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Study of thermoelectric potential of FeNbBi Half Heusler compound

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Abstract : The paper investigates the structural and electronic properties of the FeNbBi half-Heusler alloy using density functional theory (DFT)and explores its lattice structure, phonon dispersion and band structure to assess its suitability for thermoelectric applications. The results confirm the dynamic stability, a moderate indirect band gap and the promise of FeNbBi for energy conversion technology.

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

Introduction

Half-Heusler (hH) alloys with an 18-valence electron count have attracted significant attention for their ability to convert waste heat into electrical energy making them promising candidates for thermoelectric applications[1–4] Among the iron-based compounds like FeNbSb and Cobalt-based materials such as CoZrBi have shown considerable thermoelectric potential. However, the overall efficiency of many hH alloys remains hindered by high thermal conductivity[5–7]. To overcome this limitation, the inclusion of heavier elements like bismuth has emerged as a promising strategy that indicates their ability to suppress lattice thermal conductivity. Although Bi doping has been used to enhance transport properties in some hH systems, synthesizing ordered hH compositions with elements of widely differing atomic masses and melting points poses a challenge[8,9]. However, recent experimental studies have reported hH alloys containing heavy elements like Ta and Bi, such as CoTaSn[10], CoZrBi[11], and FeTaSb[12]. Bi-based half-Heusler compounds such as FeNbBi and CoZrBi have not been extensively studied due to challenges in synthesizing ordered structures with elements of contrasting atomic masses and melting points. 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]

Notably, recent experimental results on CoZrBi have demonstrated remarkably low thermal conductivity compared to traditional hH alloys, positioning it as a strong reference point for the development of other Bi containing materials. Motivated by these findings, we carried out a theoretical investigation of FeNbBi and compared its properties with CoZrBi focusing on structural stability, phonon dispersion, and electronic structure using first-principles calculations, Boltzmann transport theory and the rigid band approximation within the cubic F-43m symmetry. The organization of this work is as follows: Section II, Section III and Section IV

Experimental

II. Computational Details

Two distinct first-principles density functional theory (DFT) methods have been utilized: 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 structures while 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, Scalar-relativistic norm-conserving pseudopotentials with a plane-wave cutoff energy of 100 Ry have been employed. 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

A. Structural Optimization and Phonon Stability: It discusses the results for structure, phonons, and electronic bands; the ground-state properties of FeNbBi and CoZrBi were computed using the GGA-PBEsol functional within the WIEN2k framework, a well-established approach for determining reliable structural parameters20. Both compounds were crystallized in the cubic MgAgAs-type half-Heusler structure, which can be viewed as a combination of rock salt and zinc blende substructures21. Structural optimization was performed under the cubic F-43m symmetry, and the total energy was minimized as a function of volume by fitting the results to the Birch-Murnaghan equation of state22. The optimized lattice constant for FeNbBi was found to be 6.013 Å, while that of CoZrBi was 6.1357 Å, closely matching the experimental value of 6.18 Å reported in the literature23. The calculated electronic band gaps are 0.64 eV for FeNbBi and 1.00 eV for CoZrBi, indicating their semiconductor nature, which is essential for efficient thermoelectric performance as depicted below in table I.

System	a (Å)	E_g (eV)
CoZrBi	6.1357	1.00
FeNbBi	6.0130	0.64

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

To assess the dynamic stability of these compounds, phonon dispersion relations were calculated using density functional perturbation theory (DFPT) implemented in Quantum Espresso. The phonon spectra were generated after structural relaxation, using a 2×2×2 q-point mesh in the phonon Brillouin zone. The absence of imaginary phonon modes across the entire Brillouin zone for both FeNbBi and CoZrBi confirms their dynamical stability within the cubic F-43m symmetry as shown in figure 1[24,25]. This, combined with the presence of a band gap, further supports their potential suitability for thermoelectric applications.

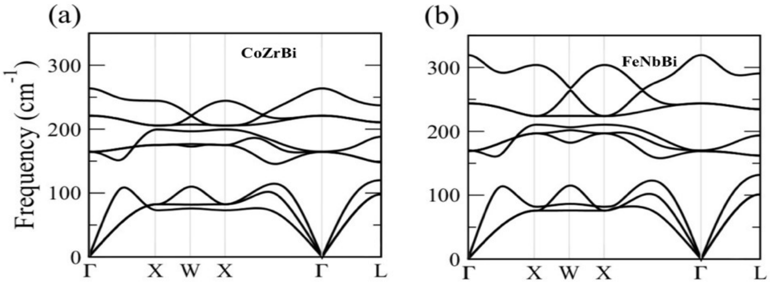

Figure 1. As obtained plots illustrating phonon dispersion in (a) CoZrBi (b) FeNbBi.

B. Electronic Structure

The electronic structures of CoZrBi and FeNbBi were calculated using the Becke-Johnson potential as implemented in Wien2k. As shown in figure 2, both compounds exhibit an indirect band gap, with the valence band maximum (VBM) located at the L point and the conduction band minimum (CBM) at the X point. This band configuration is characteristic of indirect semiconductors. In both systems, the VBM shows a twofold degeneracy, which has a significant influence on transport properties. The coexistence of heavy and light bands at the VBM benefits P-type doping: heavy bands enhance the See beck coefficient due to their higher effective mass, while light bands support better carrier mobility[26–29].

In FeNbBi, the density of states (DOS) reveals that the VBM mainly originates from Fe d-orbitals, with additional contribution from Nb. The CBM also consists of a mix of Fe and Nb d-states. Bismuth has negligible influence on both the VBM and CBM, and its states are omitted in the figure for clarity. This indicates that Bi-site doping—targeting thermal conductivity reduction—can be pursued without adversely affecting the electronic structure, preserving favourable electrical properties.

Experimental evidence supports this strategy: in CoZrBi, Sn doping at the Bi-site, as reported by Zhu et al., led to a substantial improvement in power factor. A value of 25 μW cm?^{1}K?^{2} was recorded at room temperature, with a maximum reaching 40 μW cm?^{1}K?^{2}. These results confirm that electronic bands in these materials are well-suited for effective transport under feasible doping conditions.

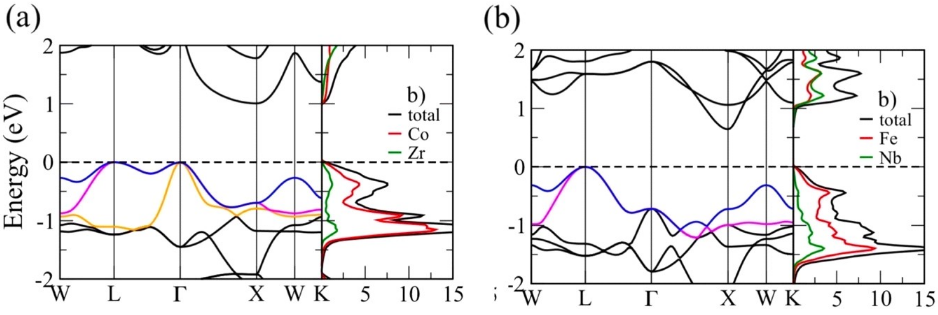

Figure 2. Electronic bands and corresponding density of states of a) CoZrBi, b) FeVBi and c) FeNbBi in cubic F 43m symmetry. Note that the top of the valence band is taken as 0 eV energy.

IV. CONCLUSION

A theoretical investigation has been conducted on bismuth-based half-Heusler alloys CoZrBi and FeNbBi. 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, it is sure that these compounds will be an efficient thermoelectric material. 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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