First-principles Study of Semiconducting Heusler Alloys for High Temperature Thermoelectric Applications

A Thesis

submitted

by

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Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis is the result of investigations carried out by me in the ***School of Engineering***, Indian Institute of Technology Mandi, under the supervision of ***Dr. Sudhir Kumar Pandey***, and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigations.

Place: IIT Mandi
Date: 25-01-2022

Signature:
Name: Shivprasad Shivaram Shastri

Declaration by the Research Advisor

I hereby certify that the entire work in this Thesis has been carried out by ***Shivprasad Shivaram Shastri*** under my supervision in the ***School of Engineering***, Indian Institute of Technology Mandi, and that no part of it has been submitted elsewhere for any Degree or Diploma.

Signature:
Name of the Guide: Dr. Sudhir Kumar Pandey
Date: 25-01-2022

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Abstract

The aim of the thesis is to study, understand and prediction of thermoelectric properties of semiconducting Heusler compounds by using first-principles methods for high temperature thermoelectric applications. In this direction the electronic structure, phonon spectrum, the derived transport properties and heat and charge carrier lifetimes are studied. The figure of merit zT and efficiency are predicted for the few Heusler thermoelectric materials. The density functional theory (DFT), semiclassical transport theory, DFT based harmonic and anharmonic phonon calculations are mainly applied.

The present thesis is divided into seven chapters. In chapter one, we give an introduction to the thermoelectric energy conversion, the efficiency of thermoelectric generator (TEG), and Heusler family of materials. The formula for efficiency of TEG and its relation to material's properties connected through zT are described. Next, the cause of limitation in conversion efficiency, need for high zT materials, desired material's features for good thermoelectric material, conflicting relation among transport coefficients and criteria for high zT are discussed. We provide some of the general properties of Heusler family of compounds, crystal structure, possible disorders and the features of Heusler materials that attract them to explore for thermoelectric applications. After this, we discuss a brief theoretical background of DFT, phonon calculations, semiclassical transport theory and a short overview of carrier lifetime calculations approaches in chapter two.

Chapter three explains the effect of exchange-correlation (XC) functionals on the electronic and phonon properties of Fe_2VAl and Fe_2TiSn. Using different functionals electronic dispersion and density of states (DOS) are calculated to see the effect on electronic structure. Mainly, the effect on E_g and band features and effective mass are checked. Further, the effect on the phonon properties is studied by comparing the phonon dispersion and thermal properties. The mBJ functional is found to be suitable to obtain proper E_g values. However, the

band features described by mBJ shows reasonable differences compared to other functionals which is also observed through effective mass. Comparison of phonon energy in dispersion and DOS from various functionals shows the lowest phonon energies from PBE while LDA and SCAN are giving higher energy values. The change in XC functionals has negligible effect on thermal properties.

The dynamical stability and thermoelectric properties of Fe_2ScX (X=P, As, Sb) Heuser compounds are predicted in chapter four. We use the two functionals approach *i.e.*, mBJ for the E_g and SCAN functional to describe band features in reliable prediction of properties of these new compounds. The total energy calculations suggested the ground state structure of these compounds is ordered $L2_1$ phase compared to other possible Heusler structure. The phonon calculations showed the dynamical stability in the $L2_1$ phase. The zT predicted for the n- and p-type compounds suggested Fe_2ScX compounds are worth considering for high temperature thermoelectric applications on successful synthesis.

In chapter five, we try to explain the experimental Seebeck coefficient S of a ZrNiSn sample using combined DFT and semiclassical transport calculations. The ZrNiSn is a promising thermoelectric material with high S and moderately high electrical conductivity. The thermal expansion behaviour is calculated which can be helpful in TEG design. The analysis of S suggested the E_g in sample could be $\sim$0.18 eV with the possibility of disorder or defect. Based on this result, we further predict the zT and efficiency obtainable by doping the pure (stoichiometric and ordered, E_g of $\sim$0.54 eV) ZrNiSn. The highest zT predicted for the n-type and p-type compounds are $\sim$0.5 and $\sim$0.6 at 1200 K, respectively.

The study of electronic structure, phonon properties, thermal expansion, prediction of zT and efficiency, as well as calculation of carrier lifetimes of FeVSb are carried out in chapter six. We try to understand the experimental S of two samples using combined DFT and transport calculations. The best possible explanation to experimental S is found for E_g of 0.7 eV which is also in agreement to E_g from mBJ calculation. From *ab-initio* anharmonic lattice dynamics calculations the lattice thermal conductivity of FeVSb is calculated by considering phonon-phonon interaction under single mode relaxation time approximation. Further, we extend our study on FeVSb by calculating the charge and heat carrier lifetimes from first-principles considering the three intrinsic scattering mechanisms *viz.* electron-

electron interaction, electron-phonon interaction and phonon-phonon interaction. Using the calculated lifetime values thermoelectric properties are predicted.

At last in chapter seven, we summarize the thesis, with a brief overview of the significant conclusions drawn and give direction for future work.

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