

**CRYSTAL GROWTH AND CHARACTERISATION OF
[(CH₃)₂NH₂]Mn_{0.25}Ni_{0.25}Co_{0.5}(CHOO)₃ and
[(CH₃)₂NH₂]Co_{0.9}Fe_{0.1}(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 in physics

By

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**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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May 2023



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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of S.DIVYALAKSHMI, (Reg No:41590005) who carried out the project entitled "SYNTHESIS "CRYSTAL GROWTH AND CHARACTERISATION OF $[(CH_3)_2NH_2]Mn_{0.25}Ni_{0.25}Co_{0.5}(CHOO)_3$ and $[(CH_3)_2NH_2]Co_{0.9}Fe_{0.1}(CHOO)_3$ PEROVSKITE TYPE MULTIFERROIC METAL ORGANIC FRAMEWORKS BY SOLVOTHERMAL METHOD" under my supervision from November 2022 to May 2023.

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I **S.DIVYALAKSHMI**, doing my M.Sc. (physics) at Sathyabama Institute Of Science And Technology Chennai-600119, hereby declare that this project report titled GROWTH AND CHARACTERIZATION OF PEROVSKITE TYPE HETEROGENIOUS MULTIFERROIC METAL ORGANIC FRAME WORKS $[(CH_3)_2NH_2]Mn_{1-x}Ni_{1-x}Co_x(HCOO)_3$ AND $[(CH_3)_2NH_2]Co_{1-x}Fe_x(HCOO)_3$ - BY SOLVOTHERMAL METHOD is an authentic report of work done by me under the guidance of **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 and **DR.S.ANANDHI** ,(Internal), professor, Department of physics, Sathyabama institute of science and technology is submitted in partial fulfilment of the requirements for the award of Master of science degree in physics.

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ABSTRACT

Multiferroic behavior is observed in perovskite-type metal–organic frameworks with general formula $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{1-x}\text{Ni}_{1-x}\text{Co}_x(\text{HCOO})_3, [(\text{CH}_3)_2\text{NH}_2]\text{Co}_{0.9}\text{Fe}_{0.1}(\text{HCOO})_3$. I report this synthesis of the heterogenous MOF $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{1-x}\text{Ni}_{1-x}\text{Co}_x(\text{HCOO})_3, [(\text{CH}_3)_2\text{NH}_2]\text{Co}_{0.9}\text{Fe}_{0.1}(\text{HCOO})_3$ crystallizing in a perovskite type structure, synthesis has been done by using solvothermal method and characterisations like x-ray powder diffraction, Single Crystal Xrd, FTIR 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 to magnetic storage, novel circuits, sensors, microwave and high-power applications. However, up to date single phase multiferroics are rare as the conventional mechanism 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 are 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.

TABLE OF CONTENTS

S.NO	Contents	Page No
CHAPTER-1 INTRODUCTION		
1.1	General Introduction	1
1.2	Multiferriocs	2
1.3	Type1Multiferriocs	3
1.4	Type2 Multiferriocs	3
1.5	Pervoskite structure	3
1.6	Spintronics	4
1.7	Organic and Inorganic	4
CHAPTER-2 LITERAUTRE SURVEY		
2.1	Literature	
2.2	Literature explanation	
CHAPTER-3 AIM AND SCOPE		
3.1	Trimettalic and Dimettallic samples	5
3.1.1	Co _{0.5} Mn _{0.25} Ni _{0.25}	6
3.2	Scope of crystal growth in MOFs	7
CHAPTER – 4 EXPERIMENTAL OR MATERIALS AND METHODS		
4.1	Crystal growth by solvothermal method	8
4.2	Solvothermal Method	9
4.3	Microscopic Observation on grown crystal	10
4.4	X-ray diffraction on singe crystal	11
4.5	2-D xrd on grown crystal	14
4.6	FTIR Studies on the sample	14
CHAPTER -5 RESULTS AND DISCUSSION , PERFOMANCE ANALYSIS		
5.1	Analysing the single XRD peaks in origin	17

5.2	Converting the 2-D XRD result in Fit-2D	18
5.3	Analysing single peak XRD with ICCD	20
5.4	Analysing Fit-2D peaks in Origin	23
5.5	FTIR characterisation	26

CHAPTER- 6

SUMMARY AND CONCLUSIONS

6.1	Conclusion	30
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CHAPTER -7

REFERENCES

7.1	References	35
-----	------------	----

LIST OF FIGURES

Figure no	Title	Page no
1.2	Hysteresis of ferroelectric materials	3
1.3	Ferroelectrically	5
1.5	Perovskite crystal structure	5
1.6	Spintronic structure	7
4.1	Dried crystal	15
4.1.1	Filtration process	17
4.2	Teflon with solution	19
4.3	Optical microscope photograph of $[(\text{CH}_3)_2\text{NH}_2]\text{Co}_{0.9}\text{Fe}_{0.1}(\text{CHOO})_3$.	21
4.3.1	Optical microscope photograph of $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.5}(\text{CHOO})_3$.	23
4.4	Single crystal XRD machine	25
4.5	2-D XRay Diffraction machine	27
4.6	Grown Crystal	28
4.6.1	FTIR Machine	28
5.1	Intensity v/s 2 theta of $\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.5}$ of single crystal XRD	31
5.2	Fit-2D software uses to analysis the 2D xrd.	32
5.4	The Fit-2D output graph of $\text{Co}_{0.9}\text{Fe}_{0.1}$	34
5.4.1	Fit-2D graph analysis the $\text{Co}_{0.9}\text{Fe}_{0.1}$ in Origin software with intensity	35

CHAPTER-1

1.1 GENERAL INTRODUCTION:

Crystal growth in Metal-Organic Frameworks (MOFs) is a process of forming ordered and crystalline structures by combining metal nodes with organic ligands in a controlled manner. MOFs are highly porous materials with a unique structure consisting of metal ions or clusters coordinated to organic ligands, forming a network of cavities and channels that can accommodate guest molecules. MOFs are of interest in many fields, including gas storage, catalysis, drug delivery, and sensing.

The crystal growth process of MOFs involves the self-assembly of metal nodes and organic ligands into ordered structures, forming crystals with well-defined shapes and sizes. This process can be influenced by several factors, including the concentration and composition of the precursor molecules, the temperature and pressure of the growth environment, and the presence of impurities.

The growth of MOF crystals can be achieved through various methods, such as solvothermal, hydrothermal, and microwave-assisted synthesis. In solvothermal and hydrothermal synthesis, the precursor materials are mixed in a solvent and heated to a high temperature and pressure to promote crystal growth. Microwave-assisted synthesis uses microwave irradiation to promote crystal growth in a shorter time period.

Controlling the crystal growth process is important for achieving the desired crystal structure and properties of MOFs. The crystal structure can be tailored by changing the metal nodes and organic ligands used in the synthesis process. The pore size and shape can also be controlled by selecting appropriate precursor materials.

Overall, the growth of MOF crystals is a critical step in the development of these materials for various applications. By developing new methods for synthesizing and studying MOFs, researchers can continue to uncover new and innovative uses for these materials.

1.2 MULTIFERROICS

Multiferroics are materials that exhibit both ferroelectric and ferromagnetic properties simultaneously. Ferroelectricity is the property of materials that have a permanent electric polarization even in the absence of an external electric field, while ferromagnetism is the property of materials that exhibit a permanent magnetization in the absence of an external magnetic field. The coupling of ferroelectric and ferromagnetic properties in multiferroics provides unique opportunities for the development of new technologies, such as magnetoelectric memory, sensors, and energy harvesting devices. The magnetoelectric effect is the ability of the material to control magnetic properties with an applied electric field or vice versa. This property can be used to design more efficient devices with lower power consumption and higher sensitivity.

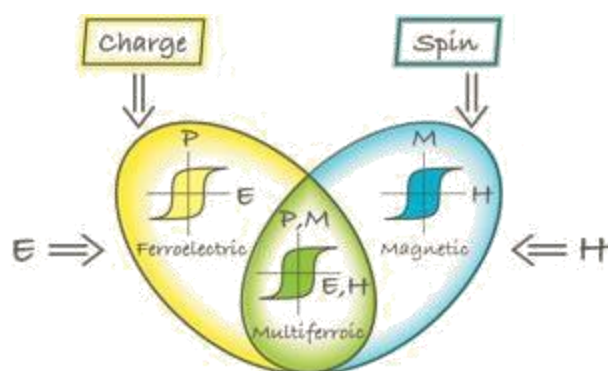


Figure 1.2 - Blue circle displays the hysteresis of ferromagnetic materials, yellow circle displays usual hysteresis of ferroelectric materials and the circle displays hysteresis of multiferroics where magneto coupling occurs.[D. Khomskii, Phys. 77, 50937 (2009)]

There are two main types of multiferroic materials: single-phase and composite. Single-phase multiferroics are materials that exhibit both ferroelectric and ferromagnetic properties in a single crystal structure. Composite multiferroics are materials that combine separate ferroelectric and ferromagnetic phases in a single material.

Research in the field of multiferroics is focused on developing new materials with improved ferroelectric and ferromagnetic properties, as well as investigating the fundamental physics behind the coupling of these properties. Some of the challenges in the field include improving the strength of the coupling between the two properties, as well as developing new methods for synthesizing and processing these materials.

1.3 Type 1 Multiferroics

The materials that exhibit both ferroelectric and antiferromagnetic properties. Antiferromagnetism 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 antiferromagnetism arises from the magnetic ordering of the ions.

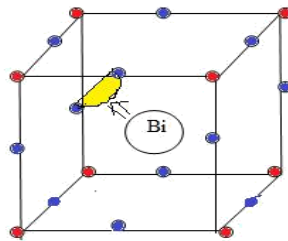


Figure1.3- Green circles are ferroelectrically active d^0 ions and red are magnetic d^n ions, yellow plaquettes are shifts of d^0 ions from the centres of O_6 octahedral, green arrows are polarization and red arrows are magnetic order

Type 1 multiferroics are of great interest because they exhibit strong coupling between the ferroelectric and antiferromagnetic properties, which allows for the control of magnetism by an electric field. This property is known as magnetoelectric coupling, and it is an important aspect of many potential applications of multiferroic materials. The study of type 1 multiferroics is an active area of research, and researchers are working to identify new materials that exhibit these properties, as well as to understand the fundamental physics behind the coupling between ferroelectricity and antiferromagnetism. Some of the challenges in the field include improving the strength of the magnetoelectric coupling, as well as developing new methods for synthesizing and processing these

materials. The type 1 multiferroics are an exciting 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 1 multiferroics, the range of potential applications for these materials is expected to continue to expand.

1.4 Type 2 Multiferroics

This materials that exhibit both ferromagnetic and ferroelectric properties simultaneously. In contrast to type 1 multiferroics, where the magnetism is antiferromagnetic, type 2 multiferroics exhibit ferromagnetic ordering, meaning the magnetic moments of neighboring ions are aligned. Type 2 multiferroics are of interest due to the possibility of strong magnetoelectric coupling, which could enable the manipulation of magnetism by an electric field. This could lead to the development of more efficient and versatile devices, such as magnetoelectric memories and sensors.

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.

1.5 Perovskite structure

Perovskite is a mineral composed of calcium titanate (CaTiO_3), and the term "perovskite type structure" refers to a crystal structure that is similar to the structure of perovskite. The perovskite crystal structure has the general formula ABX_3 , where A and B are cations and X is an anion. In a perovskite crystal structure, the A cation occupies a large octahedral site

in the center of the unit cell, and the B cation occupies smaller octahedral sites around the edges of the unit cell. The X anion is located at the corners of the unit cell. The resulting crystal structure is a three-dimensional network of corner-sharing octahedra. The perovskite structure is very versatile and can accommodate a wide range of cations and anions, leading to the formation of a large number of different compounds with diverse properties. Perovskite-type materials have been synthesized for a variety of applications, including superconductors, fuel cells, catalysts, and electronic and magnetic materials. In recent years, perovskite-type materials have gained significant attention for their potential use in photovoltaic cells, due to their high absorption coefficients, long carrier lifetimes, and low-cost synthesis methods. Perovskite solar cells have shown remarkable progress in efficiency, reaching over 25% in just a few years of development.

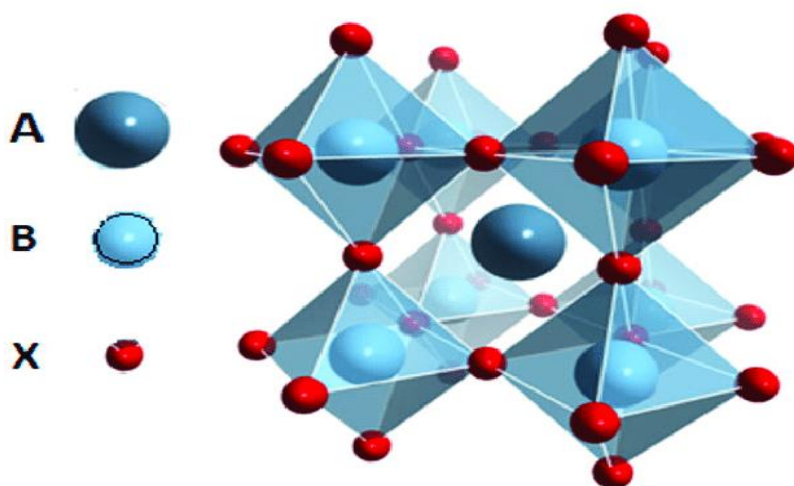


FIG1.5 The mineral calcium titanium oxide, the first perovskite crystal to be identified, has the same crystal structure as a substance known as a perovskite.

The perovskite-type structure is a versatile and promising area of research with potential applications in a wide range of fields. As researchers continue to uncover new materials and methods for synthesizing and studying perovskite-type materials, the range of

potential applications for these materials is expected to continue to expand.

1.6 Spintronics

Spintronics is a field of research that involves the use of the spin of electrons, in addition to their charge, to manipulate and store information. Spintronics devices have the potential to be faster, more energy-efficient, and more versatile than traditional electronics, which rely solely on the charge of electrons.

Perovskite-type materials have shown promise for use in spintronics applications due to their unique electronic and magnetic properties. For example, certain perovskite-type materials exhibit magnetic and ferroelectric ordering at room temperature, making them attractive candidates for multifunctional spintronic devices that combine spin and charge functionality.

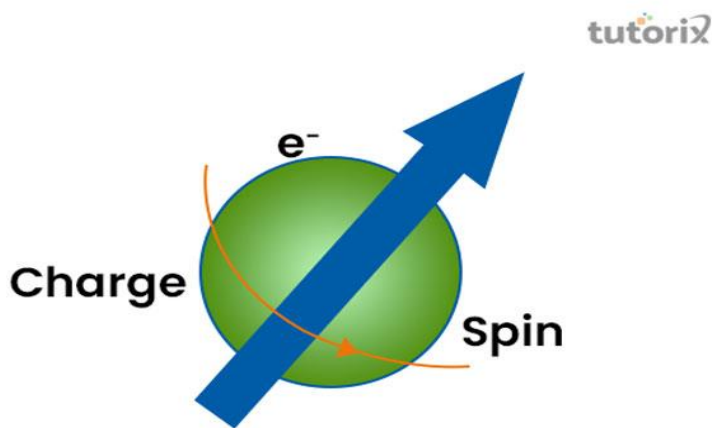


FIG 1.6 Spintronic devices are used in the field of mass-storage devices. It is used to compress massive amounts of data into a small area

Additionally, perovskite-type materials can be engineered to have specific magnetic and electronic properties by varying the composition of the A, B, and X elements. This tunability allows for the design of materials with specific properties that are tailored for spintronics applications. Furthermore, perovskite-type materials have been shown to have a high spin lifetime, which is the amount of time that a spin can be maintained without being lost or degraded. This property is important for spintronics applications, as it allows for the efficient manipulation and

transport of spins. The unique properties of perovskite-type materials use in spintronics applications, and research in this area is ongoing.

1.7 ORGANIC AND INORGANIC

Organic and inorganic crystal growth refer to two different types of materials used to grow crystals. Inorganic crystal growth involves the use of inorganic materials, which are typically metals, metalloids, and non-metals, to grow crystals. Inorganic crystals are often highly ordered and have well-defined structures. Inorganic crystal growth techniques include chemical vapour deposition, sol-gel methods, and hydrothermal synthesis.

On the other hand, organic crystal growth involves the use of organic materials, which are typically carbon-based compounds, to grow crystals. Organic crystals tend to be less ordered than inorganic crystals, and their structures are often more complex. Organic crystal growth techniques include solution growth, melt growth, and epitaxial growth. Organic crystals are often used in applications such as organic light-emitting diodes (OLEDs), organic solar cells, and organic field-effect.

CHAPTER 2

LITERATURE SURVEY

2.1 LITERATURE

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

D. Sornadurai,^{1,a)} R. M. Sarguna,¹ and V. Sridharan^{1,2} ¹ Condensed Matter Physics Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu, India ² HBNI, Kalpakkam, Tamil Nadu, India (Received 18 October 2018; accepted 13 March 2019).

2.2 LITERATURE EXPLANATION

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. [doi:10.1017/S0885715619000307] Key words: Metal Organic Frameworks, Crystal Structure, Laue diffraction, Powder XRD method, Rietveld refinement, Shannon ionic radius

CHAPTER 3

AIM AND SCOPE

3.1 TRIMETALLIC AND DIMETALLIC SAMPLES

Co_{0.9}Fe_{0.1} and Co_{0.5}Mn_{0.25}Ni_{0.25} are both materials that have been studied for their various properties and potential applications. The aims of research on these materials can vary depending on the specific field and application. Here are a few examples of research aims for Co_{0.9}Fe_{0.1} and Co_{0.5}Mn_{0.25}Ni_{0.25}:

Magnetic properties: Co_{0.9}Fe_{0.1} is a magnetic material, and one aim of research on this material is to study and optimize its magnetic properties. This can include measuring its magnetic moment, coercivity, and magnetic anisotropy, as well as exploring the effect of temperature, pressure, and magnetic field on these properties.

Structural properties: Co_{0.9}Fe_{0.1} can exist in different crystal structures, and one aim of research can be to study and optimize the crystal structure of this material. This can include studying its crystal growth, crystallographic orientation, and defects in the crystal structure.

Catalytic properties: Co_{0.9}Fe_{0.1} has been studied for its potential catalytic properties, and one aim of research can be to explore and optimize its catalytic activity for various reactions. This can include studying the effect of different parameters such as temperature, pressure, and reactant concentrations on the catalytic activity.

Electronic properties: Co_{0.9}Fe_{0.1} is a metallic material, and one aim of research can be to study and optimize its electronic properties. This can include measuring its resistivity, conductivity, and Hall coefficient, as well as exploring the effect of impurities and defects on these properties.

The **aim** of research on Co_{0.9}Fe_{0.1} can vary depending on the specific field and application, but it typically involves studying and optimizing its various properties for potential applications in magnetic, structural, catalytic, or electronic fields.

3.1.1 Co_{0.5}Mn_{0.25}Ni_{0.25}:

Magnetic properties: Co_{0.5}Mn_{0.25}Ni_{0.25} is also a magnetic material, and one aim of research on this material is to study and optimize its magnetic properties. This can include measuring its magnetic moment, coercivity, and magnetic anisotropy, as well as exploring the effect of temperature, pressure, and magnetic field on these properties.

Structural properties: Co_{0.5}Mn_{0.25}Ni_{0.25} can exist in different crystal structures, and one aim of research can be to study and optimize the crystal structure of this material. This can include studying its crystal growth, crystallographic orientation, and defects in the crystal structure.

Catalytic properties: Co_{0.5}Mn_{0.25}Ni_{0.25} has also been studied for its potential catalytic properties, and one aim of research can be to explore and optimize its catalytic activity for various reactions. This can include studying the effect of different parameters such as temperature, pressure, and reactant concentrations on the catalytic activity.

Magnetocaloric properties: Co_{0.5}Mn_{0.25}Ni_{0.25} has been studied for its magnetocaloric properties, which could potentially be used for magnetic refrigeration. One aim of research can be to optimize these properties by studying the effect of temperature and magnetic field on the magnetocaloric effect.

The aims of research on Co_{0.9}Fe_{0.1} and Co_{0.5}Mn_{0.25}Ni_{0.25} can vary depending on the specific field and application, but they typically involve studying and optimizing the various properties of these materials for potential applications in magnetic, structural, catalytic, or magnetocaloric fields.

3.2 SCOPE OF CRYSTAL GROWTH IN MOFs

Metal-organic frameworks (MOFs) are a class of porous materials that are composed of metal ions or clusters connected by organic ligands. MOFs have a high surface area and tunable pore size, making them attractive for a variety of applications such as gas storage, catalysis, and drug delivery.

The crystal growth of MOFs is an important area of research, as it can affect the morphology, size, and properties of the resulting materials. The scope of crystal growth in MOFs is quite broad and includes many different techniques and approaches.

Some examples of crystal growth techniques for MOFs include:

Solvothermal synthesis: This involves dissolving the metal ions and organic ligands in a suitable solvent and heating the solution under high pressure to promote crystal growth.

Hydrothermal synthesis: This is similar to solvothermal synthesis, but the reaction is carried out under lower pressure and at a lower temperature.

Microwave-assisted synthesis: This involves using microwave radiation to heat the reaction mixture and promote crystal growth.

Template-directed synthesis: In this approach, a pre-formed template is used to direct the crystal growth of the MOF, resulting in materials with specific shapes and sizes.

Layer-by-layer assembly: This technique involves growing MOF crystals layer by layer on a substrate, resulting in thin films of the material.

Seed-mediated growth: This involves using pre-formed MOF crystals as seeds to promote the growth of larger crystals.

The scope of crystal growth in MOFs is vast, and there are many different factors that can influence the process, such as the choice of solvent, temperature, and reaction time. Researchers are continuing to explore new synthesis methods and approaches to optimize the crystal growth of MOFs for specific applications.

CHAPTER 4

EXPERIMENTAL OR MATERIALS AND METHODS:ALGORITHMS USED

4.1 CRYSTAL GROWTH BY SOLVOTHERMAL SYNTHESIS

The $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ alloys can be synthesized using the solvothermal method, which involves the use of a solvent under high temperature and high pressure to promote crystal growth. Here is a detailed procedure for the solvothermal synthesis of $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ alloys.

Formula:

$$\text{Molecular mass} = \text{Sum of atomic masses}$$

CALCULATION:

Formula:

$$\text{Molecular mass} = \text{Sum of atomic masses}$$

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
	28	Nickel	58.693

Molecular masses:

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

5mM of Co_{0.5}Ni_{0.25}Mn_{0.25} 80ml of solution:

S.No	Compound name	Molarity(M)	Calculated mass
1	Cobalt Chloride Hexa-Hydrate	2.5	0.5948
2	Nickel Chloride Hexa-Hydrate	1.25	0.2971
3	Manganese chloride tetra-hydrate	1.25	0.4947

5mM of Co_{0.9}Fe_{0.1} 80ml of solution:

S.No	Compound name	Molarity(M)	Calculated mass(g)
1	Cobalt Chloride Hexa-Hydrate	0.9	1.07150
2	Ferrous Chloride Tetra-Hydrate	0.1	0.29541

Preparation of reactants: The reactants used for the synthesis of Co_{0.9}Fe_{0.1} with the calculation by the molecular formula of Cobalt and Ferrous in the dimetallic and in trimetallic Co,Mn,Ni molecular weights. Alloy include cobalt (II) nitrate hexahydrate (Co(NO₃)₂.6H₂O), iron (III) nitrate non hydrate (Fe(NO₃)₃.9H₂O), and 1,4-benzenedicarboxylic acid

(BDC). The metal salts and BDC are dissolved in a suitable solvent, such as N,N-dimethylformamide (DMF), to prepare a clear solution.

Mixing and stirring: In a typical crystal growth of Mn-MOF, 5 mM of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 40 ml dimethylformamide and 40 ml deionized water stirred vigorously for a minimum of 30 minutes to ensure complete dissolution of the metal salts.

Transfer to autoclave: The solution was transferred to a Teflon-lined stainless steel autoclave of 100 ml capacity which is then sealed to prevent any leakage of the solvent.

Heating: The autoclave is heated to a temperature ranging 140°C for several hours, typically for 72 hours. The reaction can be carried out at high pressure to ensure the solvent remains in liquid state.

Cooling and transferring: After the reaction, the autoclave is allowed to cool at room temperature, and the solution is poured into a clean beaker and leave it for 7 days to crystal growing.

Washing: After 7 days the crystals were washed with a suitable solvent, such as ethanol for 4-5 times, to remove any unreacted materials.

Drying and annealing: The washed crystals are then dried at low temperature, followed by annealing at higher temperatures (typically 200-500 °C) to further improve crystal quality.

By optimizing the reaction conditions, such as the temperature, pressure, and reaction time, the crystal size, morphology, and quality of the $\text{Co}_{0.9}\text{Fe}_{0.1}$ alloy can be controlled. The resulting material can be characterized using various techniques such as X-ray diffraction.



FIG 4.1 The above photograph crystals are taken after washed in ethanol for several times.



FIG 4.1.1 The crystals are undergoing in the process of filtration and washed with ethanol.

4.2 SOLVOTHERMAL METHOD

Solvothermal method is a technique for synthesizing crystalline materials by using a solvent at high temperature and high pressure. The method involves the dissolution of precursor materials in a suitable solvent, which is then subjected to high temperature and pressure conditions in a sealed vessel to promote crystal growth. The solvent acts as a medium for transporting the dissolved **precursors** and also serves as a reaction medium for crystal growth.

The solvothermal method is widely used for synthesizing a variety of materials including metals, metal oxides, metal sulfides, metal-organic

frameworks (MOFs), and other inorganic compounds. The method offers several advantages over other synthesis methods, such as:

Controlled crystal growth: Solvothermal method provides a controlled environment for crystal growth, which allows for the synthesis of materials with well-defined crystal structures, morphologies, and sizes.

Homogeneous materials: The solvothermal method promotes homogeneous crystal growth, which leads to the formation of materials with uniform properties.

High purity: The high temperature and pressure conditions of the solvothermal method can promote the removal of impurities, leading to high-purity materials.

Versatility: The solvothermal method can be used to synthesize a wide range of materials, including those that are difficult to synthesize by other methods

Some of the disadvantages of the solvothermal method include the need for specialized equipment, the potential for the solvent to react with the precursor materials, and the difficulty in controlling the reaction conditions. Despite these limitations, the solvothermal method remains a popular and effective technique for synthesizing a variety of materials with controlled properties.

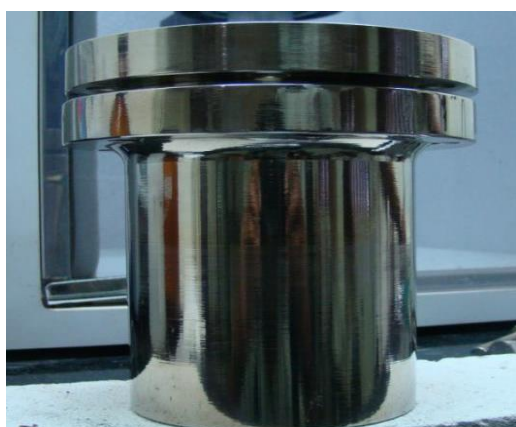


FIG:4.2 This is called Teflon which is used to pour the solution and kept in Autoclave for solvothermal synthesis.

4.3 MICROSCOPIC OBSERVATION OF GROWN CRYSTAL

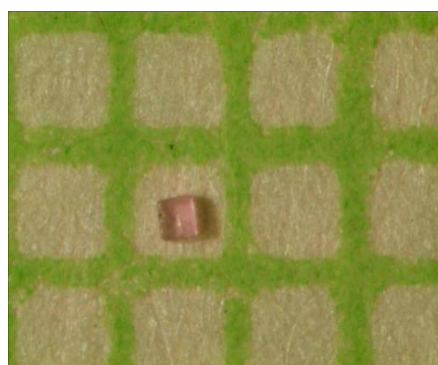
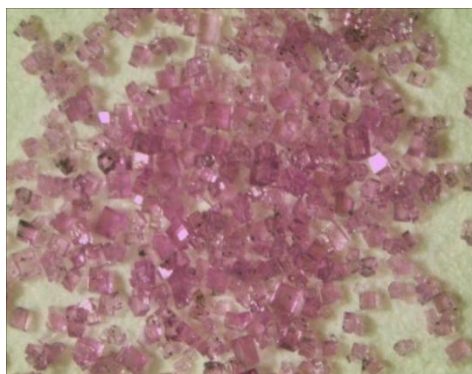


FIG4.3 Optical micrograph of $[(\text{CH}_3)_2\text{NH}_2]\text{Co}_{0.9}\text{Fe}_{0.1}(\text{CHOO})_3$.

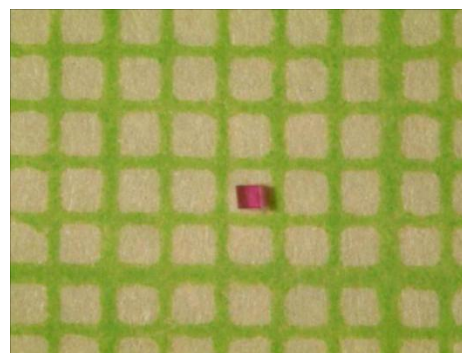


FIG4.3.1 Optical microscope photograph of $[(\text{CH}_3)_2\text{NH}_2]\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.5}(\text{HCOO})_3$

4.4 X-RAY DIFFRACTION ON SINGLE CRYSTAL

X-ray crystallography is a powerful tool to determine the crystal structure of macromolecules at an atomic resolution . This technique enhances understanding of the biological and chemical mechanisms underlying macromolecular reactions . Moreover, this structural information provides insights for drug design and rational engineering of enzymes for food and pharmaceutical industries . The X-ray crystallography workflow necessitates the crystallization of the target molecule, which provides the diffraction pattern that enables structure determination . In traditional X-ray crystallography, in order to provide accurate indexing of

Bragg peaks from diffraction patterns and improve the signal-to-noise , it is preferred to collect single-crystal diffraction patterns . Accordingly, in typical X-ray crystallography, researchers focus on growing a single large crystal, which aids in obtaining high-resolution diffraction data . Various crystallization methods, such as sitting drop vapor diffusion, hanging drop vapor diffusion, microbatch, microdialysis and free-interface diffusion, are applied to obtain high-quality single crystals . Multiple studies have reported this single crystal growth method , whereas little is known about growing large numbers of crystals.



FIG 4.4 Single crystal XRD machine

XRD can be performed on both powder and single crystals. In the case of single crystals, a small crystal is mounted on a sample holder and aligned with the X-ray beam. The X-ray beam is then directed onto the crystal at a specific angle, and the diffracted beams are collected by a detector. The collected data is processed using software to determine the positions and intensities of the diffracted spots. From this information, the crystal structure can be determined using various computational methods.

The advantage of using XRD on single crystals is that it provides highly accurate information on the crystal structure, including bond lengths, angles, and other structural parameters. It is also possible to obtain information on the orientation of the crystal and the presence of defects or impurities.

However, the main disadvantage of XRD on single crystals is that it requires high-quality crystals with large dimensions. Growing single crystals can be a challenging process, and the crystals must be of sufficient size and quality to provide accurate data. Additionally, XRD on single crystals is a time-consuming process and requires specialized equipment and expertise.

XRD on single crystals is a valuable tool for determining the crystal structure of materials and is widely used in various fields, including materials science, chemistry, and solid-state physics.

4.5 2-D xrd on grown crystal

2D X-ray diffraction (XRD) is a technique that provides more detailed information about the crystal structure of a material than conventional XRD. In 2D XRD, a 2D detector is used to collect diffraction patterns at multiple angles simultaneously, allowing for the reconstruction of a 3D diffraction pattern.

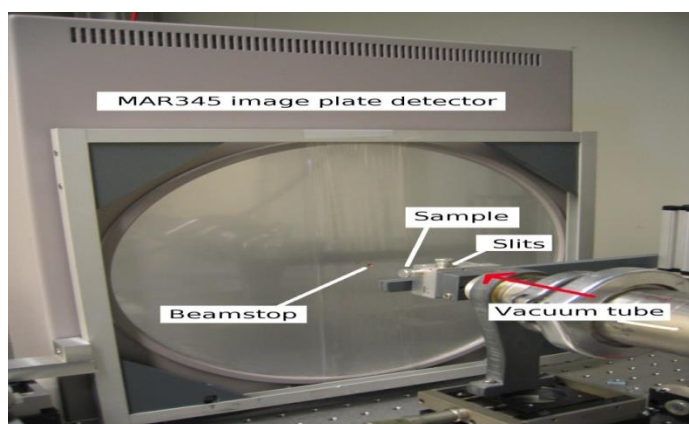


FIG 4.5 2-D XRay Diffraction machine

The collected data can be analyzed using specialized software, which allows for the determination of crystal structure. The technique can also be used to determine the crystallographic orientation of the crystal, which is important for studying the anisotropic properties of the material.

The advantage of using 2D XRD over conventional XRD is that it provides more detailed information about the crystal structure and allows for the characterization of materials with more complex structures. For example, the technique can be used to analyze polycrystalline materials,

which have multiple grains with different orientations, and can provide information about the preferred orientation of the grains.

Regarding $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ crystal growth, 2D XRD can provide valuable information on the crystal structure, phase purity, and crystal orientation. The technique can also be used to analyze the quality of the crystal, such as the presence of defects, grain boundaries, or twinning. The 2D XRD data can be analyzed using specialized software, which allows for the determination of crystal structure and other crystallographic parameters such as lattice constants, unit cell dimensions, and atomic positions. The technique can also be used to determine the crystallographic orientation of the crystal, which is important for studying the anisotropic properties of the material.

In summary, 2D XRD can provide detailed information about the crystal structure and quality of $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ crystals grown by solvothermal synthesis. The technique can help to optimize the crystal growth process and to characterize the materials for potential applications in various fields such as magnetic and electronic devices, catalysis, and energy storage.

4.6 FTIR Studies on the sample

FTIR (Fourier Transform Infrared) spectroscopy is a technique that is widely used for the analysis of the functional groups and molecular structure of materials. It involves the measurement of the absorption or transmission of infrared radiation by a material, which is related to the vibrations of the molecules within the sample.

In FTIR, a beam of infrared radiation is passed through a sample and the amount of radiation absorbed or transmitted by the sample is measured. The resulting spectrum provides information about the types of chemical bonds and functional groups present in the sample. The spectrum can be analyzed using specialized software to identify the specific vibrations associated with different functional groups, such as C-H, O-H, or N-H bonds.

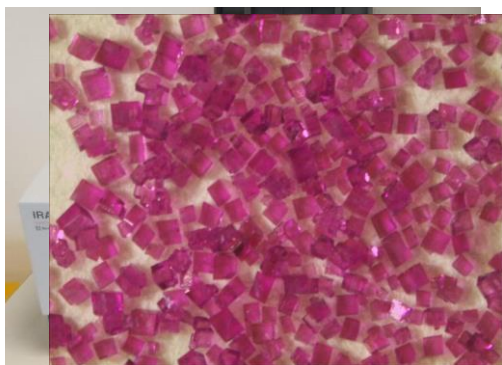


FIG4.6 GROWN CRYSTAL

FIG 4.6.1 FTIR MACHINE

FTIR can be used to analyze a wide range of materials, including solids, liquids, and gases. It is a non-destructive technique that requires minimal sample preparation and can be performed on very small samples. It is also a relatively quick and easy technique, making it a popular choice for routine analysis in research and industrial settings.

Regarding crystal growth of $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$, FTIR spectroscopy can provide valuable information about the chemical bonding and molecular structure of the crystals. FTIR can be used to analyze the functional groups present in the crystal lattice, such as metal-ligand bonds or organic ligands, and to study the effects of crystal growth conditions on the crystal structure.

The FTIR spectra obtained from the crystals can be compared with reference spectra or simulated spectra obtained from computational methods to identify the functional groups and molecular structure of the crystal. This information can be used to confirm the crystal structure obtained from X-ray diffraction analysis and to study the properties of the crystal, such as its thermal stability or reactivity.

The FTIR spectroscopy is a valuable tool for the analysis of the crystal growth of $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$, providing information about the chemical bonding and molecular structure of the crystals. The technique can help to optimize crystal growth conditions and to understand the properties of the materials for potential applications in various fields such as catalysis, sensors, and energy storage.

CHAPTER 5

RESULTS AND DISCUSSIONS, PERFORMANCE ANALYSIS

5.1 Analysing the single XRD peaks in origin

Origin is a powerful software package commonly used for data analysis and visualization in various fields of research, including X-ray diffraction (XRD) analysis. When analyzing single XRD peaks in Origin, there are several steps that can be followed to extract meaningful information from the data.

Import the XRD data into Origin: The XRD data can be imported into Origin using the "Import Wizard" or by copying and pasting the data into a new worksheet. The data should be arranged in columns with the two-theta angles in the first column and the corresponding intensities in the second column.

Fit the XRD peak: The XRD peak can be fitted using a peak fitting function, such as the Gaussian or Lorentzian function. The fitting function can be selected from the "Fitting Function" menu in the "Peak Analysis" toolbar. The peak fitting parameters can be adjusted until the fitted curve closely matches the experimental data.

Analyze the peak parameters: Once the peak has been fitted, several parameters can be extracted from the data. These include the peak position (2-theta angle), peak width (full width at half maximum, FWHM), and peak intensity. These parameters can be obtained from the "Fit

Parameters" dialog box, which can be accessed by double-clicking on the fitted curve.

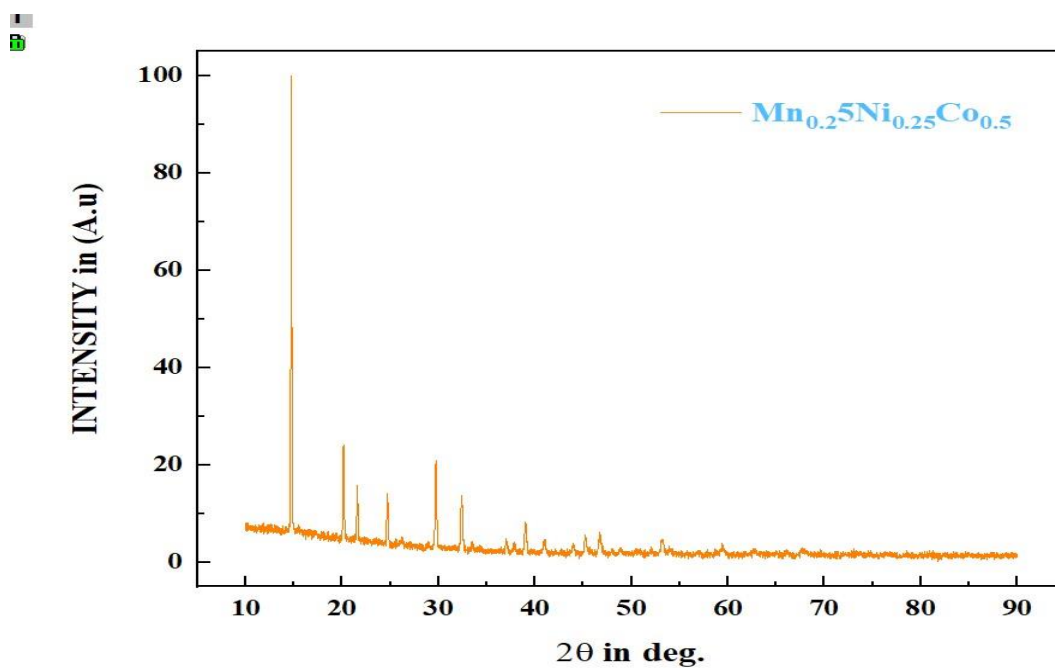


FIG5.1: Intensity v/s 2 theta of $\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.5}$ of single crystal XRD

Compare the peak parameters: The peak parameters obtained from the XRD data can be compared with the expected values for the crystal structure being studied. This can help to confirm the identity of the crystal and to determine if the crystal is in the correct phase. Any discrepancies between the expected and observed values may indicate a problem with the crystal structure or the experimental conditions.

Analyzing single XRD peaks in Origin involves fitting the peak using a suitable function and extracting the peak parameters, which can then be compared with the expected values for the crystal structure being studied. This can provide valuable information about the crystal structure and help to identify any issues with the experimental setup.

5.2 Converting the 2-D XRD result in Fit-2D

FIT2D is a software package commonly used for analyzing 2D X-ray diffraction (XRD) data. When analyzing crystals using 2D XRD data in FIT2D, the following steps can be taken:

Import the 2D XRD data: The 2D XRD data can be imported into FIT2D using the "Open" command under the "File" menu. The data should be in the form of an image file, such as a TIFF or BMP file.



FIG 5.2 Fit-2D software uses to analysis the 2D xrd.

Calibration: The 2D XRD pattern needs to be calibrated to determine the two-theta (2θ) angle of the diffraction peaks. This can be done using a calibration standard, such as a standard powder diffraction pattern or a LaB6 calibration standard. The calibration can be performed using the "Calibration" command under the "Calibration" menu.

Integration: The 2D XRD pattern can be integrated along one or more directions to produce a 1D or 2D plot of the intensity versus the 2θ angle. This can be done using the "Integrate" command under the "Integration" menu. The integration can be performed along a single line or a region of interest.

Background subtraction: The background can be subtracted from the integrated pattern using the "Background Subtraction" command under the "Background" menu. This can help to improve the accuracy of the peak fitting.

Peak fitting: The integrated pattern can be analyzed using the "Fit Peaks" command under the "Fitting" menu. The peaks can be fitted using a variety of fitting functions, such as Gaussian or Lorentzian functions. The fitted parameters, such as the position, width, and intensity of the peaks, can be obtained from the peak fitting results.

Data analysis: The fitted parameters can be used to analyze the crystal structure, such as determining the lattice parameters or identifying the crystal phase. FIT2D is a versatile software package for analyzing 2D XRD data and provides a range of tools for calibration, integration, peak fitting, and data analysis.

5.3 Analysing single peak XRD with ICDD

Single crystal X-ray diffraction (XRD) is a powerful analytical technique used to determine the crystal structure of a material at the atomic level. The International Centre for Diffraction Data (ICDD) is an organization that provides a comprehensive database of X-ray diffraction patterns for a wide range of materials.

To analyze the single crystal XRD pattern of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ and $\text{Co}_{0.9}\text{Fe}_{0.1}$ using the ICDD database, you would need to follow these steps:

Collect the XRD data: This involves obtaining a high-quality X-ray diffraction pattern of the single crystal using an X-ray diffractometer.

Index the crystal: The first step in analyzing the XRD pattern is to index the crystal to determine the crystal system, lattice parameters, and space group. This can be done using software such as CrysAlisPro or APEX3

Refine the structure: Once the crystal has been indexed, the crystal structure can be refined using software such as CRYSTALS. This involves fitting the observed diffraction pattern to a model of the crystal structure to determine the positions of the atoms within the unit cell.

Compare with ICDD database: Once the crystal structure has been refined, you can compare it with the database of known crystal structures provided by the ICDD. This will allow you to identify the phase(s) present in the sample and confirm the crystal structure.

Interpret the results: Finally, you can interpret the results of the analysis to gain insights into the structure-property relationships of the material. For example, you can determine the bonding characteristics, identify any defects or impurities in the crystal structure, and relate the crystal structure to the physical properties of the material.

TABLE 5.3

The table shows the observed and calculated values of $\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.5}$ with ICDD and origin:

d observed	d calculated	2 theta (observed)	2theta (calculated)	2 theta (observed- calculated)	intensity	h	k	l
6.0111	6.0145	14.725	14.717	-0.008	0	0	1	2
4.4035	4.3994	20.149	20.168	0.019	0	1	0	4
4.1201	4.1156	21.575	21.551	-0.024	0	1	1	3
3.6069	3.6055	24.663	24.672	0.010	0	1	1	3
3.0033	3.0072	29.723	29.683	-0.040	0	0	2	4
2.7622	2.7631	32.386	32.375	-0.011	0	0	1	1
2.4302	2.4290	36.959	36.978	0.019	0	2	1	4
2.3110	2.3094	38.942	38.969	0.028	0	1	2	5
2.1999	2.1997	40.994	40.997	0.003	0	2	0	8
2.0588	2.0601	43.944	43.915	-0.029	0	2	2	0
2.0049	2.0048	45.189	45.191	0.002	0	3	0	6
1.9485	1.9489	46.573	46.563	-0.010	0	1	2	8
1.7208	1.7210	53.186	53.180	-0.006	0	2	1	10
1.5571	1.5573	59.299	59.294	-0.005	0	4	1	0
1.4899	1.4900	62.264	62.260	-0.004	0	0	0	15
1.4127	1.4125	66.087	66.096	0.010	0	0	2	3

The single crystal XRD pattern of $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Ni}_{0.25}$ using the ICDD database involves indexing the crystal, refining the crystal structure, comparing it with the ICDD database, and interpreting the results to gain insights into the material's properties.

5.4. Analysing Fit-2D peaks in Origin with ICDD

FIT2D is a software package commonly used for analyzing X-ray diffraction data from single-crystal and powder samples. On the other hand, Origin is a data analysis and graphing software commonly used in the scientific and engineering fields.

To analyze FIT2D peaks in Origin, you would need to follow these steps:

Export the FIT2D data: This involves exporting the processed FIT2D data into a format that can be read by Origin. The data can be exported as a text file or a CSV file.

Import the data into Origin: Once the data has been exported, it can be imported into Origin for analysis. This can be done by using the File > Import menu in Origin and selecting the appropriate file format.

Plot the data: Using Origin, you can plot the X-ray diffraction data to visualize the crystal peaks. You can customize the plot to show the diffraction angle (2θ) on the x-axis and the intensity on the y-axis.

Fit the peaks: Once the data has been plotted, you can fit the crystal peaks using a peak fitting function in Origin. This involves selecting the appropriate peak shape and adjusting the peak parameters to fit the data.

Identify the crystal structure: Once the peaks have been fitted, you can compare the peak positions and intensities to those in the ICDD database to identify the crystal structure.

Interpret the results: Finally, you can interpret the results of the analysis to gain insights into the crystal structure and its properties. For

example, you can determine the bonding characteristics, identify any defects or impurities in the crystal structure, and relate the crystal structure to the physical properties of the material.

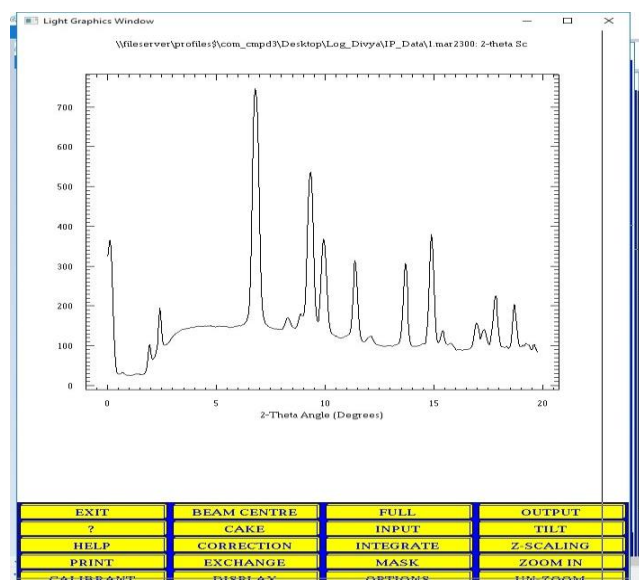


Fig 5.4 The Fit-2D output graph of $\text{Co}_{0.9}\text{Fe}_{0.1}$

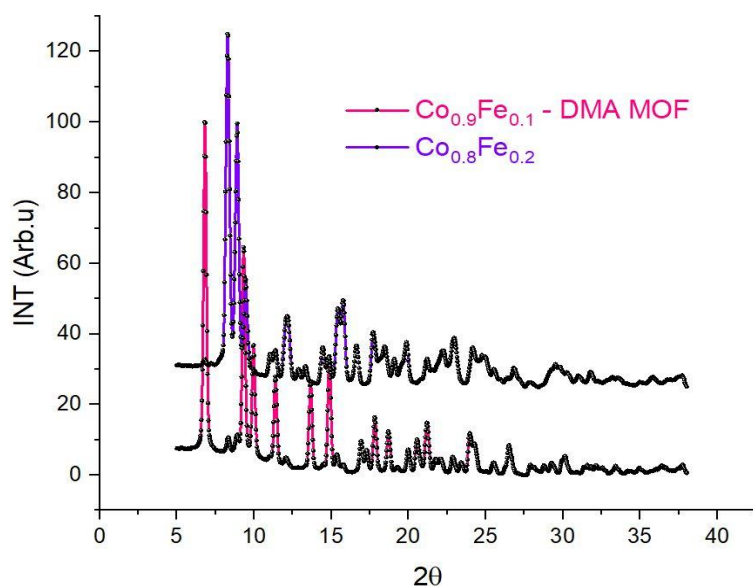


Fig 5.4.1 Fit-2D graph analysis the $\text{Co}_{0.9}\text{Fe}_{0.1}$ in Origin software with intensity

Table5.4

The table shows the observed and calculated values of $\text{Co}_{0.9}\text{Fe}_{0.1}$ with ICDD and origin

d observed	d calculated	2 theta observed	2 theta calculaed	2 theta (obs-calc)	intensity	h	k	l
5.9838	5.9792	6.812	6.817	-0.005	0	0	1	2
4.3737	4.3721	9.324	9.328	0.004	0	1	0	4
4.0946	4.103	9.962	9.941	-0.021	0	1	0	4
3.7627	3.7634	10.843	10.841	-0.002	0	0	1	5
3.582	3.5877	11.392	11.373	-0.018	0	1	1	3
3.3822	3.3839	12.067	12.061	-0.006	0	2	0	2
3.0018	2.9919	13.603	13.648	0.045	0	0	2	4
2.7756	2.7735	14.717	14.729	0.011	0	2	0	5
2.6629	2.6666	15.344	15.323	-0.021	0	2	1	1
2.4138	2.4174	16.939	16.913	-0.0026	0	2	1	4
2.3657	2.3651	17.285	17.29	0.005	0	0	2	7
2.2954	2.2978	17.819	17.801	-0.08	0	1	2	5
2.1875	2.186	18.705	18.718	0.013	0	2	0	8
2.049	2.0488	19.985	19.982	-0.003	0	2	1	7
1.9907	1.9946	20.574	20.534	-0.041	0	3	0	6
1.9326	1.9293	21.2	21.236	0.036	0	1	2	8
1.8814	1.8572	22.076	22.071	-0.005	0	0	2	10
1.7919	1.7939	22.886	22.861	-0.025	0	2	2	6
1.7515	1.7539	23.422	23.389	-0.032	0	2	0	11
1.7133	1.7104	23.951	23.992	0.041	0	2	1	10
1.6919	1.692	24.259	24.258	-0.001	0	4	0	4
1.6097	1.6127	25.517	25.459	-0.048	1	2	11	
1.5493	1.5497	26.53	26.523	-0.007	0	4	0	7
1.4747	1.4734	27.899	27.923	0.025	0	1	3	10
1.4295	1.4301	28.799	28.788	-0.012	0	4	1	6
1.3778	1.3768	29.906	29.927	0.021	0	0	5	4
1.3683	1.3677	30.118	30.132	0.014	0	3	3	0
1.346	1.3449	30.628	30.655	0.028	0	3	3	3
1.3349	1.3333	30.891	30.928	0.037	0	4	2	2
1.3152	1.3137	31.365	31.401	0.035	0	3	2	10
1.2965	1.2969	31.83	31.819	-0.011	0	0	5	7
1.2844	1.2834	32.138	32.162	0.024	0	0	1	17
1.2695	1.268	32.524	32.563	0.039	0	1	5	2
1.2359	1.2366	33.434	33.415	-0.019	0	2	4	7

1.21	1.2087	34.17	34.209	0.039	0	4	2	8
1.1829	1.825	34.978	34.99	0.013	0	0	4	14
1.1607	1.1618	35.67	35.636	-0.034	0	5	0	11
1.1478	1.14898	36.085	36.05	-0.036	0	2	4	10
1.1068	1.1063	37.471	37.481	0.017	0	5	1	10
1.10986	1.10995	37.76	37.73	-0.03	0	3	3	12

The FIT2D peaks in Origin involves exporting the data from FIT2D, importing it into Origin, plotting the data, fitting the peaks, identifying the crystal structure, and interpreting the results. This process allows for a detailed analysis of the crystal structure and its properties using two powerful software tools.

5.5. FTIR CHARACTERISATION

FTIR (Fourier transform infrared spectroscopy) is a commonly used analytical technique for characterizing the vibrational modes of molecules and materials. It can be used to identify functional groups, determine the purity of a sample, and provide information about the crystal structure and bonding.

To characterize the crystals $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Fe}_{0.25}$ using FTIR, you would typically follow these steps:

Preparation of the sample: The sample should be prepared by grinding it into a fine powder to ensure that the sample is homogenous and the spectrum is representative of the entire sample.

Instrumentation: An FTIR spectrometer should be used to obtain the FTIR spectrum. This involves shining an infrared beam through the sample and measuring the absorption or transmission of the light at different frequencies.

Sample measurement: The sample is placed into the FTIR spectrometer and the measurement is taken in transmission mode, where the infrared beam passes through the sample.

Spectral interpretation: The FTIR spectrum obtained can be used to identify the functional groups present in the sample. The spectra of $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Fe}_{0.25}$ may show characteristic absorption bands that are specific to each crystal structure.

Analysis and interpretation of the results: The FTIR spectrum can be analyzed to obtain information about the crystal structure, bonding, and purity of the sample. For example, the positions and intensities of the absorption bands can provide information about the types of atoms present in the crystal, the strength of the bonding between the atoms, and any impurities or defects in the crystal structure

The FTIR characterization of crystals such as $\text{Co}_{0.9}\text{Fe}_{0.1}$ and $\text{Co}_{0.5}\text{Mn}_{0.25}\text{Fe}_{0.25}$ involves the preparation of the sample, the measurement of the FTIR spectrum using an FTIR spectrometer, interpretation of the spectral data to identify the functional groups present, and analysis and interpretation of the results to gain insights into the crystal structure and bonding. FTIR is a powerful analytical technique that can be used in a wide range of scientific and industrial applications.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Successfully grown the single crystals of Metal-Organic Frameworks (MOF) with perovskite structure using solvothermal method. And successfully grown the Fe-doped Co-MOF with the molecular formula $[(CH_3)_2NH_2]Co_{0.9}Fe_{0.1}(HCCO)_3$ and another ternary metallic MOF with the chemical formula $[(CH_3)_2NH_2]Co_{0.5}Mn_{0.25}Ni_{0.25}(HCOO)_3$. She recorded the powder diffraction pattern of the as grown crystal which showed only a few peaks which were satisfying 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 recorded for both the crystals with a two dimensional X-ray detector . The 2D XRD patterns unwrapped into a 1D data with X-Y format and further analysis carried on this data .The powdered samples were 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 refined using the NBS* AIDS83 program. Finally, the lattice parameters of these materials found and the patterns were indexed.

CHAPTER 7

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CERTIFICATES



