

Structural and Dielectric studies on layered transition metal oxides

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By

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CERTIFICATE

This is to certify that the project report which is entitled by “Structural and dielectric studies of layered transition metal oxides” is submitted by Mr. Smruti Ranjan Mohanty in partial contentment of the restraint toward the MSc degree in Physics at NIT, Rourkela. This is a bonfied work carried out by him under my regulation and supervision in the laboratory of Department of Physics and Astronomy.

To the best of my knowledge, the matter presents in the thesis has not been submitted to any other university or institution.

Prof. S.N. Dash
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I express my genuine thanks to all the faculty members of Department of Physics and Astronomy, NIT Rourkela.

I also thank the entire research scholars and all my friends of Department of Physics And Astronomy for their endless motivation and support.

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Abstract

We want to characterize the outcome, when an alkali material Sr is substituted on rare earth site of Nickelate ($\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$) and Cobaltate ($\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$). The samples are primed by using Sol-gel procedure. It is found that the samples are in single phase when the structural analysis is done by Rietveld analysis of the XRD data. Through SEM microscopic analysis, we have surveyed the granular information and size. The band gap of both samples is measured by UV Visible spectroscopy method which shows the semiconducting behavior of the samples. To find out the dielectric loss and the dielectric constant, the dielectric measurement of two samples is done with respect to frequency. The results are discussed from different graphs.

Contents

1 Introduction	1
1.1 TRANSITION METAL OXIDE:	1
1.2 PEROVSKITE STRUCTURE:-	2
1.3 RUDDLESDEN-POPPER PHASE:-	3
1.4 LAYERED COMPOUNDS:-	3
1.5 CHARGE ORDERING:-	4
1.6 OBJECTIVE OF THE PRESENT WORK:-	5
1.7 BRIEF DESCRIPTION OF THE SAMPLES:-	6
1.7.1: LaSrNiO ₄ :-	6
1.7.2: LaSrCoO ₄ :-	6
2 SAMPLE PREPARATION	7
2.1 PREPARATION OF SAMPLES BY SOL GEL METHOD:-	7
2.2 FLOW CHART FOR PREPARATION:	9
3 CHARACTERIZATION	10
3.1 X-RAY DIFFRACTION AND RIETVELD ANALYSIS:-	10
3.2 SCANNING ELECTRON MICROSCOPE:-	11
3.3 UV SPECTROSCOPY:-	12
3.3 DIELECTRIC MEASUREMENT:-	12
4 RESULTS AND DISCUSSIONS	13
4.1 Structure by X-ray diffraction and Rietveld Analysis:	13
4.2 SEM:	14
4.3 UV-VIS SPECTROSCOPY:	15
4.4 DIELECTRIC STUDIES:	16
5 CONCLUSION AND SCOPE OF FUTURE WORK	17
REFERENCES	18

1 INTRODUCTION

In physical world, transition metal describes those elements in which the atom has incompletely filled d subshell. These also can be defined as elements giving rise to cations with partially filled d subshell. The periodic table can be divided into 4 group i.e. main group element, actinide, lanthanide and transition metal. The transition metals act as of a bridge between main group elements. Lanthanides and actinides can also be represented by inner transition metals. Transition metals have several interesting properties like they can form colored compounds because of the d-d electron transition. Another important property is they can form paramagnetic compounds because of the presence of unpaired electron. Due to very small resistivity, they can also form compounds having many number of oxidation states. Transition metals generally have very high melting and boiling points density as well as high density. The reason behind this is the metallic bonding between delocalized electrons of d subshell [1]

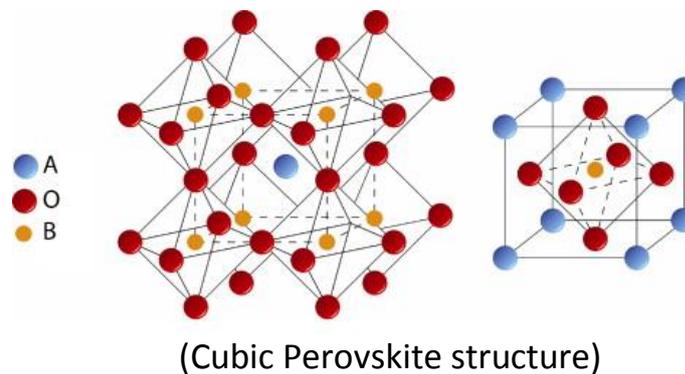
1.1 TRANSITION METAL OXIDE:

Transition metal oxides are those compounds in which there is oxygen atoms bonded with the transition metals. An important feature of transition metal oxide is that the same metals can show metallic (poor) behavior and also can show insulating behavior if there is some changes in temperature and pressure. These transitions are classified as metal insulator transition and can be described by Mott's transition. In these oxides, the oxide crystal structure is constituted of metal cations at interstitial sites with oxygen anions in form of closed pack array. The FCC(face centered cubic) and HCP(hexagonal close packed) which are the closed pack arrays have tetrahedral as well as octahedral interstices. The transition metals are widely used because of their semiconductive properties as well as catalytic activity. These transition metals have different kinds of surface structure and this affect the energy of surface of the compound and due to this the chemical property also get influenced. Although there is very less data or idea about the surface structure of these metal oxides, but the bulk structure property is known after several researches. While deriving the property of the oxides, we have to keep in mind that the oxides present are ideal crystals and the atomic arrangement is well maintained and the surface plan is maintained too. After the creation of newly formed structure, the newly created surface will minimize the Gibb's surface energy by reconstruction in order to attain most thermodynamically stable state. The stability of these can be seen by evaluating defect sites

and the surface polarity. According to the bulk surface structure we can have 4 types of surface types. These 4 types can be classified as Monoxides, Dioxides, Trioxides and Ternary oxides. Out of all the structures, the Perovskite structure is most widely used ternary phase. In below there is a brief discussion about the Perovskite structure and the Ruddleson-Popper phase which is based on Perovskite structure and layered compounds [2][3].

1.2 PEROVSKITE STRUCTURE:-

The Perovskite compounds usually have the chemical formula like ABX_3 in which A and B represents cations of different sizes and X represents the anion that is bounded with both A and B [4]. generally the A atoms are larger in size than B atoms. The B cation has 6 fold coordination and it has an ideal cubic symmetry structure and it is surrounded by octahedral anions. Cation A has 12 fold octahedral coordination. In order to attain stability, it depends mainly open the ion size, a little buckle and bending can produce lower symmetry distorted version in which coordination number of A and B or of both are changed or decreased.



The Perovskite structure is shown by oxides which have the chemical formula of ABO_3 . In such compounds, the A atom fits at corner position of cube where as B atom fits body centered position of cube. At the face centered position, there is oxygen atom. As we discussed above about the stability of the structure, it depends mainly open the ion size, if there will be little buckle or some bending, then that can give rise to distort version of symmetry in which coordination of A and B are changed. If there presents some slanting in octahedral structure of BO_6 , the coordination number will be changed. Now the coordination number of A will become 8, but the slanting will allow B to attain stable bonding. The electric dipole that results is responsible for ferroelectric property and this is shown by Perovskite structures.[5]

1.3 RUDDLESDEN-POPPER PHASE:-

The RP phase or Ruddlesden-Popper phase is of a appearance of coated Perovskite construction. It has two dimensional Perovskite slab intercovered with many cations. It can be shown by



in above, X represents an anion and A,A* and B represents cation.m is the number of coat of octahedral in structure of Perovskite

In general, A and A* describes the alkaline, alkali or rare earth metal. Here B describes the transition metal. The A Cations are positioned at edge of Perovskite structure and do have a 9 coordination number. Similarly there is 6 coordination numbers for B. the preparation of RP compounds can be done by sol gel method, solid state method or it can also be prepared using soft chemistry technique which is similar to solid state technique in some ways. In soft chemistry technique there is exchange of ions and reaction takes place of solid coated Perovskite and also ion exchange and reaction which involves interpolated structure unit.

The most important and interesting characteristics of Perovskite structure is they are very appropriate for carrier doping procedure. The reason is that the structure being very strong or stout against the modification that happens chemically at A site. RP series can also be resulted from Perovskite structure. The other representation of RP phase is done by



In which R represents the rare earth material or element, A represents the alkali earth material or elements.[6]

Now we will talk about the property of layered compounds or what actually layered compounds means.

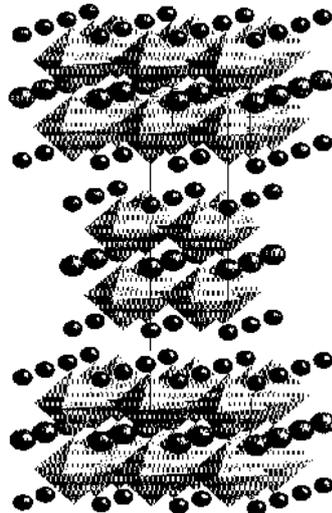
1.4 LAYERED COMPOUNDS:-

The layered compounds can also be termed as RP phase or Ruddlesden-Popper phase. The compounds can be described by the formula



In which m represents the number of corner which is shared by the transition metal oxides. The electronic as well as the magnetic state of the layered compounds is strongly affected by ionic shape and size as well as concentration of various dopants. The case is alike to Perovskite structure case. Although the layered compounds are generally derived or prepared from Perovskite structure, their responses of structure to the metal insulator transition or ferromagnetism fluctuate remarkably.[7]

Now putting the value of m equal to 1 in the above formula then the compound will become A_2BO_4 . This represents the RP phase materials. Materials like La, Pr, Nd etc. can be taken in place of A while materials like Ni, Co, Mn etc. can be taken in place of B. if some impurity are added like Sr, Ba, Ca etc. to these compounds, then it will be the desired compounds. This will be in the form $A_{1-n}A_n^*BO_4$



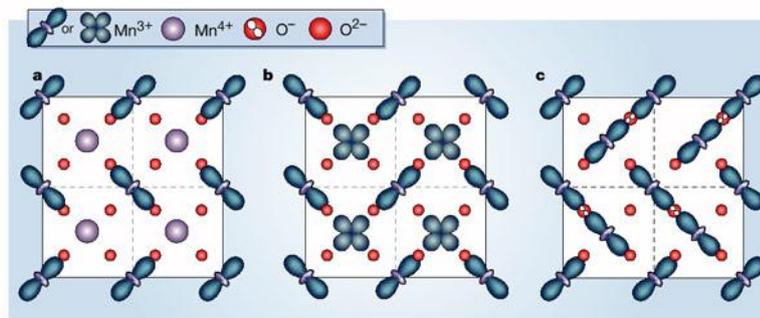
(Crystal structure for the $m = 2$ Ruddlesden-Popper Structure that show the two A cation sites. Large lightly colored circles represent the perovskite cations, and the small dark circles represent the rock-salt cations[7]) The below compound are some examples of layered compounds. $La_{1-x}Sr_xNiO_4$, $La_{1-x}Sr_xMnO_4$, $La_{1-x}Sr_xCoO_4$ etc.

1.5 CHARGE ORDERING:-

Charge ordering is generally a phase transition that takes place mostly in system which is strongly correlated. The strongly correlated system includes organic conductor or transition metal oxide. There results a disproportion and an ordered super lattice because of charge localization at different sites due to tough interface among the electrons. This results at different shape and size which range from horizontal and vertical stripes or can result a shape of checkerboard like shape. This transition may lead to ferroelectricity which happens due to

symmetry breaking. Most famous transition metal oxide that shows charge ordering is magnetite which has a formula Fe_3O_4 . This is because the fact that it is a mixed valence oxide in which iron atoms have algebraic allotment of Fe^{2+} and Fe^{3+} above the transition temperature.

Generally some mixed valent transition metal oxide shows charge ordering property. One of the important examples of this is manganates Perovskite which generally have the formula $\text{La}_{1-x}\text{Sr}_x\text{MnO}_4$. This is important because of long range of Mn^{4+} and Mn^{3+} ions in materials like above. Charge ordering happens if the temperature is much larger than the spin ordering temperature. And we can describe this charge ordering and the relation of it with orbital and spin ordering by many ways like giving consideration to cation size, dimensionality, chemical substitution, pressure etc.



In above diagram, 'a' represents the charge ordered arrangement of Mn^{4+} and Mn^{3+} ion in form of checkerboard. Again 'b' represents orbital order of manganese ion and 'c' represents the ordered arrangement of oxygen ion in between Mn^{3+} ions.[8]

1.6 OBJECTIVE OF THE PRESENT WORK:-

In this thesis, we will try to study the effect when there is some Sr is doped on the rare earth site of the nickelate and cobaltate. We will also see about the structural and other properties of the doped compound. We will check the dielectric properties of the layered materials after doping. The properties of this layered compound will depend upon the interaction between rare earth material and dopants. Here Sr is doped in accordance with alike ionic radii to that of rare earth material (La).

1.7 BRIEF DESCRIPTION OF THE SAMPLES:-

1.7.1: LaSrNiO₄:-

The nickelate is one member of fascinating family of pseudo-cubic Perovskite compounds. They are known for their Mott metal-insulator transition which is controlled by the bandwidth. The properties of nickelate have been studied for decades but still there are much confusion on the theory and properties of nickelate.[9]

When the temperature is very high the nickelates show paramagnetic property but when the temperature is low, they show semiconducting property which exhibit a unique antiferromagnetic ordering along with the charge disproportion. Both charge ordering and antiferromagnetism are observed by neutron scattering (elastic). Upon the selection of rare earth element the transition temperature may vary since the transition temperature is correlated with the shape and size of the rare earth material. All the nickelate shows magnetic ordering having an up-up-down-down spin configuration that quadruples the unit cell in reference to ideal cubic structure[10]. Here we can only observe the contraction and expansion of the octahedral oxygen atom. The interesting factor about nickelate is that if it becomes more metallic, then there is both charge and spin ordering which will take place simultaneously. And also charge ordering will happen independently if the nickelate is more insulating type. The nature of insulating and metallic depends upon what rare earth metal we have chosen. It has been found that half doped nickelate has excellent dielectric properties. This happens because of charge ordering of Ni³⁺ and Ni²⁺ below T_c.

1.7.2: LaSrCoO₄:-

Like Nickelate, cobaltate is also a member of pseudo-cubic Perovskite compounds and it satisfies the properties that are shown by nickelate. Like nickelate, it also shows high dielectric constant. The Sr doped La₂CoO₄ show high dielectric constant if charge ordering leads to high dielectric response. Since charge ordering can persists as high as 850K, there will be high dielectric constant at high temp. it has been found that if the value of x is not equal to 0.5 in La_{2-x}Sr_xCoO₄, the Co²⁺ and Co³⁺ ions can't be arranged in order way which lead to decrease in dielectric constant.[11]

2 SAMPLE PREPARATION

The samples can be prepared by solid state and sol gel method.

In solid state method [12] [13], the preparation of the layered compound starts from taking stoichiometric amount of salts and mixing followed by grinding them together. Then they are hard-pressed to pellets and again subjected to heat at various temperatures with in-between grinding. Again this is followed by cooling of material to find the resultant material. The solid state process includes certain processes like calcinations, grinding, mixing, pressing to pellets, sintering etc. Although in solid state process, we have various advantages which include preparation of material in precise size and shape which is very much required for practical application. But the processes are very lengthy. The synthesis process can extend to several days.

Sol gel method has another advantage of low temperature synthesizing method and it provides ways to prevail over the difficulties achieved while intimate addition of reagents during the reaction. The sol gel method also helps in controlling not only the distribution of particles, but it also helps in controlling the shape and size.[14]

In order to prepare samples, I have used sol gel method. The sol gel method includes preparation of sol which is a dispersal of solid particles and discrete phase in a liquid medium. The solution is prepared in this by mixing of the concentrated solution which contains cation with an organic solvent as the dispersal medium. Again the solution is diluted by adding water. The water pressure modifies the pH value of solution and hence it reduces the repulsion between the elements. This in turn leads to increase in viscosity which again leads to formation of gel. The next step is followed by preparation of powder which can be made by passing the fine droplets of gel into alcohol. The final result can be obtained by sintering and compaction of powder at suitable temperature.[15]

2.1 PREPARATION OF SAMPLES BY SOL GEL METHOD:-

The Nickelate can be prepared by the use of Pachini method or sol gel method by using lanthanum oxide (La_2O_3), Strontium Carbonate (SrCO_3) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as first or starting material. Stoichiometric preparation of high purity material e.g. rare earth oxides and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and SrCO_3 are taken and next changed into nitrates using nitric acid which is 30% pure. Next product nitrates are dissolved in water to obtain clear and precise solution.

Strontium carbonate was also taken and next dissolved in water. This again added to above solution. And next the solution is heated to vanish nitric acid.

The next part involves conversion of all ions present in solution as metal citrates by the addition of 1M citric acid. Before making this we have to consider whether all of the nitric acid presents inside the solution is completely heated out. Then we have to add 1M of citric acid for every 1M of metals ions present in the solutions with stirring so that all the metals are completely turned into citrates.

The next step is the geletion process. In order to achieve this, ethylene glycol is added as geleting reagent. We have to mix ethylene glycol in proportion of 10% v/v carefully. The geleting reagent is added to viscous mass in the ratio of 1:1.2 (metal to ethylene glycol). This mixture was heated in hot plate for the geletion. The solution will convert to a grey colored gel. Temperature required for the geletion ranges between 60⁰ to 200⁰ Celsius. The matter which is organic in nature is decomposed at 400⁰C.

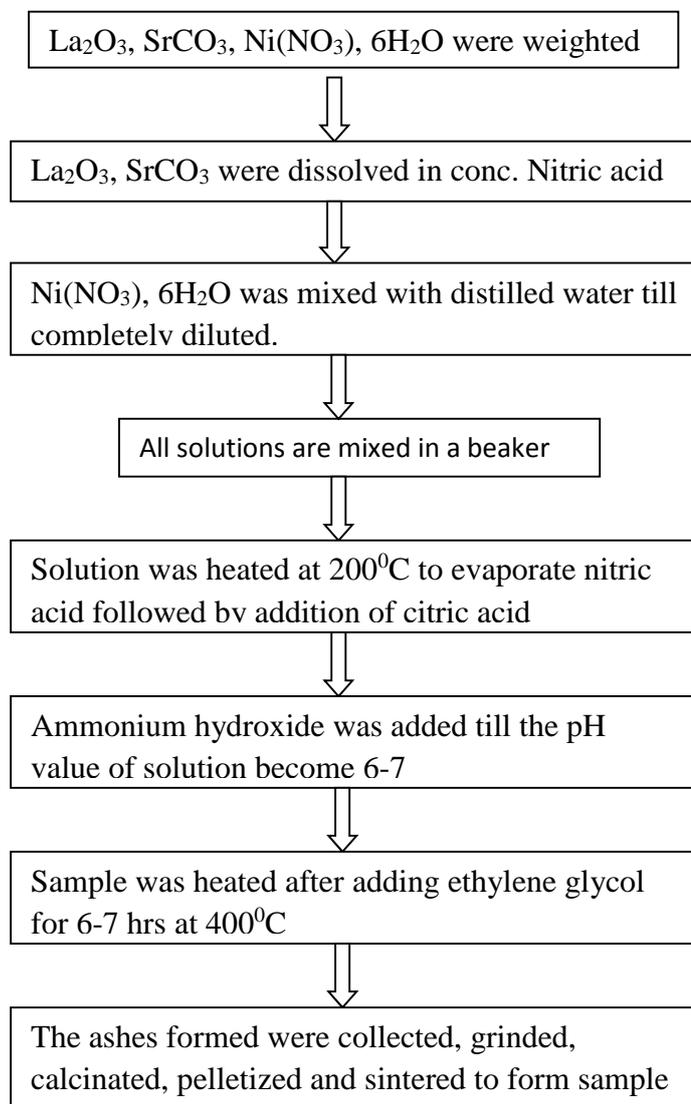
After the deposition, the next procedure to be followed is calcinations process. For this the gel which we got is grinded and is calcinated between 600⁰C to 800⁰C for 12 hours.

The final step is the process of pelletization and sintering. The black colored powder i.e. obtained after calcinations is pressed into pellets in cylindrical form with about 1 cm diameter and about 2.4 mm thickness.[16][17]

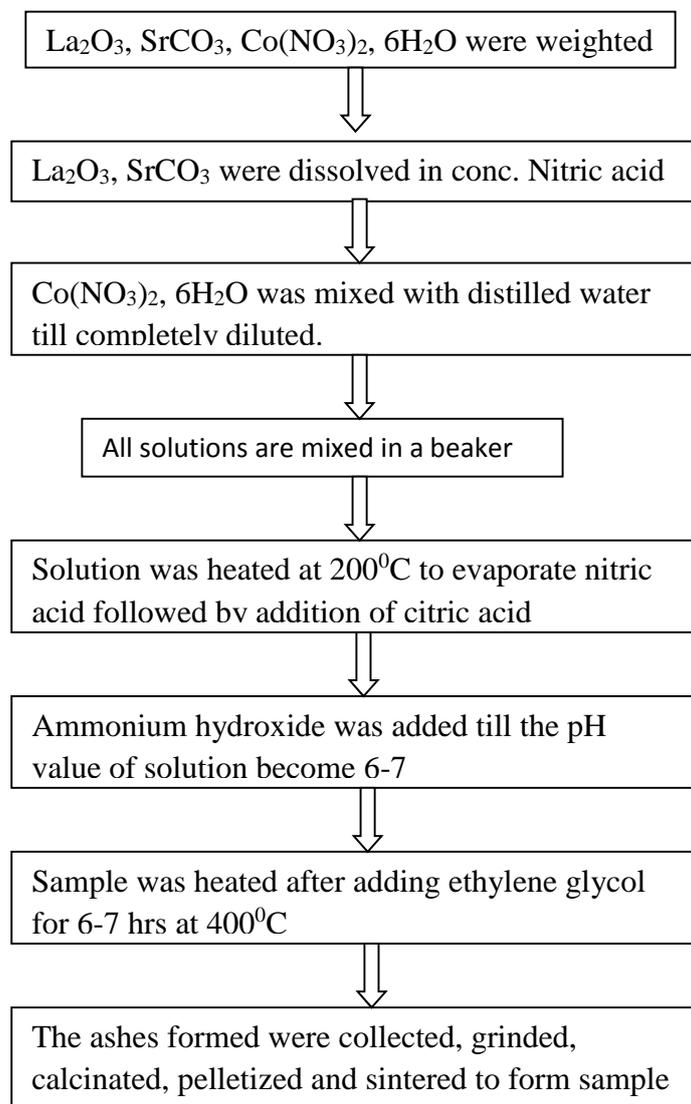
In a similar process other sample $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ is prepared. The detail flow chart for the preparation method is followed

2.2 FLOW CHART FOR PREPARATION:

FOR NICKELATE: -



FOR COBALTATE:-



3 CHARACTERIZATION

The samples are characterized by the following technique.

3.1 X-RAY DIFFRACTION AND RIETVELD ANALYSIS:-

XRD technique is a very dominant and common technique in order to describe the materials and to know the structural clarification in details. The determination of structure of crystal is very important since many of the physical properties like ferroelectric, optical, magnetic properties depend upon the arrangement of atoms in sample. XRD pattern are generally used to found the collection of material or atomic arrangement because of the d-spacing in diffraction planes is some order of x-ray wavelength.

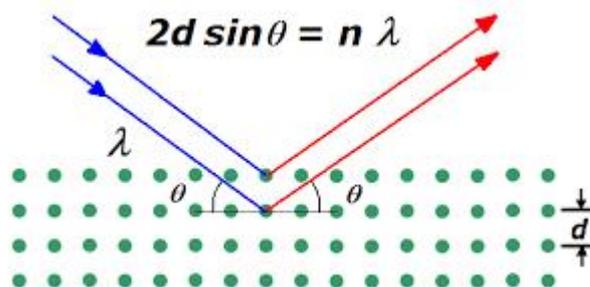
When high energetic beam of X-ray incident upon the sample of consideration, it can penetrate very deep into sample and thus can provide many useful data about the crystal structure. In collision between a X-ray photon and atom, some of photon deflect away from their original direction of travelling. When the scattering is considered to be elastic, only there will be change in momentum and won't be any change of energy or wavelength. After the transfer of momentum from photon to atom, the diffracted X-ray will carry the information about the distribution of atoms in the lattice.[18]

The XRD peak and the d-spacing are directly related to each other by the formula which is known as the Bragg's law which is given by

$$2d \sin \theta = n \lambda$$

Where d is the spacing between 2 planes θ is the incident angle λ is the wavelength of X ray

(Bragg's law for X-ray Diffraction)



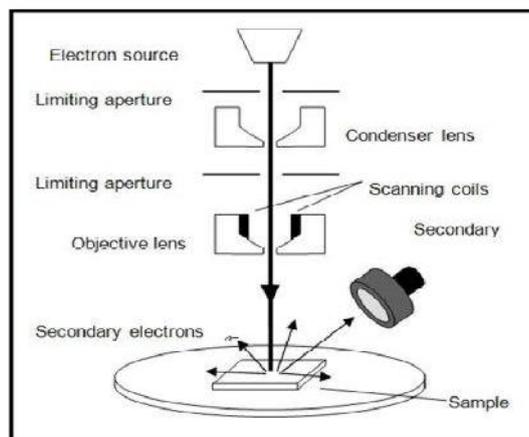
The above image represents the Bragg's law diffraction for a crystal lattice having distance between two planes d and wavelength of X-ray as λ . [19]

The Rietveld analysis which was designed to describe the properties of crystalline materials was developed by Hugo Rietveld. There occur peaks in intensity in diffraction pattern at certain position when the sample is characterized by x-ray diffraction. Many aspects of materials properties can be determined by the use of these peaks' height, position and width. This process includes using of a least square approach to refine theoretical line profile till it matches with the experimental profile. It was specially designed to deal with the peaks which are strongly overlapped.

3.2 SCANNING ELECTRON MICROSCOPE:-

In SEM (scanning Electron Microscope), there is production of images of a sample by scanning it with focused high energetic beam of electrons. The electrons that are incident upon the sample interact with the sample atoms and produce various signals which can be detected and the information which is contained in the signal can be derived to know about the sample composition and topography.

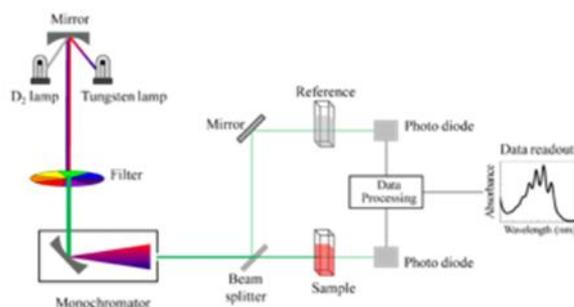
X-rays, back scattered electron as well as secondary electrons are emitted from a sample surface when high energy electron beam is made incident upon a sample under consideration. The SEM detector generally collect the back scattered and secondary electrons. The detector then converts these into signals which are displayed on SEM screen. SEM gives only the information about the surface of sample since it doesn't have the ability to scan deep inside the sample surface. SEM provides us the information or data about the surface orientation, morphology and crystal composition.[20]



3.3 UV SPECTROSCOPY:-

UV spectroscopy is a kind of absorption spectroscopy in which molecules absorb ultraviolet light. By absorbing the ultraviolet radiations, electrons from ground state jump to higher energy state. Now the energy of this ultraviolet radiation will be equal to the difference in energy between the higher energy state and the ground state.

This technique is complementary to fluorescence technology which deals with transitions involving an excited state to the ground state. The basic principle of this technique is that a molecule that has a pi electron has the ability to absorb radiations (UV) in order to excite the electrons to an anti-bonding orbital. If the electron is easily excited, then it can absorb longer wavelengths. This spectroscopy technique is used to measure the band gap of samples from the graph between reflectance vs wavelength or from absorbance vs energy.[21]



(Schematic diagram for UV spectroscopy)

3.3 DIELECTRIC MEASUREMENT:-

The measurements of dielectric constant by parallel plate capacitor have become very simple due to the relation between capacitance and plate separation of an ideal parallel plate capacitor. The determination of dielectric constant is based on the formula

$$C = k \epsilon_0 A / D$$

Where C is the capacitance, k is the dielectric constant, ϵ_0 is the permittivity of free space and D is the separation. Here the task is to determine the dielectric constant and verify the relation between capacitance and inverse dielectric thickness. This experiment results in a non-linear relation between them.[22][23]

4 RESULTS AND DISCUSSIONS

4.1 STRUCTURE BY X-RAY DIFFRACTION AND RIETVELD ANALYSIS:

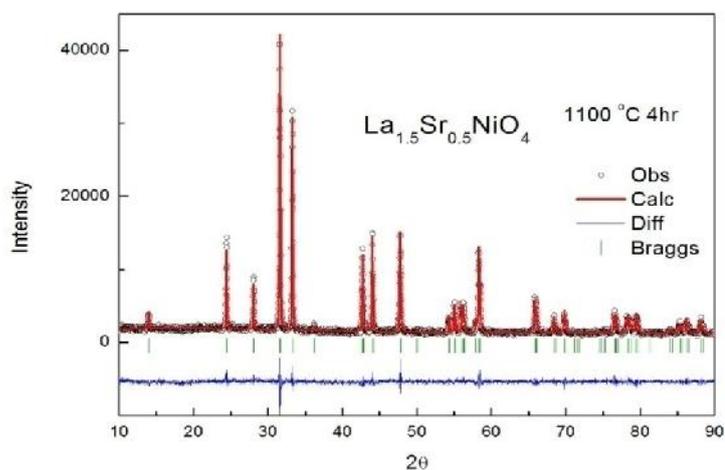


Fig 4.1(a)

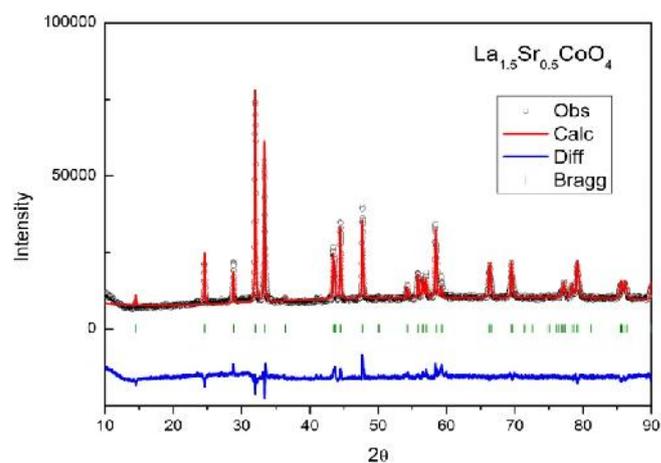


Fig 4.1(b)

The figure 4.1(a) and figure 4.1(b) represents the XRD data and Rietveld analysis of nickelate and cobaltate respectively. From this we can see the samples are in single phase tetragonal structure with space group $I4/mmm$ and stoichiometric. For Nickelate, we have used parameters,

ATOMS	X	Y	Z
La	0.0000	0.0000	0.3615
Sr	0.0000	0.0000	0.3615
Ni	0.0000	0.0000	0.0000
O ₁	0.0000	0.0000	0.1707
O ₂	0.5000	0.0000	0.0000

$a=3.81356, b=3.81356, c=12.72823$

$R_p= 32.3, R_{wp}= 24.3, R_e= 5.34, \chi^2=2.11,$

Bragg R-factor= 5.92, R_f factor= 5.30

For Cobaltate, we have used structural parameters,

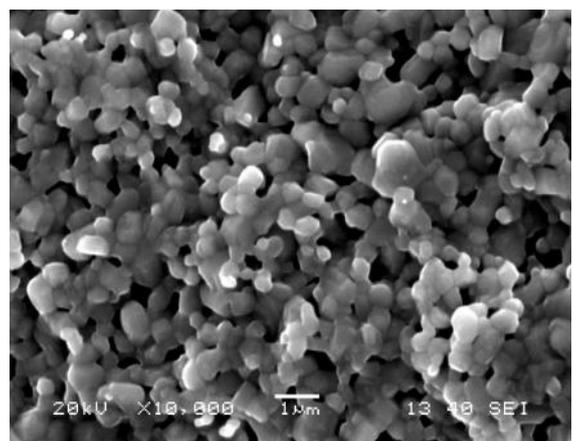
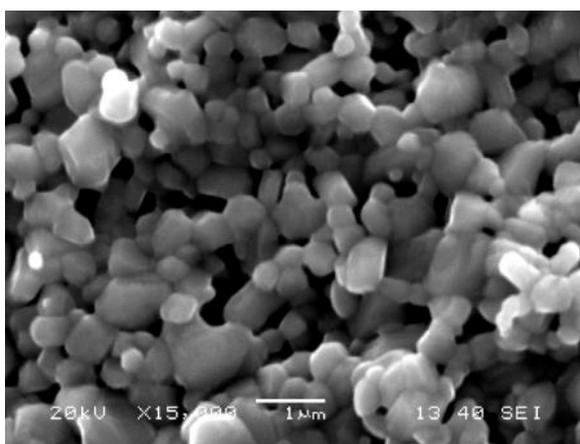
ATOMS	X	Y	Z
La	0.0000	0.0000	0.3618
Sr	0.0000	0.0000	0.3618
Co	0.0000	0.0000	0.0000
O ₁	0.0000	0.0000	0.1685
O ₂	0.5000	0.0000	0.0000

$a=3.81356, b=3.81356, c=12.72823$

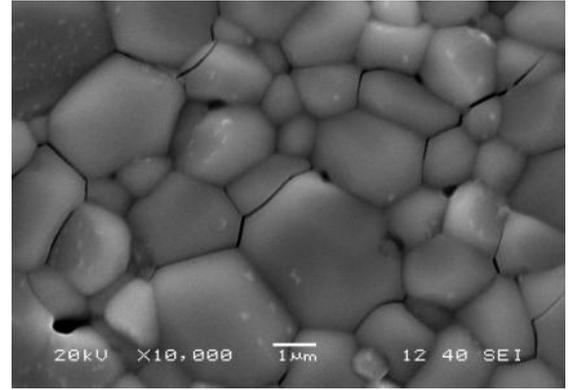
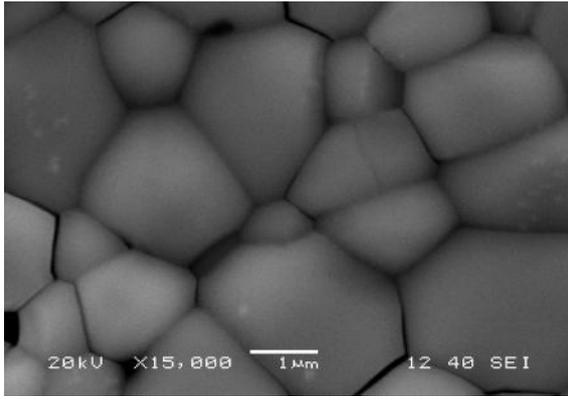
$R_p= 43.6, R_{wp}= 28.3, R_e= 4.04, \chi^2=1.92,$

Bragg R-factor= 8.92, R_f factor= 7.80

4.2 SEM:



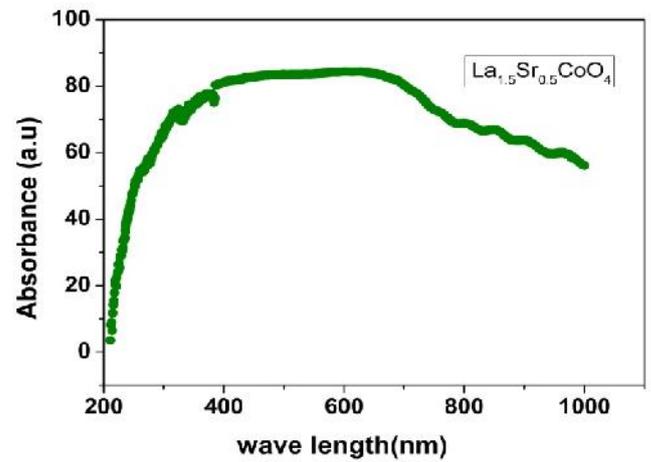
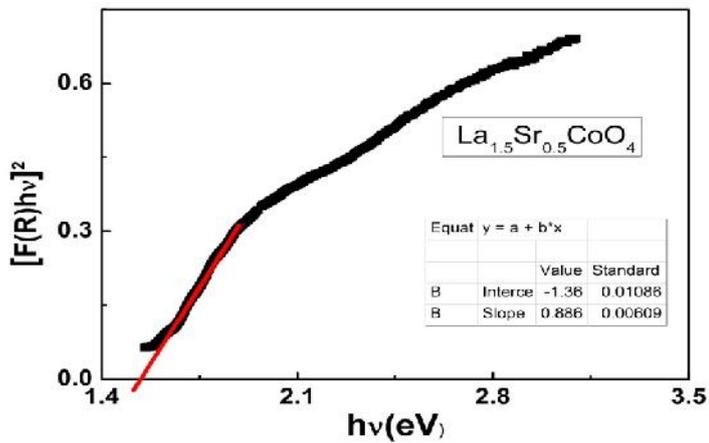
(fig 4.2(a))



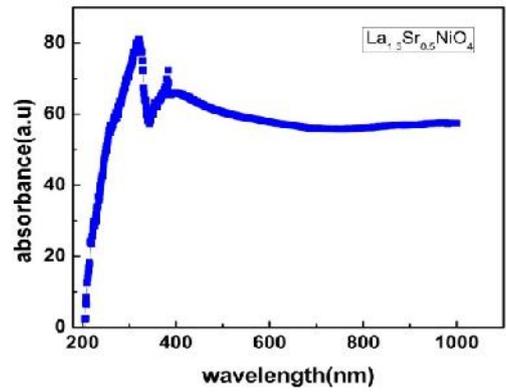
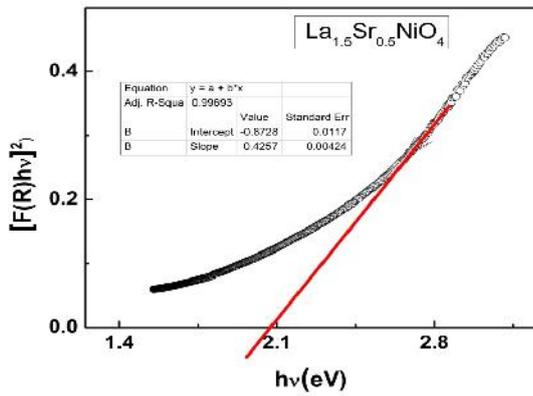
(fig 4.2(b))

The SEM microscopy image of Nickelate and Cobaltate is obtained. The Figure 4.2(a) represents the SEM image of Nickelate and figure 4.2(b) represents the SEM image of Cobaltate at different magnification. From the image 4.2(a) it is observed that the average grain size of Nickelate is .563µm and from 4.2(b), average grain size of cobaltate is 2.302µm.

4.3 UV-VIS SPECTROSCOPY:



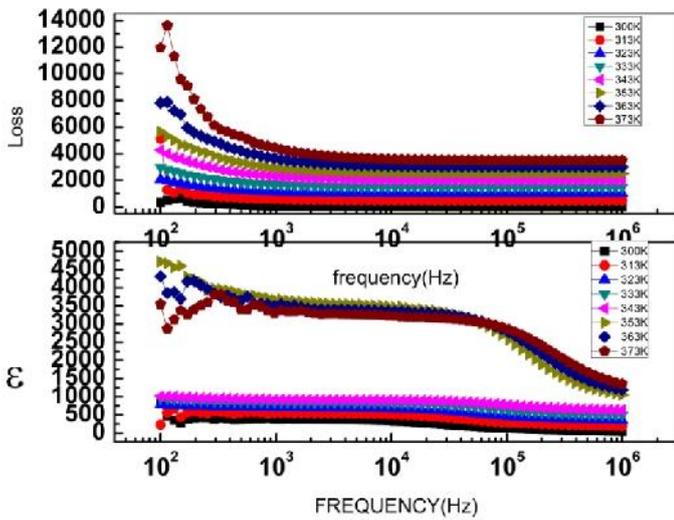
(fig 4.3(a))



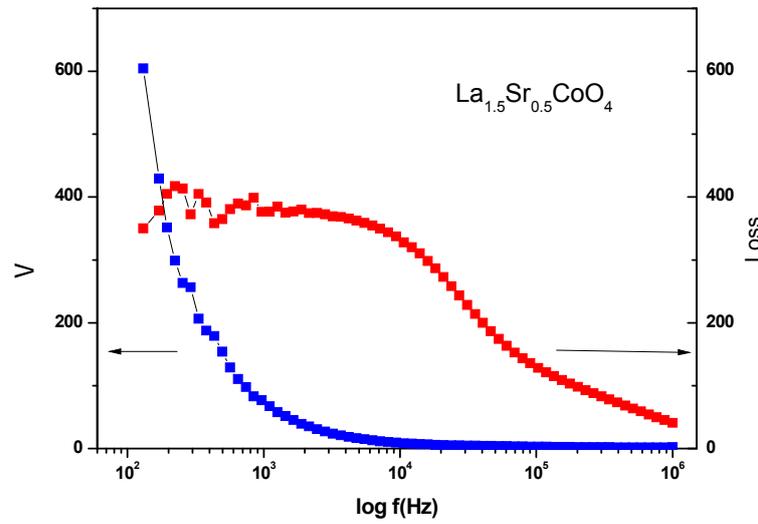
(fig. 4.3 (b))

The figure 4.3(a) figure 4.3(b) represents the UV visible absorption spectra for Cobaltate and Nickelate respectively. The direct band gap energy E_g was determined by fitting absorption data to direct transition equation $(h F(R))^2 = A(h - E_g)$. The extrapolation of the linear portion of curve towards absorption gives E_g for the direct transition. The value of E_g is found to be 2.06ev for Nickelate and 1.53ev for Cobaltate which shows the Semiconductive property of samples.

4.4 DIELECTRIC STUDIES:



(fig 4.4(a))



(fig 4.4(b))

(cobaltate)

The dielectric study of the Cobaltate was done at room temperature and at different frequency.

5 CONCLUSION AND SCOPE OF FUTURE WORK

The effect when an alkali metal like Sr is doped at rare earth material site like La is studied with details structural, image, band gap measurement and dielectric studies. The samples are prepared by Sol-gel method. The structural analysis of samples is carried out by details Rietveld analysis of XRD data which shows samples are in single phase. The sizes and granular information are probed by SEM analysis. The band gaps of the samples are measured by UV VIS spectroscopy method which proves these are semiconducting in nature. Next the dielectric measurement is done of both the samples and results are discussed.

There are several scopes that have been opened in this area. The magnetic behavior of the samples can be studied in details. We can also use different rare earth materials in order to find the effect of those on sample properties. One can also try to study the property in details of different form of material like thin film or nano material.

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