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Investigation of structural, electronic and anisotropic elastic properties of *Ru*-doped WB_2 compound by increased valence electron concentration

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HIGHLIGHTS

- Effects of Ru substitution in WB_2 using increased valence electron concentration.
- Structural, electronic, mechanic and elastic properties for increasing *Ru* content.
- Considered alloys are incompressible, brittle, stiffer and high hard materials.

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ABSTRACT

First principles density functional theory (DFT) calculations have been used to investigate the structural, anisotropic elastic and electronic properties of ruthenium doped tungsten-diboride ternary compounds ($W_{1-x}Ru_xB_2$) for an increasing molar fraction of Ru atom from 0.1 to 0.9 by 0.1. Among the nine different compositions, $W_{0.3}Ru_{0.7}B_2$ has been found as the most stable one due to the formation energy and band filling theory calculations. Moreover, the band structures and partial density of states (PDOS) have been computed for each *x* composition. After obtaining the elastic constants for all *x* compositions, the secondary results such as Bulk modulus, Young's modulus, Poisson's ratio, Shear modulus, and Vickers Hardness of polycrystalline aggregates have been derived and the relevant mechanical properties have been discussed. In addition, the elastic anisotropy has been visualized in detail by plotting the directional dependence of compressibility, Poisson ratio, Young's and Shear moduli.

1. Introduction

Super-hard materials (SHM) are important for their wide usage area from cutting and polishing tools to wear and scratch resistant coatings [1–3]. Since diamond and cubic boron nitride failed to satisfy the need of some emerging industrial applications, most studies have been focused on the combination of transition metals (TM) with light elements to design new SHMs [4–6]. Here, while the high valence electron density of the heavy TM atom leads to a high bulk modulus which causes high incompressibility due to the greater repulsive forces within the material; the light element of the compound provides strong covalent bonding network in the structure which is responsible for the elastic and plastic deformation resistance [7–10]. In accordance with this designing strategy, carbides, oxides, nitrides and borides of TMs have been in the center of interest to meet the requirements of new technologies [1,5,11,12]. The physical and chemical properties of these alloys such as high melting point, excellent oxidation resistance, lower diffusion coefficient, good thermal and electrical conductivity are unique [13,14]. However, only borides among these groups are easy to synthesize under ambient temperature and pressure [5,15].

Especially, tungsten-boron combinations, which constitute an important group of ceramics, have become prominent among all other TM borides due to their relative inexpensiveness [8]. Hence,

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many theoretical and experimental works have been done for different combinations including W_2B, WB, WB_2, W_2B_5, WB_4, WB_{12}, W_8B_7 and W_2B_3 phases [8,9,16–22]. Among these, P6$_3$/mmc-WB_2 phase has come to the forefront as a candidate to replace the traditional SHMs due to its high hardness and incompressibility values [21,22].

Recent works have started to discuss whether another TM atom addition induces a change in the microstructure of the ceramic to improve its mechanical properties. For example, Mohammadi et al. [15] have examined molybdenum addition into the WB_4 by arc melting method while Akopov et al. [23] have done a similar work with titanium, zirconium and hafnium metals. Also, the experimental work done by Yeung et al. [10] and the theoretical work done by Feng et al. [24] have reported the addition of tantalum and rhenium into the WB and W_2B_5 phases, respectively. As for WB_2 phase, besides the work of Cao et al. [25] in which nickel doping have been studied experimentally, two other theoretical studies have been done by Surucu et al. [26] and Euchner et al. [6] for technetium, aluminum, titanium and vanadium dopants. As can be seen from above-mentioned studies, adding another TM atom into the tungsten-boride systems has an improving impact on the mechanical properties of these materials. Also, other works done for similar systems support the same doping strategy [27–30].

Consequently, finding optimal doping rates of different TM atoms into TM borides can be helpful to design new materials in parallel with the technological requirements. Based on this idea and above-stated studies, we have decided to introduce ruthenium as an additive to WB_2 phase due to the high performance of Ru–B systems as hard materials [31–33]. Moreover, ruthenium is the least compressible element in its own row of the periodic table [7]. Also, it has a high bulk modulus, namely a high valence electron concentration (VEC) [34]. Therefore we nominate it as a suitable dopant to the WB_2.

To the best of our knowledge, there is only one experimental work done by Rogl et al., in 1970 for $x = 0.7$ composition [35]. Crystal structure of $W_{0.3}Ru_{0.7}B_2$ was investigated in this work, but mechanical and electronic properties of the $W_{1-x}Ru_xB_2$ are still missing. In this context, we aim to study the detailed structural, electronic and anisotropic elastic properties of $W_{1-x}Ru_xB_2$ compounds ($x = 0.1$–0.9) as a function of increased VEC using first principle calculations for the first time in the literature.

2. Calculation methods

All of the simulations in this work were performed by the self-consistent density functional theory (DFT) with a plane-wave pseudopotential approach implemented in the CASTEP code [36,37]. Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) was used for the exchange-correlation terms in the electron–electron interaction [38,39]. The interactions between the ions and the electrons were described by using the Ultrasoft Vanderbilt pseudopotential [40]. The electronic valence configurations for each atomic species were chosen as W:$5s^25p^65d^46s^2$, Ru:$4s^24p^6\ 4d^75s^1$, and B:$2s^22p^1$ within the virtual crystal approximation (VCA) [41]. The electronic wave functions were expanded in the plane waves up to a 500 eV kinetic energy cutoff. Self-consistent solutions were obtained by employing a set ($20 \times 20 \times 8$) Monkhorst–Pack [42] grid of k-points in the irreducible Brillouin zone. The molar fraction (x) of Ru atom in the structure was increased from 0.1 to 0.9 by 0.1 maintaining an integer number of electrons per unit cell. The VEC numbers were calculated using the following Formula (1), where valence electron numbers of constituent atoms are 6 for W, 8 for Ru, and 3 for B.

$$\mathrm{VEC} = \frac{[(1-\mathrm{x}).\mathrm{W} + \mathrm{x}.\mathrm{Ru} + 2.\mathrm{B}]}{3} \quad (1)$$

In addition, spin-polarization effect was also taken into account to determine whether there is a difference between the results. However, no significant difference was observed between spin- and nonspin-polarized calculations.

3. Results and discussion

3.1. Structural and electronic properties

In our calculations, $W_{1-x}Ru_xB_2$ compounds have been modeled to find the most stable structure for increasing doping rates of Ru atom. Within this framework, molar fraction x has been increased from 0.1 to 0.9 by 0.1 steps while keeping the well-known P6$_3$/mmc (space group:194) symmetry of the host WB_2 [17,20,43]. In this structure, TM atoms occupy $2c$ sites (1/3, 2/3, 1/4), while B atoms occupy $4f$ sites (1/3, 2/3, z). The optimized lattice parameters and the VEC values calculated according to the Formula (1) as a function of x composition are given in Table 1 and shown in Fig. 1. The dashed lines in this figure correspond to a linear and biquadratic equation, obtained from least squares fitting, for a and c parameters, respectively. As can be seen from this table and figure, increasing VEC and x content leads to an almost linear decrease in the optimized lattice parameter c while the lattice parameter a exhibits a downward bowing with a minimum point at $x = 0.7$. This deviation of a from Vegard's Law [44], which was also similarly observed for $Os_xW_{1-x}B_2$ [30], might be attributed to the mismatch of the lattice constants of WB_2 and RuB_2 sublattices.

The formation energy (ΔH_f) of the present system has been calculated using the following Formula (2) and listed in Table 1 for each x value.

$$\mathrm{E}^{\mathrm{W_{1-x}Ru_xB_2}}_{\mathrm{formation}} = \mathrm{E}^{\mathrm{W_{1-x}Ru_xB_2}}_{\mathrm{total}} - \left[(1-\mathrm{x})\mathrm{E}^{\mathrm{W}}_{\mathrm{solid}} + \mathrm{xE}^{\mathrm{Ru}}_{\mathrm{solid}} + 2\mathrm{E}^{\mathrm{B}}_{\mathrm{solid}}\right] \quad (2)$$

The negative formation energies in the table indicate that all of the x compositions are structurally stable and synthesizable. The lowest ΔH_f value is at $x = 0.7$ ($\Delta H_f = -0.329$ eV/f.u.).

Another way to determine the stability of a structure is calculating the ratio of the occupied states width to the bonding states width (W_{occ}/W_b), because according to the band filling theory, the stability of a material increases along with the increase (decrease) in the numbers of bonding (anti-bonding) states [45,46]. When this ratio is closer to 1.0, one can observe that the stability increases. Table 1 shows the computed pseudogaps (W_p, the nearest valley to the Fermi level), occupation gaps (W_{occ}), bonding gaps (W_b) and the W_{occ}/W_b ratios for all x compositions. As it can be seen from the table, $W_{occ}/W_b = 0.987$ (for $x = 0.7$) is the closest value to 1.0, which means $W_{0.3}Ru_{0.7}B_2$ is the most stable one as predicted from formation energy calculations above.

Also, the variation of electron numbers (n) at Fermi level is another indicator of the structural stability, so the lowest n value can be expected to refer to the most stable structure. According to Fig. 2, $W_{1-x}Ru_xB_2$ achieves the minimum point at $x = 0.7$ with a value of $n = 0.935$. In consequence of above-stated structural stability calculations, $W_{0.3}Ru_{0.7}B_2$ is found to be the most stable composition among others.

To obtain information about the electronic properties of the $W_{1-x}Ru_xB_2$, partial density of states (PDOS) have been calculated for each x composition, but only illustrated for the most stable $x = 0.7$ composition to save space in the journal (Fig. 3). Hereby, the bonding character demonstrated by the PDOS gives information on hybridization and the orbital character of the states. For