\text{ThO}_2} - E_{\text{He}},$$

(14)

where $E_{\text{tot}}$ is the energy of the ThO$_2$ supercell with an incorporated helium, $E_{\text{ThO}_2}$ is the energy of the ThO$_2$ supercell with or without defects, and $E_{\text{He}}$ the energy of an isolated helium atom. Three different kinds of incorporation are systematically considered here, i.e., a helium atom at the oxygen (O) and thorium vacancy (Th) sites in defective ThO$_2$, and a helium atom at the octahedral interstitial site (OIS). The
calculated incorporation energies are 2.48, 0.21, and 0.77 eV respectively. We can see that the most possible incorporation site for helium is the thorium vacancy site in defective ThO$_2$. In comparison, the oxygen vacancy site is much less possible for helium incorporation.

The structural influence of helium on ThO$_2$ is determined not only by the incorporation energy, but also by the minimum energy path for helium diffusion. The climbing image nudged elastic band (CINEB) method [58] is then employed to find the minimum energy diffusion pathways. Based on the obtained incorporation results for helium in ThO$_2$, we here investigate the diffusion of helium from OIS to OIS in both defect-free and defective ThO$_2$. Figures 10(a)–(c) depict our considered diffusion pathways, and the energy profiles along these paths are shown in figures 11(a)–(c) respectively. We can see from figure 11(a) that in intrinsic ThO$_2$, the incorporated helium atom needs to overcome a 3.34 eV energy barrier in order to diffuse from one OIS to another. This huge diffusion energy barrier means that at normal temperatures, helium diffusion in intrinsic ThO$_2$ is almost impossible. In the corresponding saddle point along this diffusion path, the helium atom is in the middle of the two OISs, and the nearest oxygen atoms along the [001] direction are repelled from each other by about 0.80 Å.

From the calculated energy profile shown in figure 11(b), we see that the energy barrier for an incorporated helium atom to diffuse from one OIS to another by passing an oxygen vacancy is lowered down to be 1.58 eV. This energy barrier is, however, still too large for the diffusion to occur at room temperature. The only possible way for helium to diffuse in ThO$_2$ is found to be by passing through a thorium vacancy, as depicted in figure 10(c). We can see from figure 11(c) that the helium atom only needs to overcome a 0.10 eV energy barrier to diffuse from an OIS to the thorium vacancy, and a 0.52 eV energy barrier to diffuse from the thorium vacancy to another OIS. Note that the van der Waals (vdW) interactions between helium and ThO$_2$ are not specially considered in our calculations, thus the obtained diffusion energy barriers might contain small fluctuations. However, since helium is a full-shell element with a small mass, the dispersion forces between helium and ThO$_2$ are expected to be very small. Thus, our result that helium atoms can only diffuse freely around thorium vacancies remains unperturbed by the tiny correction of vdW interaction.
The small energy barriers for helium to diffuse in thorium vacancy-included ThO$_2$ indicate that thorium vacancies might lead to helium aggregation causing failure of the ThO$_2$ material. Fortunately, from our above defect formation studies, the formation of thorium vacancies is almost forbidden when the Fermi energy is not upshifted, because their formation energy is too large in ThO$_2$. Therefore, to prevent structural damage to ThO$_2$ from helium incorporation, any kind of factor possibly leading to upshifts of the Fermi energy should be avoided.

### 4. Summary

In summary, we have performed a systematic first-principles study to investigate the thermodynamic properties and structural stabilities of ThO$_2$. Based on the calculated phonon dispersion curves for ThO$_2$, we systematically analyzed its thermodynamic properties and obtained the values of its thermal expansion coefficient, bulk modulus, and heat capacities at different temperatures, which are in good agreement with corresponding experimental measurements. The agreement between our calculations and experiments also proves the validity of our methods and model, and the effectiveness of the quasi-harmonic approximation. According to the Umklapp interaction mechanism between different phonon branches, we systematically obtained the mode Gr"uneisen parameters, and further calculated the thermal conductivities of ThO$_2$. Within the temperature range from Debye temperature to about 1500 K, our calculated thermal conductivities accord very well with experimental results.

In addition to studying the thermodynamic properties of ThO$_2$, we also investigated its structural stability by calculating the formation energy of different defects, and the diffusion behavior of helium, during which different charge states of the defects were considered. The formation energy results indicate that without any shifts of the Fermi energy, it is very probable for the interstitial Th$^{4+}$ defect to appear in ThO$_2$ with an energy release of 1.74 eV. On changing the Fermi energy to different values, the formation possibilities of different defects vary. For helium incorporation, it was found that the helium atom tends to occupy a thorium vacancy in defective ThO$_2$ or occupy the octahedral interstitial site in intrinsic ThO$_2$. It was further revealed that incorporated helium atoms can only diffuse freely in thorium vacancy containing ThO$_2$, with small energy barriers of 0.10 and 0.52 eV. Our studies show that to avoid helium damage, the electronic Fermi energy of ThO$_2$ should not be upshifted because it can make the formation of thorium vacancies more possible.

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