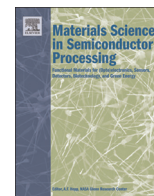




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Vibrational spectra of Ruthenium Carbide structures yielded by the structure search employing evolutionary algorithm

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ABSTRACT

Out of the three dynamically stable structures of Ruthenium Carbides yielded by the exhaustive structure search employing evolutionary algorithm, Born effective charges are computed for the semiconducting RuC in Zinc blende structure using density functional perturbation theory. Using the phonon frequencies and the Born effective charge tensors of Ru and C in this structure, infrared spectrum is generated for this system. Computations of these dynamical quantities and IR spectra from first principles can be helpful in the unambiguous determination of the stoichiometry and structure by comparison of the experimental measurements with the computational predictions. The positive formation energies of the three systems show that high pressure and possibly high temperature may be necessary for their synthesis. Formation energies of these systems at different pressures are computed. One of the structurally stable systems, Ru₃C with hexagonal structure (*P6m2*), has negative formation energy at 200 GPa. The system reported from the first synthesis of Ruthenium Carbide also has the same symmetry, though it has a different stoichiometry.

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1. Introduction

Ruthenium Carbide belongs to the class of potentially hard compounds of the transition metal elements with B, C or N [1–3]. A high charge density of valence electrons supplied by the transition metal atom and p–d hybridized strong covalent bonds formed between B, C or N atom and transition metal atom are the reasons for the potential high hardness of borides, carbides and nitrides of transition metals. Transition metal carbides and nitrides have many industrial applications such as cutting and polishing tools, wear-resistant coatings etc. because of their high melting point, high hardness, good thermal conductivity and high resistance to wear and corrosion [4]. In many applications they could be economically viable substitutes for diamond and cubic Boron Nitride. The diverse applications of these systems have motivated many electronic structure studies to investigate their stability and structural properties [5–14].

Two reported synthesis of Ruthenium Carbide gave tungsten carbide (WC) type hexagonal structure with the space group *P6m2* (187) in RuC stoichiometry [15] and Fe₂N type hexagonal structure with the space group *P3m1* (164) in Ru₂C stoichiometry [16]. The

computational studies on Ruthenium Carbide had so far been concentrating exclusively on RuC stoichiometry [17–22]. In studies using the density functional theory (DFT), only the Zinc blende structure of RuC was found to be dynamically as well as mechanically stable [20,21]. Though tungsten carbide structure was mechanically stable, it lacked dynamical stability in RuC stoichiometry. From the electronic energy band calculation using DFT, RuC–Zinc blende system was found to be a semiconductor and it was estimated to have a Vickers hardness ~37 GPa [20,21]. A recent structure search for RuC stoichiometry using particle swarm optimization algorithm [22] reported *R3m* structure as the ground state. Using Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) to the exchange–correlation functional, it was shown [22] that the *R3m* structure had mechanical and dynamical stability and that it was metallic.

In the present work, we undertake an exhaustive structure search of Ruthenium Carbides using evolutionary algorithm with no assumptions about the possible outcomes. We investigate the possible structures of three stoichiometries, Ru₁C₁, Ru₂C₁ and Ru₃C₁. For the distinct structures yielded by our structure search, the analysis the dynamical stability through the phonon spectra have resulted in three dynamically stable systems. We also calculate two important dynamical properties, the Born effective charges and the IR spectrum, of the semiconducting Zinc blende system in RuC stoichiometry yielded by the structure search. IR

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spectra of Ruthenium Carbide systems are being investigated for the first time in this work. These computational predictions would be helpful indicators for future experimental measurements.

2. Computational methods

The possible crystal structures of Ruthenium Carbides are investigated using the evolutionary algorithm based tool Universal Structure Predictor: Evolutionary Xtallography (USPEX) [23,24]. The local optimization and energy calculation of various structures are done in our USPEX calculations using the electronic density functional theory as employed in, Vienna Ab initio Simulation Package (VASP) [25,26]. Further relaxation and properties calculation are done using VASP. Projector augmented wave (PAW) pseudopotentials [27,28] as supplied with VASP are used, with 4p, 4d and 5s as the valence states for Ru, and 2s and 2p for C. All our total energy calculations are tested for convergence with respect to both plane wave energy cutoff and that of k-grid to a precision of 0.1 meV/atom. The value of plane wave energy cutoff used is 900 eV which is 2.25 times the default value as per the pseudo-potential files of Ru and C. Monkhorst–Pack k-point meshes [29] are used except for hexagonal systems for which Gamma centered k-meshes are used. The Perdew–Burke–Ernzerhof (PBE) [30] generalized gradient approximation (GGA) to the exchange–correlation functional is used. The states are smeared using Methfessel–Paxton scheme [31] with a smearing parameter of 0.1 eV. Both the lattice parameters and the atomic coordinates of all the structures were relaxed such that energies converge to a precision of less than 10^{-10} eV/atom and Hellmann–Feynman forces to less than 10^{-5} eV/Å. Phonons are calculated with force constants generated on $2 \times 2 \times 2$ supercells using density functional perturbation theory (DFPT) [32,33]. The phonon dispersion curves for the relevant systems are calculated by using PHONOPY code [34]. Born effective charges (BEC) are computed using DFPT [33] and IR spectra are generated using phonons and BEC tensors [33].

3. Results and discussion

3.1. Structures

The dynamically stable structures are given in Fig. 1 and their structural data in Table 1 along with their enthalpies of formation. In Fig. 1 the green larger spheres represent Ru atoms and the brown smaller ones represent C atoms. All the nearest neighbors are not explicitly shown and only the labeled atoms belong to the given unit cell. The crystal visualization program VESTA [35] is used to generate the images. In Table 1 lattice parameter of RuC–Zinc blende structure from other computational works are given in brackets. We have obtained Rhombohedral structure (R3m) in Ru₂C stoichiometry but the phonon data has shown that it is not dynamically stable and hence it is not included here. At ambient pressure enthalpy is the same as total energy. In VASP the total energy is computed with respect to the energies of the constituent atoms. Therefore the total energy reported by VASP is the negative of the cohesive energy. Hence the enthalpy/formula unit given in Table 1 represents the negative of the cohesive energy of the system. Negative values of the total energy of these three systems with respect to constituent atoms imply that the cohesive energy values are positive and it shows that the three systems are energetically stable. However, thermodynamical stability has to be determined with respect to the enthalpy of formation. If it is negative, it means that the system can be spontaneously formed from its constituent elements. The enthalpies of formation of these Ruthenium Carbide systems are calculated with reference to

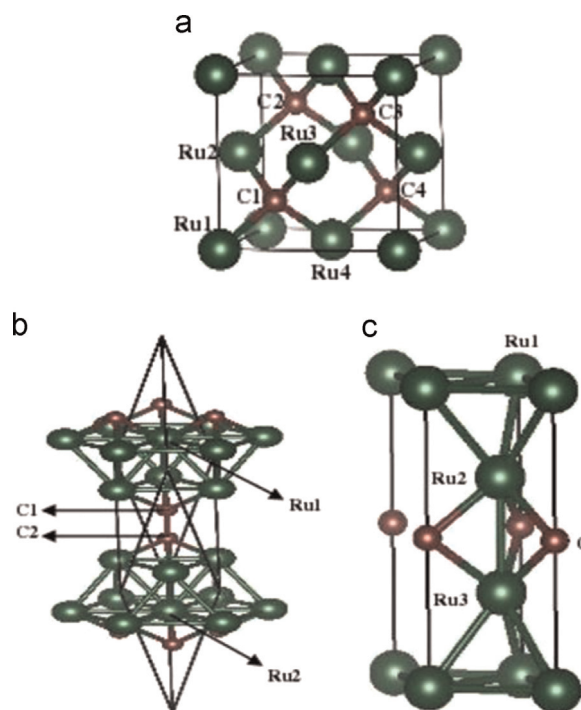


Fig. 1. Dynamically stable structures yielded by the structure search. (a) RuC–Zinc blende (b) RuC–Rhombohedral (c) Ru₃C–Hexagonal. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

crystalline Ruthenium and Graphite. To get the enthalpy per atom of Ruthenium and Graphite, convergence of k -grid is done for both using plane wave energy cut-off of 900 eV and the structures are fully relaxed. For Graphite enthalpy/atom of -9.2320 eV is obtained with a k -grid of $19 \times 19 \times 7$ and for Ruthenium, -9.2751 eV with a k -grid of $31 \times 31 \times 20$. For a structure with unit cell stoichiometry of Ru_aC_b, the enthalpy of formation ΔH_f is calculated by the formula

$$\Delta H_f = \text{Enthalpy of Ru}_a\text{C}_b - a \times (\text{Enthalpy per atom of Ruthenium}) - b \times (\text{Enthalpy per atom of Graphite}) \quad (1)$$

Fig. 2 presents the variation of energy with unit cell volume for the two systems in RuC stoichiometry and Fig. 3, for the Ru₃C system. The symbols represent the energy values from DFT calculation and the solid lines correspond to the fits with Murnaghan equation of state [36]. The energy and volume values are normalized to formula units.

All the structures have positive enthalpies of formation (Table 1) that show that they are not thermodynamically stable, i.e. they cannot be spontaneously formed under ambient conditions. In order to synthesize them, sufficient energy should be supplied and possibly high temperature and pressure. The synthesis of Ruthenium Carbide [15,16] under high pressure and high temperature testifies to this result. In order to make an estimate of optimal synthesis conditions the enthalpies of formation have been calculated at different pressures, ranging from 0 to 200 GPa. Since enthalpies of Graphite and Ruthenium are also required for this purpose, they are also calculated accurately using $19 \times 19 \times 7$ and $31 \times 31 \times 20$ k -grids, respectively, for Graphite and Ruthenium. The values for enthalpy per atom of Graphite and Ruthenium for different pressures are given in Table 2.

Enthalpies of formation ΔH_f of Ruthenium Carbides are

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