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First principles study of structural, electronic, elastic and thermodynamic properties of cubic HfO_2 under pressure

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Abstract

In this paper, we report the results of the density functional theory (DFT)-based theoretical calculations of structural, electronic and elastic properties of HfO_2 in cubic phase (c-HfO_2) under pressure up to 30 GPa using full-potential linearized augmented plane wave (FP-LAPW) approach as implemented in Wien2k package. The generalized gradient approximation as parameterized by Wu-Cohen (GGA-WC) and the Tran-Blaha modified Becke-Johnson exchange potential (mBJ) with improved parameterization by Koller were used for the exchange-correlaton effect, the later was employed with objetive of obtaining accurate band gap of the compound. Our results of structural optimization are in good agreement with other available theoretical ones and experimental datas, and we found that the volume of c-HfO_2 decreases with pressure. Our electronic calculations indicate that c-HfO_2 has indirect band gap X-Γ whose value is 6.189 eV, and this value increases with increasing pressure. The calculated elastic properties show that this material is ductile for pressures up to 12.5 GPa, and then it becomes elastically brittle. Finally, the thermodynamic properties of c-HfO_2, such as, heat capacities, thermal expansion, Debye temperature, Grüneisen parameter and entropy under high pressures and tempratures were computed using the quasi-harmonic Debye model as embedded in GIBBS2 code and analyzed in details.

Keywords: HfO_2, structural, electronic, elastic, thermodynamic, high pressures, high temperatures.

1. Introduction

Nowaday, hafnium oxide (HfO_2), a high K-dielectric metal oxide, is gaining increased interest of scientific community due to its unique physical and chemical properties, such as, high dielectric constant ($\epsilon = 25$) [1], thermal and chemical stability [2, 3], optical transparence in large energy range as result of its wide band gap (5.68 eV) and low phonon frequencies [4], high melting temperature (2774^0C) [5], large heat of formation [6], high refractive index [7], etc. These mentioned properties make HfO_2 suitable for applications as luminiscent materials [4, 5, 8–10], in microelectronic devices [11], etc. Experimentally, HfO_2 has been synthesized by different methods and its three polymorphs have been observed: the monoclinic m-HfO_2 (space group $P2_1/c$), the tetragonal t-HfO_2 (space group $P4_2/nmc$) and the cubic c-HfO_2 in fluorite structure (space group $Fm\bar{3}m$) [12–18].

From theoretical point of view, the physical properties of c-HfO_2 have been studied extensively. Caravaca et al [19] studied the structural, electronic and elastic properties of different polymorphs of HfO_2 using pseudopotential and localized basis sets. Ponce et al [20] studied the mechanical properties of c-HfO_2 by means of the *ab*-initio all electron full-potential linear-muffin-tin orbitals method and predicted that this compound shows more ductility than brittleness. Q. Liu et al [21] investigated the structural, optical and elastic properties of c-HfO_2 using the plane-wave ultrasoft pseudopotential technique based on the first-principles density-functional theory (DFT), obtained a band gap of 2.8 eV. Yang et al [22] studied the structural and electronic properties of c-HfO_2 using the projected augmented plane wave (PAW) with hybrid functionals and obtained band gap of 5.10 eV and 5.38 eV with HSE03 and HSE06, respectively. Jiang et al [23] calculated band gap of c-HfO_2 using advanced functionals G_0W_0 and GW_0 and obtained band gap values of 4.92 eV and 5.20 eV, respectively. Li et al [24] tried to improve band gap of c-HfO_2 computed with GGA by introducing

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