STRUCTURAL, ELECTRONIC, ELASTIC, PHONON AND THERMAL PROPERTIES OF L12 INTERMETALLIC COMPOUNDS BASED ON IRIDIUM (Ir3Hf)

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Abstract: We present ab initio calculations of the structural, electronic structures, elastic, thermodynamic and vibrational properties of the Ir3Hf compound in the L12 structure. The calculated lattice constants, bulk modulus, and first-order pressure derivative of the bulk modulus are reported for the L12 structure and compared with the earlier values. The elastic constants (C11, C12 and C44) in the L12 phase for Ir3Hf compound is calculated using the energy-strain method. The calculated elastic constants satisfy the mechanical stability criterion. Electronic band structures and partial and total densities of states have been derived for Ir3Hf. The band structures show metallic character; the conductivity is mostly governed by Ir 5d states. The phonon-dispersion curves and phonon total density of states based on the linear-response method have been investigated for this compound. Temperature variations of specific heat capacity in the range of 0–1000 K are obtained using the quasi-harmonic model.

Keywords: DENSITY FUNCTIONAL THEORY, ELECTRONIC STRUCTURE, VIBRATIONAL PROPERTIES

1. Introduction

Ir-based intermetallic compounds are of great interest due to their high melting point, good mechanical properties, and thermal stability at high temperatures and excellent oxidation resistance at elevated temperatures [1–4]. L12 intermetallic compound Ir3Hf is widely used in the automobiles, space power applications [5] and interest in their high temperature applications is increasing. The L12 intermetallic compound Ir3Hf has aroused the interest of many researchers both experimentally and theoretically because of their high strengths and high melting points, and the coherent structures [6-11], mechanical [5, 12], structural [11, 13-17], thermal [9, 10, 17], thermodynamic [6, 8, 18, 19], elastic and electronic properties [11, 13, 19], microstructure [20, 21], phase diagrams (stability) [5, 6, 14, 17] and oxidation [20, 21] of Ir3Hf has been studied by many research groups, employing different experimental and theoretical methods. Kontsevii et al. [13] have investigated the mobility and structural properties in Ir3Hf and Ir3Nb with L12 phase in the framework of modified Peierls-Nabarro (PN) model with first principle generalized stocking fault energetic calculated by using FLAPW. The morphology evolution of Ir-Nb-Hf system have been measured by Huang et al. [21] with the microstructure observation, using SEM, composition map-analysis by EPMA, and phase determination using X-ray diffraction (XRD) pattern. Yamabe-Mitarai et al. [18] investigated using compression tests between -196 and 1200 °C of Ir3Nb in the L12 phase. They observed that the strength degreased with increasing temperature from -196 to room temperature while the strength increased with increasing temperature between room temperature to 800 °C. Gu et al. [10] investigated the ultra high temperature deformation properties of directionally solidified (DS) and polycrystalline (PC) L12 Ir3Nb compound. Their results show that directionally solidified (DS) compound has higher creep resistance and large creep life than polycrystalline compound under experimental conditions. Terada et al. [9, 17] measured by using employing the laser-flash method thermal conductivity and thermal expansion in the temperature range from 300 to 1100 °C for Ir3Hf compound. Their measurements indicated that Ir3Hf and Ir3Nb compounds have large conductivities and smaller temperature coefficients. The elastic constants and other mechanical parameters of Ir3Hf compound has been calculated using Vienna ab initio simulation package (VASP) by Gong [11]. A first-principle calculation on the electronic structures of the Ir3Hf L12 intermetallic compound has been studied by several groups [11, 13, 19] and electronic structures for Ir3Hf compound in the L12 phase has not been studied in detail so far in the available literature. Liang and Gong [19] have studied the temperature dependence heat capacity, thermal expansion coefficient, elastic constants, and lattice misfit for Ir3Hf compound.

In addition, they have computed electronic and phonon density of states using VASP-PAW code. The phonon properties are important to understand the microstructure of the lattice dynamics. The knowledge of the phonon spectrum plays a significant role in determining various material properties such as phase transition, thermodynamic stability, transport and thermal properties. The full phonon properties of Ir3Hf have not yet been studied by using any theoretical or experimental method.

2. Computational Methods

The Quantum-ESPRESSO software package [22] is used in the present calculations based on DFT [23, 24]. Ultrasoft pseudopotentials were used, and the cut-off energy for the plane wave basis set was 40 Ry. The electronic exchange-correlation energy was treated under generalized gradient approximation (GGA) parameterized by Peredew–Burke–Ernzerhof [25]. Self-consistent solutions of Khon–Sham equations were obtained by employing a set of 60 k-points within the irreducible part of the Brillouin zone. Eight dynamical matrices were calculated on a 4×4×4 q-point mesh to obtain complete phonon dispersions and vibrational density of states. The dynamical matrices at the arbitrary wave vectors were evaluated using the Fourier deconvolution on this mesh. Specific heat at constant volume versus temperature was calculated using the quasi-harmonic approximation (QHA) [26].

Elastic constants were obtained by calculating the total energy as a function of volume-conserving strain. The symmetry of the total energy was investigated under generalized gradient approximation (GGA) parameterized by Peredew–Burke–Ernzerhof [25]. The elastic constants of Ir3Hf are obtained using the generalized gradient approximation (GGA) along the higher symmetry direction, and are shown in Fig. 1, in which EF = 0 is taken. The character of the band states for Rh3Hf compound has been identified by calculating their total and partial densities of states (DOS) (in Fig. 2). It is seen that there is no gap at the Fermi level and the total density of state...
This exhibits normal metallic behavior with bands crossing the Fermi level along various directions, which results in a finite DOS at the Fermi level, as shown in Fig. 2. The results indicate that the predominant contributions of the density of states at the Fermi level come from the Ir 5d states for Ir₃Hf compound. From the calculated total DOS of Ir₃Hf compound, it can be seen that there is one peak below the Fermi level. This peak is centered 3 eV, which is mainly dominated by the Ir 5d state and Hf 5d state.

The calculated phonon dispersion curves for Ir₃Hf compound along the high-symmetry directions and the phonon density of states are illustrated in Fig. 3. The primitive cell of Ir₃Hf compound contains three atoms, leading to a total of 9 phonon branches. Due to the symmetry, the distinct number of phonon branches is reduced along the principal symmetry directions Γ -X and M-R-Γ. All phonon frequency this material is positive that there are no phonon branches with dispersion that dip toward the zero frequency. This indicates that the both of the materials are dynamically stable.

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Fig. 4 shows the calculated specific heat capacity at constant volume (Cᵥ) of Ir₃Hf compound as a function of temperature. The Cᵥ increases rapidly in the range 0–500 K before it starts to saturate. The calculated specific heat capacity Cᵥ is very close to the Dulong-Petit limit [30] at high temperature, which is commonly satisfied with all solids at high temperatures. For all materials, the Cᵥ functions flatten out as the temperature increases above 300 K. The optic and acoustic modes have large effects on the heat capacity.

The calculated lattice constants (a Å), bulk modulus, pressure derivative of the bulk modulus and second order elastic constants (all in GPa) for Ir₃Hf in the L₁₂ structure are shown in Table 1. All phonon dispersion curves and their corresponding total and projected densities of states for Ir₃Hf compound in the L₁₂ phase were calculated for the first time in the framework of the density-functional perturbation theory. It is found that the heat capacity, internal energy and entropy increase with temperature, but free energy exhibits different trend.

4. Conclusion

The structural, elastic, electronic and phonon properties of states of Ir₃Hf compound have been studied. Pseudopotential method was used in the framework of the density functional theory (DFT) with the generalized gradient approximation (GGA). We have also studied the mechanical properties of these compounds. The elastic constants have been calculated using the approach, the energy-strain method. Band structure and density of states diagrams confirm the metallicity of Ir₃Hf compound in the L₁₂ phase. Phonon dispersion curves and their corresponding total and projected densities of states for Ir₃Hf compound in the L₁₂ phase were calculated for the first time in the framework of the density-functional perturbation theory. It is found that the heat capacity, internal energy and entropy increase with temperature, but free energy exhibits different trend.

References