

**CRYSTAL GROWTH AND CHARACTERISATION OF $[(\text{CH}_3)_2\text{NH}_2]$
 $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}(\text{CHOO})_3$ and $[(\text{CH}_3)_2\text{NH}_2]$ $\text{Ni}_{0.9}\text{Fe}_{0.1}(\text{CHOO})_3$
PEROVSKITE TYPE MULTIFERROIC METAL ORGANIC
FRAMEWORKS BY SOLVOTHERMAL METHOD**

Submitted in partial fulfillment of the requirements for the award of
Master of Science degree in Physics

By

G. LOKESHWARI

(41590011)



**DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCE AND HUMANITIES**

SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited with "A" grade by NAAC I 12B Status by
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JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119.

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of G. LOKESHWARI (41590011) who carried out the project entitled "CRYSTAL GROWTH AND CHARACTERISATION OF $[(CH_3)_2NH_2] Mn_{0.5}Ni_{0.25}Co_{0.25}(CHOO)_3$ and $[(CH_3)_2NH_2] Ni_{0.9}Fe_{0.1}(CHOO)_3$ PEROVSKITE TYPE MULTIFERROIC METAL ORGANIC FRAMEWORKS BY SOLVOTHERMAL METHOD" under my supervision and jointly with Dr. D. SORNADURAI (external supervisor from IGCAR, Kalpakkam) from November 2022 to May 2023.

Internal Guide

(Dr. Helen Merina Albert)

External Guide

(Dr. Sornadurai)

Head of the Department

(Dr.S. Ravichandran)

Submitted for Viva voce Examination held on 9.5.2023 2023

INTERNAL EXAMINER

EXTERNAL EXAMINER

D. D. DINESH KUMAR

Associate Professor (Research)

DECLARATION

I G. LOKESHWARI hereby declare that the Project Report entitled “CRYSTAL GROWTH AND CHARACTERISATION OF $[(\text{CH}_3)_2\text{NH}_2] \text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}(\text{CHOO})_3$ and $[(\text{CH}_3)_2\text{NH}_2] \text{Ni}_{0.9}\text{Fe}_{0.1}(\text{CHOO})_3$ PEROVSKITE TYPE MULTIFERROIC METAL ORGANIC FRAMEWORKS BY SOLVOTHERMAL METHOD” done by me under the guidance of Dr. Helen Merina Albert (Internal), Department of Physics, Sathyabama Institute of Science and Technology, Chennai and Dr. D. Sornadurai (External) Scientific Officer-F, X-ray scattering and Crystal Growth section, Condensed matter Physics Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, is submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Physics.

DATE: 09-05-2023

PLACE: CHENNAI



SIGNATURE OF THE CANDIDATE

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ABSTRACT

Multiferroic behaviour is observed in perovskite-type metal–organic frameworks with general formula report this synthesis of the heterogeneous $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}(\text{HCOO})_3$ AND $[(\text{CH}_3)_2\text{NH}_2]\text{Ni}_{0.9}\text{Fe}_{0.1}(\text{HCOO})_3$ MOF $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}(\text{HCOO})_3$ AND $[(\text{CH}_3)_2\text{NH}_2]\text{Ni}_{0.9}\text{Fe}_{0.1}(\text{HCOO})_3$, Crystallizing in a perovskite-type structure, synthesis has been done by using solvothermal method and characterizations like x-ray powder diffraction, single crystal xrd have been done.

Multiferroic materials, in which magnetic and electrical ordering coexist in a single phase, have received much attention in the last few years in view of their potential applications for magnetic storage, novel circuits, sensors, microwaves, and high-power applications. However, up-to-date single-phase multiferroics are rare as the conventional mechanisms for ferroelectric and cooperative magnetism are mutually exclusive. Beyond transition-metal oxides like BiFeO_3 , TbMnO_3 , GdMnO_3 etc. that have been extensively investigated, the family of hybrid inorganic-organic materials is attracting increased attention.

Recently the dense perovskite structure type (ABX_3) metal–organic frameworks (P- MOF) of formula $[(\text{CH}_3)_2\text{NH}_2][\text{M}(\text{HCOO})_3]$ (with $\text{M}_{2+} = \text{Mn}_{2+}$, Co_{2+} , Ni_{2+} and Fe_{2+}) (where $\text{A} = [(\text{CH}_3)_2\text{NH}_2]^+$, $\text{B} = \text{M}_{2+}$, $\text{X} = (\text{HCOO})^-$) are specially interesting as type I- multiferroics: they combine structural flexibility, relatively good stability, low density and cooperative magnetic and electrical properties.

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Chapter 1

1.1 INTRODUCTION

The term "MOF" refers to a group of porous materials made up of metal ions or clusters coordinated with organic ligands. Because of their high surface area and well-defined crystalline structure, MOFs are excellent for a variety of uses, such as gas storage, catalysis, drug delivery, and sensing. Metal nodes and organic linkers are joined in a controlled way to create three-dimensional structures in MOFs. By acting as dividers between the metal nodes, the organic linkers create a network of cavities and channels that can hold extracellular molecules. By adjusting the metal nodes and organic linkers, these cavities and channels may be modified, providing fine control over the pore size and shape.

One of the key advantages of MOFs is their tunability. By selecting different metal nodes and organic linkers, researchers can tailor the properties of the material to a specific application. An example of a trimetallic crystal with three separate metallic elements in particular ratios is $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$. This material's crystal structure is particularly intriguing because of its potential uses in catalysis, energy storage, and electrical devices. The cubic L12 crystal structure, which is characterized by a face-centered cubic (FCC) lattice with alternating layers of Co and Ni atoms and a third layer of Mn atoms, includes the $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ crystal structure. The Heusler alloy structure is another name for this crystal structure, which was given to Fritz Heusler, who made the initial discovery of this class of minerals in 1903. The $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ crystal possesses a high degree of structural symmetry and a variety of peculiar electrical and magnetic properties.

1.2 MULTIFERROICS

Multiferroics are substances that concurrently display ferromagnetic and ferroelectric characteristics. In contrast to ferromagnetism, which is the property of materials that display permanent magnetization in the absence of an external magnetic field, ferroelectricity is the attribute of materials that exhibit permanent electric polarization even in the absence of an external electric field. Multiferroics offer exceptional prospects for the creation of novel technologies, including magnetoelectric memory, sensors, and energy harvesting devices.

Multiferroics combine ferroelectric and ferromagnetic capabilities. The ability of a material to regulate its magnetic properties with an applied electric field or vice versa is known as the magnetoelectric effect. Devices with higher sensitivity and lower power consumption can be designed using this characteristic.

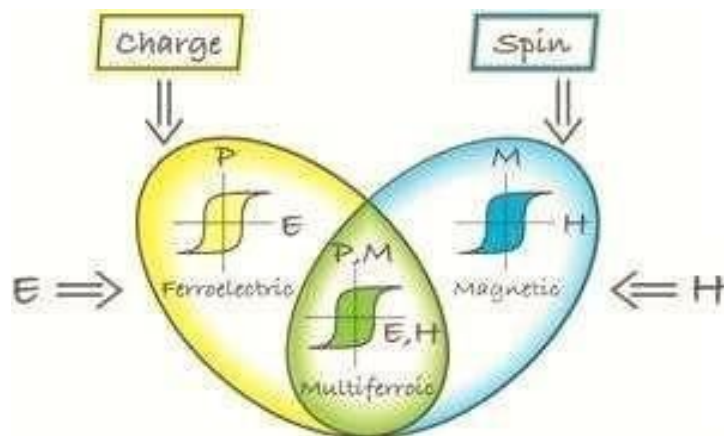


Figure 1.2 - The blue circle displays the hysteresis of ferromagnetic materials, the yellow circle displays usual hysteresis of ferroelectric materials and the circle displays hysteresis of multiferroics where magneto coupling occurs. [D. Khomskii, Phys. 77, 50937 (2009)]

Multiferroic materials can be divided into two categories: single-phase and composite. Materials with a single crystal structure and ferromagnetic and ferroelectric characteristics are known as single-phase multiferroics.

Composite multiferroics are substances that incorporate distinct ferromagnetic and ferroelectric phases into one substance.

The goal of multiferroics research is to create new materials with enhanced ferroelectric and ferromagnetic capabilities while also examining the underlying physics that underlies the connection of these phenomena. Improving the strength of the connection between the two qualities as well as creating new techniques for the synthesis and processing of these materials are some of the problems in the subject.

1.3 TYPE 1 MULTIFERROICS

The materials exhibit both ferroelectric and antiferromagnetic properties. Antiferromagnetic is the property of materials that exhibit a net magnetic moment of zero due to the cancellation of magnetic moments in adjacent atoms or ions. In type 1 multiferroics, the ferroelectricity arises from a polar crystal structure, while the antiferromagnetic arises from the magnetic ordering of the ions.

Due to their strong antiferromagnetic and ferroelectric coupling, type 1 multiferroics are of particular interest because they enable the control of magnetism by an electric field. This characteristic, referred to as magnetoelectric coupling, is crucial for many possible uses of multiferroic materials. A lot of work is being done to understand the fundamental physics behind the interaction between ferroelectricity and antiferromagnetism in type 1 multiferroics, as well as to find new materials that show these features. The development of novel techniques for the synthesis and processing of these materials, as well as strengthening the magnetoelectric interaction, are some of the difficulties facing the sector. A fascinating area of study, type 1 multiferroics have the potential to be used in a number of industries, including data storage, sensing, and energy conversion. The spectrum of possible uses for type 1 multiferroics is predicted to continue to grow as scientists unearth new components and techniques for creating and understanding them.

1.4 TYPE 2 MULTIFERROICS

Ferroelectric and ferromagnetic characteristics can both be seen in these materials at the same time. The magnetism in type 2 multiferroics is ferromagnetic, which means that the magnetic moments of nearby ions are aligned, in contrast to type 1 multiferroics, where it is antiferromagnetic. The likelihood of significant magnetoelectric coupling in type 2 multiferroics, which would allow for the control of magnetism by an electric field, is a factor in their attractiveness. Magnetoelectric memory and sensors might be created as a result, which would make technology more effective and adaptable.

One of the challenges in the field of type 2 multiferroics is the difficulty in finding materials that exhibit both strong ferroelectricity and ferromagnetism. However, researchers are continuing to search for new materials that exhibit these properties, as well as to understand the fundamental physics behind the coupling of ferroelectricity and ferromagnetism. Therefore, type 2 multiferroics represent a promising area of research with potential applications in a variety of fields, including data storage, sensing, and energy conversion. As researchers continue to uncover new materials and methods for synthesizing and studying type 2 multiferroics, the potential applications for these materials are expected to continue to expand.

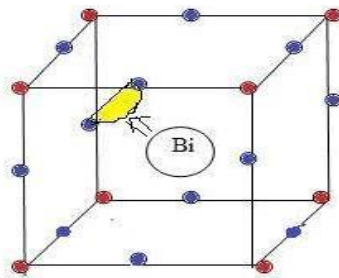


Figure 1.4 - Green circles are ferroelectrically active d^0 ions and red are magnetic d^n ions, yellow plaquettes are shifts of d^0 ions from the centers of O_6 octahedral, green arrows are polarization and red arrows are magnetic order.

Finding materials that demonstrate both strong ferroelectricity and ferromagnetism is one of the difficulties in the field of type 2 multiferroics. To learn more about the underlying physics of the coupling of ferroelectricity and

ferromagnetism, researchers are still looking for new materials with these characteristics. As a result, type 2 multiferroics are an exciting area of study with potential applications in a number of areas, such as data storage, sensing, and energy conversion. Applications for type 2 multiferroics are anticipated to increase as scientists continue to learn about novel components and techniques for synthesis and study.

1.5 PEROVSKITE STRUCTURE

Calcium titanate (CaTiO_3) makes up the mineral known as perovskite, therefore the phrase "perovskite-type structure" describes a crystal structure that is comparable to that of perovskite. A and B are cations, and X is an anion in the perovskite crystal structure, which has the general formula ABX_3 . A cation takes up a sizable octahedral site in the center of the unit cell of a perovskite crystal, whereas the B cation takes up smaller octahedral sites on the unit cell's periphery. The corners of the unit cell are where the X anion is found. A three-dimensional network of octahedra that share corners is the resulting crystal structure. As a result of the perovskite structure's flexibility and ability to hold a variety of cations and anions, numerous distinct compounds with various characteristics can be formed.

Superconductors, fuel cells, catalysts, as well as electrical and magnetic materials are just a few of the uses for perovskite-type materials that have been created. Due to their high absorption coefficients, extended carrier lifetimes, and inexpensive synthesis techniques, perovskite-type materials have recently attracted a lot of attention for their possible use in solar cells. With an efficiency increase of over 25% in just a few years of development, perovskite solar cells have made significant strides.

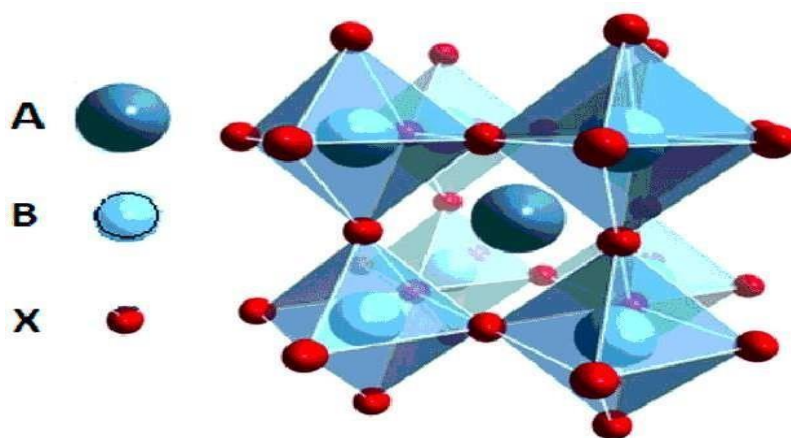


FIG 1.5 The mineral calcium titanium oxide, the first perovskite crystal to be identified, has the same crystal structure as a substance known as perovskite.

The chemical formula for perovskite compounds is typically ABX_3 , where 'A' and 'B' stand for cations and 'X' is an anion that bonds to both of them. The perovskite-type structure is a diverse and promising area of study with potential applications in a variety of industries. The number of possible uses for perovskite-type materials is anticipated to grow as scientists continue to unearth novel substances and techniques for investigating and synthesizing them.

1.6 Organic and Inorganic

The two different types of substances utilized to form crystals are referred to as organic and inorganic crystal growth. Inorganic materials, which are mainly metals, metalloids, and non-metals, are used in inorganic crystal development to create crystals. Inorganic crystals frequently have well-defined structures and are highly organized. Techniques for growing inorganic crystals include hydrothermal synthesis, sol-gel processes, and chemical vapour deposition. The use of organic materials, which are primarily carbon-based chemicals, to produce crystals, on the other hand, is known as organic crystal growth. In comparison to inorganic crystals, organic crystals typically have less order and more complicated structures. Solution growth, melt growth, and epitaxial growth are methods used to grow organic crystals. Applications including

organic light-emitting diodes (OLEDs), organic solar cells, and organic field effects frequently use organic crystals.

CHAPTER 2

LITERATURE SURVEY

1. Sornadurai, D., Sarguna, R., & Sridharan, V, Variation of structural parameters in dimethylammonium manganese formate $[(CH_3)_2NH_2]Mn(HCOO)_3$ by substitution of transition metals (M = Zn, Co and Ni): By powder XRD method. *Powder Diffraction*, 34(2), 124-129 (2019). [doi:10.1017/S0885715619000307](https://doi.org/10.1017/S0885715619000307)
2. Sornadurai D, Sarguna R.M, Vinod K, Sridharan V, Structural and magnetic properties study of cobalt substituted dimethylammonium manganese formate single crystals $[(CH_3)_2NH_2]Mn_{1-x}Co_x$ ($x=0, 0.1, 0.2$ and 0.3). *AIP Conf. Proc.* 2115, 030416 (2019). <https://doi.org/10.1063/1.5113255>

2.2 LITERATURE EXPLANATION

1. Variation of structural parameters of dimethylammonium manganese formate $[(CH_3)_2NH_2]Mn [(HCOO)_3]$ upon substitution by the transition elements Zn, Co, and Ni is studied by powder X- ray diffraction (PXRD) technique. These metal–organic framework (MOF) crystals were grown by solvothermal method. The PXRD patterns of all MOFs exhibited rhombohedral structure. PXRD patterns of MOFs were analyzed using Rietveld refinement method. While the parent MnMOF and $Mn_{0.9}Zn_{0.1}MOF$ are found to have similar structural parameters, Co and Ni substituted Mn- MOFs have smaller structural parameters than that of parent Mn- MOF. The reason for this variation in the lattice parameters is explained based on the Shannon ionic radii. © 2019 International Centre for Diffraction Data.

2. The Perovskite type metal organic framework (MOF) dimethylammonium manganese formate (Mn-MOF) and cobalt substituted Mn-MOFs ($\text{Mn}_{1-x}\text{Co}_x$; $x=0.1, 0.2$ and 0.3) were grown by solvothermal method. The single crystalline nature of these crystals was confirmed by Laue diffraction. The lattice parameters as well as the unit cell volume are found to linearly decrease with the increase of Co substitution. The magnetic measurements of the crystals $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{1-x}\text{Co}_x(\text{HCOO})_3$ ($x = 0.1, 0.2, 0.3$) were carried out using vibrating sample magnetometer. $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.9}\text{Co}_{0.1}(\text{HCOO})_3$ showed both the metastable magnetic phase formation as well as the Neel temperature (T_N) at 9.5 K and 8.5 K respectively. The M-H curves at 4 K showed the ferromagnetic behavior and at 20 K showed the paramagnetic nature. $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.8}\text{Co}_{0.2}(\text{HCOO})_3$ showed metastable magnetic phase formation at 10.3 K and T_N at 9 K. $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.7}\text{Co}_{0.3}(\text{HCOO})_3$ showed metastable magnetic phase formation at 12.5 K and T_N at 10.5 K.

CHAPTER 3

AIM AND SCOPE

3.1 TRIMETALLIC AND BIMETALLIC COMPOUND

Both the material $\text{Ni}_{0.9}\text{Fe}_{0.1}$ and the material $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ have been investigated for their varied characteristics and possible uses. Depending on the particular field and application, different goals may be pursued in research on these materials. Several examples of $\text{Ni}_{0.9}\text{Fe}_{0.1}$ and $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ research objectives are given below:

Magnetic property: Studying and improving the magnetic characteristics of the magnetic substance $\text{Ni}_{0.9}\text{Fe}_{0.1}$ is one of the goals of research on this material. This may entail calculating the magnetic moment, coercivity, and magnetic anisotropy of the material as well as investigating how these characteristics are affected by the environment's temperature, pressure, and magnetic field.

Structural properties: Research may be conducted with the goal of analyzing and improving the crystal structure of $\text{Ni}_{0.9}\text{Fe}_{0.1}$, which can exist in a variety of forms. Studying its crystallographic orientation, development, and structural flaws in the crystal are some examples of what can be done in this regard.

Catalytic properties: Research may look into and improve the catalytic activity of $\text{Ni}_{0.9}\text{Fe}_{0.1}$ for a variety of reactions after it has been investigated for its possible catalytic features. Studying how various factors, such as temperature, pressure, and reactant concentrations, affect the catalytic activity might be a part of this.

Electronic properties: Considering that $\text{Ni}_{0.9}\text{Fe}_{0.1}$ is a metallic substance, one goal of research might be to examine and improve upon its electronic properties. This can involve determining the material's conductivity, resistivity, and Hall coefficient as well as investigating the impact of impurities and flaws on these characteristics. Depending on the subject and application, the goal of

research on $\text{Ni}_{0.9}\text{Fe}_{0.1}$ can change, but it often entails analyzing and improving its many properties for prospective applications in the disciplines of magnetism, structure, catalysis, and electronics.

3.2 $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$

Magnetic properties: $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ is also a magnetic material, and one goal of research on this material is to examine and enhance its magnetic properties. This may entail measuring the material's magnetic moment, coercivity, and magnetic anisotropy as well as investigating how temperature, pressure, and magnetic field affect these characteristics.

Structural properties: Research may focus on understanding and improving the crystal structure of $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$, which can exist in a variety of forms. This can involve researching the crystal's crystallographic orientation, crystal development, and crystal structure flaws.

Catalytic properties: The possible catalytic characteristics of $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ have also been investigated, and one goal of research may be to discover and enhance its catalytic activity for different reactions. This may entail researching how various factors, such as temperature, pressure, and reactant concentrations, affect the catalytic activity.

Magnetocaloric properties: Its magnetocaloric characteristics, which might be utilized for magnetic refrigeration, have been examined for $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$. The study of the influence of temperature and magnetic field on the magnetocaloric effect can be used to optimize these features.

The objectives of research on $\text{Ni}_{0.9}\text{Fe}_{0.1}$ and $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ can vary depending on the area and application, but they usually entail analyzing and improving the many properties of these materials for prospective uses in magnetic, structural, catalytic, or magnetocaloric sectors.

3.3 SCOPE OF CRYSTAL GROWTH IN MOFs

The term "metal-organic framework" (MOF) refers to a family of porous materials made of metal ions or clusters linked by organic ligands. Due to their large surface area and adjustable pore size, MOFs are well-suited for a number of uses, including gas storage, catalysis, and drug delivery. Because it can change the morphology, size, and properties of the final materials, the crystal growth of MOFs is a crucial area of study. The range of crystal formation in MOFs is very extensive and encompasses a variety of methods and strategies. Some examples of crystal growth techniques for MOFs include:

Solvothermal synthesis: To do this, a suitable solvent is used to dissolve the metal ions and organic ligands, and the solution is heated under high pressure to encourage crystal formation.

Hydrothermal synthesis: Although the reaction takes place at a lower pressure and temperature, it is similar to solvothermal synthesis.

Microwave-assisted synthesis: This includes heating the reaction mixture with microwave energy in order to encourage crystal formation.

Template-directed synthesis: In this method, the crystal development of the MOF is guided by a pre-formed template, producing materials with predetermined shapes and sizes.

Layer-by-layer assembly: By layer-by-layer, growing MOF crystals on a substrate, thin films of the substance are produced using this method.

Seed-mediated growth: By employing MOF crystals that have already formed as seeds, bigger crystals can be encouraged to grow.

The range of crystal formation in MOFs is enormous, and a wide range of variables, including solvent selection, temperature, and reaction time, can affect the outcome. In order to optimize the crystal development of MOFs for particular purposes, researchers are still investigating novel synthesis techniques. MOFs for particular purposes, researchers are still investigating novel synthesis techniques.

CHAPTER 4

EXPERIMENTAL OR MATERIALS AND METHODS: ALGORITHMSUSED

4.1 CRYSTAL GROWTH BY SOLVOTHERMAL SYNTHESIS

The solvothermal process, which uses the use of a solvent under high temperatures and high pressure to promote crystal development, can be used to create the alloys $\text{Ni}_{0.9}\text{Fe}_{0.1}$ and $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$. The solvothermal synthesis of the alloys $\text{Ni}_{0.9}\text{Fe}_{0.1}$ and $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ is described in $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ detail here.

CALCULATION:

Atomic mass:

S. No	Atomic No	Element	Atomic Mass(g)
1	1	Hydrogen	1.008
2	8	Oxygen	15.99
3	17	Chlorine	35.45
4	25	Manganese	54.45
5	27	Cobalt	58.933
6	28	Nickel	58.693

Molecular masses:

S. No	Compound name	Molecular Mass (amu)
1	Manganese Chloride Tetra-Hydrate	197.91
2	Nickel Chloride Hexa-Hydrate	237.683
3	Ferrous Chloride Tetra-Hydrate	198.805
4	Cobalt Chloride Hexa-Hydrate	237.923

5mM of $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ 80ml of solution:

S. No	Compound name	Molarity(M)	Calculated mass
1	Manganese chloride tetra-hydrate	2.5	0.4947
2	Nickel Chloride Hexa-Hydrate	1.25	0.2971
3	Cobalt Chloride Hexa-Hydrate	1.25	0.2974

5m M of $\text{Ni}_{0.9}\text{Fe}_{0.1}$ 80ml of solution

S. No	Compound name	Molarity(M)	Calculated mass(g)
1	Nickel Chloride Hexa-Hydrate	0.9	1.06957
2	Ferrous Chloride Tetra-Hydrate	0.1	0.0994025

Preparation of reactants: In order to calculate the reactants for the synthesis of $\text{Ni}_{0.9}\text{Fe}_{0.1}$, the molecular weights of Nickel and ferrous in their bimetallic and trimetallic forms—Co, Mn and Ni—were employed. The components of the alloy are 1,4-benzenedicarboxylic acid (BDC), cNickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and iron (III) nitrate nonhydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). A suitable solvent, such as N, N- dimethylformamide (DMF), is used to dissolve the metal salts and BDCto create a transparent solution.

Mixing and stirring: In a typical crystal formation of Mn-MOF, 5 mM of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 40 ml of dimethylformamide and 40 ml of deionized water. This mixture was rapidly agitated for at least 30 minutes to guarantee complete dissolution of the metal salts.

Transfer to autoclave: The solution was transferred to a 100 cc Teflon-lined stainless-steel autoclave, which was then sealed to stop any solvent leakage.

Heating: For a period usually 72 hours, the autoclave is heated to a temperature in the range of 140°C . High pressure might be used during the process to make sure the solvent stays liquid.

Cooling and transferring: Following the reaction, the autoclave must cool to room temperature before the product is poured into a clean beaker and left to crystal for seven days.

Washing: The crystals were washed 4-5 times with a suitable solvent, such as ethanol, after 7 days to get rid of any unreacted substances.

Drying and annealing: The dried crystals are annealed at high temperatures (usually $200\text{--}500^\circ\text{C}$) after being cleaned at low temperatures, which further enhances the crystal quality.

The $\text{Ni}_{0.9}\text{Fe}_{0.1}$ alloy's crystal size, shape, and quality can be modified by adjusting the reaction parameters, such as the temperature, pressure, and reaction time. X-ray diffraction is just one of the methods that can be used to characterize the final product.



FIG 4.1 The photograph of the crystal taken after washing in ethanol.

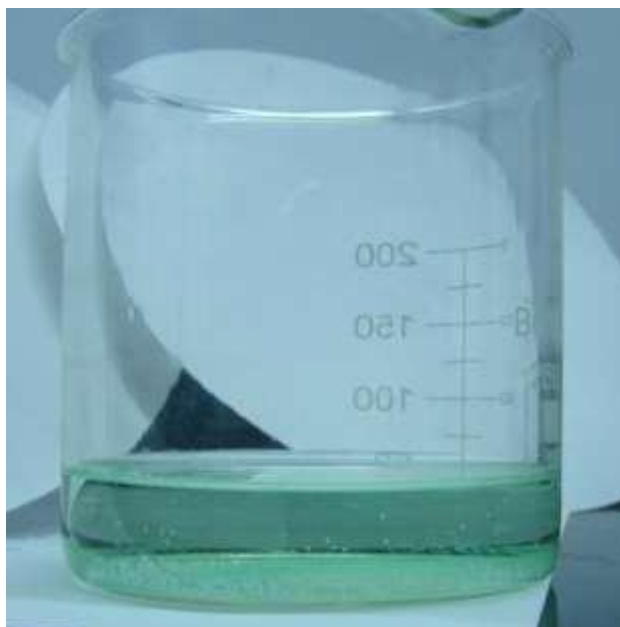


FIG 4.1.1 The process of crystal growth

4.2 SOLVOTHERMAL METHOD

The process known as the "solvothelmal method" involves heating and compressing a solvent to create crystalline crystals. In order to facilitate crystal development, the procedure includes dissolving precursor materials in a suitable solvent before exposing it to extreme heat and pressure in a sealed vessel. The solvent serves as a reaction media for crystal formation as well as a means of transport for the dissolved precursors.

A wide range of materials, including metals, metal oxides, metal sulfides, metal-organic frameworks (MOFs), and other inorganic compounds, are frequently synthesized using the solvothelmal process. The process has several benefits over other synthesis techniques, including the following:

Controlled crystal growth: The synthesis of materials with clearly defined crystal structures, morphologies, and sizes is possible thanks to the controlled environment that the solvothelmal process offers for crystal formation.

Homogeneous materials: The solvothermal process encourages homogeneous crystal development, which produces materials with consistent characteristics.

High purity: The solvothermal method's high temperature and pressure conditions can encourage the elimination of impurities, producing high- purity materials.

Versatility: Many different types of materials, including those that are challenging to synthesize using other techniques, can be created using the solvothermal method.

The requirement for specialized equipment, the possibility of the solvent reacting with the precursor ingredients, and the challenge of managing the reaction conditions are some drawbacks of the solvothermal process. The solvothermal approach is nevertheless a well-liked and efficient way to create a variety of materials with regulated properties, despite these drawbacks.



FIG. 4.2 Autoclave for solvothermal synthesis.

4.3 MICROSCOPIC OBSERVATION OF GROWN CRYSTAL

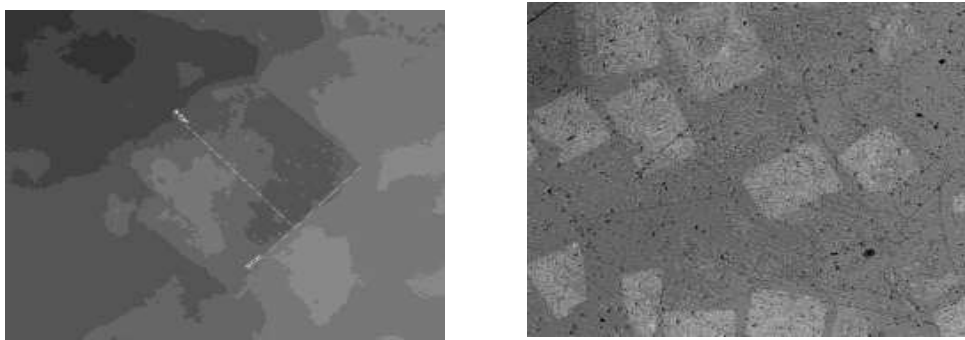


FIG 4.3 Optical microscope photograph of $[(\text{CH}_3)_2\text{NH}_2]\text{Ni}_{0.9}\text{Fe}_{0.1}(\text{CHOO})_3$.

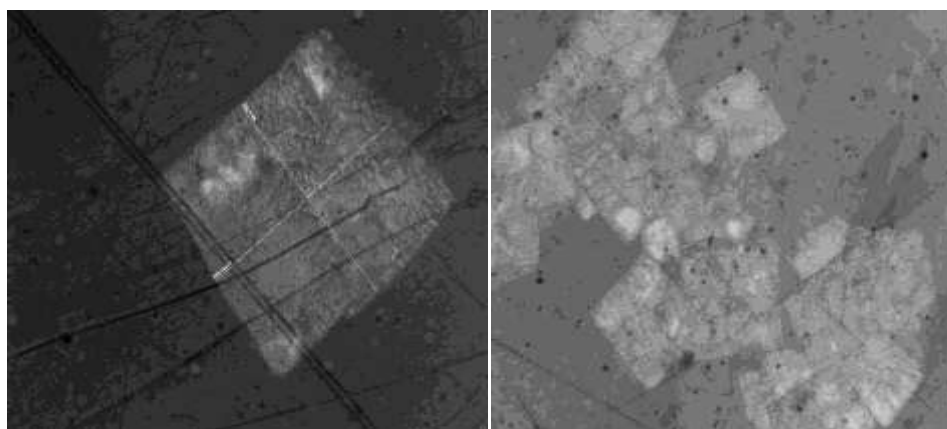


FIG. 4.3.1 Photograph of $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}(\text{HCOO})_3$

4.4 X-RAY DIFFRACTION ON SINGLE CRYSTAL

A potent method for figuring out a material's crystal structure is X-ray diffraction (XRD). X-rays are diffracted in particular directions when they interact with a crystal, leaving a pattern of spots on a detector as a result. The crystal structure affects the pattern of spots, and the crystal structure can be ascertained by examining the locations and intensities of the spots.



FIG. 4.4: Single crystal XRD machine

Both single crystals and powders can be subjected to XRD. Single crystals are examined by aligning a small crystal with the X-ray beam while it is positioned on a sample holder. A detector then gathers the diffracted beams once the X-ray beam is pointed at a precise angle towards the crystal. The positions and intensities of the diffracted spots are calculated utilizing software processing of the gathered data. Using a variety of computer techniques, the crystal structure can be ascertained from this data. When used on single crystals, XRD has the benefit of providing extremely exact data on the crystal structure, including bond lengths, angles, and other structural elements.

The requirement for large, high-quality crystals with huge dimensions is the primary drawback of XRD on single crystals. Single crystal growth can be a difficult procedure, and for reliable data to be obtained, the crystals must be large enough and of high enough quality. A time-consuming procedure that needs specialized tools and knowledge, XRD on single crystals is also a laborious task. In numerous disciplines, such as materials science, chemistry, and solid-state physics, XRD on single crystals is a useful method for determining the crystal structure of materials.

4.5 2D XRAY-DIFFRACTION IN GROWN CRYSTALS

2D X-ray diffraction (XRD) is a method that, in comparison to standard XRD, offers more precise details about a material's crystal structure. By simultaneously collecting diffraction patterns from various angles using a 2D detector, a 3D diffraction pattern can be recreated in 2D XRD.

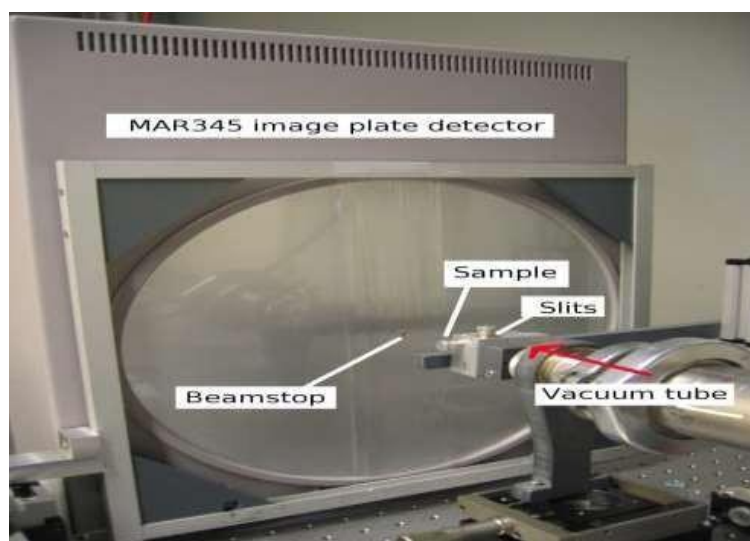


FIG. 4.5 2-D X-Ray Diffraction Machine

Utilizing specialized software, the collected data can be examined to determine the crystal structure. The method can also be used to ascertain the crystal's crystallographic orientation, which is crucial for understanding the material's anisotropic properties. With 2D XRD, you can characterize materials with more complex structures and get more detailed information about the crystal structure than you can with conventional XRD. The method, for instance, can be used to examine polycrystalline materials, which include several grains with various orientations, and it can reveal details about the grains' preferred orientation.

The crystal structure, phase purity, and crystal orientation of $\text{Ni}_{0.9}\text{Fe}_{0.1}$ and $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$ crystal development may all be learned from 2D XRD data. The method can also be used to examine the crystal's quality, including any flaws, grain boundaries, or twinning. Using specialized software, it is possible to analyze the 2D XRD data and determine the crystal structure as

well as other crystallographic parameters like lattice constants, unit cell dimensions, and atomic positions. The method can also be used to ascertain the crystal's crystallographic orientation, which is crucial for understanding the material's anisotropic properties.

In conclusion, 2D XRD can give precise details on the crystal quality and structure of $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ crystals produced by solvothermal synthesis. The method can aid in streamlining the crystallization procedure and characterizing the materials for prospective use in a variety of sectors, including catalysis, energy storage, and magnetic and electrical devices.

CHAPTER 5

RESULTS AND DISCUSSIONS, PERFORMANCE ANALYSIS

5.1 ANALYSING THE SINGLE XRD PEAKS IN ORIGIN

In many research domains, including X-ray diffraction (XRD) analysis, powerful software called Origin is frequently utilized for data processing and visualization. There are numerous methods that can be used to retrieve useful information from the data when analyzing single XRD peaks in Origin.

Import the XRD data into Origin: The "Import Wizard" or copying and pasting the data into a new spreadsheet are two ways to import the XRD data into Origin. The two-theta angles should be in the first column of the data, and the matching intensities should be in the second column.

Fit the XRD peak: A peak fitting function, such as the Gaussian or Lorentzian function, can be used to fit the XRD peak. The "Fitting Function" menu in the "Peak Analysis" toolbar allows you to choose the fitting function. You can play about with the peak fitting parameters until the fitted curve roughly resembles the experimental data.

Analyze the peak parameters: The data can be used to extract a number of parameters after the peak has been fitted. These include the peak width (full width at half maximum, FWHM), peak position (2-theta angle), and peak intensity. By double-clicking on the fitted curve, you may open the "Fit Parameters" dialogue box and find these parameters there.

Compare the peak parameters: It is possible to compare the peak parameters acquired from the XRD data with the predicted values for the crystal structure under investigation. This can assist in identifying the crystal and determining whether it is in the right phase. Any deviations from the expected values may point to an issue with the crystal structure or the experimental setup.

Using a suitable function to fit the peak and extract the peak characteristics, which may then be compared with the predicted values for the crystal structure being examined, are the first steps in analyzing single XRD peaks in Origin. This can offer important insights into the crystal structure and point out any problems with the experimental set-up.

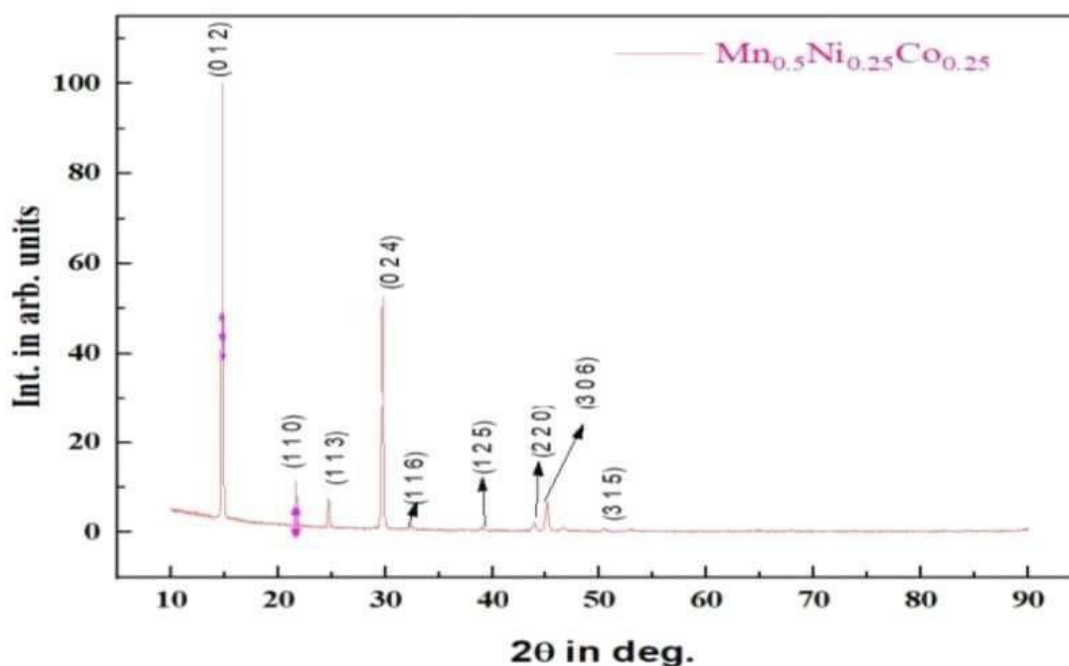


Fig 5.1 XRD pattern of $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$

5.2 CONVERTING THE 2D XRAY- DIFFRACTION CRYSTAL RESULTS IN FIT2D

A popular piece of software for studying 2D X-ray diffraction (XRD) data is called FIT2D. The following actions can be conducted to analyze crystals using 2D XRD data in FIT2D:

Import the 2D XRD data: The "Open" command found in the "File" menu can be used to import the 2D XRD data into FIT2D. The information must be contained in an image file, such as a TIFF or BMP file.

Calibration: For the purpose of figuring out the two-theta (2θ) angle of the diffraction peaks, the 2D XRD pattern needs to be calibrated. A calibration

standard, such as a standard powder diffraction pattern or a LaB6 calibration standard, can be used to do this. The "Calibration" command found in the "Calibration" menu can be used to perform the calibration.

Integration: To create a 1D or 2D plot of the intensity vs the 2 angle, the 2D XRD pattern can be combined along one or more directions. Utilizing the "Integrate" command found in the "Integration" menu, this can be done. An interest region or a single line might be used for the integration.

Background subtraction: Using the "Background Subtraction" command from the "Background" menu, the background can be removed from the integrated pattern. This may aid in increasing the peakfitting's precision.

Peak fitting: The "Fit Peaks" command found in the "Fitting" menu can be used to examine the integrated pattern. There are many fitting functions that can be used, such as Gaussian or Lorentzian functions, to fit the peaks. The findings of peak fitting can be used to determine the fitted parameters, such as the position, width, and intensity of the peaks.

Data analysis: The crystal structure can be examined using the fitted parameters, for as by figuring out the lattice parameters or detecting the crystal phase. For the examination of 2D XRD data, FIT2D is a flexible software program that offers a number of tools for calibration, integration, peak fitting, and data analysis.

5.3 XRD SINGLE PEAK ANALYSIS WITH ICDD DATA'S

An effective analytical method for pinpointing the atomic level crystal structure of a substance is single-crystal X-ray diffraction (XRD). An organization called the International Centre for Diffraction Data (ICDD) offers a vast library of X-ray diffraction patterns for a variety of materials.

The steps below should be followed in order to use the ICDD database to analyze the single crystal XRD pattern of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ and $\text{Ni}_{0.9}\text{Fe}_{0.1}$:

Collect the XRD data: Using an X-ray diffractometer, a high-quality X-ray diffraction pattern of the single crystal must be obtained.

Index the crystal: Indexing the crystal to identify the crystal system, lattice parameters, and space group is the first step in analyzing the XRD pattern. Software like APEX3 can be used for this.

Structure refinement: After the crystal has been indexed, the crystal structure can be adjusted using programs like crystals. To do this, the locations of the atoms within the unit cell are calculated by fitting the observed diffraction pattern to a model of the crystal structure.

Compare with ICDD database: After the crystal structure has been improved, you can check it against the ICDD's database of known crystal structures. You will be able to validate the crystal structure and identify the phase(s) present in the sample using this method.

Interpreting the outcomes: Finally, you can analyze the study's findings to learn more about the material's links between its structure and properties. For instance, you may figure out the bonding traits, spot any flaws or impurities in the crystal structure, and connect the crystal structure to the material's physical attributes.

TABLE 5.3 The (hkl) values of $\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}$

Observed (d)	Calculated (d)	Observed (2 θ)	Calculated (2 θ)	(observed– calculated)	intensity	h	k	l
6.0128	6.0126	6.779	6.779	0	0	0	1	2
4.403	4.4036	9.261	9.262	-0.001	0	1	0	4
4.0066	4.1145	9.913	9.908	0.005	0	1	1	0
3.6045	3.6037	11.32	11.323	0.003	0	1	1	3
3.406	3.3956	11.982	11.019	0.037	0	2	0	2
3.0062	3.0064	13.583	13.582	-0.001	0	0	2	4
2.7641	2.765	14.779	14.774	-0.005	0	1	1	6
2.6751	2.6743	15.278	15.273	0.005	0	2	1	1
2.4257	2.4274	16.855	16.843	-0.012	0	2	1	4
2.376	2.3755	17.21	17.213	0.003	0	3	0	0
2.308	2.3085	17.721	17.717	-0.005	0	1	2	5
2.2007	2.2018	18.583	18.593	-0.009	0	2	0	8
2.1386	2.1372	19.15	19.138	0.013	0	1	0	10
2.20581	2.0573	19.893	19.902	0.008	0	2	2	0
1.9431	1.9413	21.083	21.104	0.02	0	1	2	8
1.8947	1.8966	21.628	21.607	-0.021	0	0	2	10
1.8656	1.8669	21.971	21.955	-0.016	0	0	0	12
1.8015	1.8019	22.763	22.758	-0.005	0	2	2	6
1.7589	1.7595	23.313	23.322	-0.008	0	0	4	2
1.7228	1.7224	23.817	23.823	0.006	0	2	1	10
1.6999	1.7001	24.142	24.14	-0.002	0	1	1	12
1.6183	1.6178	25.38	25.388	0.008	0	2	3	2
1.5577	1.5567	26.384	26.402	0.018	0	4	0	7
1.5352	1.5359	26.779	26.766	-0.013	0	2	3	5
1.5224	1.5225	27.008	27.007	-0.002	0	4	1	3
1.482	1.4821	27.759	27.756	-0.003	0	1	3	10
1.4361	1.4356	28.665	28.675	0.01	0	4	1	6
1.4129	1.4139	29.145	29.124	-0.021	0	5	0	2
1.3812	1.3813	29.83	29.828	-0.002	0	0	5	4
1.3497	1.3489	30.542	30.56	0.018	0	3	3	3
1.3189	1.3189	31.273	31.274	0.001	0	4	1	9

1.2892	1.2898	32.407	31.999	-0.015	0	4	2	5
1.274	1.274	32.407	32.381	-0.026	0	2	3	11
1.2467	1.2478	33.136	33.106	-0.03	0	5	1	4
1.2437	1.2437	33.217	33.218	0.001	0	3	1	14
1.2152	1.2137	34.02	34.063	0.044	4	2	8	6
1.1913	1.1913	34.724	34.725	0.001	0	1	1	18
1.173	1.173	35.283	35.284	0.001	0	6	0	3
1.1542	1.1543	35.879	35.876	-0.003	0	2	4	10
1.1437	1.1436	36.22	36.222	0.002	0	2	3	14
1.1338	1.1335	36.545	36.557	0.011	0	3	4	5
1.1197	1.1194	37.022	37.033	0.011	0	0	2	19
1.0965	37.832	37.834	0.005	0	3	1	17	10

When using the ICDD database to analyze the $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ single crystal XRD pattern, the crystal is indexed, its structure is improved, it is compared to the database, and the results are then analyzed to reveal information about the material's properties.

5.4. FIT 2D PEAKS ARE ANALYSING IN ORIGIN

The software program FIT2D is frequently used to examine single-crystal and powder sample X-ray diffraction data. However, Origin is a data analysis and graphing program that is frequently employed in the scientific and engineering disciplines. You would need to do the following actions in order to analyze FIT2D peaks in Origin:

Export the data from FIT2D: In order to do this, the FIT2D data must be exported in a way that Origin can understand. Both a text file and a CSV file can be used to export the data.

Data import into Origin: After the data has been exported, Origin can be used to analyze it. By choosing the right file format from the File > Import option in

Origin, you can accomplish this.

Plot the data to see the crystal peaks: You can use Origin to plot the X-ray diffraction data. The graphic can be altered to display the intensity on the y-axis and the diffraction angle (2θ) on the x-axis.

Peak fitting function: In Origin can be used to fit the crystal peaks after the data has been plotted. In order to do this, the peak parameters must be changed to fit the data and the peak shape must be chosen appropriately.

Analyze the crystal structure Once the peaks have been fitted, the crystal structure can be determined by comparing the peak positions and intensities to those in the ICDD database.

Interpreting the outcomes: Finally, you can use the analysis's findings to interpret the crystal structure and its properties. For instance, you may figure out the bonding traits, spot any flaws or impurities in the crystal structure, and connect the crystal structure to the material's physical attributes.

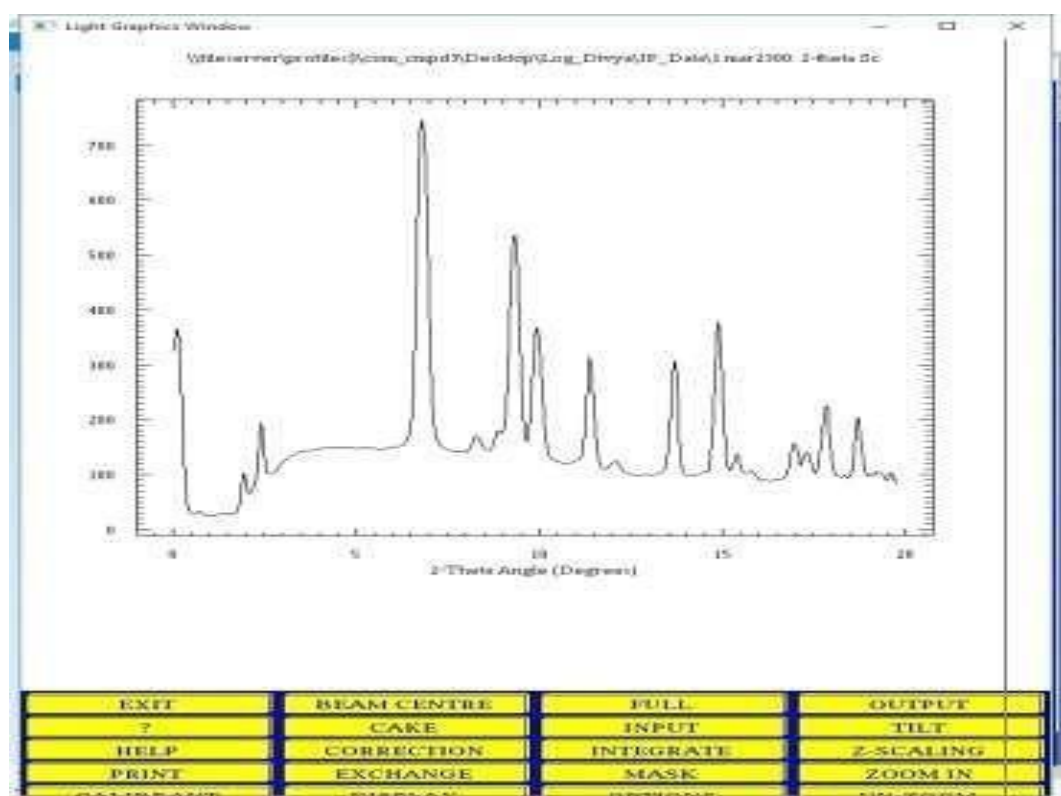


FIG 5.4 Fit 2-D graph of $\text{Ni}_{0.9}\text{Fe}_{0.1}$

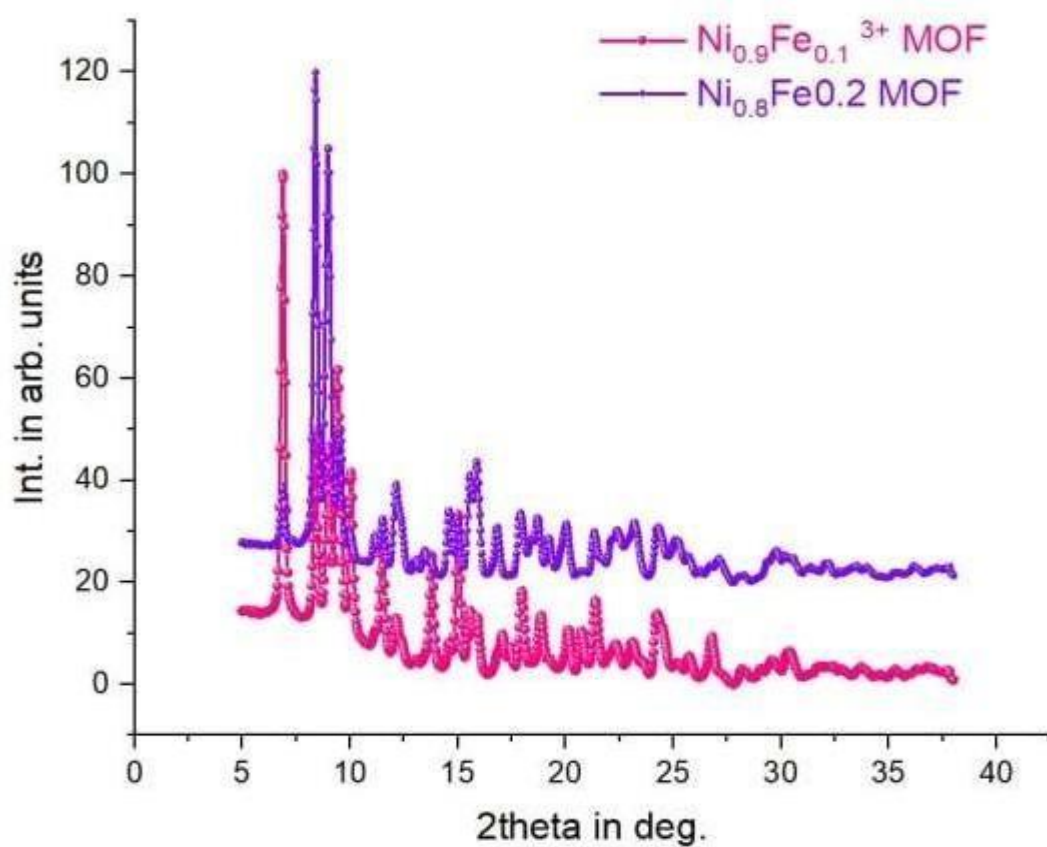


Fig 5.4.1 Fit-2D graph analysis of the $\text{Ni}_{0.9}\text{Fe}_{0.1}$

Table 5.4 The (hkl) values of $\text{Ni}_{0.9}\text{Fe}_{0.1}$

Observed (d)	Calculated (d)	Observed (2 θ)	Calculated (2 θ)	Obs- Calc)	intensity	h	k	l
5.9253	5.9293	6.879	6.875	-0.005	0	0	1	2
4.3335	4.3384	9.411	9.411	-0.011	0	1	0	4
3.5513	3.3503	11.491	11.481	-0.01	0	1	1	3
3.3503	3.3503	12.182	12.183	-0.01	0	2	0	2
2.9629	2.9646	13.782	13.774	-0.01	0	0	2	4
2.7476	2.7494	14.868	14.859	-0.01	0	2	0	5
2.7232	2.7246	15.002	14.994	-0.008	0	1	1	6
2.7246	2.7232	15.945	15.927	-0.018	0	2	1	1
2.5796	2.5842	15.843	15.927	-0.029	0	1	2	2

2.5632	2.566	17.043	17.077	-0.034	0	2	1	4
2.3436	2.3444	17.45	17.444	-0.003	0	3	0	0
2.2753	2.2766	17.978	17.967	-0.011	0	1	2	5
2.17	2.1692	18.858	18.865	0.007	0	2	0	8
2.0349	2.0315	20.157	20.122	0.035	0	2	1	7
1.9721	1.9764	20.771	20.724	-0.046	0	3	0	6
1.915	1.9133	21.397	21.416	0.019	0	1	2	8
1.8397	1.8389	22.283	22.293	0.01	0	1	3	4
1.774	1.7771	23.12	23.079	-0.041	0	2	2	6
1.6957	1.697	24.203	24.184	-0.019	0	2	1	10
1.6782	1.6751	24.46	24.505	0.045	0	4	0	4
1.6346	1.6332	25.123	25.144	0.021	0	0	4	5
1.5958	1.5965	25.744	25.732	-0.012	0	2	3	2
1.5343	1.5348	26.795	26.786	-0.009	0	4	1	0
1.4608	1.461	28.169	28.167	-0.002	0	1	3	10
1.447	1.4461	28.444	28.462	0.017	0	3	0	12
1.4181	1.4162	29.035	29.076	0.041	0	4	1	6
1.3923	1.3924	29.587	29.584	-0.004	0	2	3	8
1.3562	1.3549	30.392	30.422	0.03	0	1	2	14
1.3186	1.3196	31.281	31.257	-0.023	0	4	2	2
1.2988	1.3006	31.77	31.725	-0.045	0	4	1	9
1.2568	1.2569	32.861	32.861	-0.001	0	2	3	11
1.2246	1.2246	33.751	33.752	0.001	0	2	4	7
1.1977	1.1972	34.533	34.548	0.015	0	4	2	8
1.1907	1.906	34.741	34.746	0.004	0	2	2	15
1.1729	1.1727	35.287	35.294	-0.01	0	1	2	17
1.1446	1.1449	36.191	36.178	-0.012	0	1	0	19
1.1392	1.1383	36.367	36.397	0.03	0	2	4	10
1.1266	1.127	36.787	36.826	-0.013	0	2	3	14
1.1252	1.1255	36.826	36.826	-0.01	0	1	3	16
1.1023	1.102	37.628	37.641	0.013	0	0	2	19

The process for analyzing the FIT2D peaks in Origin includes exporting the data from FIT2D, importing it into Origin, charting the data, fitting the peaks, determining the crystal structure, and analyzing the results. This procedure enables the use of two potent software tools for a thorough investigation of the crystal structure and its characteristics.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The single crystals of Metal-Organic Frameworks (MOF) with perovskite structure were successfully grown using the solvothermal method. And successfully grown the Fe-doped Co-MOF with the molecular formula $[(\text{CH}_3)_2\text{NH}_2]\text{Ni}_{0.9}\text{Fe}_{0.1}(\text{HCCO})_3$ and another ternary metallic MOF with the chemical formula $[(\text{CH}_3)_2\text{NH}_2\text{Mn}_{0.5}\text{Ni}_{0.25}\text{Co}_{0.25}(\text{HCOO})_3$. The powder diffraction pattern of the as-grown crystal showed only a few peaks which satisfied the Bragg diffraction condition. This showed the mono-phase nature of the crystals. The same crystals were powdered and then the powder X-ray diffraction pattern was recorded for both crystals with a two-dimensional X-ray detector. The 2D XRD patterns were unwrapped into 1D data with X-Y format and further analysis was carried out on this data. The powdered samples exhibited all the possible and resolvable peaks. Since there is no standard XRD data available for these materials, the XRD patterns were indexed based on the standard XRD pattern of the same perovskite family MOFs, and the structures were refined using the NBS* AIDS83 program. Finally, the lattice parameters of these materials were found and the patterns were indexed.

CHAPTER 7

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