Study of structural and electrical Properties of few Double Perovskite Compounds

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IN

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BY

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CERTIFICATE

This is to certify that the dissertation entitled "**Study of structural and Electrical Properties of few Double Perovskite Compounds**" being submitted by **Mr Anjan Kumar Jena** to the Department of Physics, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of genuine research carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACTS

A detail structure and electrical characterization of a few double perovskite and their perovskite counterpart have been performed. All the compounds are synthesized by wet chemical route known as sol-gel process. The samples are found to be in single phase and stoichiometric. The information about the molecular bonding is obtained from the FTIR spectra. The calculated band gap from UV-Visible spectra characterises the semiconducting and insulating nature of the material. The morphology of the materials has been studied through FESEM and finally the dielectric spectroscopy has been carried out for all compounds.

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Chapter-1   Introduction

1.1 Transition metal oxide

Transition metal oxide (TMO) materials contain transition element and oxygen. Both insulator and metal of poor quality are belongs to this group. It may be happens that the same material may give both types of transport properties. When either temperature or pressure is varying, then metal-insulator transition is possible. There are few superconductors are transition metal oxide. Valence electrons are present more than one shell in such type of compound. But the most of transition metal has one oxidation state. Transition metal oxides are not associated with activation energy; hence it is better than non-transition metal oxides. Transition metals have vacant d orbitals, so they are basically called catalyst. The metal surface adsorbed the reagent and the substrate and reagent are bound between them by a clamp called d orbitals. The vacant d-orbitals behaves similar like energy gap, hence transition metals have different colours.

1.2 Properties of transition metal oxide

There are many types of distortions occurring in the ideal perovskite structure due to the flexibility inherent inside the perovskite structure. Resulting the tilting of the octahedra. Then displacement of cations takes place from the centres of their respective coordination in polyhedral. The distortion of the octahedral is accelerated by electronic factors. Most the physical properties of perovskite structure depend on these distortions. Particularly the electronic, magnetic and dielectric properties which are so important for many of the applications of perovskite materials. These materials have different useful magnetic and electronic properties. Most of the properties depends upon some defects like vacancies, dislocations, stacking faults, grain boundaries etc. The local oxygen bonding in TMO is affected due to these defects. These are used for their semi conductive properties and catalytic activities. The metal oxides surface contain acidity and basicity of the atoms. These are also affected by metal cations and oxygen anions which change the catalytic properties of TMO compounds. Hence only for those defects in structure in TMO are highly influenced their catalytic properties. By using the FTIR spectroscopy, the acidity and basicity on the surface of the compound are characterised simply. The semi conductivity of TMO is controlled by photo assisted adsorption and desorption. More properties are found during

research that these compounds are well response to electromagnetic radiation. These properties are help to metal as a use full catalyst for isotope exchange, some redox reaction and special type of surface.

1.3 Perovskite structure

The structure of perovskite compound is ABO_3, where A and B are cations and O is anions respectively. The important purpose for the study that the cations A accepted a trivalent state and and B the divalent states [1]. The ions occupying the A and B lattice sites are detailed in Figure 1.1.
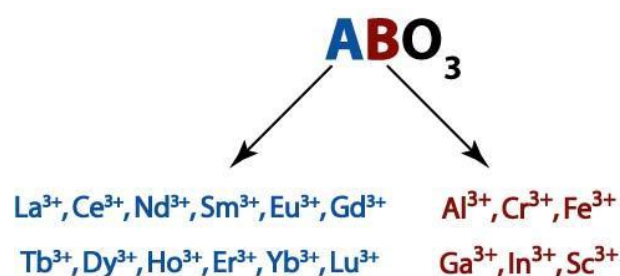
Figure 1.1: Schematic of compositions under study

In a structural point of view the perovskite lattice composed of tiny B cations within oxygen octahedra and larger cations are eleven fold coordinates of oxygen. The compound CaTiO3 having orthorhombic structure with space group Pnma was first named then the structural family of the perovskite compound was named. For example a perovskite structure of type $A^{3+}B^{3+}O_3$ has rhombohedral structure with space group R3c (e.g. LaAlO3), when it associated with a rotation of the BO6 octahedra with respect to the cubic structure. However, this distortion slightly changes from the cubic symmetry. The structure of an ideal cubic perovskite is shown in Figure 1.2.

Fig.1.2: Cubic perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen anions forming an octahedra

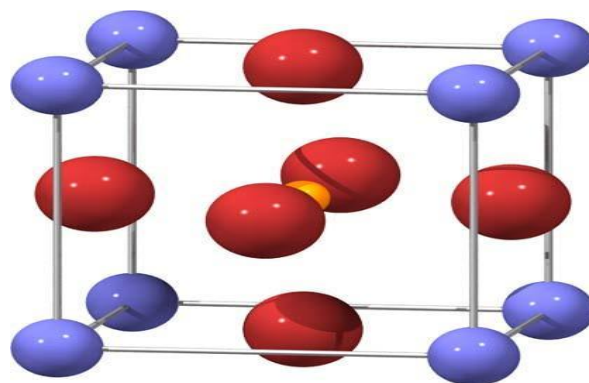Where the A cations composites with transition metal ions (TMI) on the B cations show the variety of electronics and magnetic properties. This variety is related to both chemical flexibility and complex character that transition metal ions play certain coordination with oxygen or halides. While magnetism and electronic correlations are usually related to unfilled 3d electron shells of the TMI, pronounced dielectric properties are connected with filled 3d Electron shells. Multiferrocity is the coexistence of spontaneous ferroelectric and ferromagnetic moments, which have very few phenomena due to less magnetic point groups that allow a spontaneous polarisation. The presence of competing interaction and high magneto-capacitive coupling also given. From the following examples we can studied the structure and properties of transition metal perovskite compound. These materials extends in the field of commercial application e.g. capacitors, transducers, actuators, sensors and electro optical and switching. Some examples of perovskite compound are $LaCoO_3$, $LaCrO_3$, $LaNiO_3$, $LaFeO_3$ etc. [1]

1.4 Double Perovskite Structure

Two unit cell of perovskite structure consists double perovskite. When two perovskite compounds are bombard with each other then they have the tendency to align their respective bonding to form a double perovskite structure. The structure of double perovskite compound is of type $A_2BB'O_6$. There are two types of B-site patterning in B-site ordering. One type of pattern is that more than 160 perovskite oxides, which is represented by rock-salt ordering. That cations between B and B' order into alternate octahedral and other type is layered order between B and B'. In double perovskite structure $A_2BB'O_6$ where B has partially filled and B' has empty orbitals or vise-versa. It gives an unique opportunity that provides the multiferroic behaviours due to their ferromagnetic insulator behaviours which has 180°-superexchange interactions between B and B' cations via the oxygen ions. The ordering between B and B' in $A_2BB'O_6$ gives important functional properties. Now the most important aspect is that how to achieve and control the structural ordering between B and B' in double perovskite compound and the correlation between their functional properties. Some examples of double perovskite compounds are La_2CoMnO_6, La_2CrMnO_6, La_2FeMnO_6, La_2NiMnO_6 etc.

Generally the perovskite compound behaves like antiferromagnetic insulator but when manganese is doped with it suddenly behaves like a ferromagnetic semiconductor by forming a double perovskite compound. Hence the perovskite compounds are antiferromagnetic

insulator and the double perovskite compounds are ferromagnetic semiconductor.

1.5 Antiferromagnetic Insulator

Reviewing the earlier literature, one can obtain that many of the rare earth perovskite oxides are antiferromagnetic as the magnetic state. However, the resistivity of those materials may not be measured by the instruments characterising highly insulating behaviour. The antiferromagnetic character of these materials stems from the super exchange interaction [2] from their neighbouring spins.

1.6 Ferromagnetic semiconductor

However, doping with magnetic element to the antiferromagnetic insulator compound changes the magnetic state from purely antiferromagnetic to ferromagnetic. This new magnetic state stems from the fact that the spins are interacting by the double exchange interaction. Subsequently the insulating state changes to semiconductor. Furthermore, the general concept is that ferromagnetic materials favours metalicity.

1.7 Aim of the present work

The materials with perovskite structure have numerous studies in last decade. Their structure, electrical and magnetic properties has been established up to a great extent. However, a detail study relating to double perovskite type of materials is still lacking in the literatures. In this report an effort is made to study in detail the behaviour of few double perovskite materials and then compared with their perovskite counterpart specifically their structure, morphology and electrical behaviour. These short of studies will provide a base line to select these materials for technological applications.

CHAPTER-2   SAMPLE PREAPARATION

2.1 Solid State Route

This process is generally used for prepare ceramic materials. It is one of the well-known and old technique for the preparation of the sample. This process starting with different solid materials. After that the solid materials are mixed together and intermediate grinded by using motor-vessel. The grinding is carried out for 5-6 hours. During this process we have to causes about the sample wastage and contaminated with organic and inorganic particles present in the atmosphere. After grinding the sample, it heated between 1000^0c-1500^0c for initial phase formation. Then with certain intermediate steps we get the desired compound. These steps are calcination, palletisation, sintering etc. This technique is depends on the kinetic and thermodynamic factor. In accordance to thermodynamic factor, the reaction should be possible by changing the free energy and the kinetic factor gives the rate of the reaction. This process required more physical work and also time taken. [3]

2.2 Wet Chemical Method

The sample is also prepared by chemical route. This is one of the best synthesis methods for sample formation because in this way we get the homogeneity in the sample and it requires very low sintering temperature and also less contamination. In this method the molecular level mixing of the compound is very good. This route includes sol-gel, combustion, pyrophoric route etc. [3]

2.2.1 Sol-gel Process

Very popular method for sample preparation. From this method we can easily get nanometric sized compound. For this process two initial things are required one is solvent and other is solute. When colloidal particles or polymers are immersed in the solvent then it forms sol. Then it heated with very low temperature around 200 ^0c. This method must requires the addition of fuels which accelerating the reaction. Before adding fuel the solution should be stirred and heated at 70 ^0c. Some of the reaction needs adjust the pH, which is the important in case of any sample which is more acidic or basic. By adjusting the pH the solution is reached the concentration of water. Then it was continuously heated upto the gel is not formed. The gel is a three dimensional continuous network of homogeneous chain in which all the chains are homogeneous. After the formation of gel, it was heated upto the stage where

all the sample gel is burned. Then a black floppy and dried mass is formed. It comes under gelation or sol-gel transition. Gels are classified into two types, one is physical gel and other is chemical gels. The physical gels are related with the Vander Wall bond and hydrogen bond. This process is better from others because of its unique characteristics i.e. require low temperature for sample preparation , less contamination, wastage of sample is little chance and well molecular level mixing takes place of the precursor.

During this process the concentration, temperature and pH control is very important. [3]

2.2.2 Pyrophoric Process

It is the popular wet chemical method route for fabrication of materials, favourably metal oxides. In this method aqueous solution of the requisites amount of ingredient materials are taken in stoichiometric proportion. The individual solution is heated up and concentric HNO3 is added drop wise until it becomes clear then the fuel is added with these solutions in such a way that metal ions to fuel ratio is maintained fraction 1:1:2 to make viscous solution. The clear solution of fuel complexes metal nitrates was evaporated around 200 ^{o}c with constant stirring. The continuous heating of these solutions causes foaming and puffing. During evaporation the nitrate ions provides a situ oxidation environment for fuel, which partially converts the hydroxyl group of fuel into carboxylic acid. When complete dehydration occurs, the nitrate themselves are decomposed with the voluminous. Organic based black fluffy powder i.e. precursor powder. The precursor powder after proper grinding are calcined at various temperature to get desired compound with variable particle size. In this method the TEA (Tri Ethalo Amine) is used as a fuel. [4]

2.2.3 Calcination

This is the initial heat treatment process for the initial phase formation. The solid sample is heated below its melting point. It is carried out inside a high temperature or low temperature furnace. During calcination process the impurities and ingredients are removed from the compound due to oxidation. Initially the grinded powder is placed inside a furnace, then heating it in a control manner for few hours. If the temperature is not increase in controlled manner then there is chances of splitting of sample inside the furnace when it is directly contact with high temperature. During this stage the sample have arrange themselves in a homogeneous manner. After that the sample can be easily made into pellet for sintering which is the post treatment stages of sample formation. [3]

2.2.4 Palletisation

Palletisation means to make the pellets by using die set and patizer. The calcined sample is homogeneity in nature, which will put into a die set the applying pressure to the head of the die set. Due application of high pressure the powders are packed close to each other and compact strongly to each other. There is no specific pressure for a particular compound. Most of the superconducting materials requires high pressure for the pellet formation. But in case of some perovskite and double perovskite compound it require low pressure for the pellet formation. In this process the particles are packed together by high or low pressure with decreasing the densification. Sometimes for the strength of the pellet the binder is used for to make the pellet. [3]
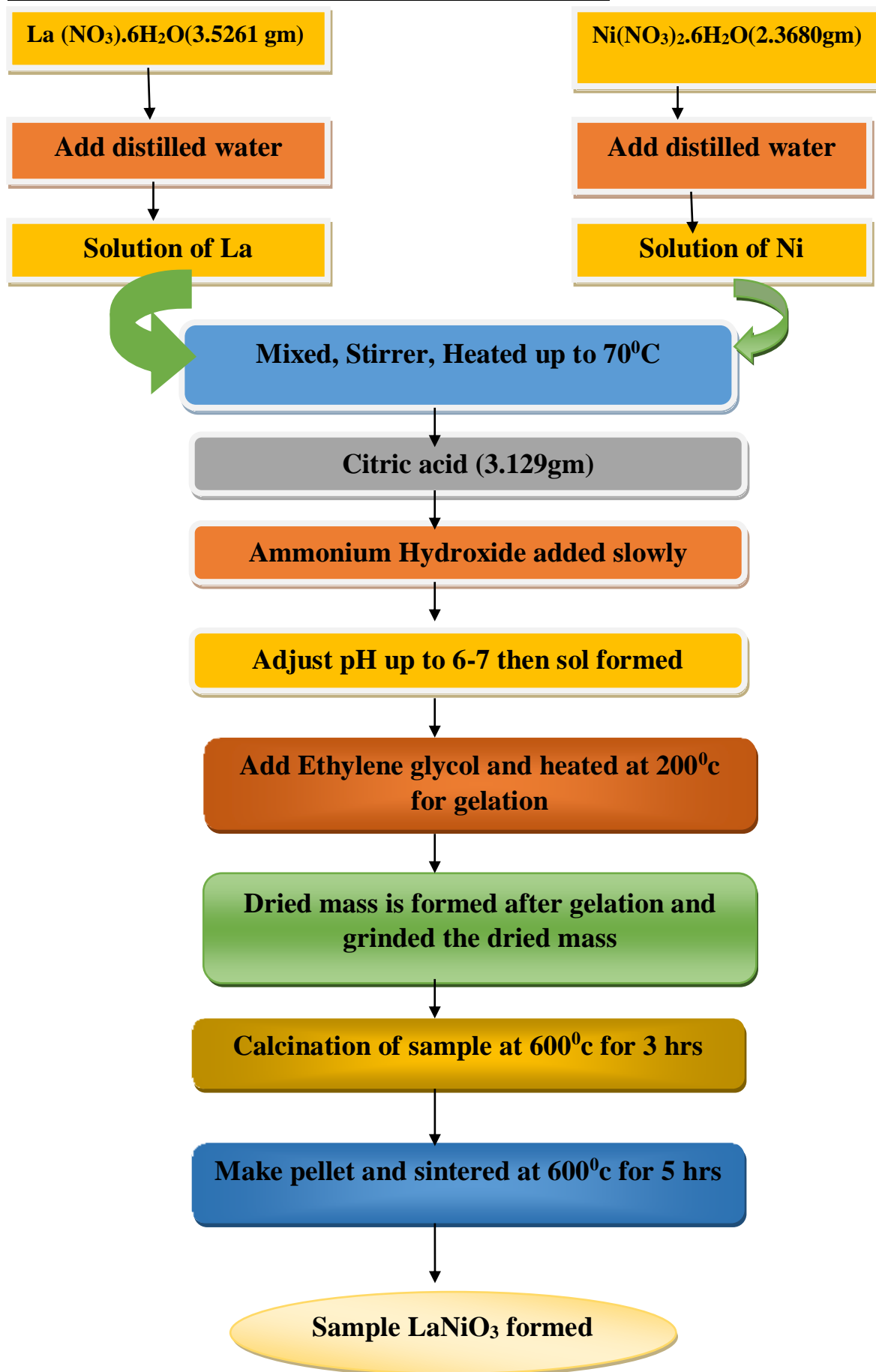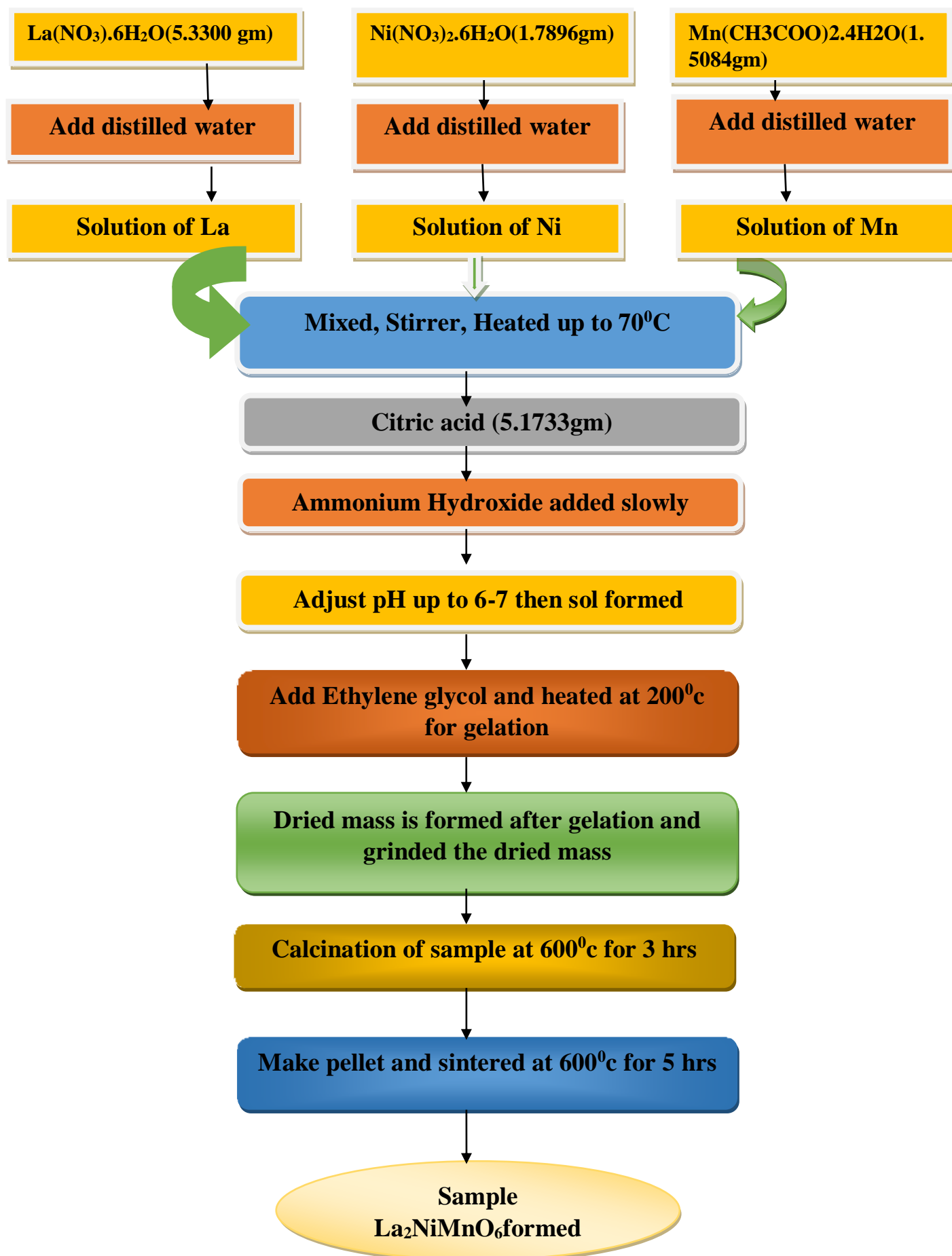
2.2.5 Sintering

It is the heat treatment process for the phase formation. After formation of pellet, it was again heated with desired temperature in a controlled manner. As a result the bonding between the particles leads to coherent, predominately solid structure of the sample. Due to increase in bonding the strength of the pellet increases significantly. Sintering process is depends on the temperature and time ratio. The temperature must be in controlled manner with time and the temperature must be below the melting temperature. If the temperature exceeds melting temperature then there is chances of phase lost and may be destruction of the sample. [3]

2.3 Preparation of samples (LaCoO3, La$_2$CoMnO$_3$, LaFeO$_3$, La$_2$FeMnO$_3$)

These samples are the series of compounds in which first parent compound show the antiferromagnetic insulator and when the Mn component doped with the parent one, it behaves like ferromagnetic semiconductor. From the above sample LaNiO3, La$_2$NiMnO$_3$, LaFeO$_3$, La$_2$FeMnO$_3$ are prepared by sol-gel method[8]. The detail process for the preparation for the sample is given in the following by flowchart. The samples are

(i)   LaNiO$_3$
(ii)   La$_2$NiMnO$_3$
(iii)   LaFeO$_3$
(iv)   La$_2$FeMnO

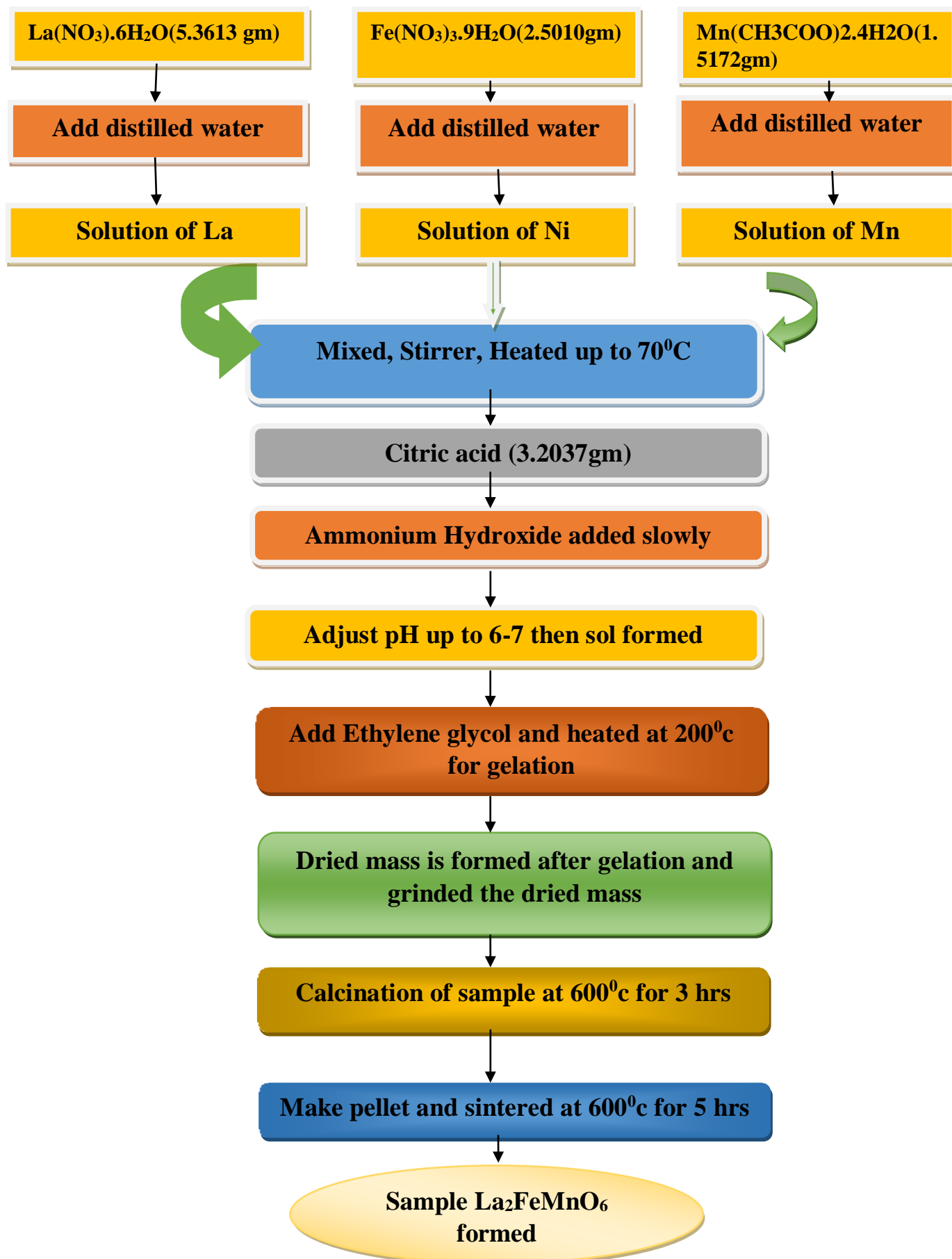## ROUTES FOR PREPARATION OF LaNiO₃:-

La $(NO_3).6H_2O$ (3.5261 gm)	Ni$(NO_3)_2.6H_2O$ (2.3680gm)

Add distilled water → **Solution of La**

Add distilled water → **Solution of Ni**

Mixed, Stirrer, Heated up to 70⁰C

Citric acid (3.129gm)

Ammonium Hydroxide added slowly

Adjust pH up to 6-7 then sol formed

Add Ethylene glycol and heated at 200⁰c for gelation

Dried mass is formed after gelation and grinded the dried mass

Calcination of sample at 600⁰c for 3 hrs

Make pellet and sintered at 600⁰c for 5 hrs

Sample LaNiO₃ formed

ROUTES FOR PREPARATION OF La$_2$NiMnO$_6$:-

La(NO$_3$).6H$_2$O(5.3300 gm)	Ni(NO$_3$)$_2$.6H$_2$O(1.7896gm)	Mn(CH3COO)2.4H2O(1.5084gm)
Add distilled water	Add distilled water	Add distilled water
Solution of La	Solution of Ni	Solution of Mn

Mixed, Stirrer, Heated up to 70^{0}C

Citric acid (5.1733gm)

Ammonium Hydroxide added slowly

Adjust pH up to 6-7 then sol formed

Add Ethylene glycol and heated at 200^{0}c for gelation

Dried mass is formed after gelation and grinded the dried mass

Calcination of sample at 600^{0}c for 3 hrs

Make pellet and sintered at 600^{0}c for 5 hrs

Sample La$_2$NiMnO$_6$ formed

ROUTES FOR PREPARATION OF LaFeO$_3$:-

La (NO$_3$).6H$_2$O(5.3513 gm)

Fe(NO$_3$)$_3$.9H$_2$O(4.9928gm)

Add distilled water

Add distilled water

Solution of La

Solution of Ni

Mixed, Stirrer, Heated up to 70^{0}C

Citric acid (5.1939gm)

Ammonium Hydroxide added slowly

Adjust pH up to 6-7 then sol formed

Add Ethylene glycol and heated at 200^{0}c for gelation

Dried mass is formed after gelation and grinded the dried mass

Calcination of sample at 600^{0}c for 3 hrs

Make pellet and sintered at 600^{0}c for 5 hrs

Sample LaFeO$_3$ formed

ROUTES FOR PREPARATION OF La$_2$FeMnO$_6$:-

La(NO$_3$).6H$_2$O(5.3613 gm)	Fe(NO$_3$)$_3$.9H$_2$O(2.5010gm)	Mn(CH3COO)2.4H2O(1.5172gm)
Add distilled water	Add distilled water	Add distilled water
Solution of La	Solution of Ni	Solution of Mn

Mixed, Stirrer, Heated up to 70^{0}C

Citric acid (3.2037gm)

Ammonium Hydroxide added slowly

Adjust pH up to 6-7 then sol formed

Add Ethylene glycol and heated at 200^{0}c for gelation

Dried mass is formed after gelation and grinded the dried mass

Calcination of sample at 600^{0}c for 3 hrs

Make pellet and sintered at 600^{0}c for 5 hrs

Sample La$_2$FeMnO$_6$ formed

CHAPTER-3   CHARACTERIZATION TECHNIQUES

3.1 X-ray Diffraction

It is one of the important characterisation techniques that give the information about crystal structure, crystal composition, lattice parameter, spacing between two crystal planes [5]. The filament inside the cathode tube is heated due to the application of alternating voltage between two electrodes. As the filament gets heated then the free electrons are travelling from cathode to anode and finally strike the anode surface. Resulting formation of X-Rays in x-ray tube. The X-ray originated from the tube is falls on the surface of the sample. As a result the X-rays are diffracted in different direction by continuous change in intensity with the incident angle. The diffracted X-ray makes the same angle as that of the incident beam. The intensity distribution is varying with the angle between incidence and diffracted beam. As a result the fine peaks are formed in the computer screen that represents the different planes called Miller indices. By knowing those plane we can calculated the structure of sample, composition of the crystal, spacing between two planes, and lattice constant etc. This technique is basically based on the principle of Bragg's law i.e.

$$2d \sin\theta = n\lambda \text{ (symbols have their usual meaning)}$$
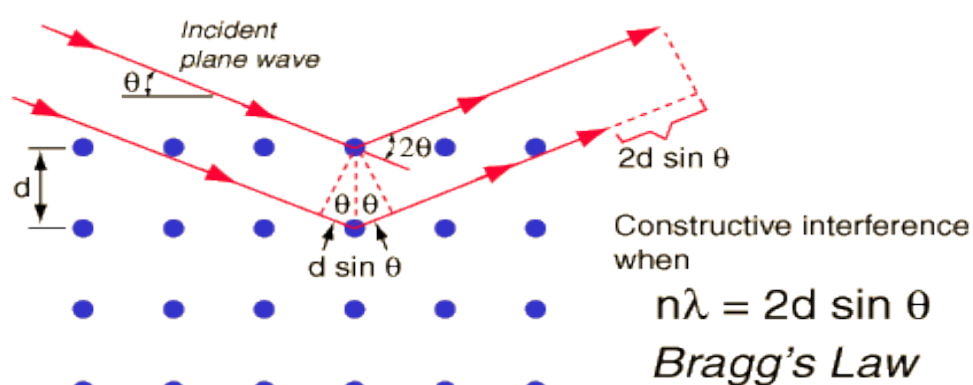
Fig 3.1 X-Ray diffraction through crystal planes

3.2 FTIR (Fourier Transform Infrared Analysis)

FTIR technique is used for knowing the infrared spectra in terms of absorbance, reflection and photoconductivity [6]. FTIR collects spectral data in wide spectral range. This technique is utilised for knowing the molecular bonding between the atoms present in the sample, resulting confirmation about its structure. In this technique the sample cannot be directly characterised, but few samples like thin film may able to direct measurement. For the ceramic sample, there is a base of potassium bromide (KBr). The light source falls on the sample surface that present in front of the base KBr. The IR spectrum forms in form of stretching peaks on the computer screen. Each peaks formed at different wave number. Particularly these peaks are given the bonding range between the atoms present in the materials. The FTIR principle based on the Michelson's Interferometer, i.e shown diagrammatically given below
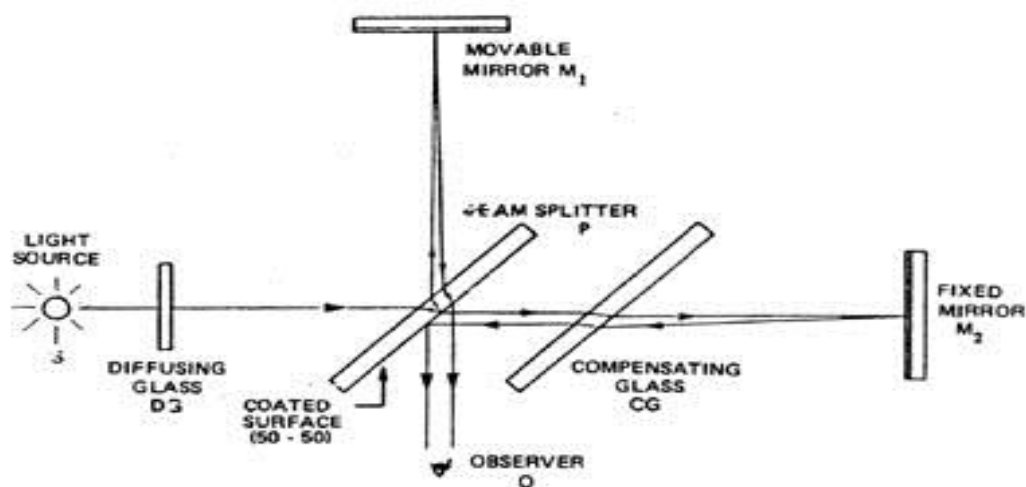
Fig 3.2 shows the Michelson Interferometer for the principle of FTIR

3.3 UV-Visible Spectroscopy

UV-visibility spectroscopy means that the absorbance or reflectance found in the visible spectral region. In this region there is transition between electromagnetic spectra and molecules. As a result the electrons are exited from ground state to exited state. When these excitation rate is high, the spectra of larger wavelength is found in visible region. It is used for characterisation for different materials like transition metal ions, organic and biological

compounds. This technique is utilised for knowing the band bap of the sample. As a result the conductivity of the sample is known easily. This technique is based on Beer's law i.e.

$$A = \varepsilon.c.l$$

where the symbols have their usual meaning(ε= molar absorptivity, c = concentration, and l = path length)

3.4 FESEM (Field Emission Scanning Electron Microscope)

The SEM technology is used to study the morphological structure and compositional analysis of the material. But it could not able to give better resolution. By the application of field emission in the electron gun of the SEM which has thinner probing having high electron energy. As a result the resolution is 3-6 times better than the simple SEM. It also benefits in minimize the sample damage. In the FESEM we get the grain boundaries in nanometric range [7].
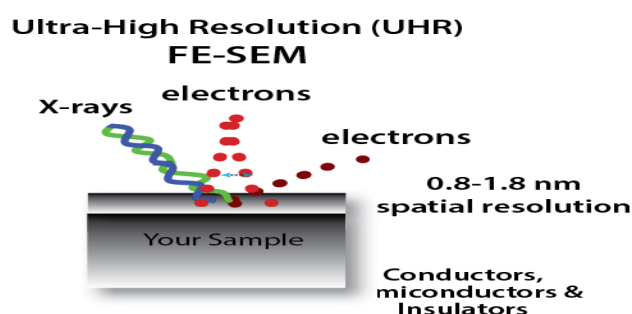
(FIG 3.3 UHR FESEM)

3.5 Dielectric Spectroscopy

It is use to determine the dielectric, electrical and optical properties of compounds. To study the correlation among complex dielectric constant and electrical susceptibility, electrical conductivity and refractive index. Using this technique we can found the dielectric constant, dielectric loss, impedance, conductivity etc. It is the one of the best instrument which can study several numbers of properties. Use of dielectrics in fabrication of capacitors, filtering out noise from signals as part of a resonant circuit and in a camera flash system. Dielectric constant is helpful in determining other properties i.e. n, χ_e. This is useful for the study of resonance phenomena in dielectrics, and critical phenomena at ferroelectric transitions. The ultralow dielectric constant is useful for high-frequency switching applications.

CHAPTER-4   RESULT AND DISCUSSION

4.1 Structure Determination by XRD

The XRD of 4 samples is shown in fig4.1. All the samples are found to be single phase. The $LaNiO_3$ crystallizes in rhombocentred where as $LaFeO_3$ in cubic. The doubled peroskite compounds are indexed with reference to the JCPDS data.
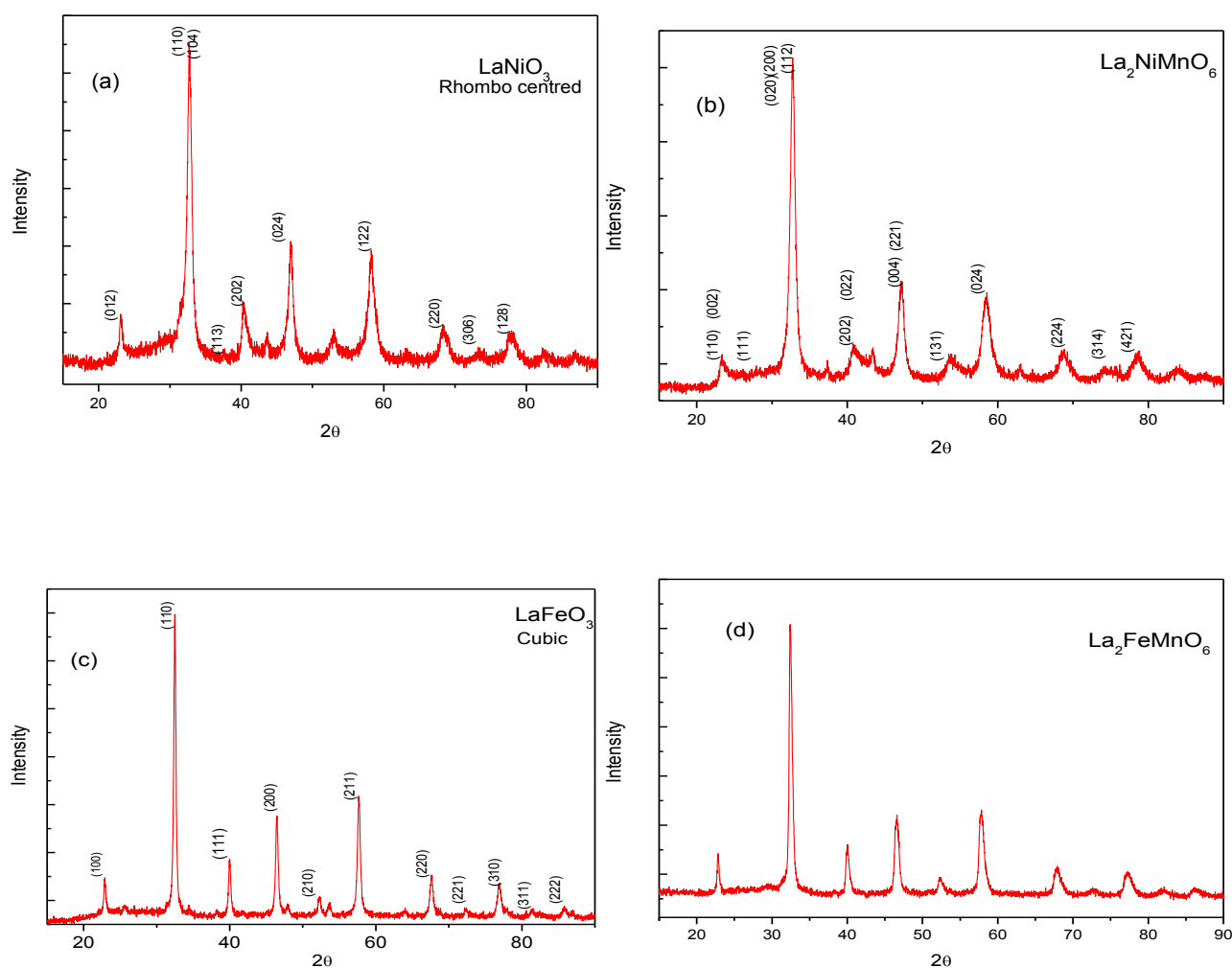

Fig4.1: XRD pattern of (a) LaNiO₃ (b) La₂NiMnO₆ (c) LaFeO₃ and (d) La₂FeMnO₆

4.2 Characteristics of Bonding by FTIR

The FTIR data for the four samples are given below. We get the characteristic bonding, its vibration, and intensity from the range of its absorbance. Generally the metal oxide bonds are in the range 400-650 and presence of water composition lies above 3000 cm^{-1} in the entire

sample   (O-H)   which   is   a   strong   bond.
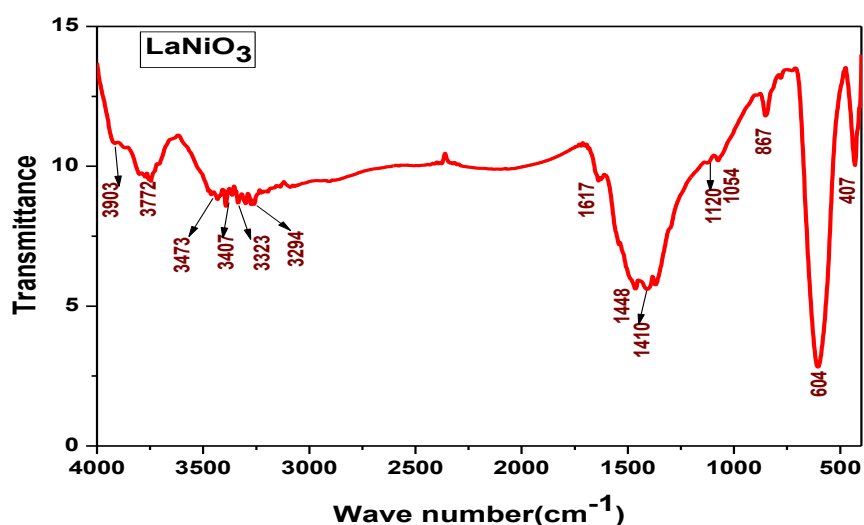
Fig. 4.2.1 FTIR spectra of LaNiO₃

In LaNiO$_3$, the range 1410-1500 cm^{-1} gives C-F bond which is stretched and having strong intensity and 1120-1054 gives C-N bond, which is stretched.
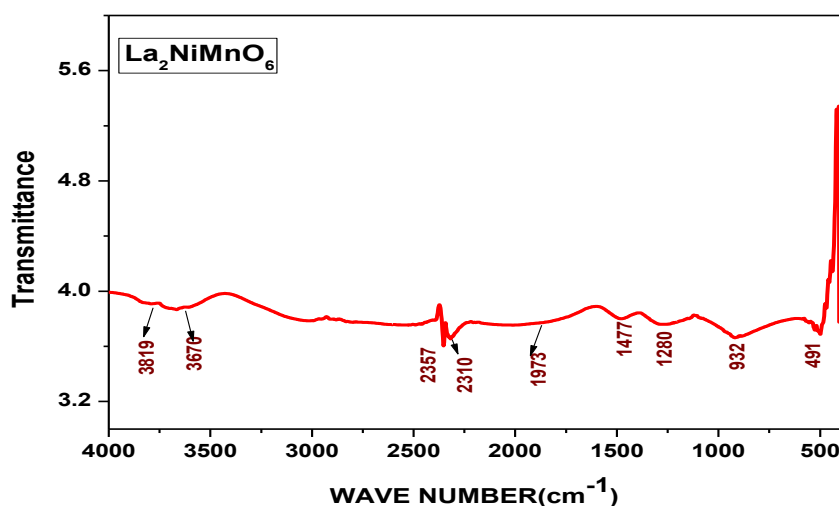
Fig. 4.2.2 FTIR spectra of La₂NiMnO3

In La$_2$NiMnO$_6$ CN bond is present (IR carbonyl group) in the range 2367-2310 cm^{-1} with strong intensity and = C-H bond in the range 1280-1477 cm^{-1} with strong frequency. In LaFeO3 the bonds C=C are formed in the range 1400-1600 cm^{-1}, they are stretched in the weak intensity.
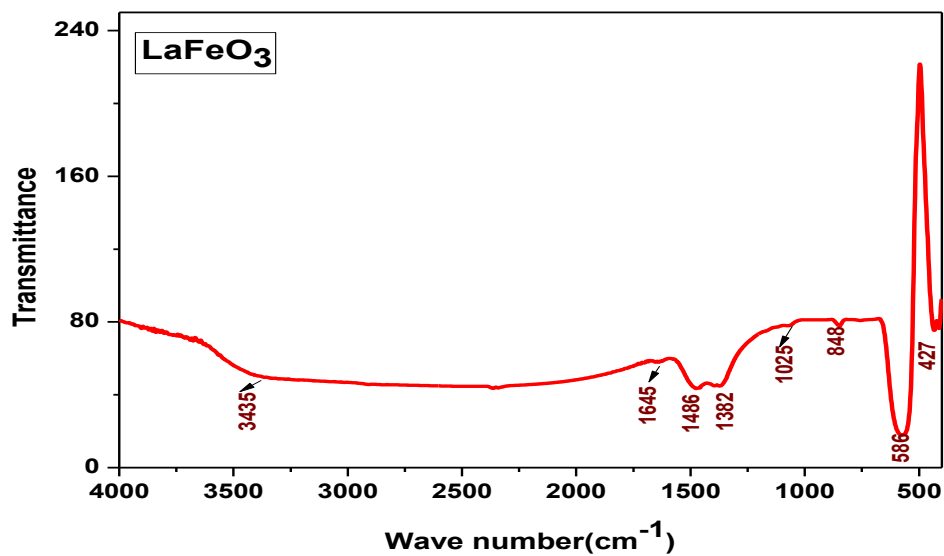
Fig. 4.2.3 FTIR spectra of LaFeO₃

In La$_2$FeMnO$_6$ the bonds C=C are formed in the range 1400-1600 cm^{-1} with strong intensity.
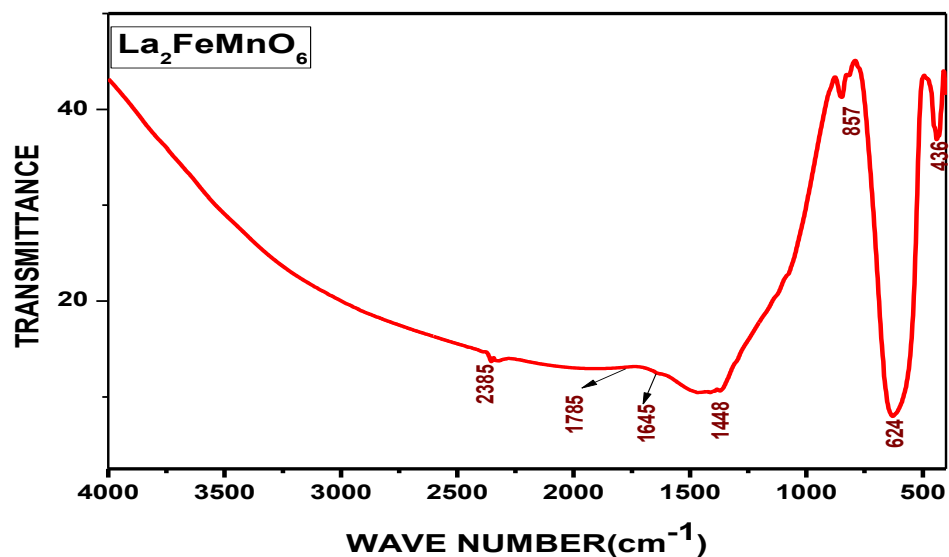
Fig. 4.2.4 FTIR spectra of La$_2$FeMnO$_6$

4.3 Band Gap study by UV-visible Spectroscopy

From the UV-visible data it is confirmed that the double perovskite compounds are semiconducting in nature due to its band gap is found above 3ev. If the UV-Visible is carried out in low temperature, then it confirms the insulating nature of perovskite compound with high band gap.
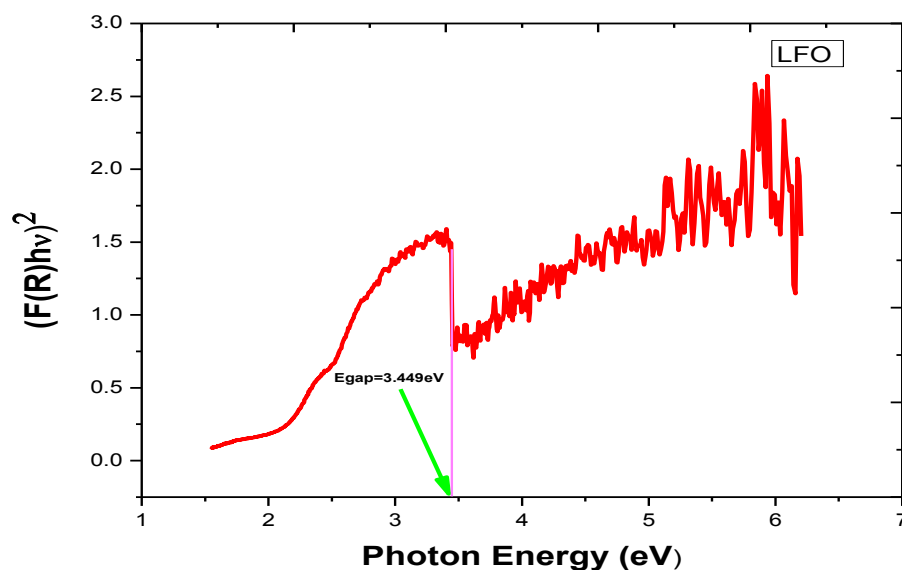
Fig. 4.3.1 UV-visible graph for LaFeO₃
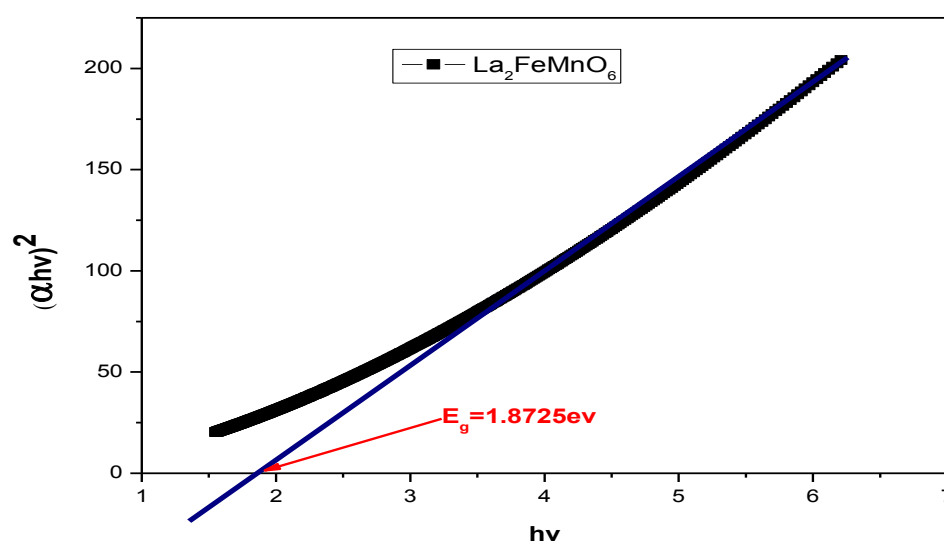
Fig. 4.3.2 UV-visible graph for La₂FeMnO₆
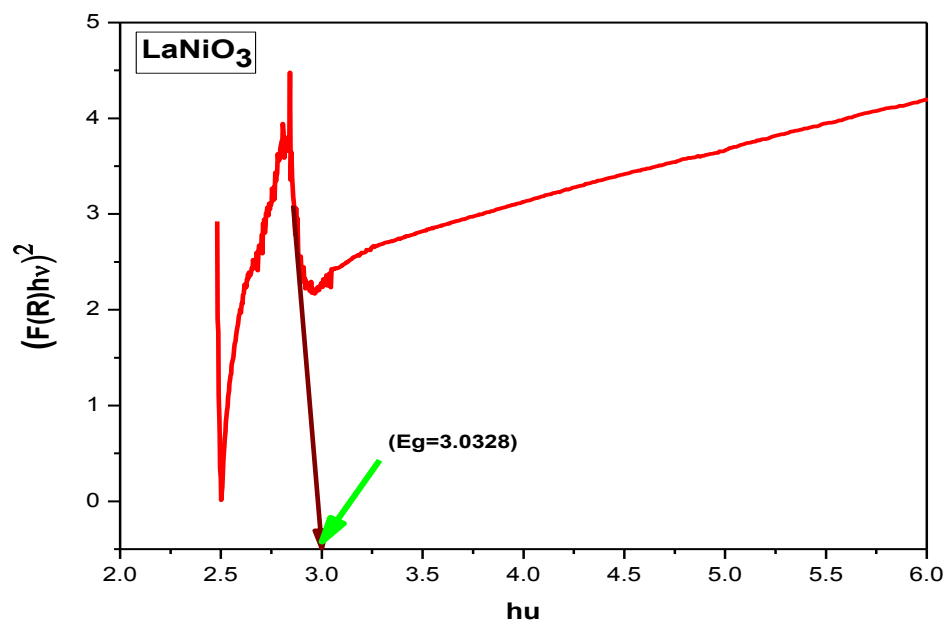
Fig. 4.3.3 UV-visible graph for LaNiO₃
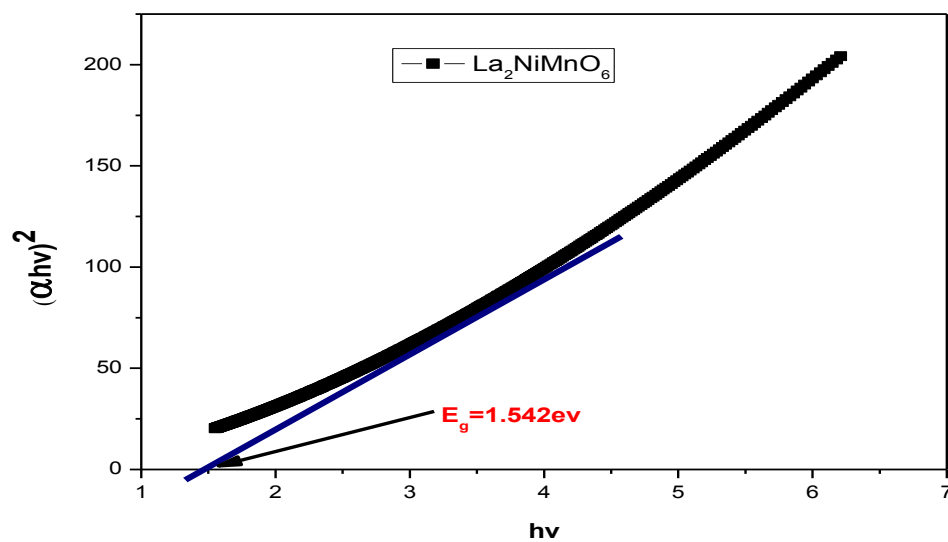
Fig. 4.3.4 UV-visible graph for La₂NiMnO₆

4.4 Microstructure by FESEM

The morphology of the double perovskite compounds has been studied through FESEM. From that the size of the grains is found to be in micron. In addition there is porosity found in samples. This is probably due to the low sintering temperature of the materials.
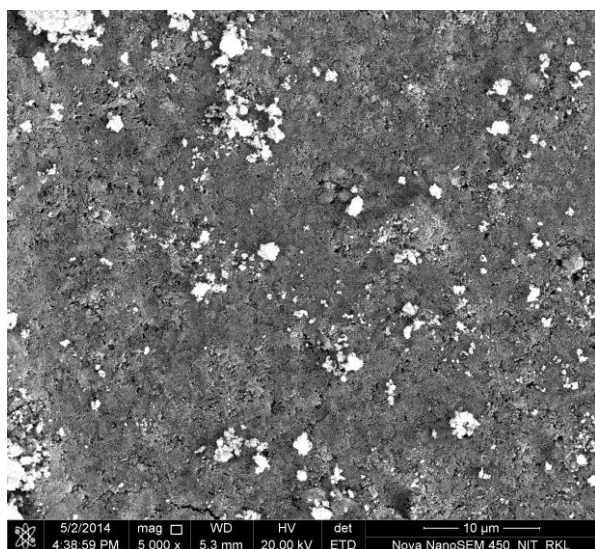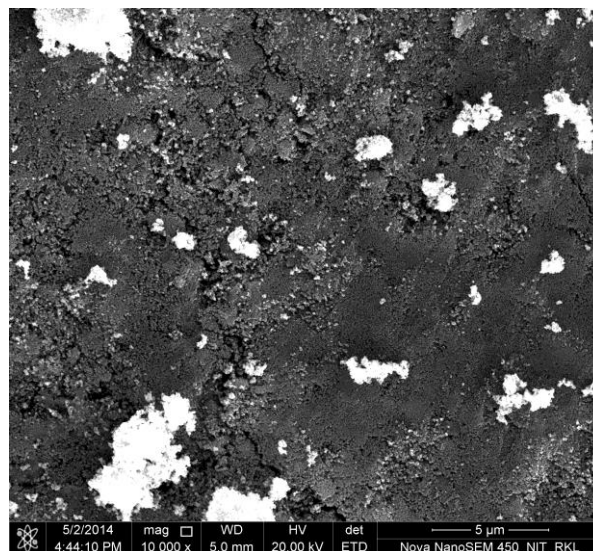

Fig 4.4.1 FESEM of La$_2$FeMnO$_6$

Fig. 4.4.2   FESEM ofLa$_2$NiMnO$_6$

Moreover, the EDAX spectra confirm the presence of elements in the respective compounds which is tally with their atomic weight percentage.

4.5 Dielectric study:

The material capacitance (source of dielectric constant) and loss has been plotted as a function of frequency for both LaFeO3 and La2FeMnO6 at room temperature. With increase in frequency the dielectric constant decreases as similar to many of the dielectric materials.
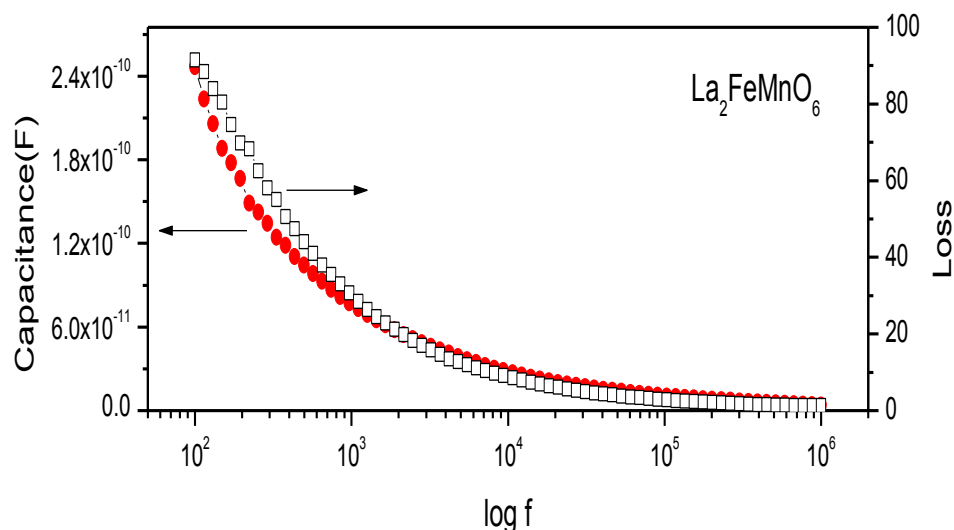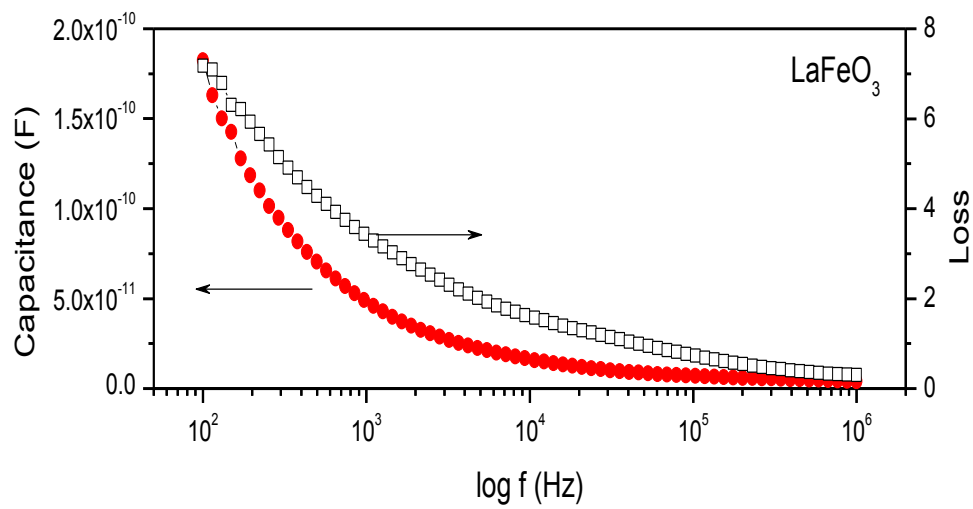
Fig 4.8: Capacitance and loss tangent vs log of frequency for La2FeMnO6 and LaFeO3

CHAPTER 5. Conclusion and scope of future work

We have studied the structure and electrical properties of several perovskite and double perovskite compound and also got how properties changes from perovskite compound to double perovskite compound significantly. Compounds are synthesized by sol-gel process. The samples are found to be in single phase and stoichiometric. The information about the molecular bonding is obtained from the FTIR spectra. The calculated band gap from UV-Visible spectra characterises the semiconducting and insulating nature of the material. Perovskite compound behaves like insulator when manganese is doped with these compounds it behaves like semiconductor. The morphology of the materials has been studied through FESEM and finally the dielectric spectroscopy has been carriedout for all compounds.

Furthermore, one can study the correlation between different electric and magnetic order parameter for this materials, to use as a potential candidate for multiferroics. The magnetization dynamics can be studied to know the spin-spin interactions. Low temperature dielectric spectroscopy can be studied to know whether this materials undergoes any transition or not and if so what is the inside story of this transition and many more work can be done related to these materials.

REFERENCES

1. http://abulafia.mt.ic.ac.uk/publications/theses/levy/Chapter3.pdf
2. P W Anderson, Phys. Rev. **79**, 350(1950)
3. A.R. West, Solid state chemistry and its applications, John willey sons, Singapore 1887
4. R. K. Pati, J. C. Ray, P. Pramanik, J. Am. Ceram. Soc. 84, 2849 (2001).
5. http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html
6. http://pe2bz.philpem.me.uk/Lights/-%20Laser/Info-999-LaserCourse/C10-M04-MichelsonInterferometers/Module10-4.htm
7. http://www.nanolabtechnologies.com/fe-sem
8. Ferromagnetism in Mn-half doped LaCrO3 perovskite, Petrucio Barrazo and J. Albino Aguiar
9. http://www.slideshare.net/avocado1111/magneticsppt-compatibility-mode