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A new phase of ThC at high pressure predicted from a first-principles study

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ABSTRACT

The phase transition of thorium monocarbide (ThC) at high pressure has been studied by means of density functional theory. Through structure search, a new phase with space group $P4/nmm$ has been predicted. The calculated phonons demonstrate that this new phase and the previous $B2$ phase are dynamically stable as the external pressure is greater than 60 GPa and 120 GPa, respectively. The transformation from $B1$ to $P4/nmm$ is predicted to be a first-order transition, while that from $P4/nmm$ to $B2$ is found to be a second-order transition.

1. Introduction

For the purpose of high-performance nuclear fuel, there has been a renewed interest in thorium carbide since this material is suitable for high-burnup and high-temperature operations with a reduced “margin to melting” in the framework of the Generation IV nuclear systems [1]. Additionally, thorium is thought to be ~3.1 times more naturally abundant than uranium in the terrestrial upper mantle as inferred from analyses of mid-ocean-ridge basalts [2,3]. And usually a thorium fuel cycle can produce negligible amounts of plutonium and fewer long-lived minor actinides than a uranium cycle [4].

In principle, there may be extreme conditions of high temperature and high pressure inside the nuclear reactor, thus it is necessary to comprehensively understand the structural stability of ThC in the condition of high pressure. At ambient conditions, thorium monocarbide (ThC) has a rock-salt type structure (denoted as $B1$ phase). The structural, electronic, elastic, and thermodynamic properties of the $B1$ phase have been extensively studied by many groups [5–16]. At high pressure, the research on ThC is still limited. Experimentally, Gerward et al. and Staun Olsen et al. did not observe the structural phase transition from the $B1$ phase to the $B2$ phase ($Pm\bar{3}m$) up to 50 GPa [12–14]. Recently, Sahoo et al. [16] proposed that $B1$ may be transformed to $B2$ at around 40 GPa based on their first-principles calculations, however, their dynamical stability was not carefully discussed in their work.

One interesting question remains unanswered “Is there any possible phase transition for ThC under high pressure?” It is well known that the dynamical instability of crystal structure is associated with soft phonon modes with imaginary frequencies. To check the stability of the ground-state structure of ThC, the phonon dispersion curves at different volumes were calculated and illustrated in Fig. 1. The figure shows that the longitudinal acoustic branch has soft modes at a compressed volume $V/V_0 = 0.809$, indicating that the $B1$ phase is dynamically unstable at high pressure. Then we have performed a structure search for ThC by using the *ab initio* evolutionary algorithm **USPEX** [17,18]. Interestingly, a new crystal structure ($P4/nmm$ phase) of ThC was discovered, as illustrated in Fig. 2(b). Meanwhile, the ground-state structure ($B1$) and the previous theoretical predication ($B2$) [16] were also successfully reproduced, as illustrated in Fig. 2. In this paper, the dynamic stability of these structures will be extensively studied by using first-principles calculations based on density functional theory (DFT). The transition paths and energy barriers among the $B1$, $P4/nmm$ and $B2$ phases will be studied by using the variable cell nudged elastic band (VC-NEB) method [19], which can provide a broad way

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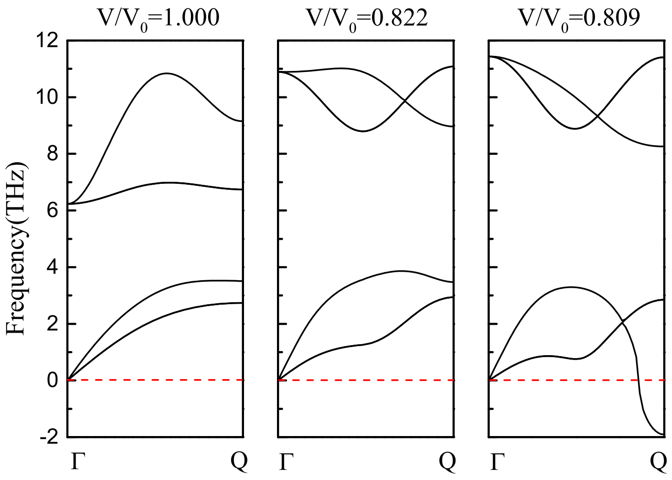

Fig. 1. Phonon dispersion relation along Γ–Q for the $B1$ phase of ThC at different volumes. V_0 is the equilibrium volume.

to find the minimum energy path and to investigate the activation energies between the two given phases for a phase transition process within a larger configuration space. This technique has proven to be efficient for studying the paths and mechanisms of reconstructive phase transitions [20].

2. Theoretical methods

All of the density-functional-theory (DFT) calculations in this study were carried out using the Vienna *Ab initio* Simulation Package (**VASP**) [21,22] with the projector augmented wave scheme (PAW) [23,24]. The exchange-correlation functional with generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [25] was used to solve the Kohn–Sham equations with a kinetic energy cutoff of 600 eV. Since none of the localized $5f$-like band is occupied in Th, the DFT with the GGA approximation was proved to be enough to describe the structural and vibrational properties of ThC [6–8,11]. We have searched the crystal structure of ThC by using the evolutionary algorithm **USPEX** [17,18]. For the structural relaxations, we performed with ions, cell volume, and cell shape being allowed to change. The Brillouin zone was sampled with a 16 × 16 × 16 k-point mesh and a 12 × 12 × 16 k-point mesh generated via the Monkhorst-pack scheme [26] for cubic structure ($B1$ and $B2$ phases) and tetragonal structure ($P4/nmm$ phase), respectively. The geometries were considered to be converged when the forces on each ion became less than 0.001 eV/Å. The convergence threshold was set to be 10^{-7} eV/atom for the total energy calculations in the electronic self-consistent loop. For the fitting of equation of state (EoS), the third-order Brich–Murnaghan equation of state [27] was used. The phonon calculations were carried out by using a supercell approach [28] as implemented in the **PHONOPY** code [29]. Structural transition paths and energy barriers were explored with the VC-NEB method [19], which can deal with the variation of the unit cell during solid–solid transformations. The convergence criteria for the force and energy were 0.001 eV/Å and 0.0001 eV for each image, respectively.

Table 1
Calculated lattice constants and equilibrium volumes for the $B1$, $P4/nmm$ and $B2$ phases in comparison with available experimental and theoretical data.

		a_0 (Å)	c_0 (Å)	V_0 (Å^3/f.u.)
$B1$	Our results	5.352		38.32
	Experimental	5.3221 [12]		37.68 [12]
		5.335–5.344 [30]		
	Theoretical	5.3879 [6]		38.75 [6]
		5.341, 5.269 [10]		38.09 [16]
$P4/nmm$	Our results	4.509	3.683	37.45
$B2$	Our results	3.193		32.55
	Theoretical	3.205 [16]		32.91 [16]

3. Results and discussions

Crystal structure of ThC is a NaCl-type structure (denoted as $B1$ phase; space group $Fm\bar{3}m$) at ambient conditions [12], as shown in Fig. 2(a). At high pressure, we performed the extensive structure search through the **USPEX** code [17,18] without any prior structural information. As a result, the $B1$ phase and the previous $B2$ phase (CsCl-type, shown in Fig. 2(c)) [16] have been successfully reproduced in our calculations. Meanwhile, a new structure with the space group $P4/nmm$ has been predicted herein, as illustrated in Fig. 2(b). This new phase is a tetragonal structure including two ThC formula units (f.u.) in a primitive cell. The atomic positions are given as follows: the basis C atom occupies 2a Wyckoff position (0.5, 0.5, 0.0), the basis Th atom occupies 2c Wyckoff position (0.5, 0.0, 0.7268). The calculated lattice parameters for $B1$, $B2$ and newly predicted ThC are shown in Table 1. The table shows that our calculated constants for the $B1$ and $B2$ phases are in very good agreement with the experiments [12,30] and the previous calculations [6,10,16].

The equation of state (EoS) of a material is of fundamental importance in high-pressure physics since it gives the relationship between the pressure and volume. The EoS for the three phase of ThC are shown in Fig. 3. It can be seen that the $B1$ phase is more stable than the new phase ($P4/nmm$), which in turn is more stable than the $B2$ phase. To obtain the transition pressure among the three phase, the enthalpy as a function of pressure was calculated, and presented in the inset of Fig. 3. The figure shows that the new

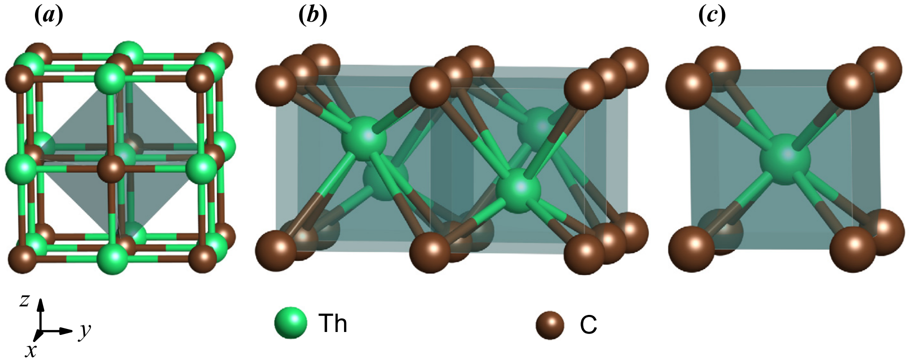

Fig. 2. Crystal structures (a), (b), and (c) represent the $B1$ phase, the newly predicted phase ($P4/nmm$), and the $B2$ phase, respectively. For the $P4/nmm$ phase, the lattice constants are $a = b = 4.509$ Å, $c = 3.683$ Å, and $\alpha = \beta = \gamma = 90°$, with atomic positions of C at 2a (0.5, 0.5, 0.0) and Th at 2c (0.5, 0.0, 0.7268).