Structural phase stability and elastic properties of refractory carbides

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ABSTRACT

In the present paper, we have investigated the high-pressure structural phase transition of refractory carbides (ZrC, HfC, NbC and TaC). A Modified Interaction Potential Model with Covalency (MIPMC$_v$) has been applied. Phase transition pressures are associated with a sudden collapse in volume showing the occurrence of first order phase transition. At compressed volumes, these compounds are found in CsCl phase. The phase transition pressures and associated volume collapses obtained from present potential model show a generally better agreement with available experimental data than others. The elastic constants and bulk modulus are also reported. Our results are in general in good agreement with experimental and theoretical data where they are available, and provide predictions where they are unavailable.

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1. Introduction

The 'interstitial' carbides of group IV and group V elements are refractory with interesting properties like high hardness and strength and often a high thermal and electrical conductivity. This makes them interesting materials for applications such as coatings and diffusion barriers. The carbides of refractory metals ZrC, HfC, NbC and TaC have recently drawn considerable attention in research for many special properties. These properties are important not only because of their technological applications in industries as dispersion hardening particles in cutting tools but also for potential applications in information storage technology, high power industry, and opto-electronic devices. These refractory carbides (RC) show unique combination of properties such as high-melting temperature, high hardness, good high-temperature strength, and good electrical and thermal conductivity. Hence carbides have long been used as high-temperature structural materials in the form of hard constituents in metal matrix composites or coatings on cutting tools. Therefore, the searching for materials with hardness exceeding or comparable to diamond has always fascinated humans and is also a great challenge. Because of their unique physical properties and degeneracy in optical vibration frequencies at the zone center, these carbides have always been fascinating and challenging both experimentally and theoretically [1–3].

Zirconium carbide ZrC belongs to a large family of highly refractory interstitial compounds. Some of the carbides like NbC and HfC have the highest known melting point. ZrC is used in the high temperature nuclear reactors and alloys. ZrC is widely used as the main constituent in cutting tools [4] for its very hard property. Especially, ZrC is characterized by the ultra-high melting point, solid-state phase stability, and good thermo mechanical and thermo chemical properties [5]. These properties promote further investigations on ZrC. A lot of work is available on ZrC. Thermodynamic properties of cubic ZrC under high pressure have been performed by first principle calculations [6]. The elastic properties of cubic ZrC under high pressure have been studied by ab initio plane-wave pseudo potential density function theory (DFT) method [7] together with local density approximation (LDA). Along with high pressure studies on lattice dynamics of carbides are also available. The lattice dynamics of HfC has been studied by coherent inelastic neutron scattering [8]. The lattice dynamics of ZrC, NbC, and HfC had been studied long back [9]. Their results strongly support the covalent model, where the extreme physical properties of these carbides are also mainly attributed to strong covalent bond between metal and non-metal atoms in these compounds. The type of the bonding found for the RC systems is not typically ionic but more covalent [10] and the occurrence of ionic-like structure in combination with covalent-like hardness is very interesting.

Further the electronic band structure and X-ray photoelectron spectra of ZrC, HfC and TaC have been performed by Ihara et al. [11]. Wu et al. [12] studied the trends in elasticity and electronic structure of transition metal nitrides and carbides. Recently high pressure phase transitions in carbides of Ti, Hf, V, Nb and Ta are reported by Shrivastava et al. [13] using the first principle calculations. The FPLAPW investigations of electronic structure and bonding mechanism of NbC have been studied by Amriou et al. [14]. The first principle calculations on the electronic structure have been performed on alloys TiC$_x$N$_{1-x}$, Zr$_x$Nb$_{1-x}$C and HfC$_x$N$_{1-x}$ [15]. High pressure behavior and structural properties of TiC, ZrC, NbC, HfC and TaC have been predicted by Singh et al. [16,17] using an interionic potential theory based on two body interaction potential model.

Even with the many efforts of first-principle calculations for the electronic properties of rare earth and transition metal compounds,

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the developments in theoretical modeling have made promising attempts of the calculation of structural, mechanical and thermal properties of different groups of compounds. These developments have created new opportunities for studying these hard materials. It is well known that the carbides of refractory metals are highly covalent due to the presence of two electrons in the outer most orbits. Since the previous calculations [16,17] ignored the covalency effect in their calculations, we thought it pertinent to apply a Modified Interaction Potential Model with Covalency (MIPMC$_v$) which includes the covalence effect in the potential model. This model consists of Coulomb interaction, three body interactions, van der Waal interaction, overlap repulsive interaction and covalent interaction. Among these the significance of van der Waal (vdW) attraction due to the dipole–dipole (d–d) and dipole–quadruple (d–q) interactions to describe the cohesion in ionic solids have been emphasized by Tosi and coworkers [18] which are generally ignored in the first principle calculations.

In the present paper, we have used the model theory to calculate the high pressure structural and elastic properties of RCs and compared them with available theoretical and experimental data to judge the suitability of the potential and our predictions for these properties. The organization of this paper is as follows: the method of calculation of structural phase transition pressure and model theory are given in Section 2, while in Section 3, we present interesting results on structural and elastic properties of refractory carbides, namely ZrC, NbC, HfC, and TaC.

2. Potential model and method of calculation

The natural consequence of application of pressure on the crystals is the compression, which in turn leads to an increased charge transfer (or three-body interaction effects) [19] due to the existence of the deformed (or exchanged) charge between the overlapping electron shells of the adjacent ions.

These effects have been incorporated in the Gibbs free energy (G = U + PV − TS) as a function of pressure and three body interactions (TBI), which are the most dominant among the many body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At temperature T = 0 K and pressure (P) the Gibbs free energies for BX (X = 1,2) phase are:

$$G_{BX}(r) = \frac{-\alpha_m{}^X Z^2 e^2}{r^X} - \frac{12\alpha_m{}^X Z e^2 f_m(r)}{r^X} - \left[\frac{C^X}{r^{X6}} + \frac{D^X}{r^{X8}}\right]$$
$$+ 6b\beta_{ij} \exp\left[\left(r_i + r_j - r^X\right)/\rho\right] + 6b\beta_{ii} \exp\left[\left(2r_i - Y_X r^X\right)/\rho\right] \quad (1)$$
$$+ 6b\beta_{jj} \exp\left[\left(2r_j - Y_X r^X\right)/\rho\right] + PV_{BX}\left(r^X\right)$$

where X = 1 (Phase 1 = B1), 2(Phase 2 = B2), and Y_x = 1.414, 1.154, for NaCl and CsCl structures respectively.

With α_m^X as the Madelung constant. C and D are the overall van der Waal coefficients for NaCl and CsCl structure respectively, β_{ij} (i,j = 1,2) are the Pauling coefficients defined as $\beta_{ij} = 1 + (Z_i/n_i) + (Z_j/n_j)$ with Z_i (Z_j) and n_i (n_j) as the valence and the number of electrons of the i(j) th ion. Ze is the ionic charge and b (ρ) is the hardness (range) parameters, r is the nearest neighbor separations $f_m(r)$ is the modified three body force parameter which includes the covalency effect with three body interaction and r_i (r_j) are the ionic radii of ions i (j).

These lattice energies consist of long range Coulomb energy (first term), three body interactions corresponding to the nearest neighbor separation r (second term), vdW (van der Waal) interaction (third term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) [20] type potential and extended up to the second neighbor ions (fourth, fifth and sixth terms).

Covalency effects have been included in three-body interaction in the second terms of lattice energies given by Eq. (1) parameter on the lines of Motida [21]. Now modified three body parameter $f_m(r)$ becomes

$$f_m(r) = f_{TBI}(r) + f_{cov}(r). \quad (2)$$

The relevant expressions of f_{TBI} (r) and fcov(r) are given in our earlier work [22].

3. Results and discussion

The Gibbs free energy contains three model parameters [b, ρ, $f_m(r)$]. The values of these parameters have been evaluated using lattice parameter, the first space derivatives of the lattice energy (U) and equilibrium condition expressed as:

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 \quad (3)$$

$$\left[\frac{d^2U}{dr^2}\right]_{r=r_0} = 9kr_0 B_T \quad (4)$$

and after following method adopted earlier [22–25]. Using these model parameters and the minimization technique, phase transition pressures of refractory carbides have been computed. The input data [26] of the crystal and calculated model parameters are listed in Table 1.

3.1. Structural properties

The B1 (NaCl) structure is most stable in present compounds and at high pressure they transform to body centered B2 (CsCl) structure. As, the stable phase is associated with minimum free energy of the crystal, we have followed the technique of minimization of Gibbs free energies of real and hypothetical phases. The phase transition occurs when Gibbs free energy difference ΔG approaches zero (ΔG → 0). At phase transition pressure (P$_t$) these compounds undergo a (B1–B2) transition associated with a sudden collapse in volume showing a first order phase transition.

Fig. 1 shows our present computed phase transition pressure for B1–B2 structural transition in ZrC at 99 GPa, HfC at 87 GPa, NbC at 92 GPa, and TaC at 94 GPa respectively. The present phase transition pressures have been illustrated by arrows in Fig. 1 and have been listed in Table 2 with comparisons with the experimental and other theoretical results. It is interesting to note from Table 2 and Fig. 1 that the phase transition pressures (P$_t$), obtained from the MIPM model are in general in closer agreement with other theoretical data [13,16,17] for present carbides.

At elevated pressures, the materials undergo structural phase transition associated with a sudden change in the arrangement of the atoms. The atoms are rearranged in new positions leading to a new structure. Experimentally one usually studies the relative volume changes associated with the compressions. The discontinuity in volume at the transition pressure is obtained from the phase diagram. We have also computed the relative volume changes V(P)/V(0) corresponding to the values of r and r′ at different pressures and plotted them against the pressure in Fig. 2(a–d) for ZrC, HfC, NbC and TaC. The values of the volume collapses (%) are depicted in Table 2. It is clear from Table 2 and Fig. 2(a–d) that our calculated volume collapses − ΔV$_{(p)}$/V$_{(0)}$ from our MIPM model for ZrC is 8.5%, HfC is 5.3%, NbC is 6.2% and TaC is 7.0%. We have compared our results of volume collapse with the first principle calculations by Shrivastava et al. [13], the interionic potential theory by Singh et al. [16] and a two body interionic potential model by Singh et al. [17]. It is clear from Table 2 that our results on volume collapses are close to other