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Investigation of Thermal Properties of Half-Heusler Alloy FeVZ (Z= As, P, Sb) within Density Functioal Theory

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Abstrak. Figure of merit (ZT) memegang peran penting dalam material termoelektrik yang menunjukkan efisiensi dari sebuah devais termoelektrik (TE). Semakin tinggi nilai ZT, semakin tinggi pula efisiensi yang akan diperoleh sebuah devais TE. Salah satu sub-kelas material yang memiliki potensi tinggi untuk aplikasi termoelektrik adalah paduan Half-Heusler (HH). Untuk mengetahui nilai ZT dari HH dilakukan simulasi untuk mengetahui nilai ZT dari paduan HH FeVZ (Z = As, P, Sb) dengan menggunakan *Density Functional Theory* (DFT). Hasil penelitian kami menunjukkan bahwa FeVAs memiliki nilai ZT yang lebih tinggi dari FeVP dan FeVSb pada kisaran temperatur 150-900 K. Semua paduan material masih memiliki nilai ZT yang baik sekitar ~ 0,7 bahkan pada nilai temperatur 900 K dan menunjukkan trend yang baik untuk material termoelektrik tipe-p.

***Kata Kunci**: Half-Heusler, Figure of merit, Termoelektrik*

Abstract. The figure of merit (ZT) holds an important role in thermoelectric material that indicates the efficiency of thermoelectric (TE) devices. The higher ZT value, the higher efficiency would be obtained of TE devices. One of the sub-class materials that has high potential application for thermoelectric material is Half-Heusler (HH) alloy. In order to investigate the ZT value of HH conduct simulation using to investigate the ZT value of HH alloy FeVZ (Z= As, P, Sb) by using density-functional theory (DFT). Our research results show that FeVAs has higher ZT values than FeVP and FeVSb in the range temperature of 150-900 K. All of those compounds still have good ZT value around ~0.7 even in the temperature regime of 900 K, and shows a good trend for p-type thermoelectric materials.

***Keywords**: Half-Heusler, Figure of merit, Thermoelectric*

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INTRODUCTION

The discovery of the Heusler Alloy (HA) was founded by F. Heusler at the end of the 20th century, which reveals that Cu_2MnAl is magnetic although its constituent elements are not [1]. HA has a general formula of X_2YZ for full-Heusler (FH) and XYZ for half-Heusler (HH) where X and Y are transition metal elements, and Z is the main group element, and surprisingly, its magnetic moment can be predicted by simple rule calculation called Slater-Pauling rule [1], [2].

HA has a high tuning capacity because the properties of this material can be modified by changing its compounds through chemical substitutions and structural motifs [3] and the exploration of HA has been extensively explored due to its fascinating properties that can be implemented in the technology such as spintronic technology [4], shape-memory materials [5], superconductors [6], and thermoelectric (TE) devices [7].

Thermoelectric as one of the HA properties has been extensively studied to obtain high figures of merit (ZT) which describes the efficiency of the TE material. The higher the ZT, the higher the efficiency of the TE material. Half-Heusler (HH) alloy as one of the HA families and as one of the promising candidates for TE materials [7], has high ZT values around $ZT \approx 1$ [8]. Nano-sized grains is used experimentally in order to reduce the thermal conductivity between grain boundaries mediated by phonon scattering [9]. Another approach such as nanocomposites is also used by certain metal combinations that have been preferred to reduce thermal conductivity due to the difference in atomic size [10].

Due to of its high potential application as thermoelectric materials, therefore, we try to explore the iron-based of half-Heusler FeVZ (Z= As, P, Sb) by performing the density-functional theory (DFT) calculation using Quantum-Espresso package [11], [12] to obtain its electronic properties and BoltzTraP calculation to obtain the thermal properties (electronic part) of the FeVZ systems [13].

COMPUTATIONAL METHODS

In order to acquire the density of states (DOS) and the chemical potential information of FeVZ, we perform the DFT calculations by running Quantum-Espresso (QE) package [11], [12]. We also incorporate the Message Passing Interface (MPI) for parallel computing to reduce the computational time [14]. The Pseudopotential type that is used in this work is the Local Density Approximation (LDA) type pseudopotential of the Psilibrary [15]. After we obtain the DOS and the chemical potential, we then perform BoltzTraP calculation to get the electrical conductivity, thermal conductivity, Seebeck coefficient, and ZT of FeVZ systems [13].

(a) (b)

Figure 1. The $C1_b$ crystal structure of FeVZ with the lattice constant of 5.4855 Å, 5.3138 Å, and 5.7758 Å for FeVAs, FeVP, and FeVSb, respectively. (a) Conventional unit cell of FeVZ systems occupy the Wyckoff positions of Fe (red), V (grey), and As/P/Sb (yellow) placed at (0,0,0), (0.25,0.25,0.25), and (0.75,0.75,0.75), respectively. (b) Primitive unit cell of FeVZ systems.

RESULTS AND DISCUSSION

Density of States (DOS)

We use 12×12×12 k-points grid mesh in the self-consistent field (SCF) of QE calculation for all compounds and 36×36×36 k-points grid mesh for the non-self-consistency field (NSCF) calculation in order to obtain a good quality DOS and accurate chemical potential value. The chemical potential values obtained from QE calculation of FeVAs, FeVP, and FeVSb which are 14.26 eV, 15.31 eV, and 12.98 eV, respectively. All of those chemical potential values lies on the edge of the DOS that indicate all of the systems are p-type semiconductor (see figure 2).

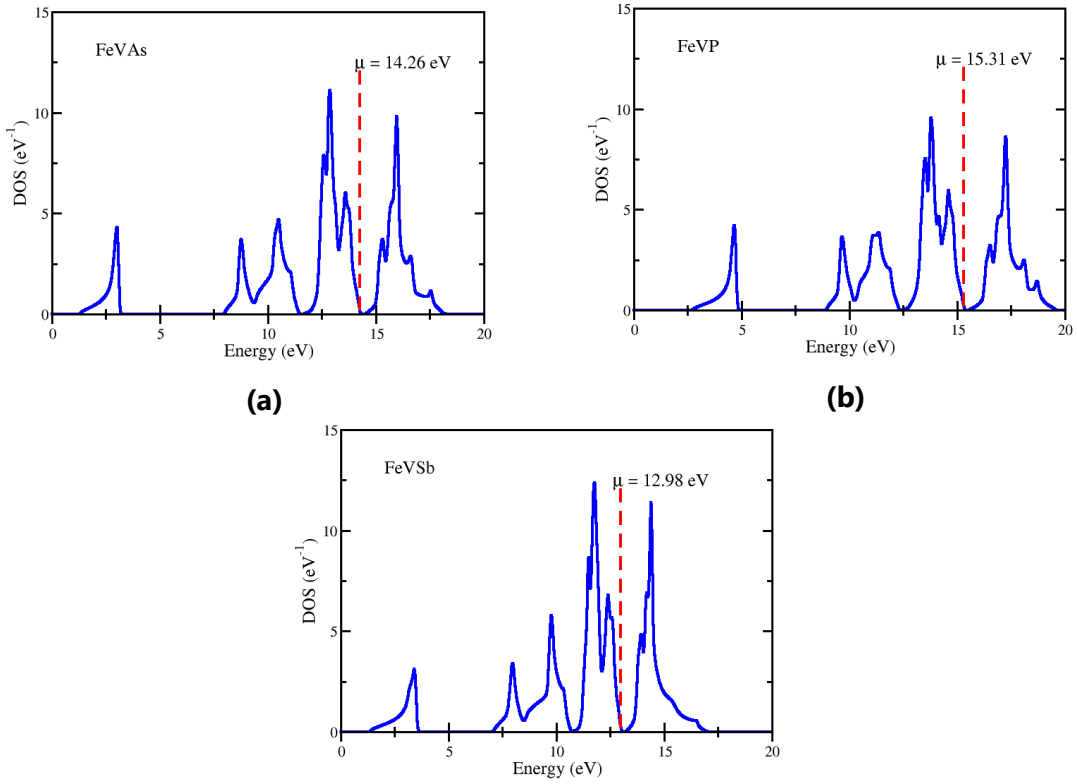

Figure 2. The DOS of: (a) FeVAs, (b) FeVP, and (c) FeVSb.

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Electrical and Thermal Conductivity

Figure 3 shows the temperature-dependent electrical conductivity per relaxation time τ of FeVZ systems obtained from the BoltzTraP calculation. τ value is assumed to be a constant, and its typical value is around 10^{-14} s [16].

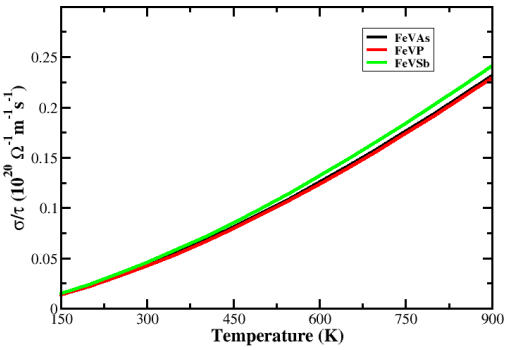

Figure 3. The temperature-dependent electrical conductivity (σ) of the FeVZ systems.

As shown in figure 3, the value of σ increases as the temperature is increased for all system, and typically are similar for all system indicating that all of those materials have good electrical conductivity even for high temperature of 900 K.

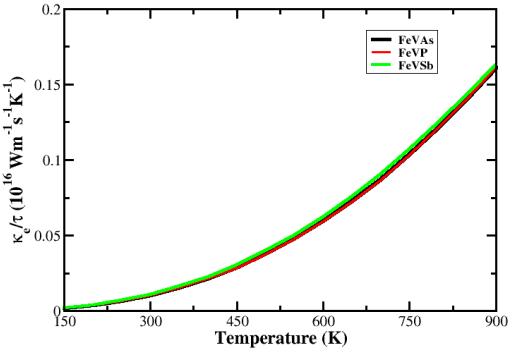

Figure 4. The temperature-dependent electron thermal conductivity (κ_e) of the FeVZ systems.

Figure 4 shows the electron thermal conductivity (ETC) of the FeVZ systems which increase as the temperature increases. From the information above, all κ_e of FeVZ systems almost give the same values in the temperature range of 150-900 K. However, we should note that the real κ obtained through experimental result contains two contribution formulated as

$$\kappa = \kappa_e + \kappa_{ph}, \tag{1}$$

where κ_e is the thermal conductivity contributed by electron, while κ_{ph} is the thermal conductivity contributed by phonon. Because the calculation to obtain the thermal conductivity of the phonon contribution need an expensive calculation and took a very long computational time, we restrict our calculation only to the thermal conductivity of the electron contribution to give a rough interpretation about the figure of merit of the FeVZ systems. However, we realize that a very good approximation should include the thermal conductivity of the phonon contribution to give very accurate ZT values.

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Seebeck Coefficient and Figure of Merit

Figures 5 shows the Seebeck coefficient of FeVZ in the range temperature of 150 – 900 K.

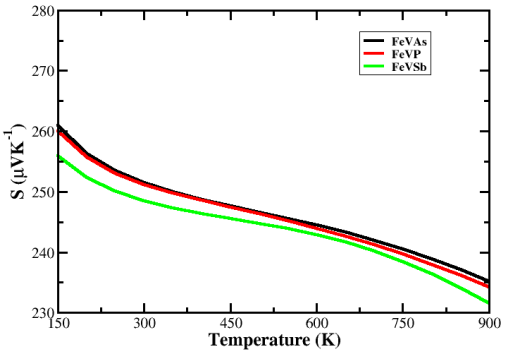

Figure 5. The temperature-dependent Seebeck coefficient (*S*) of FeVZ.

In figure 5, we see that FeVSb trend is quite shifted from the other, while the FeVP trend is slightly different from the FeVAs system. The Seebeck coefficient decreases as the temperature increases and shows a good trend of the p-type thermoelectric material even for high-temperature regime.

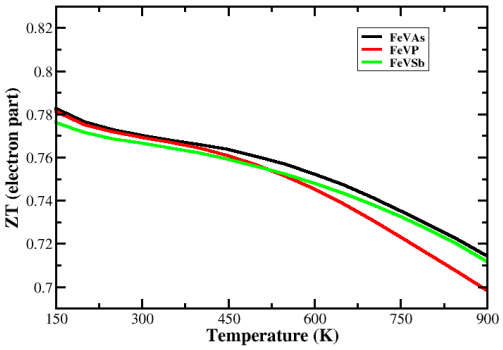

Figure 6. The temperature-dependent figure of merit (ZT) of FeVZ.

From the figure of merit data shown in figure 6, we obtain that FeVAs has higher ZT value than FeVP and FeVSb. At 900 K, we can see the difference that FeVP is quite different from FeVAs and FeVSb. However, that all of those materials still give high ZT value around 0.7 for FeVP, 0.71 for FeVSb, and 0.715 for FeVAs. Those ZT values range are still acceptable for HH material and in agreement with other HH material conducted by Vandu et al. which obtain the ZT value around 0.8-1 for TiNiSn system doped with Zr and Hf [17].

CONCLUSION

We have done the first-principles density functional theory calculation to study the thermoelectric behavior of half-Heusler FeVZ (Z=As, P, Sb). Our results show that FeVAs has higher ZT value than FeVP and FeVSb. We obtain that all of the FeVZ systems behave as p-type semiconductor signatured by the positive sigh of their Seebeck coefficient values. The Seebeck coefficient and figure of merit (electron part) of

all of FeVZ systems in the room temperature are around ~250 μV/K and ~0.75, respectively. All FeVZ systems in 900 K still gives a high Seebeck coefficient and figure of merit (electron part) around ~230 μV/K and ~0.7, respectively. We realize that our results may not yet give a fully realistic prediction for the real material due to the phonon contribution which is neglected to the calculation of the figure of merit (ZT). We acknowledge that the phonon thermal conductivity must be considered in the calculation in order to obtain a more realistic prediction of ZT values.

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