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First principles density functional theory prediction of the crystal structure and the elastic properties of Mo_2ZrB_2 and Mo_2HfB_2

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Introduction

The most challenging goal to develop new high-temperature materials is that they should provide balanced properties in a wide temperature range, i. e., sufficient fracture toughness at low and ambient temperatures, as well as creep strength and appropriate oxidation resistance at ultra-high temperatures. This target could be met by tailored refractory metal alloys, e.g., those based on molybdenum [1–4]. Mostly, the alloying strategy is due to the formation of temperature and oxidation-resistant intermetallic phases in a molybdenum solid solution matrix, like different silicides and borides [5,6]. Recently, systems that incorporate borides as strengthening phases were described in terms of their microstructural evolution and mechanical properties, namely the ternary systems Mo-Hf-B and Mo-Zr-B [7–9]. It could be shown that this class of materials is very attractive in terms of a promising combination of high fracture toughness and outstanding creep resistance. The borides especially, e.g. ZrB, HfB or Mo_2B, and the respective ternary borides that form in Mo-rich alloys, provide excellent creep resistance. However, there is a lack of data on the properties of the ternary phases, especially their thermodynamic stability within the ternary systems Mo-Hf-B and Mo-Zr-B. In our preliminary work so far, we found undescribed ternary phases, which were provisionally named Mo_2HfB_x and Mo_2ZrB_x in previous publications [8, 9]. More precise information on the exact chemical composition of the phases was derived from Atom Probe Tomography (APT) measurements [10]. These results give evidence on the type of phases to be Mo_2MB_2 (M = Zr, Hf), but the crystal structure and stability of the phases is still unclear.

The prediction of the crystal structure of new materials or of known crystals at extreme conditions is an ongoing research topic. Diverse methods exist, e.g., Random Sampling [11], Simulated Annealing [12] and Evolutionary Algorithms [13], often in combination with Density Functional Theory (DFT) calculations. One drawback of using these methods, however, can be the high demand of calculation power and/or time. To overcome these drawbacks, a different approach was used to predict the crystal structure of Mo_2MB_2 (M = Zr, Hf) by simply using known crystals structures of intermetallics with the 2-1-2 or 3-2 chemical composition within our DFT calculations.

Materials and Methods

Based on the measured chemical composition 2-1-2 for Mo, M (M = Zr, Hf) and B, respectively, for the new compounds, we took 50 crystal structures of already known 2-1-2 and 3-2 intermetallics that fulfill the above-mentioned criterion of composition. First-principles calculation were carried out with Quickstep [14], as implemented in CP2K [15] for quick estimation of the total energy. Additionally, the PHONOPY program [16] was used to check for the dynamically most stable structure.

The Density-Of-States calculation and the chemical bonding analysis was done by calculation of the crystal orbital Hamilton population (COHP) [17] and its integrals (ICOHP) of the most stable energy ground-state structure using the tight-binding, linear muffin-tin orbitals with the atomic spheres approximation (TB-LMTO-ASA) [18, 19] as implemented in the TB-LMTO 4.7 program.

For the calculation of the elastic properties, a further structure optimization of the most stable crystal structure was carried out with Quantum ESPRESSO [20, 21]. The elastic properties were determined with thermo_pw. To calculate the Vickers hardness, Tian et al.'s formula [22] was used.

Results and Discussion

The crystal structure of Mo_2ZrB_2 and Mo_2HfB_2 is predicted to be of the $AlMn_2B_2$ type structure, as it is the most stable in terms of energy (see Fig. 1) and there are no signs of electronic or dynamical instability (see Fig. 2) found in the electronic and phononic density-of-states, respectively. Further the elastic properties of these ternary borides and the isotropic and anisotropic elastic moduli like the bulk, shear and Young's modulus, as well as the Vickers hardness were investigated. It can be shown that the respective values of Mo_2HfB_2 are higher than those of Mo_2ZrB_2 because of the chemical bonding situation. Also, it is depicted that Mo_2HfB_2 is less elastically anisotropic than Mo_2ZrB_2.

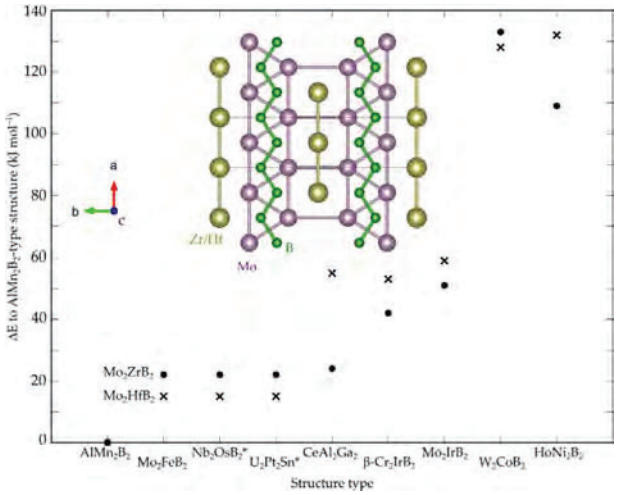

Fig. 1: Crystal structure of the $AlMn_2B_2$ type and energies of nine crystal structure types for Mo_2MB_2 (M = Zr, Hf) relative to the $AlMn_2B_2$ type

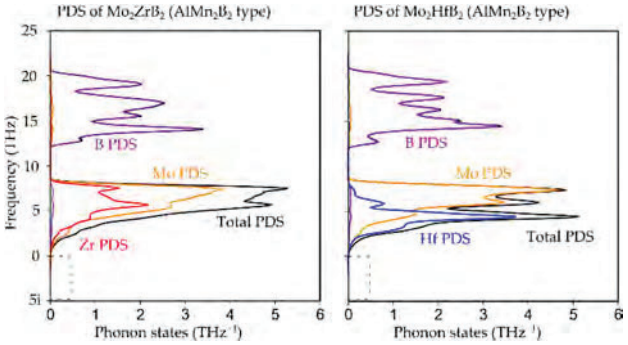

Fig. 2: Phononic density-of-states of Mo_2ZrB_2 (left) and Mo_2HfB_2 (right)

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