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A DFT study of FeVBi, a half Heusler alloy as a potential thermoelectric material

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Abstract : We explored the thermoelectric potential of bismuth-based 18-valence electron count (VEC) half-Heusler alloy, FeVBi using first-principles calculations. Our motivation stems from the anticipated lower thermal conductivity of these Bi materials and the recent discovery of promising thermoelectric properties in CoZrBi-based compounds. Notably, our calculations reveal the electronic bands and density of states that can be helpful in understanding the high power factor value of this systemcompared to the reported p-type CoTiSb. Based on their electronic properties, we suggest that doping at the Bi site could further enhance the power factor value. Overall, our findings highlight bismuth-based ternary compound as a promising candidate for high thermoelectric efficiency.

(Keywords : Half Heusler, thermoelectricity, Bismuth, band structure, Density of states (DOS), phonons).

Introduction

Half-Heusler (hH) alloys with an 18-valence electron count have been widely studied over the past few decades for their potential in converting waste heat into electricity for thermoelectric applications[1–3]. Among the most efficient experimentally investigated hH alloys are stannides and antimonides of cobalt, nickel, and iron, combined with a third element from group IV or V of the periodic table, such as MNiSn, MCoSb, and MFeSb (where M represents Ti, Zr, Hf for Ni-based compounds, and V, Nb for Fe-based compounds). Density Functional theory calculations were carried out to investigate the thermoelectric performance of p-type FeVBi, focusing on scattering mechanisms[4]. While n-type MNiSn, p-type MCoSb, and MFeSb alloys exhibit notable power factor values, their thermoelectric performance is limited by inherently high thermal conductivity[5–7].

Despite significant progress in reducing thermal conductivity, exploring bismuth-based counterparts of previously studied half-Heusler (hH) alloys remains intriguing, given the potential for lower thermal conductivity contributions from heavy elements. While Bi doping has been employed to enhance transport properties[8,9], Bi-based hH alloys have received relatively little attention. Synthesizing ordered hH compositions with elements of widely differing atomic masses and melting points poses a challenge. However, recent experimental studies have reported hH alloys containing heavy elements like Ta and Bi, such as CoTaSn[10], CoZrBi[11], and FeTaSb[12]. Notably, the discovery of CoZrBi based hH alloys serves as a promising reference point for the development of other Bi-based compounds. Importantly, pristine CoZrBi has been found to exhibit significantly lower thermal conductivity than conventional hH alloys[12]. The most efficient experimentally studied half Heusler alloys are antimonides of iron, combined with a third element from group IV or V of the periodic table, such as MFeSb (where M is V). The role of Bi doping tends to enhance the thermoelectric properties of compounds owing to its contribution to low lattice thermal conductivity. V is a transition metal that influences the density

of states near the Fermi level. Fe has a strong interaction with V, resulting in a narrow band gap, making it a semiconductor, which is the most desirable material for thermoelectricity[8,10,13]

Therefore, investigating Bi-based hH alloys as potential thermoelectric materials is crucial.In this study, we employ an ab initio approach, to theoretically examine the static and dynamic stability of novel Bi-based hH alloy-FeVBi, within the cubic F 43m symmetry, alongside the previously reported CoZrBi. The paper is structured as follows.

In Sec. II, we discuss the computational details of structural optimization and electronic structure. In Sec. III, we discuss the results of structural optimization, static and dynamic stability (phonons), and electronic structure (band structure and density of states (DOS)). The results are concluded in Sec. IV.

II. Computational Details

We utilized two distinct first-principles density functional theory (DFT) methods: the full-potential linearized augmented plane wave (FLAPW)[14]approach, implemented in Wien2k[15], and the plane-wave pseudopotential method, available in the Quantum Espresso package[16]. The FLAPW method was employed to determine equilibrium lattice constants and electronic structureswhile Quantum Espresso was used to confirm structural stability through phonon spectrum calculations. For FLAPW calculations, we applied the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof functional modified for solids (PBEsol)[17]. Band structure calculations were conducted with the Becke-Johnson potential[18]. A scalar relativistic approximation was used for all computations, though we also performed fully relativistic calculations to assess the influence of spin-orbit coupling. However, spin-orbit effects were found to be negligible near the Fermi level. The muffin-tin radii (RMT) were set between 2.32 and 2.50 Bohr radii for all atoms, with a plane-wave cutoff defined as RMTxkmax = 9. Self-consistent calculations were performed using a dense k-point mesh of 125,000 points in the full Brillouin zone, with energy and charge convergence criteria set to 10^{-6}Ry and 10^{-5} e, respectively.

In the plane-wave pseudopotential approach, we employed scalar-relativistic norm-conserving pseudopotentials with a plane-wave cutoff energy of 100 Ry. The exchange-correlation energy functional was treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) parametrization[19].The Brillouin zone was sampled using a 20×20×20 Monkhorst-Pack k-point mesh, while phonon calculations were performed on a 2×2×2 q-mesh in the phonon Brillouin zone.

III. Results and Discussion

A. Structural Optimization and Phonon Stability

The ground state properties of the systems were calculated by the GGA-PBEsol functional of Wien2k. This is a reliable approximation for calculating the ground state properties[20]. The structure of hH alloys crystallizes in MgAgAs-type structure and can be seen as a stuffed combination of rock salt and zinc blende structure[21]. The structure of both XYZ hH alloys was optimized in cubic F 43m symmetry, where X = Co, Fe, Y = V, Zr and Z = Bi. For optimization, fitted with the Birch-Murnaghan equation of state[22], the total energy was minimized as a function of volume for each system. The optimized lattice parameters and band gap values are listed in Table I.

System	a (Å)	E_g (eV)
CoZrBi	6.1357	1.00
FeVBi	5.8603	0.48

Table 1 : The optimized lattice constant, a and band gap, Eg values of XYZ half-Heusler alloys (X = Co, Fe Y = Zr, V and Z = Bi) in cubic F 43m symmetry.

The calculated lattice parameter of CoZrBi is in good agreement with the experimental value of 6.18 Å[11]. Importantly, the band gap survives in both the cases and the values range from 0.4–1.0 eV, the lowest and highest values are for FeVBi and CoZrBi, respectively. The calculated band gap in the case of CoZrBi is in agreement with previously calculated values[23]. No experimental band gap value of CoZrBi is reported for comparison. Nevertheless, the existence of a band gap in these cases is important as semiconductors are the best choices for thermoelectric materials. Following this, the optimized ground state structures were studied for dynamic stability with phonon calculations.

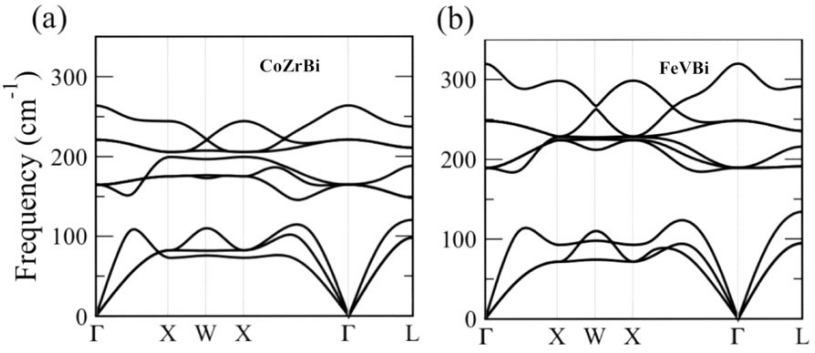

Figure 1. As obtained plots illustrating phonon dispersion in (a) CoZrBi and (b) FeVBi

Phonon calculations were conducted using Quantum Espresso, which employs density functional theory (DFT) and the plane-wave pseudopotential method. This process consists of two steps: first, optimizing the ground-state structure, and second, computing phonon dispersions using density functional perturbation theory (DFPT) as implemented in Quantum Espresso. The calculations were performed on a 2×2×2 q-mesh within the phonon Brillouin zone, with force constants in real space extracted from this data to interpolate between q-points, allowing for the construction of continuous phonon dispersion curves. For a system to be dynamically stable, all phonon frequencies must be real, without imaginary values[24,25]. As shown in Fig. 1, our results confirm that the proposed systems exhibit real phonon frequencies throughout the Brillouin zone, demonstrating their dynamical stability in the cubic $F\bar{4}3m$ symmetry. The presence of a band gap and the confirmed dynamical stability of these systems further motivate an investigation into their electronic structure.

B. Electronic Structure

The electronic structures of both the systems were computed using the Becke-Johnson potential, as implemented in Wien2k. Figure 2 presents the electronic band structure and the density of states (DOS) for FeVBi and CoZrBi. In both the systems, the valence band maximum (VBM) is located at the L point, while the conduction band minimum (CBM) is at the X point, confirming that these materials are indirect band gap semiconductors. The VBM in the FeVBi exhibits a twofold degeneracy, which plays a crucial role in influencing transport properties. The combination of heavy and light bands at the VBM enhances electrical transport in p-type doping. Heavy bands contribute to an increased Seebeck coefficient due to their larger effective mass, whereas light bands aid in charge carrier mobility[26–29].

The DOS analysis indicates that the VBM is primarily composed of Fe d-states with some contribution from Y (= V), while the CBM is

nearly equally shared between Fe and Y d-states. Interestingly, Bi does not significantly contribute to either the VBM or CBM, as omitted in the figure for clarity. This suggests that doping at the Bi-site to reduce lattice thermal conductivity would be highly effective, as it would not disrupt the fundamental band structure, thereby preserving electrical transport properties. Therefore, we anticipate that p-type doping at the Bi-site will significantly enhance the electrical transport properties of these Bi-based half-Heusler alloys. This assertion can be checked by comparing the two different experimental works on CoZrBi. Recently, Zhu et al. doped CoZrBi at Bi-site by Sn and obtained impressive power factor values. The room temperature power factor value was reported to be 25 μW $cm^{-1}k^{-2}$ and the peak value obtained was 40 [11]. Furthermore, the electronic bands favourable for efficient transport properties align with experimentally achievable doping levels.

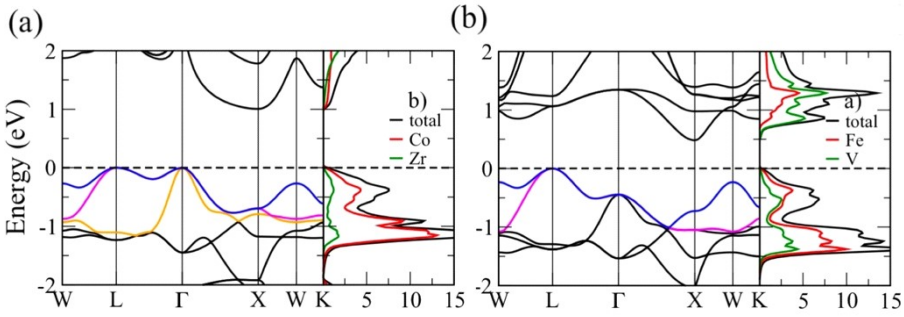

Figure 2. Electronic bands and corresponding density of states of a) CoZrBi, b) FeVBi and in cubic F 43m symmetry. Note that the top of the valence band is taken as 0 eV energy.

We have successfully demonstrated that Bi-based half-Heusler (hH) alloy hold promise as a potential thermoelectric material. Given that these alloys have only recently begun to receive attention, we hope our findings will encourage further experimental research. While theoretical predictions of new materials are relatively straightforward, their experimental realization can be both challenging and costly. Therefore, ensuring both thermodynamic and dynamic stability is crucial for the feasibility of these systems. Our calculations confirm the dynamic stability of all the proposed alloys. However, data from the Open Quantum Materials Database (OQMD)[30,31] suggest that the thermodynamic stability of FeVBi remains uncertain. It is important to highlight that our proposed values are based on p-type doped systems rather than the parent compounds. While the parent compositions may appear thermodynamically unstable, this does not necessarily preclude the fabrication of their doped counterparts. Notably, CoVSn has been predicted to be thermodynamically unstable[10,30,31], yet Lue et al.[32] successfully synthesized it experimentally, albeit with partial atomic ordering. Their study further revealed that CoVSn exhibits properties closely resembling those of hH alloys. This suggests that optimizing experimental conditions could be a key to synthesizing the doped Fe-group compositions, even if the parent compounds remain challenging to realize.

IV. Conclusion

A theoretical investigation has been conducted on bismuth-based half-Heusler alloys CoZrBi and FeVBi The electronic properties indicate that p-type doping at the Bi-site is more favourable for achieving high power factor values. Owing to the contribution of heavy metal

like Bi, we can be assured that these compounds will be an efficient thermoelectric material. We anticipate that our findings, highlighting the promising thermoelectric potential of bismuth-based half-Heusler alloys, will serve as a foundation for future experimental research.

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