Physica B 410 (2013) 57–62

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

First-principle calculations of thermodynamic properties of ZrC and ZrN at high pressures and high temperatures

Arash Abdollahi *

Department of Physics, Faculty of Science, Urmia Branch, Islamic Azad University, Urmia, Iran

ARTICLE INFO

Article history:
Received 25 June 2012
Received in revised form
27 October 2012
Accepted 31 October 2012
Available online 10 November 2012

Keywords:
ZrC
ZrN
First-principle calculation
Quasi-harmonic
Thermodynamic properties
High pressure

ABSTRACT

Ab initio calculations for the thermal properties of ZrC and ZrN have been performed by using the projector augmented-wave (PAW) method within the generalized gradient approximation (GGA). Pressure–temperature-dependent thermodynamic properties including the bulk modulus, thermal expansion, thermal expansion coefficient, heat capacity at constant volume and constant pressure were calculated using three different models based on the quasi-harmonic approximation (QHA): the Debye–Slater model, Debye–Grüneisen model and full quasi-harmonic model (that requires the phonon density of states at each calculated volume). Also the empirical energy corrections are applied to the results of three models. The calculated values are in good agreement with experimental results. It is found that the full quasi-harmonic model provides more accurate estimates in comparison with the other models.

1. Introduction

Zirconium nitride (ZrN) and Zirconium carbide (ZrC) ceramics are characterized by high melting point, high stiffness, wear resistance and solid-state phase stability [1–3]. They also have high hardness, high thermal and electrical conductivity and low evaporation which make them widely used for cutting tools, and also wear-resistant coatings, manufacturing of electrodes and filaments [4]. Because of the special properties of maintained ceramics, they have been extensively studied both experimentally and theoretically. Méçabih et al. [5] and Saha et al. [6] have studied the structure and electronic properties of ZrC and ZrN, respectively. There are a number of experimental reports on the thermal expansion of ZrC [7,8] and ZrN [9–12]. Also, several measurements have been made to determine the heat capacities of ZrC [13–16] and ZrN [17–19]. There have been a number of theoretical studies of the thermodynamic properties of ZrC and ZrN. In the framework of the quasi-harmonic approximation, the heat capacities of the cubic metal nitrides have been investigated by Iikubo et al. [20] and Wang et al. [21]. Lu et al. [22,23] evaluated the thermodynamic properties of nitrides and carbides at temperatures up to 3000 K by using the Debye–Grüneisen model [24]. Jun et al. [25] and Fu et al. [26] have investigated the thermodynamic properties of ZrC and also Hao et al. [27] have calculated the thermodynamic properties for ZrN, by using quasi-harmonic Debye model [28]. Also there are a few theoretical studies of the structural phase transformation from the NaCl-type (B1) structure to CsCl-type (B2) structure of the ZrC and ZrN. Theoretical results for phase transition pressures are 295 GPa [27] and 303 GPa [29] for ZrC, also 205 GPa [27] for ZrN. In this paper, I report my theoretical study of the thermal properties of zirconium carbide and zirconium nitride and compare the results of Debye–Slater model [30], Debye–Grüneisen model and full quasi-harmonic model [31]. The results obtained from all three models for the bulk modulus, thermal expansion, coefficient of volume thermal expansion (CVTE), heat capacity at constant volume (C_V) and constant pressure (C_P) are reported and discussed.

2. Theoretical method

2.1. First-principles and phonon calculations

The ab initio calculations were performed within the density functional theory (DFT), using the plane-wave pseudo-potential method as implemented in the Quantum-ESPRESSO package [32] with the ultrasoft Vanderbilt pseudo-potentials [33]. For the exchange and correlation terms in the electron–electron interaction, the generalized gradient approximation (GGA) of Perdew–Burke–Eruzerhof (PBE) [34] has been used. The plane-wave energy cutoff was 80 Ry and the k-grids used in total energy were $16 \times 16 \times 16$ Monkhorst–Pack (MP) meshes [35]. Density

* Tel.: +98 9111136472.
E-mail address: arash_abdollahi60@yahoo.com

0921-4526/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.10.035

functional perturbation theory (DFPT) [36] as implemented in Quantum-ESPRESSO was used for phonon calculations. For the phonon calculations we have used 80 Ry energy cutoff for all atoms together with an $8\times8\times8$ mesh of k-points. The self-consistent threshold value for convergence was 10^{-10} Ry, and for phonon calculations it was set to 10^{-16} Ry. The dynamical matrices are produced in a k-point grid of $12\times12\times12$ in irreducible wedge of the Brillouin zone. For Brillouin zone integration, the first-order Methfessel–Paxton method [37] was used with a smearing width of 0.05 Ry.

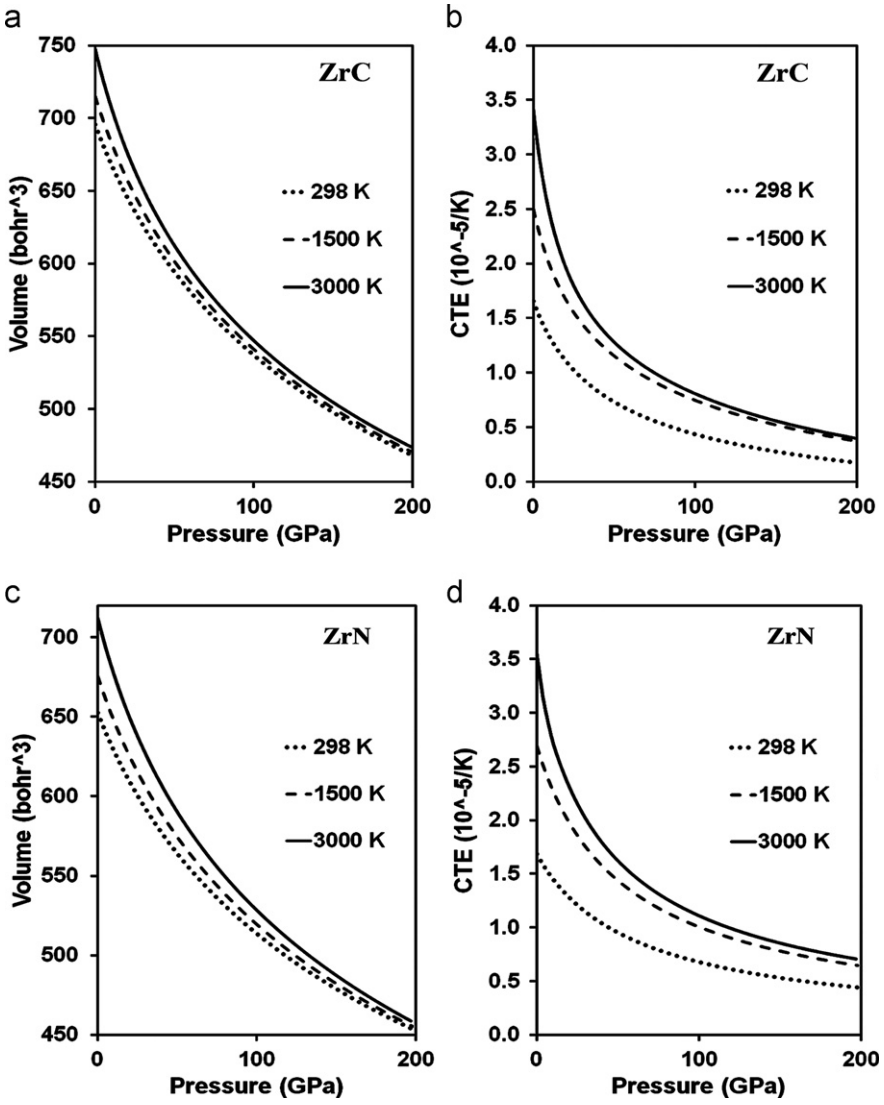

Fig. 1. Equation of states of ZrC (a) and ZrN (c). The coefficient of volume thermal expansion of ZrC (b) and ZrN (d).

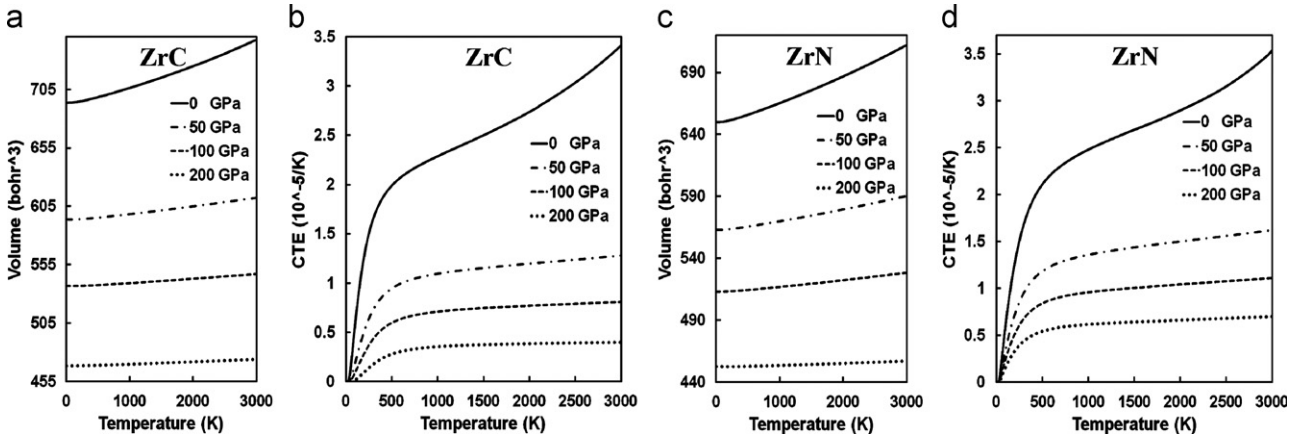

Fig. 2. Temperature dependence of the volume of ZrC (a) and ZrN (c). The coefficient of volume thermal expansion of ZrC (b) and ZrN (d) as a function of temperature.