Study of Thermoelectric Properties of Oxide Materials in High-Temperature Region

A Thesis

submitted

by

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This thesis is dedicated to my parents.

Declaration by the Research Guide

This is to certify that the thesis entitled **"Study of Thermoelectric Properties of Oxide Materials in High-Temperature Region",** submitted by Mr. Saurabh Singh to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Sudhir Kumar Pandey
May, 2018

Declaration by the Research Scholar

This is to certify that the thesis entitled **"Study of Thermoelectric Properties of Oxide Materials in High-Temperature Region",** submitted by me to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by me under the supervision of Dr. Sudhir Kumar Pandey. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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Abstract

The aim of the present thesis is the study of thermoelectric properties of oxide materials in the high-temperature region. In search of high temperature thermoelectric (TE) materials, the investigations on oxide materials have more advantages due to its nontoxic character, availability in nature, structural and chemical stability, oxidation resistance properties over the conventional TE materials (Be-Te, Pb-Te based alloys). For the selection of any material for TE applications, detailed investigation and proper understanding of the TE properties in the high-temperature region are necessary. In the high-temperature region, various scattering factors affect the TE properties of the materials. To include all these scattering factors, detailed information of materials parameters such as acoustic deformation, potential coupling constant for conduction and valence band, static and high-frequency dielectric constants, screening length of the optical phonons, etc. are required, which is itself a challenging task. In the doped oxide materials such as strongly correlated electron systems, Heikes formula has been widely used to study the thermopower (also known as Seebeck coefficient) behavior at a very high temperature (T $\longrightarrow \infty$), but it does not explain the temperature dependent behavior of thermopower (α). In the strongly correlated systems such as transition-metal oxides, the spin and orbital degrees of freedom of the charge carrier play an important role in the contribution of thermopower. In this scenario, estimation of the effective masses of the charge carriers becomes very effective to understand the sign of α. Therefore, the high-temperature TE properties of oxide materials have been explored by using experimental tools; and electronic structure and transport coefficients calculations using DFT + U method and BoltzTraP code, respectively.

The present thesis is divided into seven chapters. We begin with the basic introduction of thermoelectric effects and various thermoelectric parameters which are responsible for showing the thermoelectric properties in the different type of materials. In chapter ***1***, we have described the thermoelectric materials, their characterization and various applications in different places. The structure of chapter ***1*** is based on the important aspects of thermoelectric materials which are (i) overview of thermoelectric materials, (ii) thermoelectric effects and applications of thermoelectric materials, (iii) thermoelectric efficiency, *figure-of-merit* along with the description of Seebeck coefficient, electrical resistivity, and thermal conductivity

parameters, (iv) measurement methods of Seebeck coefficient and electrical resistivity, (v) *state-of-the-art* thermoelectric materials and advantages of oxide materials for high-temperature thermoelectric applications. Further in chapter ***2***, we have described the synthesis methods for sample preparation and structural characterization technique along with a brief introduction of Rietveld refinement methods. In the second part of chapter ***2***, a brief introduction of DFT + U method and transport coefficients calculations using BoltzTraP code are discussed.

In order to study the TE properties of the oxide materials, we have fabricated a simple and low-cost instrument for high-temperature Seebeck coefficient and electrical resistivity measurements, suitable for the temperature range 300-620 K. The details about the fabrication, measurement methodology and calibration of these setups are discussed in chapter ***3***. Components used in the fabrication of setups are low cost, easily available, and can be replaced in case of any damage occurs. In the Seebeck coefficient (α) measurement setup, the single heater is used to maintain the temperature gradient as well as to reach the desired sample temperature. The same set of K-type thermocouples are used for measurement of sample temperature and thermo-emf voltage, which minimizes the number of sensors and wires used in the setup. Measurement method used for α does not require the accurate measurement of hot and cold end temperature, thus high-cost temperature controller is not the necessary part to obtain the accurate values of α. In the resistivity measurement, very thin copper wires are used for the current supply and voltage measurement. This helps to minimize the heat loss due to cold finger effect. A rectangular gypsum block is used in the sample holder to minimize the heat loss from the heater through conduction process. A small heater is made on the sample holder to reduce the heat loss and its small size make the system compact. Both the setup is user-friendly and suitable for the measurement of metal and semiconductor materials. Using the home-made setup, thermoelectric parameters of ZnV_2O_4, $LaCoO_3$, $La_{0.82}Ba_{0.18}CoO_3$, and $La_{0.75}Ba_{0.25}CoO_3$ compounds were characterized in 300-600 K temperature range.

In chapter ***4*** & ***5***, we have understood the thermoelectric properties of these compounds using DFT + U tools. From the theoretical studies, it is found that DFT + U tools are capable of explaining the high temperature experimental data of these compounds in 230-600 K temperature range. In chapter ***4*** it is shown that consideration of temperature dependent band gap is more effective in understanding the temperature dependent behavior of α in ZnV_2O_4 and $LaCoO_3$ compounds. Also, the dependency of chemical potential on effective mass of charge carriers through temperature plays a crucial role in the study of the thermoelectric behavior of ZnV_2O_4 and $LaCoO_3$ compounds. Theoretically calculated values of ZT for *p-type* doped ZnV_2O_4 (in 900-1400 K) and *n-type* doped $LaCoO_3$ (in 600-1100 K) were

predicted to be ∼0.3 and ∼0.35, respectively. These values of *ZT* are nearly one-third of the well known thermoelectric oxide Na_xCoO_2 (*ZT* ∼1 in 700-1000 K), this suggests that doped ZnV_2O_4 and $LaCoO_3$ compound can be good materials for the thermoelectric applications in the thermal power plant, spacecraft exhaust, armoured vehicles exhaust, steel industry, etc. In order to understand the thermoelectric properties of doped compound, we have performed the DFT + *U* calculation and result shows the half-metallic character for $La_{0.82}Ba_{0.18}CoO_3$ and $La_{0.75}Ba_{0.25}CoO_3$ compounds. In both the compound, consideration of temperature-dependent relaxation time of up and down-spin channel gives a reasonably good matching between experimental and calculated values of α in 300-600 K range. For $La_{0.82}Ba_{0.18}CoO_3$, and $La_{0.75}Ba_{0.25}CoO_3$, electrical conductivity measurement was also carried out in 300-600 K range. DFT+ *U* method was used to estimate the values of σ/τ for both up and down channels. Further, temperature dependent values of relaxation time (τ), almost linear for up-spin (τ_{up}) and non-linear for dn-spin (τ_{dn}), were used in two current model and estimated values of total electrical conductivity were found to be in good agreement with experimental data in the entire temperature range.

Chapter ***6*** discusses the search of oxide materials for high-temperature thermoelectric applications, where we have studied the TE properties of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) compound with different crystallite sizes. For the crystallite size of ∼41 nm, the value of *ZT* at 600 K was found to be ∼0.017, and based on the behavior of thermoelectric parameters calculated values of *ZT* suggest that it can be further increased up to ∼0.045 around 650 K temperature. The predicted value of *ZT* suggests that LSMO can be suitable oxide material for TE applications at high temperature. In addition to this, we have also explored the thermoelectric properties of $(La_{0.7}Sr_{0.3}MnO_3)_{0.5}(NiO)_{0.5}$ (LSMO-NiO) composite in 300-600 K range, and an improvement in the *ZT* value is noticed. For LSMO-NiO composite, the value of *ZT* at ∼600 K is found to be ∼0.05, which is almost three times that of the experimentally observed *ZT* of LSMO compound.

In chapter ***7***, we have summarized the study of high-temperature thermoelectric properties of oxide materials. Further, based on our current study, we have given an overview of the future work which can be carried out in a direction to explore the high-temperature thermoelectric properties of various systems.

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