Structural and Magnetic Properties of Co2FeMn Full Heusler Alloys Synthesized by Hydrothermal Method

Muhammad Ayoub, Fuqiong Wang*, and Aatir Saeed

***Abstract*—** This paper focuses on the preparation and characterization of Co2FeMn full Heusler alloys using a hydrothermal route. These intermetallic compounds have a face-centered cubic crystal structure and are magnetic. The molarities used in the synthesis process were varied from 1.2 M to 2.0 M, and the resulting samples were analyzed for their structural and magnetic properties. X-ray diffraction analysis confirmed the formation of Co2FeMn Heusler alloys at molarities of 1.6 M and 1.8 M. Fourier-transform infrared spectroscopy was used to determine the transmittance in the range of 500-400 cm-1, and organic bands were observed, indicating physiochemical interactions with the environment. Vibrating sample magnetometry exhibited narrow-width M-H loops, indicating ferromagnetic behavior. The maximum magnetization was observed at a molarity of 1.8. Current-voltage (I-V) characteristics were measured for the samples with different molarities, and temperature-dependent I-V characteristics were measured for the sample prepared with a 1.8 M solution, which had a pure Co2FeMn full Heusler alloy structure.

***Index Terms*—**Co2FeMn, Cubic crystal, Ferromagnetic, Heusler alloys, Hydrothermal

I. Introduction and Background

Heusler compounds are a class of magnetic intermetallic compounds that have gained considerable attention in the scientific community due to their diverse and unique properties. These compounds have a face-centered cubic crystal structure and are composed of three different elements, typically denoted as XYZ. They are named after Fritz Heusler, who discovered them in 1903[1]. Heusler compounds have been found to exhibit a variety of magnetic, electronic, and thermoelectric properties, making them suitable for use in various technological applications. In particular, the full-Heusler compounds, which have a composition of X2YZ, have been of interest due to their high magnetic moment and spin polarization, which make them promising candidates for spintronic devices.

Co2FeMn is a full-Heusler alloy that has been extensively studied due to its favorable magnetic properties, including a high Curie temperature, high magnetization, and low coercivity. These properties make it an attractive material for various applications such as magnetic sensors, magnetic data storage, and spintronics.

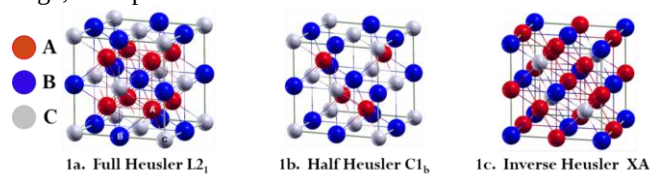

Fig. 1. Crystal structure of Full, Hall and inverse Heusler alloys

One of the most common methods used for synthesizing Heusler compounds is the solid-state reaction method, which involves heating the constituent elements in a stoichiometric ratio at high temperatures. However, this method has some limitations, such as the difficulty in achieving phase purity and the requirement for high temperatures and long reaction times. In recent years, the hydrothermal synthesis method has gained popularity as an alternative route for synthesizing Heusler compounds. This method involves using aqueous solutions at moderate temperatures and pressures, which results in highly crystalline and phase-pure products with a narrow size distribution.

In recent years, several studies have investigated the use of Co2FeMn full Heusler alloys in various technological applications. Guo et al. [2] (2021) synthesized Co2FeMn full Heusler alloys using the solid-state reaction method and found that the samples exhibited a high magnetic moment and low coercivity. Meanwhile, [3] synthesized Co2FeMn full Heusler alloys using a co-precipitation method and reported that the samples exhibited high magnetic anisotropy. Wang et al. [4], Co2FeMn full Heusler alloys were synthesized using the microwave-assisted hydrothermal method. The authors investigated the effects of annealing temperature on the structural and magnetic properties of the alloys and found that the magnetic properties of the alloys improved with increasing annealing temperature. [4] synthesized Co2FeMn full Heusler alloys using microwave-assisted hydrothermal method and found that increasing reaction time and temperature improved the magnetic properties. Deng et al. [5] investigated the effect of doping with elements such as Cu, Ni, and Pt on the magnetic properties of Co2FeMn full Heusler alloys and found that they

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could potentially be used for spintronic and magnetic storage applications.

TABLE. I: Types and crystal structure of Heusler alloy

Alloy name	Formula	Space group	Examples
Full Heusler	X:YZ (121)	Fm3m	Ru_2FeSi, Au_2CrG,
Half Heusler	XYZ(CIb)	F43m	CoMnsb, MnCrp NiMnSb, PdMnSb,
Inverse Heusler	XX'(YZ)	F43m	NiCoMnSb, NiCoMnln, NiMnSn,
Quaternary Heusler	X2YZ	F43m	CoFeMnz, CoFeCrZ CuCoMnSi,

In this study, we aim to synthesize Co2FeMn full Heusler alloys using a hydrothermal route and investigate their structural and magnetic properties as a function of molarity. We also analyze the organic bands in Fourier-transform infrared (FTIR) spectroscopy to determine any physiochemical interactions of environmental effects. Additionally, we measure the current-voltage (I-V) characteristics of the samples to gain insight into their electrical properties. Finally, we investigate the temperature-dependent I-V characteristics of the sample prepared with a 1.8 M solution, which had a pure Co2FeMn full Heusler alloy structure.

II. Experimental Techniques

A. *Hydrothermal Synthesis*

In this process of synthesis, solubility and recrystallization are sent to aqueous media or mineralizers at high temperature and pressure materials which are comparatively insoluble under normal conditions (<1000℃ → < 1000 ℃, <atm → < atm). This method of synthesis is valid for every heterogeneous chemical reaction.

The temperature is approximately below (<3000℃ → < 3000 ℃) for hydrothermal synthesis. Water is equipped with 22.1 MPa and a critical temperature of 3740℃ (→ < 3740 ℃). This hydrothermal synthesis process was adopted in the middle of the nineteenth century when Nano-sized particles from sub micrometer materials were prepared [6]. This technique has been under debate throughout the 1840s through the early 1990s due to the lack of various techniques for diagnosing nanoparticles. After replacement of Nano particles this technique was adopted in the 1980s [7]. In the 21st century, due to its successful results a hydrothermal / solvothermal synthesis process for the manufacture of nano-particles is adopted, which in fluid environments presents the reaction, environmental benefits and limited consumption of energy [8-10].

1. Instruments Used in Hydrothermal Process

In a potted reactor called an autoclave or high-pressure blast, hydrothermal reactions are studied. The autoclave (reactor) is constructed from Teflon or holds additional can or alloy coating, cup (beaker), or an entity, such as the tube formed of gold, silver, platinum and Teflon, with a structure determined by high-caustic solvents carrying high pressure and temperature.

A bourdon gauge is also connected to the autoclaves to closely inspect the pressure and autoclaves are equipped with stirring equipment for lower concentration. An autoclave that is perfectly hydrothermal should always be easy to assemble and disassemble and have an extended lifetime at the test temperature and pressure range. A general autoclave is shown in the given Fig.2.

Fig. 2 Hydrothermal Autoclave

2. Fundamental Mechanism of Crystal Growth Via Hydrothermal Process

For material synthesis, two main steps are involved from the hydrothermal method

- Crystal nucleation.
- Succeeding growth

Controlling variables such as reactant concentrations, temperature, pH values, and extracts allowed for customized particle sizes and morphologies of the final product [11]. Numerous species that make super-saturation difficult to detect the reaction equilibrium necessary are part of the hydrothermal solution. Different models have been presented formally in order to determine the solubility of organisms found in hydrothermal environments. Shock and its team were introduced to Helgeson-Kirkham-Flower (HKW) modal for the first time. Within the ranges of 250C - 1000C, 0.1MPa – 500MPa, a significant number of inorganic compounds soluble in aqueous solvents are determined [42, 43]. The mechanism of crystal growth is shown in Fig. 3.

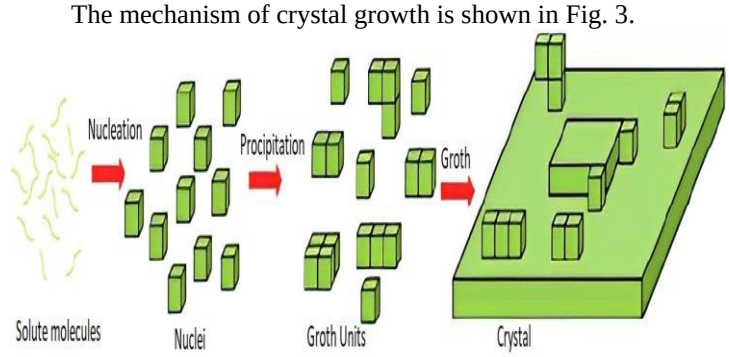

Fig. 3 Schematic representation of crystal growth mechanism under the hydrothermal/solvent synthesis

B. X-ray Diffraction (XRD) Analysis

X-ray diffraction is a widely used technique to investigate the crystallographic structures, crystallite size, and position of solid materials in polycrystalline or powdered samples. By analyzing the chemical composition and physical characteristics of a given substance, this method provides detailed information about the sample's structure, which ultimately determines its physical and chemical properties. A crystal comprises atomic lattices arranged in regular planes, which are identified by Miller indices (H, K, L) to differentiate between crystal planes and directions. The smallest repeating structure in a crystal is called the unit cell, and its angles and lengths result in various symmetries forming in the lattice, leading to the seven crystal systems. The relationship between the unit cell parameters and Miller indices is unique to each crystal class.

In X-ray diffraction, suitable X-ray wavelengths illuminate the crystal at an incidence angle theta. The X-rays scatter across the crystal, encountering lattice points where they diffract following Bragg’s law. As X-ray wavelengths are comparable to the interatomic separation of modern crystals, X-rays are commonly used in this technique. Positive interference occurs when X-rays are diffracted from atom positions in the crystal, releasing high levels of energy. The strength of the diffracted beam varies in different directions and occurs only when the diffracted X-rays follow Bragg's law [12], which was proposed by W.L. Bragg in 1912.

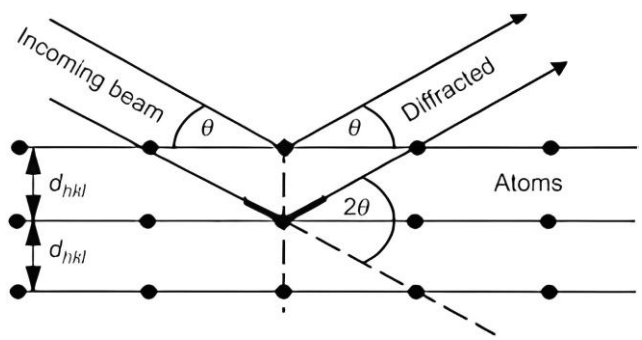

Fig. 4 Schematic of X-Ray diffraction by a crystal. (Bragg’s condition)

Various crystal structure examination methods include:

- Single crystal rotating method
- Powder method
- Laue method

In the Laue method, the wavelength is constant, while in the other two methods, the angle varies, and the wavelength is fixed.

1. Powder Method

   The powdering method is usually used to calculate the value of the lattice parameters. The magnitudes of the b and c unit vectors that categories the crystal unit cell are the lattice parameters. If a single crystal has a monochromatic beam, one or two diffracted beams can result. In this technique, a monochromatic x-ray beam is directed at a very fine powder sample material. This beam is observed in every way using the Bragg's Law of observation. Using a device known as the Goniometer, the sample is rotated in different directions. A few small crystals are oriented in planes of (110) and some in planes of (100). These beams can therefore be reflected and captured in a detector from every possible direction. The pattern is represented in Fig. 5.

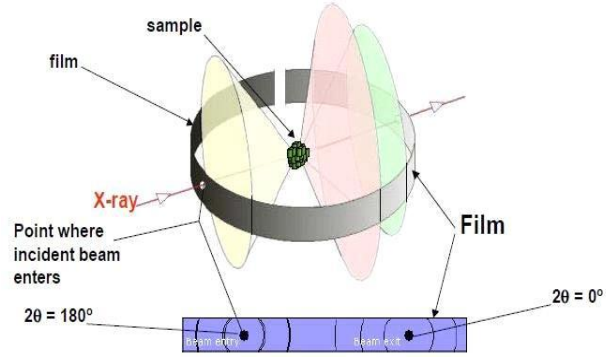

Fig. 5. The geometry of XRD powder method

C. Fourier-Transform Infrared (FTIR)

FTIR represents Fourier Transform Infrared, the favored strategy for infrared spectroscopy. In infrared spectroscopy, IR radiation is gone through an example. A portion of the infrared radiation is consumed by the example and some of it is gone through (sent). The range that comes from the molecular absorption and transmission creates a finger impression sub-atomic of the example. No two exceptional atomic designs discharge a similar infrared range, similar as fingerprints. Therefore, infrared spectroscopy can be utilized for an assortment of investigations. All in all, what data can FTIR give? It can recognize obscure materials. It can decide the quality or consistency of an example. It can decide the quantity of parts in a mixture. For numerous clarifications, Fourier change infrared spectroscopy is preferred over dispersive or channel strategies for infrared ghastly examination:

- It is a non-destructive procedure.
- It offers an accurate calculation approach that does not require external calibration.
- It has the ability to increase speed, collecting a scan per second; and it has the ability to increase sensitivity.
- It has a higher optical throughput and a simpler mechanical design with only one moving component.

The Michelson Interferometer Experimental Setup is commonly used in FTIR. It includes a beam splitter, a fixed mirror, and a moving mirror. The beam splitter splits radiation from the source into two beams, which are reflected back to the beam splitter by the mirrors. One beam goes to the detector, and the other goes back to the source of reflection. The interferogram includes information about every infrared frequency, and all frequencies are measured simultaneously, making measurements fast. Fourier transformation is used to decode individual frequencies for spectral analysis. FTIR spectra are displayed in Fig. 6.

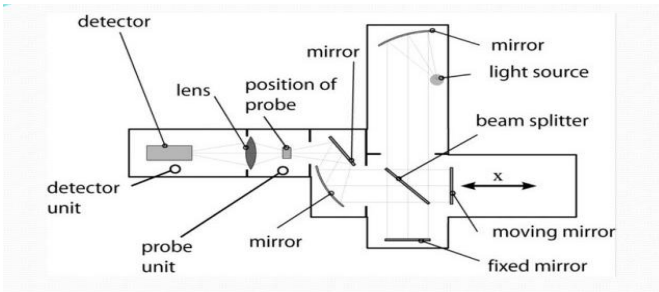

Fig. 6. Schematic diagram of FTIR

D. *Vibrating Mample Magnetometer (VSM)*

VSM measures magnetic properties of materials by first magnetizing a sample in a constant magnetic field and then vibrating it sinusoidally. Simon Foner invented the Vibrating Sample Magnetometer (VSM) at MIT Lincoln Laboratory in 1955 and it was revealed in 1959. The induced voltage is measured by a piezoelectric amplitude as a frequency analogue with a lock-in amplifier. The hysteresis curve of a material can be determined by determining the magnetic field. The construction of VSM includes a brass plate, copper coils with 3000 turns, a solenoid, and a vibrator. The pickup coils are connected to a sensitive low-pass filter circuit to eliminate external high-frequency noise, and the detection coils detect the time-varying flux generated by the vibrations. The magnetic field gradually increased and then decreased to form a hysteresis loop. The construction of VSM is shown in Fig. 7.

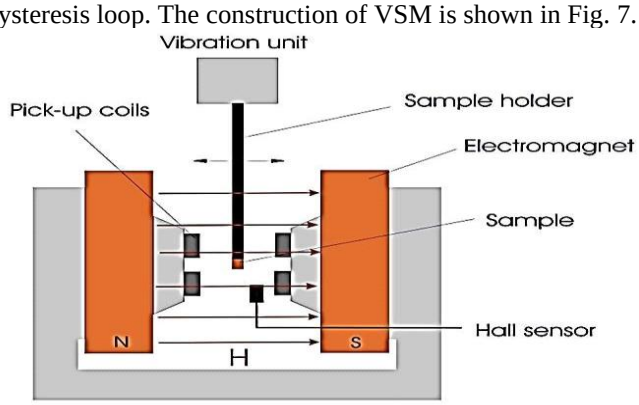

Fig.7. Schematic diagram of a vibrating-sample-magnetometer

E. *Hall Effect Measurements*

The Hall Effect is a phenomenon discovered in 1879 that characterizes materials by measuring the electrical current generated when a magnetic field is applied perpendicular to a current running through a sample. This principle is based on the Lorentz force and can be used to calculate carrier mobility, concentration, and resistivity, among other things. The technique is used in various fields, including the electronics industry, crystal making, and nanotechnology research. Most semiconductor materials and compound semiconductor materials can be characterized using Hall Effect measurements, as well as solar cells/photovoltaics, organic semiconductors, and nanomaterials.

Fig. 8. Illustration of Hall Effect

III. Results and Discussions

The hydrothermal method was utilized to synthesize Co2FeMn full Heusler alloys with varying molarities ranging from 1.2M to 2.0M. The nanoparticles obtained were subjected to characterization using different techniques. Structural analysis was carried out using X-ray diffraction (XRD) while vibrating sample magnetometer (VSM) was employed for magnetic analysis. I-V measurements were performed using Hall measurements. Detailed results for all the techniques are discussed below.

A. *Structural Analysis of Co2FeMn Full-Heusler Alloy*

Co2FeMn full-Heusler alloy nanoparticles were synthesized with varying molarities from 1.2M to 2.0M via hydrothermal method, and their XRD patterns were analyzed and shown in Fig.9.

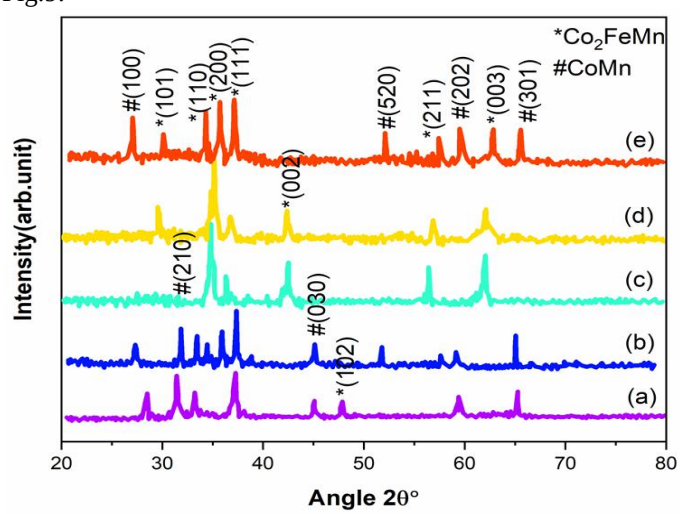

Fig. 9. XRD patterns of Co2FeMn full Heusler alloys nanoparticles with respect to molarity a) 1.2, b) 1.4, c) 1.6, d) 1.8 and e)2.0

All nanoparticles exhibited hexagonal structure with space group P63/mmc, and mixed phase was observed at 1.2M to 1.4M. Pure Co2FeMn hexagonal phase was observed at 1.6M, and phase stability and strengthening were observed at 1.8M. Mixed phases were observed again at 2.0M. Preferred orientation was along the (200) plane due to crystallites' preferential growth along certain plane.

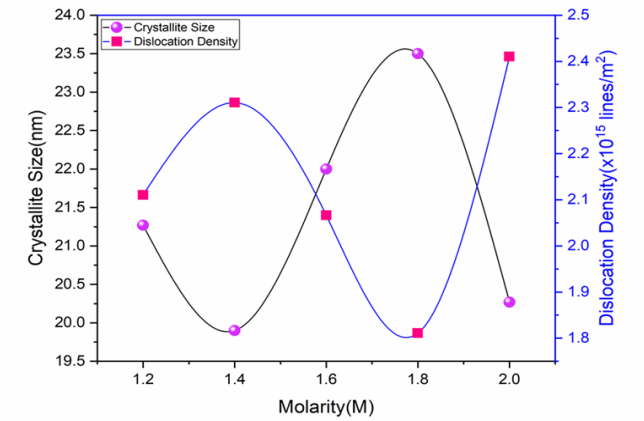

Fig. 10. Variations in Crystallite size and dislocation density of Co_2FeMn full Heusler alloys nanoparticles with respect to molarity (1.2, 1.4, 1.6, 1.8 and 2.0)

Fig 10 shows the crystallite size and dislocation density of Co2FeMn Full-Heusler Alloy nanoparticles with molarity changing from 1.2M to 2.0M. Initially, the crystallite size decreased from 1.2M to 1.4M due to mixed phases, but with an increase in molarity up to 1.6M, an increase in crystallite size was observed due to phase transformation from mixed phase to pure phase.

B. Evaluation of the Magnetic Properties of Co2FeMn Full-Heusler Alloy

Vibrating sample magnetometer (VSM) has been used to evaluate the magnetic properties of Co2FeMn full-Heusler alloy. Figure 11 shows the magnetic hysteresis (M-H) loops for Co2FeMn full-Heusler alloy nanoparticles with varying molarity (1.2M to 2.0M) is shown. All the samples show the soft ferromagnetic behavior.

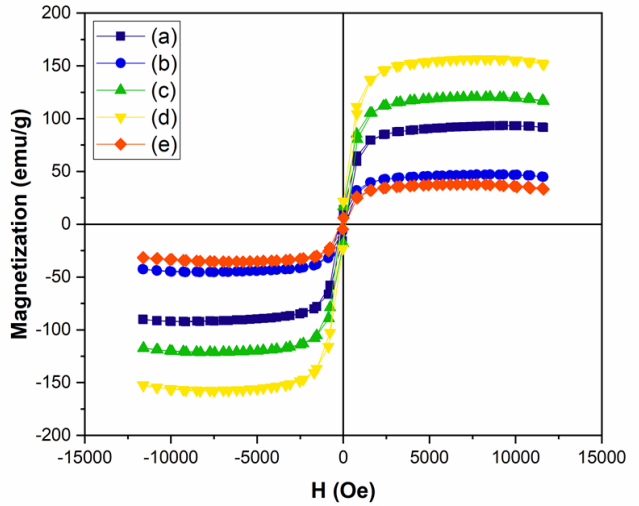

Fig. 11. MH loops of Co2FeMn full Heusler alloys nanoparticles with respect to molarity a) 1.2, b) 1.4, c) 1.6, d) 1.8 and e) 2.0

In Fig 12 and 13 shows the saturation magnetization and coercivity of Co2FeMn full Heusler alloy nanoparticles with varying molarity (1.2M-2.0M). The values of Ms have been plotted for all Co2FeMn based Heusler alloy nanoparticles with varying molarity (1.2M to 2.0M). The saturation magnetization values increase from 1.2M to 1.8M due to increasing crystallinity and crystallite size and decreases at 2.0 M due to restructuring process as decrease in crystallite size is observed. The lowest value of saturation magnetization observed at 2.0M and the highest value of saturation magnetization observed at 1.8M.

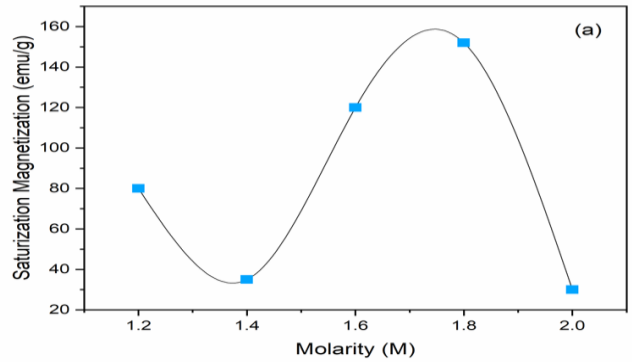

Fig. 12 Saturation Magnetization of Co2FeMn full Heusler alloys nanoparticles with respect to molarity 1.2, 1.4, 1.6, 1.8 and 2.0

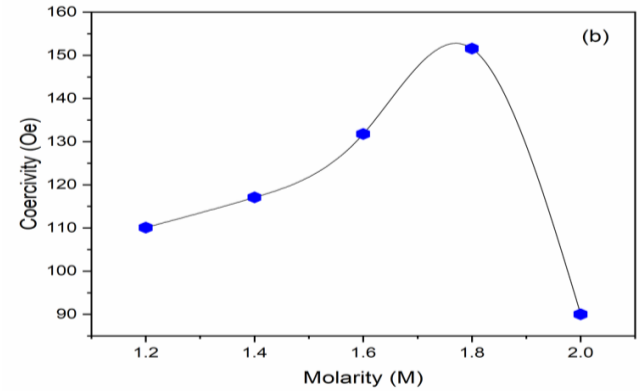

Fig. 13. Coercivity curves of Co_2FeMn full Heusler alloys nanoparticles with respect to molarity 1.2, 1.4, 1.6, 1.8 and 2.0

C. FTIR Analysis of Co2FeMn Full-Heusler Alloy

Fourier transform infrared spectra has been recorded for Co2FeMn full Heusler alloy with varying Molarity (1.2M-2.0M) in the range of mid IR (3000-500 cm-1). Fourier transform infrared spectroscopy explains chemical and structural changes due to different functional groups. Figure (4.6) of IR-spectra indicates the presence of molecular bands and several absorption bands.

FTIR is used to find out the functional groups in the sample. Bands related to alloy were not observed, however, band at 625 cm-1 represents C =C–H bending vibration mode, band at 1074 cm-1 represents C=O, band at 1438 cm-1 represents C-H and band at 1618 cm-1 shows O-H. The vibration bands at 2359 cm−1 were also assigned to CO2 modes. The vibration around 3314 cm−1 indicated C =C–H stretching vibration mode of the water.

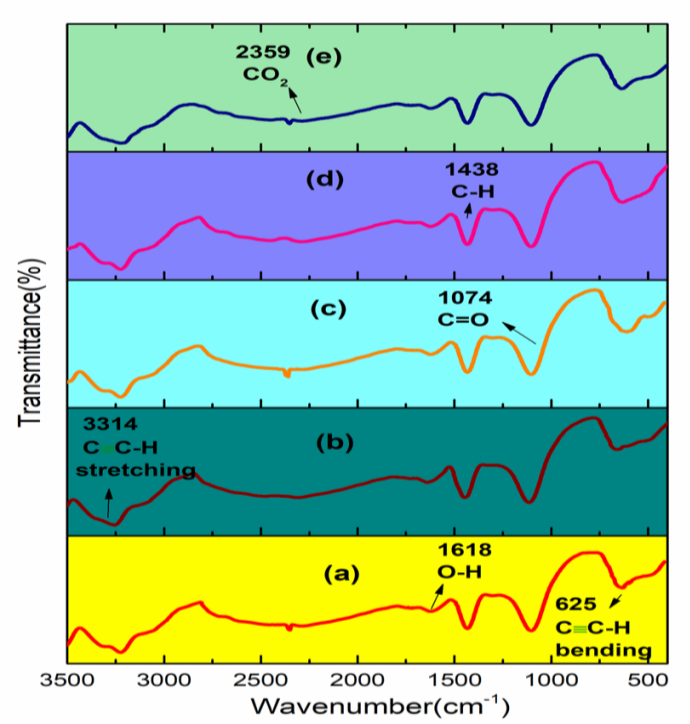

Fig. 14. FTIR spectra of Co2FeMn full Heusler alloys nanoparticles with respect to molarity a)1.2, b)1.4, c)1.6, d)1.8 and e) 2.0)

D. *Mechanical Strength of Co2FeMn Full-Heusler Alloy*

The hardness of full Heusler alloy Co2FeMn at various molarities 1.2 M, 1.4 M, 1.6 M, 1.8 M, 2.0 M alloy was determined through Shimadzu hardness HMV-2 Vickers micro indenter by applying Vickers indenter for 15 seconds at load of 4.903 N as recommended by ASTM C1327-99. Fig. 15 shows high hardness values (~9.11 -9.17 GPa) for the samples prepared at molarity of 1.6-1.8 due to pure phase formation and stabilization with increase in molarity are observed. Whereas lower values of hardness (~7.46 -8.17 GPa), in the lower majorities, are due to the presence of mixed crystal phases as discussed in XRD results.

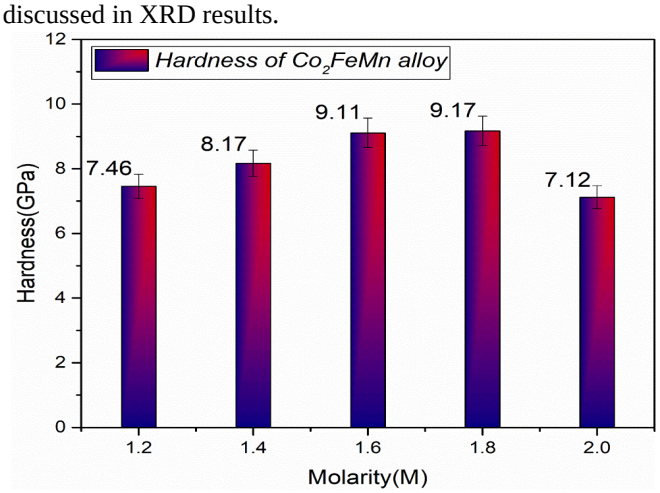

Fig. 15. Hardness values of Co2FeMn full Heusler alloys nanoparticles with respect to molarity 1.2, 1.4, 1.6, 1.8 and 2.0

E. *I-V Characteristics of Co2FeMn Full Heusler Alloys*

Fig.16 shows typical I-V characteristics of a Co2FeMn full Heusler alloys at varying molarity 1.2M to 2.0M. The I-V characteristics show linear characteristics and were almost symmetric with respect to the bias polarity, which indicated that the conduction was dominant. However, a slightly larger current was obtained for the forward bias, which was probably due to a thermionic emission current through interface for the forward bias. Fig. 17 shows the I-V characteristics at various temperatures (T) measured by three-terminal geometry. The IV curves showed linear characteristics and all of them are almost symmetric with bias. The I-V characteristics were slightly dependent on temperature.

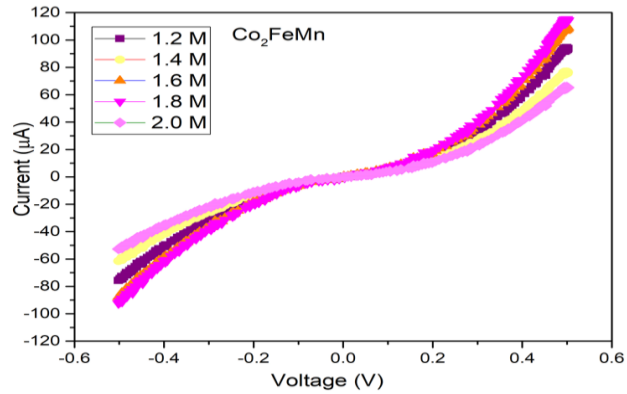

Fig. 16. I-V characteristics of Co_2FeMn alloy at different molarities (1.2, 1.4, 1.6, 1.8 and 2.0)

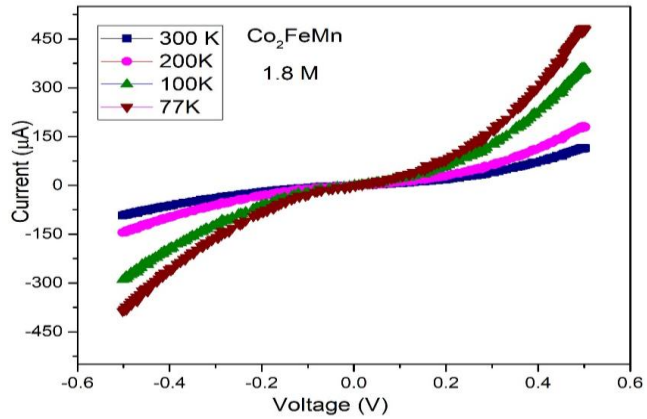

Fig. 17. Temperature dependent I-V characteristics of Co2FeMn alloy

IV. Conclusion

Co2FeMn full Heusler alloy nanoparticles were successfully synthesized via hydrothermal method at various molarities. XRD analysis showed the formation of Co2FeMn alloy at 1.6M and 1.8M. Crystallite size was calculated using Scherer's formula, and the maximum crystallite size of 24 nm was observed at 1.8M. FTIR provided information about the nature of molecular interactions, while VSM analysis showed ferromagnetic behavior with narrow M-H loops. The stabilized and strengthened hexagonal phase of Co2MnSn full Heusler alloy nanoparticles at 1.8M exhibited maximum values of saturation magnetization, coercivity, and hardness. Additionally, the phase pure sample showed maximum conduction, with increased conduction response observed at low temperatures.

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She has authored and co-authored numerous research papers, articles, and book chapters, which have been published in reputable international journals and academic platforms. Prof. Dr Wang has also received many awards and honors in recognition of her outstanding contributions to the field of materials science and her excellence in teaching and research. She is a member of several professional organizations and serves as an editorial board member of various scientific journals.

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