



Lattice dynamics and lattice thermal conductivity of thorium dicarbide



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ABSTRACT

The elastic and thermodynamic properties of ThC₂ with a monoclinic symmetry have been studied by means of density functional theory and direct force-constant method. The calculated properties including the thermal expansion, the heat capacity and the elastic constants are in a good agreement with experiment. Our results show that the vibrational property of the C₂ dimer in ThC₂ is similar to that of a free standing C₂ dimer. This indicates that the C₂ dimer in ThC₂ is not strongly bonded to Th atoms. The lattice thermal conductivity for ThC₂ was calculated by means of the Debye–Callaway model. As a comparison, the conductivity of ThC was also calculated. Our results show that the ThC and ThC₂ contributions of the lattice thermal conductivity to the total conductivity are 29% and 17%, respectively.

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1. Introduction

In the last decade, there has been renewed interest in thorium carbides since their potential application in Generation-IV reactors [1]. There are many advantages to the thorium carbides, such as the high melting point, the corrosion resistivity, the low thermal expansion coefficients and the large thermal conductivity [2]. Meanwhile, thorium is thought to be three to four times more naturally abundant than uranium [3], and a thorium fuel cycle can be developed that produces negligible amounts of plutonium and fewer long-lived minor actinides than a uranium cycle [4].

Thorium has two main types of carbides: one is thorium monocarbide (ThC) and another is thorium dicarbide (ThC₂). ThC has a rock-salt structure, while ThC₂ exists as three different phases: at the low temperature (up to 1700 K) it shows a monoclinic structure, at the temperature from 1700 K to 1754 K it shows a tetragonal structure, and at the high temperature ($T > 1754$ K) it has a cubic structure [5–7]. Currently, several first-principles studies have been performed to understand the structural, electronic, elastic, and thermodynamic properties of ThC [8–12], while the properties of ThC₂ have rarely been studied. To the best of our knowledge, only the structural and electronic properties of ThC₂ have been studied by Shein et al. [13–15]. In this work, the elastic and thermodynamic properties of ThC₂ (monoclinic phase) will be studied by means of a first-principles and a direct force-constant

method. As a comparison, we also investigate the lattice thermal conductivity of ThC.

2. Calculation methods

2.1. Computational details

All of the DFT [16] calculations in this study were carried out using the Vienna *ab initio* simulation package (VASP) [17,18] with the projector augmented wave scheme (PAW) [19]. The exchange–correlation functional with generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [20] was used to solve the Kohn–Sham equations. Some bulk properties of thorium carbides have been studied using the GGA approximation [10–13], which shows that the GGA gives reasonable results. We also found that for ThC and ThC₂ the GGA (without adding U) could give reasonable results including the lattice constants and vibrational properties. For the structural relaxations, the cutoff energy for the plane-wave expansion was chosen as 600 eV. The energy convergence of 1.0×10^{-6} eV/atom was found to be sufficient with respect to the Monkhorst–Pack [21] *k*-point meshes of $9 \times 13 \times 9$ for ThC₂ (primitive cell) and $13 \times 13 \times 13$ for ThC. The geometries were considered to be converged when the forces on each ion became less than 0.001 eV/Å. Vibrational properties were calculated using the direct force-constant method [22] as implemented in the PHONOPY code [23]. The $3 \times 3 \times 2$ ($2 \times 2 \times 2$) supercell containing 108 (64) atoms and the $3 \times 3 \times 3$ ($5 \times 5 \times 5$) Monkhorst–Pack *k*-point meshes were used to calculate the phonon for ThC₂ (ThC).

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2.2. Elastic constants and mechanical properties

Elastic constant tensor C_{ij} can be calculated by performing six finite distortions of the lattice and deriving the elastic constants from the strain–stress relationship [24]. Normally, there are twenty-one independent matrix elements in a complete anisotropic material. As for ThC₂, thirteen independent tensor elements should be considered. Bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) can be obtained through the elastic constant matrix by using the Voigt–Reuss–Hill approximation [25]. The detail of the formulas and the stability criterion can be seen in Ref. [26].

2.3. Lattice thermodynamic properties

The Helmholtz free energy at zero pressure can be expressed as:

$$F(V, T) = E(V) + F_{ph}(V, T), \quad (1)$$

where $E(V)$ is the internal energy and $F_{ph}(V, T)$ is the phonon free energy at a given temperature T and at a given volume V . Under the quasi-harmonic approximation (QHA) [27], the $F_{ph}(V, T)$ is given by

$$F_{ph}(V, T) = k_B T \int_0^\infty g(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2 k_B T} \right) \right] d\omega, \quad (2)$$

where $g(\omega)$ is the phonon density of states (DOS).

The vibrational contribution to the isochoric heat capacity C_V can be calculated by

$$C_V = k_B \int_0^\infty g(\omega) \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\frac{\hbar \omega}{k_B T}}}{\left(e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^2} d\omega, \quad (3)$$

while the heat capacity at constant pressure C_P is calculated by the thermodynamic relationship $C_P - C_V = \alpha_V^2(T) B(T) V(T) T$, where the isobaric thermal expansion coefficient and bulk modulus are expressed by formulas $\alpha_V(T) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ and $B(T) = V \left(\frac{\partial^2 F(V, T)}{\partial V^2} \right)_P$, respectively.

2.4. Lattice thermal conductivity

The total lattice thermal conductivity (κ) is written as a sum over one longitudinal (κ_{LA}) and two transverse (κ_{TA_1} and κ_{TA_2}) acoustic phonon branches [28–30]:

$$\kappa = \kappa_{LA} + \kappa_{TA_1} + \kappa_{TA_2} \quad (4)$$

These partial thermal conductivities are determined by phonon scattering rates [31,32] $1/\tau_c = 1/\tau_N + 1/\tau_U$, where $1/\tau_c$, $1/\tau_N$, and $1/\tau_U$ are the total scattering rate, the normal phonon scattering rate, and the Umklapp phonon–phonon scattering rate, respectively. The other scattering processes (such as mass-difference impurity scattering, boundary scattering, and phonon–electron scattering) were neglected since these processes are relatively insignificant in perfect crystal [33]. Using the Debye–Callaway model [29,34], the partial conductivities κ_i (i corresponds to LA, TA₁, or TA₂ modes) are given by

$$\kappa_i = \frac{1}{3} C_i T^3 \left\{ \int_0^{\Theta_i/T} \frac{\tau_c^i(x) x^4 e^x}{(e^x - 1)^2} dx + \frac{\left[\int_0^{\Theta_i/T} \frac{\tau_c^i(x) x^4 e^x}{\tau_N^i (e^x - 1)^2} dx \right]^2}{\int_0^{\Theta_i/T} \frac{\tau_c^i(x) x^4 e^x}{\tau_N^i \tau_U^i (e^x - 1)^2} dx} \right\}, \quad (5)$$

where Θ_i is the longitudinal (transverse) Debye temperature,

$$\chi = \frac{\hbar \omega}{k_B T}, \quad (6)$$

and

$$C_i = \frac{k_B^4}{2\pi^2 \hbar^3 v_i}. \quad (7)$$

where \hbar is the Planck constant, k_B is the Boltzmann constant, ω is the phonon frequency, and v_i is the longitudinal or transverse acoustic phonon velocity.

For the normal phonon scattering [29,35], we can write as,

$$\frac{1}{\tau_N^i(x)} = \frac{k_B^3 \gamma_{TA}^2 V}{M \hbar^2 v_{LA}^5} \left(\frac{k_B}{\hbar} \right)^2 x^2 T^5, \quad (8)$$

$$\frac{1}{\tau_N^{TA_1/TA_2}(x)} = \frac{k_B^4 \gamma_{TA_1/TA_2}^2 V}{M \hbar^3 v_{TA_1/TA_2}^5} \frac{k_B}{\hbar} x T^5,$$

and for the Umklapp phonon–phonon scattering [29,35], it can be written as,

$$\frac{1}{\tau_U^i(x)} = \frac{\hbar \gamma^2}{M v_i^2 \Theta_i} \left(\frac{k_B}{\hbar} \right)^2 x^2 T^3 e^{-\Theta_i/3T}, \quad (9)$$

where γ , V , and M are the Grüneisen parameter, the volume per atom, and the average mass of an atom in the crystal, respectively. The Grüneisen parameter can be defined as [36]

$$\gamma_i = - \frac{V}{\omega_i} \frac{\partial \omega_i}{\partial V}. \quad (10)$$

The detailed expressions can be found in Ref. [28] by [28].

3. Results and discussion

3.1. Structural and elastic properties

ThC₂ exists as monoclinic structure (space group C2/c) at ambient conditions [2], as shown in Fig. 1(b). It can be seen from the figure that the two carbon atoms actually form a C₂ dimer with the bond length of 1.33 Å. This bond length is quite close to that (1.28 Å) of a free standing C₂ dimer. The calculated lattice constants of ThC₂ are composed in Table 1. The table shows that our results are quite reasonable in comparison with the experimental data [6,7] and the previous calculation [13]. Since the thermal conductivity of ThC (Fm $\bar{3}$ m) will be studied in the last section of our manuscript, the lattice constant for the ThC was also calculated. The calculated constant 5.35 Å is also in a good agreement with the experimental data 5.34 Å [37].

The bulk modulus B and its derivative B_0 of ThC₂ were obtained by fitting the total energy to the third order Birch–Murnaghan equation of state. Our results show a very good agreement with the previous calculation as listed in Table 2. Using the strain–stress relationship, we have calculated elastic constants for ThC₂, which

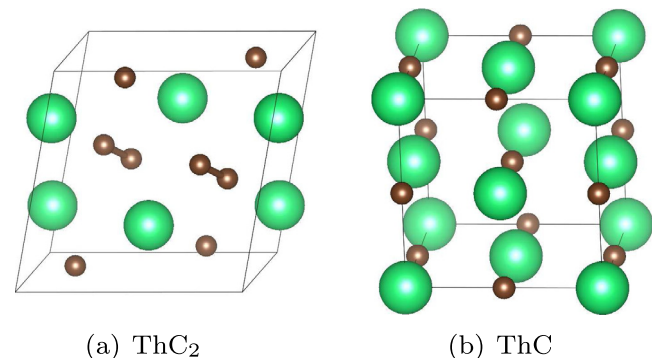


Fig. 1. The crystal structures of ThC₂ (a) and ThC (b). Big spheres and small spheres represent Th and C, respectively.

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