Investigation of Physical Properties of Bulk Metal Chalcogenide Materials for Thermoelectric Applications

A Thesis

submitted by

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for the award of the degree

of

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To My Parents

and

Brother

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Declaration by the Research Scholar

I hereby declare that the entire work embodied in the Thesis "**Investigation of Physical Properties of Bulk Metal Chalcogenide Materials for Thermoelectric Applications",** is the result of investigations carried out by me in the ***School of Basic Sciences***, Indian Institute of Technology Mandi, India, under the supervision of ***Dr. Ajay Soni***, 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 investigators.

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Declaration by the Research Advisor

I hereby certify that the entire work in the Thesis "**Investigation of Physical Properties of Bulk Metal Chalcogenide Materials for Thermoelectric Applications",** has been carried out by **Somnath Acharya** under my supervision in School of Basic Sciences, 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. Ajay Soni**

Date:

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Preface

Thermoelectric materials can directly and reversibly convert waste heat into electricity and thus can be used as power generators as well as refrigerators. Being a purely solid-state based technology, thermoelectric modules and devices are silent and reliable, which works with carbon emission free and vibration less mode. Considering these unique advantage, thermoelectric materials can be utilized to increase the green energy resources. The advancement in thermoelectric materials is associated with modification in electronic band structures and phonons dispersions caused by doping, defects, cage-rattlers, solid solutions, nanostructuring. The performance of any thermoelectric material is governed by a dimensionless figure of merit ($ZT = \alpha^2\sigma T/\kappa$), where α, σ, κ are Seebeck coefficient, electrical conductivity, thermal conductivity, respectively, and T is absolute temperature. The correlation of three interrelated parameters clarifies that there must be a minimum heat flow while maintaining a high charge flow across the material. The major challenge of thermoelectric technology is their poor efficiency which limits broader applications of thermoelectrics. Considering requirements of high performance thermoelectric materials, the decoupling of charge and phonon transport is one of the most crucial aspects. Until 1990s, it was believed that the alloy limit of the thermal conductivity cannot be defeated and the improvement in thermoelectric materials ZT had been limited to ~1, with primarily studied thermoelectric materials being Bi_2Te_3, Sb_2Te_3, PbTe, their alloys and SiGe. In the past few decades, the rapid growth in thermoelectric research have been achieved not only by quantum confinement effect and the phonon glass electron crystal concept but also by various interesting strategies such as manipulating the band structure, introducing resonant states near Fermi level and using nanostructures to control the electron and phonon transport. As a results, plenty of new thermoelectric materials have been explored with existing materials such as V_2-VI_3 compounds,

IV-VI compounds, half-Heusler alloys, filled skutterudites, and clathrates, zintl phases, superionic compounds and organic materials.

Chalcogenides (sulfur, selenium and tellurium) are basically rich in phase and structural diversity with vast range of physical properties from metallic to superconducting to semiconducting and insulating behavior, which offers an assured degree of freedom for tailoring their properties. As a consequence, these materials are suitable for thermoelectric devices, infra-red and photo detectors, solar cells and infrared lasers application. Among state of the art chalcogenides thermoelectric materials, Bi_2Te_3 and PbTe are the most studied and champion materials with high figure of merit at room temperature and high temperature applications, respectively. Recently, SnTe has gained enormous interest as a substitute to PbTe because of analogous crystal structure and electronic band structure along with non-toxic and environment friendly option. However, the intrinsic Sn vacancies resulting in high carrier concentration is the major hurdle for its efficient usage in thermoelectric application. Additionally, with the possibility of variety substitution, high ionic conductivity and inherently poor thermal conductivity, Argyrodite superionic compounds provide an interesting platform to play around with the power factor only. Therefore, it is essential to understand and tune the different thermoelectric parameters of SnTe and other superionic conductors for thermoelectric research.

The objective of the present thesis work is to investigate and understand the physical properties of environment friendly crystalline bulk metal chalcogenides such as doped-SnTe and superionic Argyrodite (Ag_8MX_6, where M is Ge, Sn and X is Se, Te), for thermoelectric applications. Conventional solid state melting reaction have been used to prepare the polycrystalline samples. Various characterization techniques and physical property measurements have been carried out on the prepared samples. In SnTe, the optimization of charge carriers have been realized by using excess Sn, and temperature dependent transport

studies demonstrate the enhanced Seebeck coefficient and poor thermal conductivity in Mn doped self-compensated $Sn_{1.03}Te$ samples. The systematic increment of magnetic moments as well as effective thermal mass of charge carriers leading to an overall enhancements in the power factor, which has been observed and investigated based on magnetization, anomalous Hall effect, heat capacity and high temperature transport measurements in doped SnTe. Further, temperature dependent transport results and first-principles calculations show that with heavy atomic mass and strong spin-orbit coupling, mild rare earth (Yb) doping in SnTe can improve thermoelectric performance over other dopants via band-engineering. In addition, the investigations have been done on argyrodite type structure Ag_8MX_6, as these compounds have intrinsically low thermal conductivity and high Seebeck coefficient. The temperature dependence thermoelectric studies are carried out on Ag_8GeSe_6, Ag_8SnSe_6 and Ag_8GeTe_6 across structural phase transition and we have demonstrated that cubic phase Ag_8SnSe_6 has an efficient thermoelectric properties over Ag_8GeSe_6. Moreover, the interesting phenomena related to thermoelectric parameters such as low energy Einstein optical modes have been discussed for Argyrodite based large unit cell superionic compounds (Ag_8GeSe_6, Ag_8SnSe_6 and Ag_8GeTe_6).

The present thesis is divided into eight chapters. The brief outline of the chapters are discussed below:

Chapter 1: Introduction

This chapter contains the background of the research problem, objectives and overview of the present thesis. Brief introduction of thermoelectric effects followed by various challenges in thermoelectric research and the adopted strategies to improve thermoelectric figure of merit such as charge carrier optimization, band structure engineering, multiple phonon

scattering and intrinsic low thermal conductivity have been discussed. At the end, detail of the investigated thermoelectric materials from the thesis have been presented.

Chapter 2: Experimental Methods

This chapter presents the details of methodology applied for synthesis and processing of the materials used in this thesis. Here, solid state melt grown technique has been used to prepare the polycrystalline compounds of doped SnTe and Argyrodites. Various techniques used for characterizations such as X-Ray Diffraction, Field Emission Scanning Electron Microscopy, Raman Spectroscopy, UV-Visible Spectroscopy and Differential Scanning Calorimetry have been elaborated in detail. For measuring the physical properties of the investigated materials, we have used Physical Property Measurement System and Magnetic Property Measurement System and the details have been presented. The details of homemade setup for Seebeck Coefficient and Resistivity Measurements are also presented.

Chapter 3: Crystal Anharmonicity and Soft-Phonons Modes in Self-compensated $Sn_{1.03}Te$ with Mn doping

This chapter describes the crystalline anharmonicity in self-compensated $Sn_{1.03}Te$ with Mn doping, which has been studied to understand the observed glassy thermal conductivity. First, the excess amount of Sn has been doped to optimize the inherent vacancies and a partial control of charge carriers have been achieved in SnTe, followed by doping of isovalent Mn. The relatively poor thermal conductivity has been understood and explained based on the point defect scattering, appearance of soft phonon modes and impurity localized modes. The observed soft phonon mode and impurity localized mode in Raman spectra have been explained based on the created anharmonicity in $Sn_{1.03}Te$ crystal with Mn doping. In addition, Mn doping

modifies the electronic band structure leading to high hole effective mass leading to enhanced Seebeck coefficient.

Chapter 4: Magnetic Entropy and Modified Thermal Transport of Mn doped $Sn_{1.03}Te$

This chapter presents magnetic and thermoelectric properties of Mn doped self-compensated $Sn_{1.03}Te$ in perspective of its dilute magnetic nature. The systematic increment of magnetic moments, increase in effective thermal mass of charge carriers and overall enhancements in power factor has been explained based on magnetization, anomalous Hall Effect, heat capacity, high temperature transport measurements, high carrier concentration and interaction between charge carriers with magnetic moments.

Chapter 5: Valence Band Engineering in Rare Earth (Yb) doped SnTe

This chapter elaborates on the strategy of rare earth element (Yb) doping to enhance the thermoelectric performance of SnTe at very low doping concentrations. Temperature dependent transport data and first-principles calculations show that with heavy atomic mass and strong spin-orbit coupling, even a 5% doping of Yb in SnTe can converge the two valence bands more effectively than Mn at the same doping level. This chapter proposes that doping with rare earth elements is an efficient alternative to improve thermoelectric performance of SnTe via effective valence band-engineering and improved electronic density of states near Fermi level.

Chapter 6: Power Factor Enhancement of Poor Thermal Conductor Argyrodite

This chapter emphasizes on thermoelectric performance of bulk chalcogenides based Argyrodites Ag_8GeSe_6 and Ag_8SnSe_6 across structural phase transition. Due to liquid-like behaviour of cations in a relatively larger unit cell, the Argyrodites exhibits inherent ultralow

lattice thermal conductivity. In this chapter, Ag_8SnSe_6 has been demonstrated as an efficient thermoelectric material over Ag_8GeSe_6 due to higher value of carrier concentration, large electronegativity difference between Ge and Sn and high mobility in high temperature cubic phase. Further, the extremely low thermal conductivity for both the samples has been explained with weakly bonded Ag ions to rigid anion sub lattice and presence of low frequency Einstein optic modes which provide the possibility of decoupling of charge and heat transport.

Chapter 7: Improved Thermoelectricity in Ag_8GeTe_6 with High Carrier Mobility

This chapter presents the thermoelectric studies of Te-based argyrodite compound Ag_8GeTe_6. The room temperature results reveal ultralow thermal conductivity and high carrier mobility leading to improved thermoelectric performance. In these compound, the ultralow lattice thermal conductivity due to weak chemical bond, complex structure and presence of optical phonon mode suggest 'liquid-like' Ag ions inside the crystal of Ag_8GeTe_6 and high electron mobility indicate the 'electron-crystal' nature.

Chapter 8: Conclusions and Future direction

This chapter summarizes the overall remarks on the results that are obtained in the current thesis work and provides the future research direction followed by new opportunities to research on bulk metal chalcogenides materials.

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