Structural and Electronic Properties of Half -Heusler Alloys

M.Sc. Thesis

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Structural and Electronic Properties of Half -Heusler Alloys

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by Bivek Ranjan Pahi



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Structural and Electronic Properties of Half -Heusler Alloys** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF PHYSICS, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from August 2022 to May 2024 under the supervision of Prof. Preeti A. Bhobe.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Biver, Ranion Pahi

Signature of the student (Bivek Ranjan Pahi) Date: 20 - OS - 22

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the Supervisor (Prof. Preeti A. Bhobe) Date: 20/05/24

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(Bivek Ranjan Pahi)

Dedicates to my

Parents and teachers.

Abstract

Nanostructured systems consisting of two separate phases hold great potential for high efficiency thermoelectrics due to the reduction in thermal conductivity brought about by the nanostructured phases. However, the choice of the forming matrix and the nanostructure phase is quite challenging. Heusler phase thermoelectrics often exhibit good electronic thermoelectric properties but relatively high thermal conductivity, making them especially appealing candidates for nanostructuring. For forming two-phase nanostructured materials, we predict the materials that have a high-power factor and also lie within the nanostructuring energy interval. In this project, we will discuss the electronic properties of Heusler alloys in HH/FH, FH/FH, and HH/HH matrix-nanostructure pairs. Additionally, our results show that isoelectronic Heuslers are suitable for forming nanostructures and are beneficial for thermoelectric applications.

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Chapter 1 Introduction

This chapter aims to clarify the importance of thermoelectricity and discuss two primary types of thermoelectric materials: Half-Heusler and Full-Heusler. I will start with the introduction of the Seebeck effect, Peltier effect, and Figures of Merit as basic concepts in thermoelectricity. subsequently, we shall talk about ZT's improvement.

1.1 Essential information about Thermoelectricity:

In most of the devices are ejecting lots of unpleasant gases like Co₂, Greenhouse gases (CFCs). So, it directly affects the Ozone layer in the stratosphere. It is only possible by using highly efficient thermoelectric materials on devices (refrigerator, heat pump, heat engines, Air Conditioner, Laser Diode). The minimum ejection of these gases can make a healthy Atmosphere. Thermoelectric Devices which can convert heat energy to electrical power, and it helps to reduce the ejection of unwanted gases and provides it into cleaner form of energy [1]. Efficiency of thermoelectric materials depends on the Zt (figure of merit values).

1.1.1 Seebeck effect:

An electrical Current flow through between two different conducting wires Subjected to temperature difference between Temperature difference is Called Seebeck effect [2]. In 1981this effect was First published by Seebeck as a temperature-dependent magnetic polarization of metals and ores [3]. It is also called net conversion of heat into electrical energy on the formation of an electric current. The Seebeck voltage refers to the net thermal electromotive force. (dT) the temperature difference between the junctions shown in figure. The potential difference between two junctions (dV) is directly proportional to the temperature difference.

$$dV \alpha dT \qquad (1-1)$$
$$dV = S dT \qquad (1-2)$$
$$S = \frac{dV}{dT} \qquad (1-3)$$

Where S is the Seebeck Coefficient.



Figure 1-1. Thermoelectric Circuits of two dissimilar materials between hot and cold junctions [4]. In Semiconductors holes and electrons are charge carriers. Then Seeback coefficient can be expressed as [2].

$$S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_n + \sigma_p} \tag{1-4}$$

Where S_p and S_n are the Seebeck coefficient of electron and hole, respectively.

 σ_n and σ_p are the Electrical Conductivity of electron and hole, respectively.

1.1.2 Peltier effect:

When an electric current passes through the circuits of two junctions of two dissimilar materials in one junction then heat gets absorbed and other junction heat gets dissipated. The effect is called the Peltier effect. In 1834 French physicist Jean Charles Athanase Peltier had discovered this effects [4]. When a current (I) is flow through a junction between two conductors, A and B, then heat generated at the junction per unit time is.

$$\dot{Q} = (\Pi_A - \Pi_B)I \tag{1-5}$$

Where Π_A and Π_B are the Peltier coefficient.

Relation between Peltier and seebeck coefficient

$$\Pi = TS \tag{1-6}$$



Figure 1-2. observation of Peltier effect at the junction between a metal M and an n-type semiconductor S [6].

1.1.3 Thomson effect:

Thomson effect first observed by Williom Thomson in 1951[7]. The Thomson effect is a phenomenon observed in conductive materials by which the flow of the charge carriers influence(electrons) is influenced by temperature gradient. It means if one end is hotter than the other the flow of the charge carriers may depend on the material properties. The rate of production of heat per unit volume is

$$\dot{q} = -KJ.\,\nabla T \tag{1-7}$$

Where J is the current density and K is the Thomson Co-efficient.



Figure 1-3. Thomson effect [8].

The Thomson coefficient can be expressed as

$$K = T \frac{dS}{dT} \tag{1-8}$$

Thomson coefficient can calculate directly of a material afterwards we can easily determine Seebeck and Peltier coefficient.

1.1.4 Figure of Merit (zT):

Figure of merit is a parameter which can determine the energy conversion efficiency of a thermoelectric material. It defined a dimensionless quantity and defined as [8]

$$zT = \frac{S^2 \sigma T}{k} \tag{1-9}$$

Where S is the seebeck coefficient, k is the total thermal conductivity, T the given temperature, σ the electrical Conductivity and the quantity S² σ represent the power factor.

Thermal Conductivity helps to conduct heat inside material. In metal heat conduction takes place due to electrical charge carriers only and in insulator heat conduction takes place only due to phonons but both charge carriers and phonons plays role in heat conduction in case of semiconductor. Total thermal conductivity is the sum thermal conductivity due to charge carriers and phonons. Total thermal conductivity [9]

$$k = k_e + k_l \tag{1-10}$$

From Wiedemann-Franz relation $k_e = LT\sigma$ [11], where L is the Lorenz number. For metals and degenerate semiconductor, $L = 2.44 \cdot 10-8 \Omega WK -2$, while for non-degenerate semiconductor $L = 1.48 \cdot 10-8 \Omega WK -2$ [10].

Total thermal conductivity can be measured using the formula.

$$k = Dc_p \alpha. \tag{1-11}$$

Where D is the density of the sample, c_p the heat capacity at Constant pressure and α the Thermal Diffusivity [8].

At temp,
$$T \le \theta_D c_p = AT + BT^3$$

$$T \ge \theta_D c_p = AT + B$$

 θ _D is the Debye temperature, and A and B are constants.

The efficiency of Thermoelectric devices for generation of electricity is defined as

$$\eta = rac{ ext{total energy provided}}{ ext{amount olf heat absorbed at hot junction}}$$

Maximum efficiency of thermoelectric device in terms of figure of merit (zT) is defined as [11]

$$\eta_{max} = \frac{T_H - T_C \sqrt{1 + z\overline{T}} - 1}{T_H \sqrt{1 + z\overline{T}} + \frac{T_C}{T_H}}$$
(1-13)

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Here T_H , T_C and \overline{T} is the temperature at hot end, cold end and mean of hot end and Cold end respectively. The efficiency of a Thermoelectric device is directly dependent on the Figure of merit [12].

1.2 Methods of Improving zT:

The figure of merit is a function of s, *k* We can improve zT values by increasing the power factor (S² σ) and decreasing the thermal conductivity. We will discuss one by one as follows.

1.2.1 By increasing the Power Factor:

The power factor is directly dependent on the Seebeck coefficient and electrical conductivity. The dependency can be illustrated by Motts formula for the Seebeck coefficient and Drude model for electrical conductivity carrier concentration must be greater than 10^{20} c.m⁻¹.

$$\sigma = ne\mu = \frac{ne\Im}{m_c^*}$$
(1-14)
$$\mathbf{S} = \frac{8\Pi^2 k_B^2 T}{3eh^2} m_s^* \left(\frac{\Pi}{3n}\right)^{\frac{2}{3}}$$
(1-15)

From equations (1-14) and (1-15) both the Seebeck coefficient and electrical conductivity inversely depend on effective mass and carrier concentration. With the increase in carrier concentration Seebeck coefficient gets reduced and thermal conductivity increases as shown in fig 1-5 [18]. The effective mass of the Seebeck coefficient and electrical conductivity is different it related through the formula.

$$m_{s=N_{V}^{*}K^{*}m_{c}^{*}}^{*} \tag{1-16}$$

This relation was established by Gibbs, et.al.[2] Where the effective contribution of both the effective valley degeneracy N_v^* and the Fermi surface complexity factor carrier pocket anisotropy which is effective K* means both Seebeck coefficient and electrical conductivity become high when the factor $N_v^*K^*$ is high. That factor represents Band utility. For low value of m_c^* Band utility should be high or vice versa. Low m_c^* value of should be achieved by increasing the doping concentration. Hence the change in chemical potential is higher than the high m_c^* [17] shown in Figure 1-4 [17]. only compounds below $m_c^* \leq 0.25$ are considered high power factors as shown in Fig 5.



Figure 1-4. Figure showing the band filling at a given carrier concentration for low m_c^* and high m_c^* [18].



Figure 1-5. The plotting of Seebeck, electrical conductivity, and power factor as a function of carrier concentration shows how peak power factor arises by optimizing carrier concentration. The dotted line divides the plot into two areas, to the left and right of the peak power factor, respectively. On each side of the diagram, the power factor's dependence on carrier concentration is shown. The exponent, a, in the equation on the left-hand side shows how the power factor varies with carrier concentration and has a value between 0 and 1[18].



Figure 1-6. Band degeneracy and inertial effective mass are correlated strongly in $(N_v^*K^* vs m_c^*)$ or both p-type and n-type compounds; low inertial effective mass is associated with higher band degeneracy. (b) Maximum power factor estimates for 1617 p-type and n-type compounds at 300 K as a function of inertial effective mass [18].

1.2.2 By reducing lattice thermal conductivity:

Acoustic phonons are responsible for transporting heat energy within solids. If we can minimize the presence of acoustic phonons, conducting heat inside the solids becomes more challenging.



Figure 1-6. Dispersion relation of one-dimensional diatomic lattice [19]

Isoelectronic alloying is the best way to scatter high frequency acoustics phonons, which leads to reduced thermal conductivity in half Heusler system [20] due to mass and strain fluctuations around point defect centers, which lower the thermal conductivity (k_l). It opposes the charge carriers due to the perturbation of periodic potential. Hence mobility decreases [21]. To minimize the perturbing potential, we must take smaller radius difference materials (period -5 and period -6) to construct alloys [22]. so that the minimum

free path increases, or relaxation time increases so, conductivity increases. To satisfy both conditions we must use solid solutions of p-type (Nb, Ta) FeSb[23], n-type (Zr,Hf)NiSn[24], and (Zr,Hf)CoSb[22].

By Producing Grain boundaries, we can scatter the low frequency phonons and reduce thermal conductivity. But by producing grain boundaries increase zT value is limited in case of MNiSn but for p-type Half Heusler we can achieve maximum zT value by producing grain boundaries.

It has been reported that creating composites and introducing nano-precipitates are efficient methods for scattering middle-frequency phonons [25]. It has been shown that even after several hours of post-annealing, the arc-melted (Ti,Zr,Hf)-based HH compounds clearly show phase separation, with micro scale Ti-rich and (Zr,Hf)-rich regions in the matrix [26][27]. Composites with this type of microstructure show significant phonon scattering, which reduces k_l . Therefore, peak zT values of roughly 1.2 were obtained for phase-separated p-type (Ti, Hf) CoSb[27] and n-type (Ti,Zr,Hf) NiSn [28] near 900 K.

1.3 Introduction to Heusler Alloys:

In 1903 people started doing research on Heusler alloys [34][35]. This system is named the Heusler system in honor of Fritz Heusler. who initially created an alloy Cu2MnAl, a ferromagnetic (FM) member of this family [36]. Many elements, including transition metals, post transition metal s and p -elements (group IIIA, IVA, and VA of the periodic table), and rare-earth elements, combine to form the Heusler compounds and alloys. Heusler compounds and alloys can be synthesized using a wide variety of elemental combinations because of this remarkable flexibility. It shows magnetic, electronic, mechanical, thermal and chemical properties [40]. It has applications in optoelectronics properties [41], magnetic shape memory effect (SME) [43][44]. Based on arrangement and different structure, the Heusler system divided into three categories named as Full Heusler, Half Heusler and Inverse Heusler system has shown in the figure below. The full Heusler system is characterized by a chemical formula X_2YZ and L21 structure consisting of eight sacked body centered cubic lattice. The half Heusler system has cubic C1b structure and is characterized by XYZ and the Inverse Heusler system with stoichiometry X_2YZ has a structure XA-type structure.



Figure1-7. Crystal structure of Half Heusler alloys.



Figure 1-8. Crystal structure of Full Heusler allovs.

1.3 Project plan:

To make high zT value, i am taking high power factor Heusler's compounds as matrix (taking large quantity atomic percentage as 95%) and mix with nano Structure (taking small amount (5%)) Heusler's compound which Solubility limit become lies in between mixing energy Interval [13]. I am expecting that the power factor of matrix/NS pair will be larger. The main reason for taking Matrix/Ns pair to make two phases grain boundary within it and low frequency acoustic phonon gets Scatter more and more [14]. Hence, Thermal Conductivity gets reduced. But the necessary condition is that composite must show Semiconductor behavior [15].



Figure 1-9. schematic Diagram matrix/NS phase pair [13].

Here My plan is to form matrix/NS phase pairs of HH (matrix)/HH (NS), FH (matrix)/HH (NS), FH (matrix)/FH (NS) as shown below. Then we will study the figure of merit of the respective compound as shown below.



Chapter 2 Experimental

2.1 SAMPLE PREPARATION

Heusler alloys are inter metallic compounds, which vary in melting temperatures e.g. 1855 °C for Zr and 232 °C for Sn [28]. For sample preparation Commercial powders have been used in stoichiometric proportions for this study. Purity percentages lie in between (99.99/99.98). samples have been prepared through arc – melting process through argon atmosphere twice and thrice, we obtained a button-shaped alloys [29][30]. If samples get spotter grind it through mortar and pestle. Heusler samples I have selected for the project Menson below.

Name of the Samples	Samples taken in gm.	Total weight of the sample(gm.) Before melting	Weight after melting
NiTiSn	Ni (0.3421), Ti (0.2791), Sn (0.6921)	1.3133	1.2706
NiZrSn	Ni (0.1711), Zr (0.2659), Sn (0.6916)	0.7831	0.9981
Ni ₂ MnSn	Ni (0.5146), Mn (0.2409), Sn (0.5205)	1.2760	0.9835
Fe ₂ TaGa	Fe (0.3087), Ta (0.4992), Ga (0.1940)	1.00019	0.9979
Co2TaGa	Co (0.3137), Ta (0.4816), Ga (0.1874)	0.9219	0.9186
Fe ₂ TiAl	Fe (0.6165), Ti (0.2621), Al (0.1479)	1.02	0.99

Table 1: Data of Samples before melting and after melting.





Figure 2-1. Arc melting Device.



After arc melting, the samples were subjected to a process called vacuum sealing. For vacuum sealing, a rotary pump is commonly used. When sealing samples within quartz ampoules, a high vacuum setting is frequently used, typically in between pressures below 10^{-3} millibars and sometimes even lower, reaching ultra-high vacuum levels below 10^{-6} millibars. This completely vacuumed environment. Maintains the authenticity of the samples, which makes them perfect delicate substances.



Figure 2-3. Sealing sample through Quartz tube.



Figure 2-2. Rotary pump.

To ensure a single-phase sample, we subject it to annealing. This process involves placing the samples inside a furnace and heating them to a specific temperature for a set duration.

Name of the sample	Annealing temperature (in degree Celsius)	Annealing Time
NiZrSn	1073	50hours
NiTiSn	850	192` hours
Ni ₂ MnSn	800	48 hours
Fe ₂ TaGa	800	24 hours
Co ₂ TaGa	800	24 hours
Fe ₂ TiAl	850	48 hours

Table 2-1. Annealing temperature and time of the sample.

After annealing, these samples are cooled through Ice-water. The process is called Ice-water quenching. This helps to freeze the material's microstructure in a desired state.



Figure 2-4. Put the sample in ice and water.

From the XRD analysis of the samples in Chapter 3, it was determined that ZrNiSn, NiTiSn, Fe₂TiAl, and Ni₂MnSn, consist of a single phase whereas samples like Co₂TaGa, Fe₂TaGa exhibit more than one phase. Consequently, I plan to create composites of two single-phase materials, HH-HH, HH-FH, and FH-FH represented by (Fe₂TiAl)_{0.95}(Ni₂MnSn)_{0.25}, (Ni₂mnSn)_{0.95}(Fe₂TiAl)_{0.95}(ZrNiSn)_{0.25} and (ZrNiSn)_{0.95}(NiTiSn)_{0.05}, through arc melting by giving current in between 50-100 amps.

2.2 CHARACTERIZATION TECHNIQUES:

Characterization techniques are used to investigate and measure various properties of materials [31]. Here we are going to discuss XRD and FESEM of the material.

2.2.1 X-ray diffraction:

It is a technique used to determine the geometrical structure and lattice parameter of the crystal. In general people are likely to use the powder method for determining peaks of XRD. In this method samples are in powdered form is placed in the path of monochromatic X-rays, i.e., λ is fixed while both θ and planner spacing varying. Thus, a few small crystallites with different orientations are in contact with X-rays. The reflection takes place for those values of d, θ , λ which satisfy Bragg's law.

It works by sending X-rays which interact with material, and it scattered by atoms within the crystal lattice. The scattered X-rays interfere constructively or destructively, producing a diffraction pattern. if it satisfies the Brags law (path difference between incident and diffracted wave must be integral multiple of wavelength).



Figure 2-5. Schematic representation of the Bragg law for a generic crystalline plane [45].

$$2d\sin\theta = n\lambda \tag{2-1}$$

Then we obtained a high-intensity diffraction peak at that value of theta. By analysis Where λ is the wavelength of the X-ray, d is the distance between atomic planes, θ is the angle of diffraction and n is an integer that represents the order of diffraction.

To understand the Miller indices, phase, and lattice parameters, we must collect data obtained from XRD measuring devices (intensity and theta) and match them with experimental results using software like Fullprof Suite.

2.2.2 FESEM:

SEM was invented by Manfred von Ardennes in 1937 [31]. It is used to get information about the surface configuration and composition of the sample [31]. In SEM Accelerated electron beam is incident on the various depths of the samples. It interacts elastically and inelastically with atoms within the samples and ejects secondary electrons, backscattered electrons, and diffracted backscattered electrons [32]. Secondary electrons are ejected from a few nanometers of the sample of the sample, and they constrain low energy of the order of 50 eV. It collects information about the Surface and composition of the sample and is detected by a detector Everhart-Thornley detector [33]. Scattering electrons get accelerated through the scintillator in 2000V. That energy is sufficient to emit a flash of light inside the scintillator and convert this signal to a distal signal. If the amplitude of the Distal signal is high, the scattering secondary electron is high. The backscattered electrons contain high energy and inelastic atoms of the specimen. Those Scattered electrons are emitted more in atoms of high atomic number than the low atomic number. These elections can be detected using a scintillator and semiconductor detector [33].



Figure 2-6. Schematic diagram of SEM [32].

2.2.3 Low temperature Resistivity measurement Device (Four Probe):

The 4-point probe setup is made up of four tungsten and metal tips with a limited circumference. To reduce sample damage during probing, springs at the end of each tip are used for support. Part of an auto-mechanical stage that moves up and down are the four metal tips. when taking measurements. The outer

two probes are powered by a high impedance current source, and the voltage across the inner two probes is measured by a voltmeter to ascertain the resistivity of the sample. Probe spacing is usually about 2 mm. The high input impedance voltage in the circuit prevents these inner probes from drawing any current. As a result, the unintended voltage drops (I R drop) at points B and C brought on by the sample's contact resistance between the probes is removed.



Figure 2-7. Schematic diagram of Four probe.

CHAPTER 3

Results Of Experimental Studies

We first prepared the individual compositions such as ZrNiSn, NiTiSn, Fe₂TiAl, Ni₂MnSn, Co₂TaGa, and Fe₂TaGa and then formed the composites by mixing these individual compositions in requisite ratios. For example, we prepared (ZrNiSn)_{0.95}(NiTiSn)_{0.05}, (Fe₂TiAl)_{0.95}(Ni₂MnSn)_{0.05}, (Ni₂mnSn)_{0.95}(Fe₂TiAl)_{0.05}, (Fe₂TiAl)_{0.95}(ZrNiSn)_{0.05}, composites such that it yields the combination of (HH –HH), (FH-FH), (FH-H). These samples are characterized using experimental methods as discussed in Chapter 2, and the results will be discussed in this chapter.

3.1 Structural studies (XRD)

By employing D8 diffractometers equipped with Cu targets, we can confirm the structural phase purity of the samples.

3.1.1 XRD of Half Heusler

In the given figure 3.1 powder XRD patterns of NiZrSn and NiTiSn have shown. All the patterns can be indexed to a cubic crystal structure with F4-3m. The absence of impurities and secondary phases in any of the observed patterns provides confirmation that the intended substitution was effectively executed. Rietveld refinement was performed on the XRD profiles utilizing the Full-Prof Suite, which corresponds well to the simulated pattern, based on the results of two hypothetical compositions of NiZrSn and NiTiSn.



Figure 3-1: Analysis of XRD data NiTiSn and NiZrSn using full prof.

The highest intensity peak occurs for NiZrSn at 41.9591° meanwhile for NiTiSn at 43.3193° and suggest the preferred position at (220). Lattice parameters are shown in the tabular form.

Name of the sample	Lattice parameters
NiTiSn	a=5.9288A°
	b=5.9288A°
	c=5.9288A°
NiZrSn	a=6.0966 A°
	b=6.0966 A°
	c=6.0966 A°

Table 3-1. Lattice parameters of the sample NiTiSn and NiZrSn.

3.1.2 XRD of Full Heusler

The XRD patterns of Fe₂TiAl, Ni₂MnSn, Fe₂TaGa, N₂MnSn are displayed in figure 3.2 and figure 3.3. Using Fm3m, the entire pattern can be indexed to a Cubic crystal structure. The fact that no contaminants or secondary phases were present in any of the patterns that were seen indicates that the desired substitution was carried out successfully. The Full-Prof Suite was used to perform Rietveld refinement on the XRD profiles. The results, based on two fictitious compositions of Fe₂TiAl and Ni₂MnSn, correspond well to the simulated pattern.



Figure 3-2: Analysis of XRD data of Ni₂MnSn and Fe₂TiAl using full prof.

Name of the Sample	Lattice parameters
Fe ₂ TiAl	a=5.9178 A° b=5.9178 A° c=5.9178 A°
Ni ₂ MnSn	a=6.0391 A° b=6.0391 A° c=6.0391 A°

Table 3-2: lattice parameters of Fe₂TiAl, Ni₂MnSn.



Figure 3-3: XRD curve of Co₂TaGa and Fe₂TaGa.

From the XRD analysis of both Co_2TaGa and Fe_2TaGa , it is observed that they exhibit Heusler peaks along with the presence of impurity peaks.

3.1.3 XRD of Composites

From fig 3.3 you will find that both Co₂TaGa and Fe₂TaGa form more than one phase .So, We make composites using ZrNiSn, NiTiSn, Fe₂TiAl, Ni₂MnSn using this sample make Composites of (Fe₂TiAl)_{0.95}(Ni₂MnSn)_{0.05}, (Ni₂mnSn)_{0.95}(Fe₂TiAl)_{0.05}, (Fe₂TiAl)_{0.95}(ZrNiSn)_{0.05} and (ZrNiSn)_{0.95}(NiTiSn)_{0.05}. If XRD peaks of both compounds are present in the XRD peak of composite, we can confidently say that the composite is formed solely from their combination.



Figure 3-4: XRD Curve of composite (ZrNiSn)_{0.95}(NiTiSn)_{0.05}.



Figure 3-5: XRD Curve of composite (Fe₂TiAl)_{0.95}(Ni₂MnSn)_{0.05}.



Figure 3-6: XRD Curve of composite, (Fe₂TiAl)_{0.95}(ZrNiSn)_{0.05}.



Figure 3-7: XRD Curve of composite (Ni2mnSn)0.95(Fe2TiAl)0.05.

From the above figures all peaks of compounds and some impurity peaks are found in the composites.we can used these composites for resistivity measurement.

3.2 FESEM.

SEM images and atomic percentage of samples (ZrNiSn, NiTiSn, Fe₂TiAl, Ni₂MnSn, Co₂TaGa and Fe₂TaGa) are shown below.



Figure 3-8: EDS image of Ni₂MnSn.

Elements	Atomic %(Expected)	Atomic % (Obtained)
Ni	50	48.46 ± 0.96
Mn	25	24.98 ± 0.49
Sn	25	26.56 ± 0.53

Table 3-3. Expected percentage of element and obtained one in the sample Ni₂MnSn.



Figure 3-9.EDS image of NiTiSn.

Elements	Atomic %(Expected)	Atomic % (Obtained)
Ni	33.33	34.04 ± 0.68
Ti	33.33	31.37 ± 0.62
Sn	33.33	34.58 ± 0.69

Table 3-4. Expected percentage of element and obtained one in the sample NiTiSn.



Figure 3-10: EDS image of Co₂TaGa.

Elements	Atomic %(Expected)	Atomic % (Obtained)
Со	50	53.55 ±1.07
Та	25	27.71 ± 0.55
Ga	25	18.74 ± 0.37

Table 3-5. Expected percentage of element and obtained one in the sample Co₂TaGa.



Figure 3-11. EDS image of NiZrSn

Elements	Atomic %(Expected)	Atomic % (Obtained)
Ni	33.33	32.16 ± 0.64
Zr	33.33	33.16 ± 0.66
Sn	33.33	33.16 ± 0.66

Table 3-6. Expected percentage of element and obtained one in the sample ZrNiSn .



Figure 3-12. EDS image of Fe₂TaGa.

Elements	Atomic %(Expected)	Atomic % (Obtained)
Fe	50	53.55 ±1.07
Та	25	27.71 ± 0.55
Ga	25	18.74 ± 0.37

Table 3-7. Expected percentage of element and obtained one in the sample Fe₂TaGa.

3.1.3 Conclusion Drawn from EDS Results:

The expected atomic percentage of the samples matches the obtained ones, indicating that elements are uniformly distributed in the given composition.

3.3 STUDY THE RESISTIVITY OF THE COMPOSITE AT LOW TEMPERATURE

The resistivity test is the First level to choosing thermoelectric material. For the best thermoelectric performance, the material should be a semiconductor, as described in Chapter One. Only we can know it by a Resistivity test. If resistivity decreases with an increase in temperature, then the material should be a Semiconductor, otherwise it may be a Conductor.



Figure 3-13. Resistivity vs Temperature of (ZrNiSn)0.95(NiTiSn)0.05.





of (Ni2mnSn)0.95(Fe2TiAl)0.05

Temperature of (Ni2mnSn)0.95(Fe2TiAl)0.05.

From the above graph, we can conclude that the compound (ZrNiSn)_{0.95}(NiTiSn)_{0.25} demonstrates semiconductor behavior. On the other hand, the Compounds (Fe₂TiAl)_{0.95}(ZrNiSn)_{0.25}, (Fe₂TiAl)_{0.95}(ZrNiSn)_{0.25},(Ni₂MnSn)_{0.95}(Fe₂TiAl)_{0.25} exhibit metallic behaviour.

4.1 CONCLUSION

For a good thermoelectric material, it should be semiconductor in nature. From resistivity measurements, we observe that the composite, having semiconductor compounds with the same valency electrons (for both the matrix and the added material (Ns)) exhibits semiconductor behavior. Which possesses better solubility for the matrix/Ns pair. However, in the case of the composite (ZrNiSn)0.95(NiTiSn)0.05, it shows semiconductor nature, whereas $(Fe_2TiAl)_{0.95}(Ni_2MnSn)_{0.05},$ (Ni₂MnSn)_{0.95}(Fe₂TiAl)_{0.05}, а and (Fe₂TiAl)_{0.95}(ZrNiSn)_{0.05} composites exhibit conducting behavior.

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