STRUCTURAL, OPTICAL, DIELECTRIC AND MAGNETO-DIELECTRIC STUDIES ON PURE AND DOPED PrFeO₃

M.Sc. Thesis

By

Anil Kumar



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STRUCTURAL, OPTICAL, DIELECTRIC AND MAGNETO-DIELECTRIC STUDIES ON PURE AND DOPED PrFeO₃

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

of Master of Science

By

Anil Kumar



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2017



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**Structural**, **Optical**, **Dielectric and Magneto-dielectric properties of pure and doped PrFeO**₃" in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF PHYSICS**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2015 to June 2017 under the supervision of Dr. P. R. Sagdeo. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date (ANIL KUMAR)

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Convener, DPGC Date:

Signature of PSPC Member #1 Date: Signature of PSPC Member #2 Date:

Dedicated To

My Parents

And Teachers

List of Publications

Anil Kumar, Kamal Warshi, Vikash Mishra, Shailendra K. Saxena, Rajesh Kumar and Pankaj R. Sagdeo*. "*Strain control of Urbach energy in Cr doped PrFeO*₃" (under reviewJournal of Materials Science: Materials in Electronics (JMSE)

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<u>Abstract</u>

Searching for new materials has become important from the view point of both fundamental research and practical applications. Due to their unique properties of multifunctional materials (RFeO₃) have been strongly attractive candidates due to their potential applications and interesting physics. PrFeO₃ exhibits room temperature (RT) orthorhombic crystal symmetry with *Pnma* space group and it undergoes through various structural phase transformations under different temperature and pressure conditions. However, it might be possible after, transition metal (TM) ion doped compound may have different potential scopes which have not been explored so far. Both research and industry have been widely studied these type material due to their diverse physical properties and technological applications. The unique properties of perovskite ferrite (PrFeO₃) have been strongly attractive candidates due to high dielectric constant and its possible proposed application in spintronic devices and magneto-optical properties. Modern optical spectroscopy is known to probe the electronic structure of various transition metal oxides. Keeping in view the potentials of modern optical spectroscopy, in the present thesis work we aim to investigate the optical property and dielectric properties of prepared oxides as a function of temperature and for different-2 Cr atomic concentrations doped to PrFeO₃ to probe the temperature dependent of electronic structure. The purity of structural phase of all prepared polycrystalline PrFeO₃ samples has been confirmed through X-ray diffraction (XRD) experiments by refining the XRD data with the help of Fullprof Rietveld refinement package. The band gap for all presently studied samples is determined through diffuse reflectance spectroscopy (DRS) based on the formalism of Kubelka-Munk function and Tauc's relation. Due to difference in the ionic radius and difference in electronegativity of Cr⁺³ and Fe⁺³ it is expected that with Cr doping in PrFeO₃ may lead to variation in lattice parameters and consequently variation in band gap. The variation of band gap with temperature

follows the varshni's relations that have been confirmed by temperature dependent diffuse reflectance spectroscopy. The variation of Urbach energy (Eu) for all samples for different-2 Cr percentages and as a function of temperature has been studied. There is a significant increase in Urbach energy with increase in temperature and on incorporation of impurities. In addition to this dielectric characterization has been done at room temperature and at low temperature range. The variation of dielectric constant and dielectric loss with Cr doping to $PrFeO_3$ is observed at room temperature, further these variation's with temperature is also studied in the present work.

Key Words: Crystal structure; Perovskite; Dielectric Properties; Magneto-dielectric Properties; Diffuse Reflectance; impedance spectroscopy; Scanning electron microscopy (SEM); Urbach energy; Optical spectroscopy; Structural disorder; Thermal disorder; X-ray diffraction (XRD).

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Abbreviation

| Room Temperature | RT |
|----------------------------------|--------------|
| Magneto-dielectric | MD |
| Magneto-electric | ME |
| Absorption | F(R) |
| Full Width Half Maxima | FWHM |
| Dielectric constant | ε' |
| Loss tangent | tan s |
| Impedance spectroscopy | IS |
| X-Ray diffraction | XRD |
| Transition metal | TM |
| Ferromagnetic | FM |
| Paramagnetic | PM |
| Anti ferromagnetic | AFM |
| Ferroelectric | FE |
| Scanning Electron Microscopy | SEM |
| Magneto-dielectric | MD |
| Urbach energy | Eu |
| PrFeO ₃ | PFO |
| Energy dispersive x-ray analysis | EDAX |
| Absorption coefficient | F(R) |
| Diffuse reflectance spectroscopy | DRS |

CHAPTER 1

Introduction and Origin of the Problem

Gustav Rose discovered CaTiO₃ in the Ural Mountains in 1839 and named it Perovskite after the great Russian mineralogist, Count Lev Alexevich Von Perovski. The general chemical formula for Perovskite structure is ABO₃ with type structure A representing cations present on the corners of the unit cell, B represents central cation present on the body centre and O as Oxygen (anions) present on the centre of each face of the unit cell. So we can define the perovskite structure as one that has the same configuration of the same type of crystal structure of calcium titanium oxide (CaTiO₃)^[1]. These types of materials are important from research point of view due to their diverse physical properties and technological applications ^[2]. Due to their unique properties of perovskite ferrite (RFeO₃) have been strongly attractive candidates due to high dielectric constant and its possible proposed application in spintronic devices ^[3–5] and magneto-optical properties ^[6,7].

Further perovskite ferrite (RFeO₃) will also be probe for magnetodielectric/multi-ferroic applications^[8,9]. From last two decades the research community worldwide trying to understand the coupling of electric and magnetic dipoles in multi-ferroic and magneto-dielectric system as these materials are proposed as the potential candidate for new generation of electronic devices. In this connection the efforts are being made to induce the ferromagnetism in high dielectric constant materials by doping or to search for natural systems possess such coupling. If such kind of coupling present in any system then by application of external magnetic field it is now possible to control the ferroelectric polarization and vice versa. The mutual control on the electric and magnetic polarization is called magneto-dielectric effect ^[10]. Presently the candidate materials in this category are limited and show the magneto-dielectric response either at very high value of magnetic field or at low temperatures which limits the practical application of such device. For example $TbMnO_3$ M.E. effect was observed at 23K, in CuO observed at 230K. Recently we have demonstrated the magneto-dielectric effect at room temperature in Mn doped LaGaO₃^[11].

Modern optical spectroscopy is known to probe the electronic structure of various transition metal oxides ^[12–14]. Keeping in view the potentials of modern optical spectroscopy, in the present thesis work we aim to investigate the optical property and dielectric properties of prepared transition metal oxides as a function of temperature and for different-2 Cr atomic concentrations doped to $PrFeO_3$ to probe the temperature dependent of electronic structure and also to probe the phase transition if any present in the samples.

Hence in order to understand the variation of band gap and Urbach energy as a function of temperature is of scientific and technological interest^[15,16]. From last decade various researchers have used the optical spectroscopy to probe the electronic structure of various transition metal oxides and the said optical spectroscopy is known for its potential to probe electronic disorder (thermal, polar, chemical, structural and due to defects etc.) present in the sample^[12–14].

The major contribution in Urbach energy is from various kind of disorders present in the system and the said energy increases if disorder in the system increases^[17]. The effect of temperature on Urbach energy can be easily understood by disturbance in periodicity in crystal with temperature or atoms will oscillates with higher and higher amplitudes so uncertainty in spatial arrangement of atoms increases with temperatures which increases the disorder in crystals, which further contributes to increase of Urbach energy^[18].

In the present work it has been observed that Urbach energy which is a measure of various disorders present in the system be small enough for pure un-doped system ($PrFeO_3$ in present case) and scales up with temperature and on incorporation of doping (chromium in present case), which may be due to structural disorder induced by doping.

(Possibly due to difference in the ionic radii of parent ion and dopant, lattice strain is induced).

Further room temperature dielectric study and temperature dependent dielectric study of $PrFeO_3$ on incorporation of Mn is already reported in Khalid et. al.^[19] which suggests that dielectric constant of $PrFeO_3$ increases after addition of Mn and with low dielectric loss (tan- δ) value.

Further due to difference in the ionic radius and difference in electronegativity of Cr^{+3} and Fe^{+3} it is expected that with Cr doping in PrFeO₃ may lead to variation in lattice parameters and consequently variation in band gap^[20]. Thus the PrFeO₃ appears to be the potential material for various electronic applications.

Keeping this in view in the present studies we have prepared

 $PrFe_{1-x}Cr_xO_3$ by sol gel method and studied its structural, optical dielectric and magneto-dielectric properties at room temperature. For detailed characterization of prepared samples SEM (Scanning electron Microscopy), EDAX (Energy dispersive x-ray analysis) and elemental mapping have been performed to study the morphology, chemical composition and homogeneity of the synthesized samples respectively. In the following section we have briefly discussed the important concepts related to the present work.

1.1 Magneto-electrics and Multiferroicity:

The classification of materials under investigation typically involves terms such as 'Multiferroic' and 'magneto-dielectric' whose overlap is shown in **figure-1.2.** Multiferroics and magneto-electrics involve both ferroelectric and magnetic properties of matter, so it has attracted researchers from both backgrounds: magnetism and ferro-electricity. Multiferroic materials are those materials which exhibit either two or three different ferroic orders at the same time: ferromagnetism, ferroelectricity and ferroelasticity. The materials possess the above said coupling are the part of the highly correlated electron system. In highly correlated electron system the charge, spin and lattice degree of freedoms and interactions between them critically controls the various properties of a given material. Thus by application of external magnetic field it is now possible to control the ferroelectric and magnetic polarization is called magneto-dielectric effect^[54].

Hall effect observed in most of the non-magnetic semiconductors (such as Si and Ge etc.) may be best example of magneto-electric effect. Magneto-electric coupling may arise directly due to the coupling between the two or more force ferroic orders (local electric, magnetic or strain field) present intrinsically in sample or due to coupling between internal force field and external perturbations.



Figure-1.1: Schematic diagram of multiferroics and magnetodielectrics^[54].

1.2 The Urbach tail

The character of the localised states observed in between the valance band and conduction band in optical spectroscopy for disordered semiconductors is a problem of importance with a history dating back to the fifties. It has been understood that band tail states in amorphous semiconductors arise due to the thermal disorder, This tail varies exponentially into the band gap. This exponential variation in absorption coefficient along the absorption band edge is a well-known universal feature in optical properties. The universal phenomena have been observed in all imperfect crystalline solids and amorphous solids.

Absorption coefficient (α) for Urbach tails can be written as^[21]:

$$\alpha(E,T) = \alpha' \exp \left[\sigma\left(\frac{E-E'}{KT}\right)\right] \quad \dots \quad (1)$$

Where E' and α' are constants determined by extrapolated linearly from $\ln(\alpha)$ Versus E curves at a given temperature T.

This exponential variation of absorption coefficient near the band edges was firstly observed by Urbach in 1953 in studying the optical properties of indirect band gap silver halides. Urbach described this exponential behaviour in the following form^[22]:

$$S = \frac{\partial (\ln(K))}{\partial (h\nu)} = -1/kT \qquad (1.1)$$

Where S is slope of exponent, K is absorption coefficient, hv is photon energy and k is Boltzmann's constant.

It was clear from equation given by Urbach that S has only temperature dependence and has no reliance on material properties. But experimentally it was observed that slope of exponent is a property of material as well as a function of temperature. Further Martienssen redefine the Urbach rule and wrote the same in following form ^[21]:

$$\alpha(E,T) = \alpha' \exp[\sigma\left(\frac{E-E'}{KT}\right)] \quad \dots \quad (1.2)$$

Hence behavior of α is referred in literature as **Urbach-Martienssen's** rule. It is observed that that the E_U scales up with temperature (thermal energy induces structural disorder) as the structural disorder (random vibrations) scales with temperature. Thus it appears that the scaling of Urbach energy may have the similar functional form as that of temperature^[14].

$$Eu = \frac{hv}{2\sigma'} coth(\frac{hv}{2kT}) - \dots - (1.3)$$

Here σ' is a temperature-independent constant proposed to be inversely proportional to the exciton-phonon interaction strength. The energy parameter hv is considered to be the energy of phonons involved in the formation of photon absorption edge.



Figure-1.2: Represents the exponential variation of absorption coefficient curve near band edge.

1.3 Origin of Urbach tail

The origin of Urbach tail is various kinds of disorders that are present in all crystals, either these disorders are due to temperature, chemical composition or various defects present in the crystal^[17,18,23]. From band theory of solids we know that electron is moving in periodically varying potential having period equal to lattice constant. Due to temperature variation or incorporation of impurities spatial arrangement of atoms gets disturbed (periodicity gets disturbed) and electron feels a potential which differ from place to place. Due to this variation of potential edges of valance band and conduction band gets blur i.e. localises states are formed in the form of tail in between the valance band and conduction band. This tail also arises because of various kinds of defects, structural coherency, chemical inhomogeneity etc. and due to presence of these disorders the valence band and conduction band do not have sharp cut off but have localized tails states, due to these localised states density of states distribution changes and optical absorption edge is not fall sharp and has exponential variation near the band edge. When we make Tauc plot we do not get straight line in the whole energy range.



Figure-1.3: Shows localised state formation in between the valance band and Conduction band.

Role of various factors affecting the Urbach tail

In the following section we will briefly discuss the role of temperature and structural disorders on the Urbach tail. As in our earlier discussion we discussed the effect of temperature i.e. temperature increases the lattice vibrations^[18] and changes the periodicity (spatial arrangement of atoms) which give rise the localised states formation in the form of tail in between the valance band and conduction band.



Figure-1.4 Shows the strain field generated by dopant atom.

Contribution of structural disorder to Urbach tail can be intrinsic (vacancies or dislocations) or be induced by external factors (deviation from stoichiometry, doping, ion implantation). These intrinsic and extrinsic factors contribute to formation of localized states in between the valance band and conduction band. Disordering due to composition arises due to non-homogenous distribution of dopant atoms.

1.4 Band-gap

The term "band gap" refers to the energy difference between the top of the valence band and the bottom of the conduction band. However for electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition. The required energy differs for different materials as every solid has its own characteristic energy-band structure. This variation in band structure is responsible for the wide range of electrical characteristics observed in various materials.



Figure-1.5 Band structure of solids.

The formation of bands is due to that an electron in a crystal moves in a region of periodically varying potential rather than one of constant potential. As a result diffraction effects occur that limit the electron to certain ranges of momenta that correspond to allowed energy bands. On the basis of band gap we can classified the solids in three different categories; insulator, conductor and semi-conductor.



Figure-1.6 Band diagram of different solids.

In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap^[38] as shown in **figure-1.6.**

1.5 Structure of PrFeO₃

Praseodymium ferrite (PrFeO₃) is ABO₃ type perovskite^[24,55] structure material, in which A and B are cations and O⁻ is an anion. All these anions are present at the centre of each faces and all of them are equidistant from the central atom (B-cation) which forms a Centro-symmetric octahedron around B- cation. Due to that reason, there is no net dipole moment found in the material. But once their symmetry is broken a net dipole moment arises and hence ferro-electricity (FE) may be induced in the sample. The resulting electric dipole is responsible for the property of ferro-electricity and shown by perovskite such as BaTiO₃ that distort in this fashion.



Figure-1.7 Perovskite Structure^[55].



1.6 Dielectric properties

The dielectric behaviour usually refers to the variation of the properties (dielectric constant, dielectric loss, a.c. conductivity, and other similar properties) with frequency of applied electric field, temperature, voltage an composition. In Dielectric measurements we basically analyse two fundamental characteristics of materials (1) capacitive (insulating) nature, which represents its ability to store electric charge (2) conducting nature which represents its ability to transfer electric charge. By calculating the capacitance of the sample and its conductivity dielectric constant and dielectric loss of a material can be determined respectively.

Dielectric constant results from four types of polarization are named as interfacial, dipolar, ionic, and electronic polarization contributions^[25].

Interfacial polarization

The sharp variation in the dielectric constant at very low frequencies is due to interfacial (space charge) polarization. The space-charge polarization occurs due to the diffusion of ions, present on the grain boundary along the field direction, thereby giving rise to redistribution of charges in the dielectrics. This usually happens at the grain boundaries or any other interface such as electrode-material interface.



Figure-1.8 (a) dielectric without field and (b) dielectric with electric field.

Dipolar polarization

The dipolar polarization is also known as orientation polarization. This polarization is important only in materials which contain permanent dipole moments, but due to the thermal agitation dipole's present in material are oriented randomly, therefore dipole moments of these dipoles cancels out resulting in a net dipole moment to be zero. On the application of electric field these dipoles align themselves in the direction of field leading to net dipole moment. The extent of this polarization depends on two factors:

- (1). Strength of applied field.
- (2). Thermal energy which randomize the dipoles.



Figure-1.9 (a) Shows randomly oriented dipoles without electric field, (b) Shows systematic alignment of dipoles on application of electric field.

Ionic polarization

Ionic polarization arises due to the displacement of -ve ions and + ve ions in opposite directions and it occurs in ionic solids, in the presence of electric field. The cations are displaced parallel to the field and anions are displaced in direction opposite to the field.

In absence of electric field E, the distance between the ions is d but in presence of electric field, distance between the ions increases which signifies a change in the net dipole moment. The displacement of ions on application of electric field is independent of temperature.



Figure-1.10 Shows the increase in the distance between ions on application of electric field.

Electronic polarization

Electronic Polarization occurs due to the displacement of positively charged nucleus and negatively charged electrons in opposite directions, when an external electric field is applied, and thereby a dipole moment is created in the dielectric. Electronic polarization has the major contribution in materials such as diamond, SiO_2 in which other effects are absent. The dipolar and ionic contribution are small at higher frequencies because of the inertia of the ions and molecules.



Figure-1.11 Shows position of +ve and -ve charges in an atom without field.



Figure-1.12 Shows position of +ve and -ve charges in an atom with field.

1.7 Frequency dependence of dielectric constant

Among the four types of polarizations^[25] the electronic polarization exist up to very high frequencies even up to 10^{15} Hz as it involves the displacement of the electron with respect to nucleus. Ionic polarization exists up to at lower frequencies (app. 10^{13} Hz) than electronic polarisation as it involves the displacement of ions, which are much heavier as compared to electron cloud. Orientation polarization exists up to lower frequencies than ionic polarisation due to inertia of dipoles. This type of polarization occurs only when the frequency of applied voltage is below the microwave frequency range (app. 10^{8} Hz).



Figure-1.14 Shows the variation of dielectric constant with frequencies.

Space charge polarization involves the diffusion of ions so it is the slowest process and occurs at lower frequency range (app. 50-60 Hz). Above this low frequency range the contribution to total polarization is from ionic, electronic and dipolar polarizations as shown in **figure-1.14**. From above discussion it is clear that sharp variation in the dielectric constant at low frequencies is due to space charge and dipolar polarizations. Ionic and electronic polarization is responsible for dielectric constant developed at higher frequencies and independent of temperature. Due to this reason temperature dependence of dielectric constant at higher frequencies is of little significance. The contribution to dielectric constant at low frequencies whereas at high frequencies grain contribution is dominant.

CHAPTER 2

Experimental Techniques

In this chapter we will discuss some of the experimental techniques that we have used in this project work these techniques includes

Sample Preparation Process

- 2.1 Characterization Techniques
 - (a) X- Ray Diffraction (XRD)
 - (b) Scanning electron microscopy (SEM)
 - (c) Diffuse Reflectance Spectroscopy (DRS)
 - (d) Impedance Spectroscopy (IS)

2.1 Sample preparation process

2.1.1 Solid State Reaction Method

We have prepared PrGaO₃, NdGaO₃, Fe-doped PrGaO₃ and Fe doped NdGaO₃ by conventional solid state reaction method by mixing the constituents powder oxides in their proper stoichiometry of which calculation is given below. Solid-state reaction route is the most common technique for the preparation of polycrystalline samples. In this method, very fine powders which usually do not react at room temperature are used as starting materials. Hence these powders are heated at much higher temperatures (800°C to 1600°C). The reaction may be written in the following form.

$$\Pr_{6}O_{11}+(1-x)Ga_{2}O_{3}+(x)Fe_{3}O_{4} \xrightarrow{Heat at 1350^{\circ}C} \Pr_{6}Ga_{1-x}Fe_{x}O_{3}$$

Atomic weights of $Pr_6O_{11}=1021.4396g$ Atomic weights of $Ga_2O_3=187.4442g$ Atomic weights of $Fe_3O_4=231.5386g$ Atomic weights of $PrGa_{1-x}Fe_xO_3=140.9077+69.723*(1-x)+55.847*x+47.9982$ For example x=0.05, then weight of

 $PrGa_{0.95}Fe_{0.05}O_3 = 140.9077 + 69.723 \times 0.95 + 55.847 \times 0.05 + 47.99$ = 257.931g

Weight (gm) of Pr_6O_{11} for 1 mole of $PrGa_{0.95}Fe_{0.05}O_3 =$

1021.4396/6=170.23993

Weight (gm) of Ga_2O_3 for 1 mole of $PrGa_{0.95}Fe_{0.05}O_3 = (187.4442/2)*0.95=89.03599$

Weight (gm) of Fe_3O_4 for 1 mole of $PrGa_{0.95}Fe_{0.05}O_3 =$ (231.5386/3)*0.05=3.85897

Now the weight of Pr_6O_{11} for 1 gm of =170.23993/257.9351=0.66001g

Similarly the weight of Ga_2O_3 for 1 gm of $PrGa_{0.95}Fe_{0.05}O_3$ =89.03599/257.9351=0.32192g

And the weight of Fe_3O_4 for 1 gm of $PrGa_{0.95}Fe_{0.05}O_3$ =3.85897/257.9351 =0.01496g

After weighing these oxides we have used the following steps to prepare samples:

- a) Mix the oxides and grind it by using Agate mortar and pestle in Iso-Propyl Alcohol (IPA) for 4-5 hours.
- b) Then heat the sample in furnace at 1000°C for 24 hours with a controlled heating rate of 5° per minute.
- c) After 24 hours cool the sample up to 300°C with a cooling rate of 1° per minute, after that cool the sample naturally up to room temperature after switching off the furnace.
- d) Repeat the steps (a) to (c) for second heating at 1250° C.
- e) After that the circular pellets of 1 mm thickness and about13 mm diameter (by using almost half quantity of

corresponding powder sample) were prepared by applying a high pressure by means of hydraulic pressure pelletizer.

 f) These prepared pellets and powdered samples have been sintered separately in air at 1350°C for 24 hours.

2.1.2 Material Synthesis technique Sol-Gel Method

Sol is a colloidal or molecular suspension of solid particles of ions in a solvent

Gel is a semi-rigid mass that forms when the solvent from the sol evaporates and the rigid mass left behind begin to join together in a continuous linkage.

The reaction may be written in the following form

 $Pr(NO_{3})_{3}.6H_{2}O+(1-x)Fe(NO_{3})_{3}.9H_{2}O+(x)Cr(NO_{3})_{3}.9H_{2}O+C_{6}H_{8}O_{7}+C_{2}H_{6}O_{2} \longrightarrow PrFe_{1-x}Cr_{x}O_{3}+8CO_{2}+9/2N_{2}+nH_{2}O$

We have prepared Chromium doped PFO samples via sol gel reaction route using citric acid as a chelating agent and ethylene glycol as a fuel which helps in hydrolysis process and gel formation.

In this method firstly metal nitrates were dissolved in excess of water to form stable metal chelate complex then 1 mole of citric acid per mole of metals ions is used which acts as a chelating agent.

Then after the addition of small amount of ethylene glycol the resulting sol was heated at constant temperature 70° C with a constant stirring rate until a gel is formed. This gel were dried in furnaces at 100° C and then grinded in agate mortar and heated in the air at 400° C for 4 hours with constant heating rate of 5° C/min and constant cooling rate 1° C/min. Then again grinding in agate mortar the powder was heated to 700° C for 12 hours at constant heating and cooling rates.
2.2 Characterization Techniques

2.2.1 X-Ray Diffraction (XRD)

X-ray diffraction is a very important technique that is used to get information of crystallite size, lattice parameters, lattice strain, chemical composition, state of ordering, spacing between two crystal planes structure of the sample etc.^[43]

The working principle of X-ray diffractometer is as follows:

The filament inside the cathode tube is heated by applying the voltage between the two electrodes. As the filament gets heated then the free electrons are travelling from cathode to anode with higher velocity and finally strike to the anode surface, this results the formation of X-Rays in the X-ray tube. These X-ray originated from the tube falls on the surface of the sample. As the wavelength of these originated X-rays has wavelength is of order of the lattice parameter which results the diffraction of X-rays in the different direction by continuous change in intensity with the incident angle. The intensity of these X-rays diffracted peaks depends on the electron density across that miller plane. So intensity distribution is varying with the angle between incidence and diffracted beam. By knowing those plane we can calculated the structure of sample, composition of the crystal, spacing between two planes, and lattice constant etc. The X-ray diffraction technique is basically based on the principle of Bragg's law.



Figure-2.1 Diffraction of X-ray by a crystal.

Path difference= $2dSin\theta = n\lambda$, where n is an integer

For the constructive interference the path difference should be integer multiple of wavelength λ . So the Bragg's condition for constructive interference, $2dSin\theta=n\lambda$, where n is an integer.

Whenever this condition is satisfied a diffraction peak will occur in diffraction pattern. So Bragg's law states that only for the angle θ satisfying Brag's law $2d\sin\theta = \lambda$ there is constructive interference. For all other angles, the intensity of peaks should cancels out.

2.2.2 Scherrer formula

In ideal and perfectly ordered crystals there is a periodic arrangement of all atoms and when Bragg condition is satisfied diffraction peaks would be observed. These Bragg peaks would be very narrow ideally point like. But the real crystals grown in laboratory are not perfect due to **Mosaic effect** and various kinds of disorders, (micro strain, macro strain, dislocation and vacancy). Mosaic effect states that a crystal always consists of mosaic blocks that are misaligned in relation to the idealized lattice by typically 0.3 degree's. This mosacity is responsible for the width of reflection of diffraction peaks. So we can also define mosacity in terms of (FWHM) Full width half maxima of diffraction peaks.

Second most reason for peak broadening is incorporation of impurities during the growth of the crystals which will produce the micro strain in the samples. Instead to these entire effects XRD peak broadening is also a function of crystallite size. For large sized grains diffraction peaks are very sharp and vice versa.

Thus Broadening is typically calculated as full width at half maximum (FWHM). The relation between the broadening of the X-ray peak β' is related to the size of the crystallite *L* is given by the **Scherrer formula**

 $L = 0.9\lambda / \beta' \cos\theta_B$ -----(2), where θ_B is the Bragg angle. From equation (2) it is clear that smaller the crystallite size greater is the broadening of the diffraction peak and vice versa.

2.2.3 Williamson-Hall Plot

This method was given by G.K. Williamson and W.H. Hall. It is based on the principle that the broadening of the diffraction peaks is a due to size broadening (β') and strain broadening (β_e). The relation between the broadening of the X-ray peak β' is related to the size of the crystallite *L* is given in eq. (2.2). Strain broadening is given by eq. (2.1)^[43]

$$\beta e = n' tan \theta -----(2.1)$$
$$\beta' = \frac{\kappa \lambda}{Lcos \theta} -----(2.2)$$

The contribution due to the size broadening varies as $1/\cos\theta$ and the strain contribution varies as $\tan\theta$. Williamson and Hall assume that if both contributions in broadening are present in the samples then by convolution total broadening is a simple sum of these two broadenings, then we get:

$$\beta = \beta e + \beta' = \frac{\kappa \lambda}{L \cos \theta} + n' tan \theta$$
-----(2.3)

where β is total broadening due to strain and crystallite size contribution

Now on multiplying the eq. (2.3) by $\cos\theta$ then we get:

$$\beta \cos \theta = \frac{\kappa \lambda}{L \cos \theta} + n' \sin \theta - (2.4)$$

on comparing the eq. (2.4) to general equation of straight line we can easily obtained strain component from plot of $\beta \cos\theta$ versus $\sin\theta$ and crystallite size component from the intercept ($\mathbf{K}\lambda/L$). Such a plot is known as a Williamson-Hall plot and is illustrated schematically in **figure-2.2**.



Figure-2.2 Shows systematically representation of Williamson-Hall plot.

2.3 Microscopy

Microscopy is the technical field of using microscopes to view magnified images of objects that cannot be seen with the naked eye or we can say microscopes are useful to see those objects that are not within the resolution range of the normal eye. There are three well-known branches of microscopy: optical, electron, and scanning probe microscopy.



Figure-2.3 Shows the magnified image of object

[https://emlab.umaine-biology.org/]

2.3.1 Light vs electron microscopy

The biggest advantage of electron microscopy is that electron microscopy has a higher resolution and is therefore also able of a higher magnification up to 2 million times. In Light microscopes can show a useful magnification only up to 1000-2000 times. This is a physical limit imposed by the wavelength of the light. Electron microscopes therefore allow for the visualization of structures that would normally be not visible by optical microscopy.

In scanning electron microscopy (SEM), due to the nature of electrons, electron microscopes have a greater depth of field compared to light microscopes. The higher resolution may also give the human eye the subjective impression of a higher depth of field.

2.3.2 SEM (Scanning Electron Microscopy)

The first electron microscope was constructed in 1931. The scanning electron microscope (SEM) is a type of electron microscope that uses a focused beam of high-energy electrons in producing a variety of signals at the surface of a solid specimen. These high energy electrons interact with the electron of the samples to produce the secondary electrons and some electrons gets back scattered from sample. The signals produced by these secondary electrons contain useful information such as the surface morphology, chemical composition atomic structure etc. When a electron beam is incident on the sample surface, it may be reflected, absorbed, or conducted away. The electrons that are absorbed by the sample can interact with atoms of the sample and become it unstable, force it to eject secondary electron. These secondary electrons and backscattered electrons contain very useful information. Secondary electrons are most valuable for knowing the morphology and topology of the samples and back-scattered electrons are most valuable for getting the chemical composition in multiphase samples. Different type of detectors is used, depending on what is being looked for. Due to the higher resolution of the SEM so

closely spaced specimens can be magnified to very large extent. This magnification to such a large level is possible due to use of electromagnets rather than lenses, as more precise focussing of electrons is possible by electromagnets. All of these advantages make the scanning electron microscope one of the most useful instruments in research today.

Principal and working

The process initiates with an electron gun which generates a beam of high energy electrons passes through a series of electromagnetic lenses. These electromagnetic lenses are the tubes, wrapped in coil and referred to as solenoids. These coils focus the incident electron beam on the sample. The electron beam is affected by air and water molecules, so the sample must be placed in a vacuum.



Figure-2.4 Shows systematic diagram of the SEM.

The sample must also be conductive to allow the electrons not reflected or absorbed to be conducted away. This gives some limits on

the type of sample that can be used. Samples first coated with gold/copper before they can be placed in the scanning electron microscope. This is done in order to preserve the sample and keep it from changing or decaying throughout the scanning process. When the incident high energy electron beam is incident on the sample energetic electrons (secondary and backscattered electrons) are released from the surface of the sample. These energetic electrons yield information on size, shape, texture and composition of the sample. X-rays, emitted from depth of the sample surface, can provide element and mineral information. Different types of detectors are used to detect the different types of scattered electrons, including secondary and backscattered electrons as well as x-rays.

2.4 Diffuse Reflectance Spectroscopy (DRS)

UV visible spectroscopy is a spectroscopy ^[20,26] in which in which we study the light absorbed in UV and visible regions of electromagnetic spectrum. DRS is based on the principal of diffused reflection. When light falls on the surface of a powdered sample, it is reflected in specular and non-specular directions through multiple scattering; as shown in figure-2.6. Some part of the light undergoes multiple scattering inside the sample and fraction of this part is emitted back into the detector. Since light cannot penetrate opaque (solid) samples, it is reflected on the surface of the samples. As shown in the figure, incident light scattered in different directions is called "diffuse reflection. When the UV-Visible light falls on the surface of powder sample, this incident light either gets absorbed or reflected (transmission is negligible). Due to the finite absorption coefficient of the sample, as the diffuse reflected light is reflected becomes weaker i.e. loses its intensity and this loss of intensity is a function of absorption coefficient of sample which is function of λ of incident beam. This diffused reflected light is detected by the detector and give a corresponding DRS spectrum.



Figure-2.5 Schematic Diagram of Light Scattering from a powdered sample.

In order to estimate the optical band gap the diffuse reflectance spectra has been converted to equivalent absorption spectra using Kubelka–Munk equation^[20].

$$F(R_{\infty}) = \frac{K}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} - (2.5)$$

 $R\infty = R_{Sample}/R_{Standard}$. R_{Sample} is the diffuse reflectance of the sample and $R_{Standard}$ is that of the standard (as BaSO₄ or white paper) K and S are the Kubelka–Munk absorption and scattering functions, respectively. As we have used powder samples for diffuse reflectance measurements hence the assumption of reflected light scatters in a perfectly diffuse manner holds true, for such case the scattering function S is nearly constant with wavelength and the Kubelka–Munk function can be related/proportional to the absorption coefficient (α) as:

$$F(\mathbf{R}_{\infty}) \propto \alpha \propto \frac{(h\nu - Eg)^{1/n}}{h\nu}$$
-----(2.6)

Here n has the value of 2 for direct band gap transitions, while n is equal to 1/2 for an indirect transition ^[20].

Thus, a plot between $[F(R\infty) \times hv]^n$ versus hv yields a straight line and the intercept on the energy axis gives the value of the band gap.



Figure-2.6 Experimental set up for diffuse reflectance measurement (a) Carry 60 UV-Vis spectrometer, (b) internal set up of 60 UV-Vis spectrometer (c) an integrating sphere attachment to detect diffuse reflectance.

Working

A diffuse reflectance has been measured by an attachment to an UV-VIS spectrometer. Xenon flash lamp is used for producing the UV-VIS spectrum, this spectrum passes through various filters and monochromator and after doing some optical arrangement, finally light is incident on the sample and diffused reflected light is detected by the detector. Experimental set up for diffuse reflectance spectroscopy is shown in **figure-2.6**.

2.4.1 Temperature dependent diffuse reflectance spectroscopy setup

Temperature dependent of diffuse reflectance measurement set up is shown in **figure-2.7.** A sensor is connected to the heater (which provides heat to the samples) which is further connected to the temperature controller to get the sample temperature. UV-VIS spectrum of light passing through optical fibre is incident on the sample and diffused reflected light is detected by the detector at various temperatures of sample.

2.4.1 Temperature dependent diffuse reflectance spectroscopy setup

UV-VIS Spectrometer



Figure-2.7 Experimental set up for temperature dependent diffuse reflectance measurement.

2.5 Impedance Spectroscopy (IS)

Impedance spectroscopy is a measure the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. This technique measures the impedance of a system over a range of frequencies, and therefore the frequency response of the system, including the energy storage and dissipation properties, is revealed.

LCR meter works on the principle of ac bridges, one schematic diagram of ac Bridge is shown in **figure-2.8.** The working principle of circuit is shown below



Figure-2.8 Schematic diagram of series LCR ac bridge.

Applying Kirchoff's voltage law, we obtain:

$$L\frac{d^2Q}{dt^2} + R\frac{dQ}{dt} + \frac{Q}{C} = V_o \sin \omega t$$

Solution of above equation can be given as

$$Q(t) = Q_o \cos(\omega t - \delta)$$

Where, amplitude and phase are respectively,

And
$$\tan \delta = \frac{1}{R} \left(\omega L - \frac{1}{\omega C} \right) = \frac{X_L - X_C}{R} - \dots - (2.8)$$

The corresponding current, $I_t = \frac{dQ}{dt} = I_o \sin(\omega t - \delta)$ ---(2.9)

With an amplitude
$$I_o = -Q_o \omega = -\frac{V_o}{\sqrt{R^2 + (X_L - X_C)^2}} \dots (2.10)$$

The short circuit and open circuit compensations were performed in order to get rid of contributions to the dielectric properties such as impedance, capacitance etc. due to electrodes. We have used the samples in the form of pellet coated with silver on both the side and then measure the dielectric properties by using impedance spectroscopy.

2.5.1 Low Temperature Dielectric Experimental Setup

Figure-2.9 Shows the Schematic diagram of Low Temperature Dielectric Experimental Setup. For low temperature dielectric measurements sample is cooled up to 78 K in liquid nitrogen gas. A sensor is connected to the heater (which provides heat to the samples) which is further connected to the temperature controller to get the sample temperature. By using the lab view based user interface dielectric properties of the samples at various temperatures and frequencies is measured. We have measured the dielectric loss and dielectric constant at different-2 temperatures for frequencies range 20 Hz to 5MHz frequencies and their results are discussed in chapter 3.



Figure-2.9 Schematic diagram Low Temperature Dielectric Experimental Setup.

CHAPTER-3

Results and Discussions

We have prepared the Cr doped $PrFeO_3$ samples for various Cr atomic percentages by sol-gel method and characterized these samples by using experimental techniques discussed in chapter-2 and results are discussed in this chapter.

3.1 Thermo-gravimetric analysis

Thermo-gravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which we study the change in physical and chemical properties of materials as a function of temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA analysis can provide us useful information about physical phenomena like phase sublimation, absorption, phase formation, transition and adsorption.



Figure-3.1 Shows T.G.A. analysis for 1% Cr doped PrFeO3.

Figure-3.1 Shows the TGA curve of precursors of mixed powder. The peaks present in the graph are the signature of loss of water and inorganic residues left during the process of combustion. It is clear from **figure-3.1** that as a function of temperatures various compositions are formed i.e. there is a loss of organic and inorganic

materials with temperatures. After certain temperatures there exist no further weight loss was in the mixture, the same is the minimum temperature required for reaction, i.e. $PrFeO_3$ in present case. The same is also clear through the inset of the figure where derivative of the loss as a function of temperature is plotted.

3.2 Structural studies (XRD)

To confirm the structural phase purity of the samples XRD experiments were carried out on bruker D8 diffract-meter equipped with Cu target. It is clear form figure-3.2 (a) (XRD Of gel form) shows that gel is amorphous in nature and there is completely missing of periodicity. We could get the sharp XRD peaks when sample is treated at 700°C as shown in figure-3.2 (b). Figure-3.2 (d) shows the powder XRD pattern of all prepared samples and the representative Rietveld refined diffraction data for PrFe_{0.99}Cr_{0.01}O₃ is shown in figure-3.2 (c). It is clear from figure-3.2 (d), the Rietveld refinement of 1% Cr doped PFO that it is one to one fit of experimental data with simulated data and also it is confirmed by indexing of peaks using powder diffraction data files form ICDD. This confirms the phase purity of sample as no obvious impurity peak is observed. It is clear from figure-3.3 that the peaks shift towards higher 2θ values with increase in Cr content indicating the variation of lattice parameters due to Cr doping. In order to estimate the lattice parameters with Cr doping we have used the data for indexing of the peaks of all samples and then calculated the lattice parameters by using the formula for orthorhombic crystal structure. The value of lattice parameters due to Cr doping is shown in table **3.2.1**. The decrease in the value of lattice constant can be attributed to the difference in the ionic radii of Fe³⁺ (0.645\AA) and Cr^{3+} (0.615 Å) hence overall decrease in lattice constants decreases inter planar spacing-'d' and therefore diffraction angle θ increases (according to Bragg's condition $2dSin\theta = n\lambda$). This corresponds to the shifting of Bragg's peaks towards higher 20. The variation of lattice parameters with substitution of chromium to $PrFeO_3$ is given in table 3.3.1.



Figure-3.2 (a) Shows XRD of Gel form, (b) XRD of 1% Cr doped PFO sintered at 700°C, (c) Shows the Rietveld refined diffraction data for PrFe_{0.99}Cr_{0.01}O₃, (d) Shows Powder XRD pattern of all prepared samples.



Figure-3.3 XRD Peaks shifting towards higher 2θ values with increase in chromium content

| Cr % | Lattice Parameter | Lattice Parameter | Lattice |
|------|-------------------|-------------------|-----------|
| (X) | a (Å) | b (Å) | Parameter |
| | | | c(Å) |
| 0 | 5.485(5) | 5.578(7) | 7.788(9) |
| 1 | 5.484(3) | 5.573(2) | 7.788(7) |
| 2 | 5.484(2) | 5.577(6) | 7.787(9) |
| 3 | 5.482(9) | 5.573(9) | 7.785(7) |
| 5 | 5.482(9) | 5.569(6) | 7.787(1) |
| 7 | 5.487(9) | 5.565(3) | 7.786(8) |
| 10 | 5.484(8) | 5.562(2) | 7.786(2) |
| 11 | 5.485(8) | 5.566(2) | 7.786(2) |
| 15 | 5.484(2) | 5.559(8) | 7.783(5) |
| 18 | 5.484(1) | 5.557(1) | 7.783(3) |
| 20 | 5.481(7) | 5.555(3) | 7.779(4) |

Table 3.3.1 Variation of lattice parameters with Cr doping to $PrFeO_3$

3.3 Optical Properties Analysis

Band gap by using UV-VIS Spectroscopy

The optical band gap of prepared samples has been measured using diffuse reflectivity measurements. These measurements have been performed in the 200 nm to 800 nm wavelength range using Cary-60 UV-VIZ-NIR spectrometer having Harrick Video-Barrelino diffuse reflectance probe. The beam spot size on the sample was around 1.5 mm in diameter and an integral sphere detector is used for diffuse signal detection. In order to estimate the optical band gap the diffuse reflectance spectra has been converted to equivalent absorption spectra using Kubelka–Munk equation^[20,27]

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}}$$

 $R_{\infty} = R \ (Sample)/R \ (Standard)$. R(Sample) is the diffuse reflectance of the sample and R(Standard) is that of the standard (BaSO₄ in present case). K and S are the Kubelka–Munk absorption and scattering functions, respectively. Tauc plot shows the quantity hv (the energy of the light) on the abscissa and the quantity $(\alpha hv)^{1/n}$ on the ordinate, where α is the absorption coefficient of the material. The value of the exponent n denotes the nature of the transition:

$$(\alpha h v)^{1/n} = B (hv - Eg)$$

Where n=2 (indirect allowed transition), n=1/2 (direct allowed transition)^[20,27].

Thus, a plot between $[F(R\infty) \times hv]^{1/n}$ versus hv yields a straight line and the intercept on the energy axis gives the value of the band gap. The band gap calculated by indirect band gap fitting for PrFeO₃ is 1.99 eV as shown in **figure-3.4** (b).



Figure-3.4 (a) DRS experimental data (b) The equivalent Tauc plot for indirect band-gap fitting of $PrFeO_3$ sample at room temperature.

3.3.1 Effect of Band gap after incorporation of chromium to PrFeO₃

From the band theory we know that for n- type and p- type semiconductors extra energy levels have been created by the incorporation of impurities. In n- type semiconductors these energy states arise near the top of the conduction band so that electrons can be easily excited into conduction band by gaining a very small amount of energy. In p-type semiconductors acceptor level arises close to valance band which allow excitation of valance band electrons by leaving mobile holes in the valance band.

From figure-3.5 it is clear that with Cr doping the band gap systematically decreases. This suggests that with Cr doping the Cr impurity states may be appearing in the band gap and thus the band gap reduces with Cr-doping concentrations. This could be due to higher energy of Cr-3d states than Fe-3d states as Fe is more electronegative than Cr. The same need to be confirmed using band structure calculations^[20,27]. The variation of band gap with chromium atomic concentration is shown in next page.



Figure-3.5 Variation of band gap vs chromium content at room temperature.

3.3.2 Temperature dependence band gap measurements

The energy band gap of semiconductors tends to decrease as the temperature is increased. This behaviour can be better understood if one considers that the interatomic spacing increases when the amplitude of the atomic vibrations increases due to the increased thermal energy. An increased interatomic spacing decreases the potential seen by the electrons in the material, which in turn reduces the size of the energy band gap. The decrease in band gap follows some theoretical laws given by Varshni's and Einstien's. The temperature dependence of the energy band gap has been experimentally determined yielding the following expression for E_g as a function of the temperature T known as Varshni relation^[28–30].

$$Eg(T) = Eg(0) - \frac{\alpha(T*T)}{(T+\beta)}$$
-----(3.1)

Where $E_g(0)$, α and β are the fitting parameters, calculated by doing non-linear fitting to Varshni's relation. From the nonlinear fitting of this inset of figures, **figure-3.6** (a), (b), (c), it is clear that the

decrease in band gap with increase in temperature follows the varshni's relation.



Figure-3.6 (a) Shows Temperature dependence of band gap for Cr1% doped $PrFeO_3$ (b) Shows Temperature dependence of band gap for Cr5% doped $PrFeO_3$ (c) Shows Temperature dependence of band gap for Cr7% doped $PrFeO_3$.

3.4 Urbach energy

In some crystalline materials having disorder in the form of defects, structural coherency, chemical in-homogeneity etc. the valence band and conduction band do not have sharp cut off but have localized tails states. Due to these band tails, optical absorption edge is not fall sharp and has tail at lower energies. When we make Tauc plot we do not get straight line in the whole energy range. The same phenomena has been observed in all imperfect crystalline solids and amorphous solids known as Urbach-Martienssen's rule or simply Urbach rule given by^[21]:

$$\alpha(E,T) = \alpha' \exp\left[\sigma\left(\frac{E-E'}{kT}\right)\right]$$
$$\ln(\alpha) = \ln(\alpha') + \frac{\sigma}{kT} - \dots - (3.2)$$

Where Eu is Urbach energy, α_0 is a constant, α is absorption coefficient, E' is material-dependent constant and σ is steepness parameter which is basically tells us about electron phonon interaction in material. Experimentally Urbach energy can be calculated by plotting the graph between $\ln \alpha$ and energy, inverse of slope of the linear fitted region signifies Urbach energy.

Urbach energy has contribution due to thermal disorder, structural and compositional disorders.

$$Eu(T,S) = Eu(T) + Eu(S) + Eu(C)$$

Where Eu(T) is contribution due to temperature in Urbach energy, Eu(S) is contribution due to structural disorders. Structural disorder to Urbach tail can be intrinsic (vacancies or dislocations) or be induced by external factors (deviation from stoichiometry, doping, ion implantation). These intrinsic and extrinsic factors contribute to formation of localised states in between the valance band and conduction band.

Eu (C) is compositional disordering arises due to nonhomogeneous chemical composition. So we can conclude that Urbach energy gives us idea about various kind of disorder present in real crystals. Now we will discuss effect of these various kinds of disorders on Cr doped $PrFeO_3$ samples. In next sections we will discuss contribution of these disorders one by one.

3.4.1 Temperature dependence of Urbach energy

It is clear from **figure-3.7** (b) that with increase in temperature Urbach energy increase^[14] it would be due to the random thermal disorder

increases with temperature and hence Urbach energy. There is significant decrease in absorption co-efficient ^[21] is observed with temperature as shown in **figure-3.7** (c) with increase in temperature which is in agreement with equation (3.2). In crystals even at low temperature there is exponential variation of absorption coefficient, may be due to dopant impurities randomly located/distributed introduce the disorder.



Figure-3.7 (b) Variation of Urbach energy with temperature for one percent Cr doped PrFeO₃. (c) Variation of $ln(\alpha)$ vs. energy for different-2 temperatures.

3.4.2 Chemical composition dependency on Urbach energy

The major contribution to the tail comes from those regions of crystals which are deformed. **Figure-3.8** reveals that Urbach energy is small enough for parent sample PFO, but with increase in chromium percentage to PFO Urbach energy increases this is due to the doping induced structural disorder which is further due to difference in the ionic radii of parent ion and dopant. Hence in the doping of Cr at Fe site in $PrFeO_3$ is expected to create the structural disorders and these structural disorders should increase the Urbach energy. Further the increase in structural disorders may be due to the non-homogenous strain induced by the dopant in PFO.



Figure-3.8 Variation of Urach energy vs chromium percentage at 300K.

3.5 Broadenings of FWHM in XRD diffraction peaks

For a crystal which is free from any kind of disorder (ideal crystal) have sharp absorption and Bragg's peak for these crystals is very narrow or ideally point like. But the crystals grown in laboratory a may not be perfect due to presence of various kinds of disorders in the form of strain chemical heterogeneity etc. In the case of peak broadening is due to the the strain in the samples and may also have contributions due to crystallite size^[32].

It could be clearly seen from **figure-3.9** (a) that full width half maxima of X-ray diffraction peaks increases with increase in chromium concentration to PFO, which further reveals the increase in lattice strain as does not much affect the average crystallite size after incorporation of doping (confirms from SEM images shown in section 3.7). After subtracting the instrumental broadening we have calculated the strain induced for some Cr doped $PrFeO_3$ samples by using Williamson-Hall plot as shown in **figure-3.9** (b). By doing the linear fitting of Williamson & Hall plot, slope of the plot gives the lattice strain and intercept gives the average crystallite size. Interestingly the pattern/order which strain is following for various concentrations of Cr doped PrFeO₃ samples is similar as Urbach energy has followed in **figure-3.10.** This we will discuss in section 3.6.



Figure-3.9 (a) X-ray diffraction peak width Full width at half maxima for prepared samples. (b) Williamson & Hall plot for 5% Cr doped PFO.

3.6 Strain controlled of Urbach energy in Cr doped PrFeO₃

With increase in chromium percentage to PrFeO₃ Urbach energy increases this is due to the doping induces structural disorder which is further due to difference in the ionic radii of parent ion and dopant. Hence in the doping of Cr at Fe site in PrFeO₃ is expected to create structural disorder and this structural disorder should increase the Urbach energy. It is clear from figure-3.8 that with increasing the Cr percentage to PFO, Urbach energy systematically increases. As discussed above the value of Urbach energy is a measure of disorder and has a contributions due to static structural disorder (static strain fields/structural disorder due to ionic radii miss match, defects, etc.), thermally induced disorder and chemical disorder. In the present case all the measurements were carried out at constant temperature (Room temperature), hence we assume that the thermal disorder is broadly constant in the present doping concentration. Further the elemental mapping (shown in section 3.7, figure-3.13 (b)) results also suggest that the prepared samples are chemically homogenous. Thus it appears that in the present case the value of the Urbach energy is essentially controlled by the strain field i.e. due to structural disorder.



Figure-3.10 Shows strain induced in samples after incorporation of Cr doping to PFO.

3.7 SEM analysis

The surface morphology of Cr doped PrFeO₃ pellets is studied through scanning electron microscopy (SEM) is shown in the figures below. The average grain size of prepared samples is found to be 200 nm. These Cr doped PrFeO₃ sample shows the porosity and non-homogeneous grain sizes/growth throughout the samples. It is well known fact that the formation of porosity is due to insufficient sintering time and/or temperature or pressure, which results in an inadequate grain growth and density. This porosity highly affect the dielectric properties, so in order to examine the dielectric and magneto-dielectric properties, further we anneal these samples to 1000°C. It is also clear from SEM images of pellets sintered at 700°C and 1000°C that porosity reduces at higher temperatures. Also we can see the change in morphology at different -2 temperatures. The increase in average grain size is observed at higher temperatures.



Figure-3.11, (a), (b), (c), (d) represents the SEM images of Cr 0%, Cr 11%, Cr15% and Cr 20% doped PrFeO₃ pellets sintered at 700°C respectively.

SEM images of Cr doped PFO pellets sintered at 1000°C

The Scanning electron microscope images of 0%, 15%, 13% and 18% Cr-doped PrFeO₃ samples sintered at 1000°C are shown in **figure-3.12** (a), (b), (c), (d) respectively (representative images). The particle size distribution shows that the average numbers of particles have a size of 250 nm, and clearly we can see from SEM images that doping does not affect much the grain size of the different -2 Cr doped PFO samples. It is also clear from SEM images of pellets sintered at 1000°C that porosity reduces at higher temperatures and its morphology is totally different from pellets sintered at 700°C. There is increase in average grain size is observed at higher temperatures.



Figure-3.12 (a), (b), (c), (d) represents the SEM images of Cr 0%, Cr 11%, Cr15% and Cr 20% doped PFO pellets sintered at 1000°C respectively.

Elemental mapping using energy dispersive analysis of X-rays (EDAX)

The chemical homogeneity or heterogeneity in the prepared samples was examined by elemental mapping using energy dispersive analysis of X-rays (EDAX) attachment of SEM shown in figure-3.13 (b). Element maps show the spatial distribution of elements in a sample. The sample formed is either stoichiometric or not and presence of different elements can be understood by SEM apparatus attached with EDAX attachment. It is working on the principle that when high energy electrons shine on the sample and due to interaction of these electrons with the atoms of specimen there is emission of secondary electrons. Also there is generation of X-rays by ejection of electrons from K, L, M...etc. shells of the sample. Corresponding to specific atomic number there is a specific energy, hence by knowing the energy of the emitted X-rays elements presents in the sample could be detected. It is clear from elemental mapping that samples formed for different-2 chromium percentages (here we are showing only two elemental mapping for sake of clarity) are chemically homogeneous. Figure-3.13 (a) shows the EDAX analysis of the 10% and 13% Crdoped PFO samples, showing the presence of Pr, Fe, Cr and oxygen in the nanoparticles. There is no peak of nitrogen in the EDAX, indicating removal of nitrate impurities during annealing of samples at $700^{\circ}C$



Figure-3.13 (a) EDAX analysis for 10 % and 13 % Cr doped $PrFeO_3$ samples.

Further and very important the distribution of Fe, Cr, Pr and Oxygen is uniform throughout the samples even as nanometer scale, suggesting uniform chemical distribution throughout the prepared samples.



Figure-3.13 (b) Elemental mapping for 10 % and 13 % Cr doped $PrFeO_3$ samples.

3.8 Dielectric properties

To measure the dielectric measurements single phase powdered samples were pelletized at a high pressure of 10 ton to form 1 mm thick circular discs of 13 mm diameter and these pellets were sintered in air at 1000°C for 24 hours. For dielectric measurement, thin silver paints were painted on to opposite faces of the pellets using a fine brush. The dielectric properties of prepared pellets have been measured at room temperature for a frequency range of 20Hz to 5MHz by using Wynne Kerr 65120B precision impedance analyzer with an oscillator voltage of +1 volt. The dielectric constant of the prepared samples at room temperature is estimated by measuring the capacitance and geometry of the prepared samples. The variation of the dielectric constant at room temperature for 2% Cr doped PrFeO₃ and 13% Cr doped $PrFeO_3$ is shown in figure-3.14 (a) and It is clear from figure-3.14 (a) that there is increase in dielectric constant with increase in Cr percentage, this variation of dielectric constant with Cr doping could be due to increase in AC conductivity of the respective samples. It is clear from figure-3.15 that with the increase in Cr concentration, the maximum value of both the real and imaginary parts of impedance decreases by in orders of magnitude at higher frequency side this suggests that the AC conductivity of the respective samples increases as a result (considering effective medium approach) increase in the value of dielectric constant is observed possibly due to apparent decrease in the thickness of the sample^[33]. The major contribution to dielectric constant at low frequencies is due to highly resistive grain boundaries whereas at high frequencies grain contribution is dominant. It is clear from **figure-3.14** (b) that dielectric loss vs frequency plot shows relaxation type behaviour. The increase in dielectric loss is observed at low frequencies which increases with frequency to maximum frequency called resonance frequency, after this dielectric loss decreases with frequency. This could be due to the reason that at low frequencies dipoles are able to follow the applied field so with increase in frequency dipole rotation lag behind from the applied

alternating field. So this dipole rotation lagging from applied alternating field leads to increase in dielectric loss. After resonance frequency dipoles are not able to synchronize themselves with the changing field i.e. flipping of dipoles are not possible with the applied field this may leads to decrease in dielectric loss after resonance frequency.



Figure-3.14 (a) Shows the behaviour of dielectric constant with frequency for 2% Cr doped PFO and 13 % Cr doped PFO respectively as a function of frequency (b) Shows dielectric loss vs frequency for 2% Cr doped PFO and 13% Cr doped PFO respectively as a function of frequency at 300K.



Figure-3.15 Cole-cole diagram for Cr-doped $PrFeO_3$ for whole probing frequency at 300K.

Temperature dependent dielectric studies

Dielectric constant results from four types of polarization's named as interfacial, dipolar, ionic, and electronic polarization contributions^[25] The sharp variation in the dielectric constant at low frequencies is due to space charge and dipolar polarization's. Ionic and electronic polarization is responsible for dielectric constant developed at higher frequencies and independent of temperature. Due to this reason it is clear that temperature dependence of dielectric constant at higher frequencies is of significance.



Figure-3.16 (a) Represents temperature dependence of dielectric constant for Pure PrFeO₃. (c) temperature dependence of dielectric constant for 13% Cr doped PrFeO₃.



Figure-3.17 (b) Shows temperature dependence of the dielectric loss for Pure $PrFeO_3$ (d) Show temperature dependence of the dielectric loss for 13% Cr doped $PrFeO_3$ ceramics.

It is clear from **figure-3.16**, (a) and (c), that with increase in temperature dielectric constant increases this is attributed due to the reason that with increment of temperature extra thermal energy increases the thermal mobility of the charge carriers. At low temperatures the thermal energy is not sufficient to contribute to the mobility of charge carriers so at low temperatures there is not much variation in dielectric constant. At high temperatures extra thermal energy increases the mobility of charge carriers, hence higher polarization at high temperatures increases the dielectric constant. The dielectric loss at higher frequency and the peaks position shifts to high temperatures as the measuring frequency increase, as shown in figure **figure-3.17**, (b) and (d).

This indicates that there exists thermally activated relaxation as mentioned above. The inset of Figures clearly shows a relaxor type behaviour of parent and doped samples which is a typical behaviour of ferrites.

3.9 Magneto Dielectric (MD) Properties

In addition to temperature dependent dielectric studies we have carried out room temperature magneto dielectric measurements for all prepared samples. MD effect is basically change in the dielectric constant or capacitance with applied magnetic field. No such kind of effect has been observed in all samples. **Figure-3.18** reveals that No change in capacitance is observed with the application of magnetic field, which confirms that no such kind of effect is present in Cr doped PFO samples.



Figure-3.18 Shows capacitance vs frequency for $PrFe_{0.99}Cr_{0.01}O_3$ with and without magnetic field.

CHAPTER 4

4.1 Summary and Conclusion

Summary: The XRD results show that all the prepared samples are pure and also the lattice parameters are changing with Cr doping. DRS results show that with Cr doping the band gap systematically decreases. This could be due to higher energy of Cr-3d states than Fe-3d states as Cr is more electronegative than Fe. The same need to be confirmed using band structure calculations.

With increase in chromium percentage to PFO Urbach energy increases this is due to the doping induces structural disorder which is further due to difference in the ionic radii of parent ion and dopant. Hence in the doping of Cr at Fe site in $PrFeO_3$ is expected to create structural disorder and this structural disorder should increase the urbach energy. In other words doping induces strain in $PrFe_{(1-x)}Cr_{(x)}O_3$ and the Urbach energy scales with the lattice strain. It is clear that with increasing in the Cr doping Urbach energy systematically increases. Thus the contribution due to thermal disorder is broadly remains constant as all experiments are done at 290K. Further the elemental mapping results also suggest that the prepared samples are chemically homogenous. Thus it appears that in the present case the value of the Urbach energy is essentially controlled by the strain field i.e. due to structural disorder.

Conclusion

We have prepared single phase samples of Cr doped $PrFeO_3$ by wet chemical route method. It is observed that with Cr doping the Urbach energy which is measure of disorder increases. It is observed that the value of Urbach energy is essentially controlled by structural disorder in the form of correlated strain field dues to mismatch in the ionic radius of Fe and Cr ions.

It is clear that with Cr doping the band gap systematically decreases. This suggests that with Cr doping the Cr impurity states may be appearing in the band gap and thus the band gap reduces with Cr-
doping concentrations. This could be due to higher energy of Cr-3d states than Fe-3d states as Cr is more electronegative than Fe. In addition to this dielectric characterization has been done at room temperature and at low temperature range. The variation of dielectric constant and dielectric loss with Cr doping to PrFeO₃ is observed at roo temperature, further these variation's with temperature is also studied in the present work.

4.2 New findings in this thesis work

- The value of the Urbach energy is essentially controlled by the strain field i.e. due to structural disorder.
- Tuning of the band gap on incorporation on Cr doping to PrFeO₃.
- Effect of doping and temperature on dielectric constant and dielectric loss is studied.
- Variation of band gap with temperature is also studied in temperature range 300K to 470K.

4.3 Future Research Plan

- To study the Temperature dependent Dielectric and Magnetodielectric measurements on all samples.
- The photo luminescence experiment to confirm the direct and indirect band gap.
- To study the temperature dependent susceptibility measurements to confirm the any magnetic transition if any.

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