Investigation of Structural and Optical properties of Lanthanum Gallates

M.Sc. Thesis

By

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Investigation of Structural and Optical properties of Lanthanum Gallates

A THESIS

Submitted in partial fulfillment of the Requirements for the award of the degree of

Master of Science

by **BAJRANG GUPTA**



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2019



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Investigation of Optical and Electronic properties of Lanthanum Gallates** in the partial fulfillment 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 2017 to June 2019 under the supervision of Dr. Pankaj R. Sagdeo, Associate Professor, Discipline of Physics, IIT Indore.

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.

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|------------------------------------|
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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Dedicated to my parents and Teachers

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Abstract:

Polycrystalline LGO sample has been prepared using modified chemical wet route. In order to know the structural phase purity of the prepared sample, X-ray diffraction has been carried out. Band gap of prepared sample has been determined using Diffuse Reflectance Spectroscopy (DRS) which is obtained through the mathematical relation of Kubelka-Munk function, known as Tauc plot. Behavior of band gap with temperature has been studied using temperature dependent DRS experiments. These materials show the structural phase transition from orthorhombic to rhombohedral at around 417 K temperature. In order to know about the kind of structural phase transition present in the sample, temperature dependent DRS has been carried out. On the further confirmation of structural phase transition, temperature dependent Raman spectroscopy has been carried out. Variation of Urbach energy with temperature has been also studied using TD DRS. Additionally, Temperature dependent optical band gap has been fitted using various fitting models like Varshni model and Bose-Einstein model to determine the thermodynamics of prepared sample. Both TD Diffuse Reflectance Spectroscopy and TD Raman spectroscopy confirms that LGO shows a structural phase transition from orthorhombic to rhombohedral phase at around 417 K temperature.

Key words:

Temperature dependent diffuse reflectance spectroscopy, Temperature dependent Raman spectroscopy, Solid oxide fuel cells, Structural Phase transition, Band gap and X-ray diffraction.

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Abbreviations:

| Solid oxide fuel cell | SOFC |
|----------------------------------|--------------|
| Lanthanum Gallate | LGO |
| Band gap | E_{g} |
| Urbach energy | E_{u} |
| Temperature dependent | TD |
| Diffuse reflectance spectroscopy | DRS |
| Absorption coefficient | α |
| Debye temperature | θ_{B} |
| Room temperature | RT |

Chapter 1

1.1 Introduction and origin of the problem:

As the world population is increasing rapidly, the demand of energy is becoming an ever a serious challenge for world's energy sector. At present, the supplies of energy in the world mainly depend on fossil fuels. Now a day's global warming is also one of the most serious issues faced by mankind and hence need eco-friendly products based on solidstate oxide fuel cells (SOFC) have attracted due to its high efficiency, flues flexibility and carbon free emission[1]. SOFC is used as an electrolyte in the fuel cells. The materials with perovskite structure show interesting ferroelectric, magnetic and optical properties. Amongst the various perovskite oxides, the lanthanum gallate (LaGaO₃) is known to show excellent oxygen-ion conductivity at moderate temperatures, which makes it one of the most promising solid electrolytes for intermediate temperature solid oxide fuel cell and hence studied by scientific community during the last decade[2]. With the inclusion of some transition materials like Ni, Mn and Fe lanthanum gallates show the magneto dielectric effects thus, gallates can be also used in storage devices, magnetic sensors and tunable filters. The perovskite oxide, which supplies large amount of vacancies, can be expected to obtain high oxide ion conductivity. It is known that the electronic disorder significantly modifies the ionic conductivity and optical properties are known to probe such electronic disorder. It is known that the optical absorption spectroscopy is one of the most widely used tools to investigate the electronic structure near band edge. Even though the correlation between band gap and electronic disorder is well established but the validity of such correlation near structural phase transition is not clear. In semiconductors/insulators variation of optical band gap and electronic disordered term Eu with temperature is of scientific and technological interest and has contributions due to total disorder present in the system i.e. thermal, chemical, polar and structural disorders (structural disorder induced by defects, vacancies, static strain fields, doping) etc[3]. Earlier, various efforts have been made by many research groups in order to explain the behavior of Eu, its functional form as a function of temperature (T) and structural disorder (X). Generally, it is believed that Eu scales up with temperature due to increase in random vibrations of temperature, however, for a system which shows a change in the structure, an anomaly has been observed earlier by various research groups in temperature dependent optical Eg and Eu. It is important here to note that the signature of structural phase transition and thermal disorder is clearly visible in Raman spectra for given semiconductor material. The generation or disappearance of a phonon mode in Raman spectra is attributed to change in the symmetry/structure; however, the width of Raman line shapes is essentially controlled by thermal/structural disorder. As many researchers have been studied this structural phase transition by using temperature dependent X-ray diffraction[4], neutron diffraction[5] and dielectric studies[6] on the sample. Some researchers also have been reported this structural phase transition by inducing twinning[7] in the sample but nobody has studied this structural phase transition by using temperature dependent diffuse reflectance spectroscopy. So, in present report, temperature dependent (TD) optical absorption spectroscopy and TD Raman spectroscopy experiments has been performed on one of the technologically important material LaGaO₃, in order to determine the exact structural phase transition temperature. An anomaly observed at 420 K in optical band gap and electronic disorder variation has been observed and understood in terms of change in structure from orthorhombic (Pnma) to rhombohedral (R3c), which is well conformance with Raman structural phase transition temperature. Our results clearly suggest that optical absorption spectroscopy could be an economical and non-destructive temperature dependent optical absorption spectroscopy and TD Raman spectroscopy.

1.2 Band gap:

A band gap is an energy difference between the bottom of conduction band and top of the valance band. Band gap can be understood easily that this is the minimum energy required to excite an electron from valance band to the conduction band so that this electron can take part in conduction.



Figure 1. 1: The band structure (parabolic bands) of solids.

On the basis of the band gap model, materials can be divided in to three categories conductor, semiconductor and insulator. According to the band gap model, in conductor there is no gap between the top of the valance band and bottom of the conduction band means both conduction and valance band are overlapping to each other so that electron can easily excite from valance band to conduction band. In insulator there is a more gap ($\geq 3.2 \text{ eV}$) between the top of the valance band and bottom of the conductor there is any situation from valance band to conductor there is small enough gap ($\leq 3.2 \text{ eV}$) so that electron can excite from the top of the valance band to bottom of the conductor there is small enough gap ($\leq 3.2 \text{ eV}$) so that electron can excite from the top of the valance band to bottom of the valance band to bottom band.



Figure 1. 2: The band diagram for different solids (metals, semiconductors and insulators)

1.3 Urbach energy:

In 1953, Franz Urbach was the first to observe experimentally an exponential increase of the absorption coefficient as the photon energy increases[8].

Along the absorption coefficient curve and near the band edge there is an exponential part called Urbach tail or Urbach energy. This edge comes in to view in the low crystalline, poor crystalline, the disorder and amorphous materials because these materials have localized states which extend the band gap.

Absorption coefficient for the urbach tails can be written as:

$$\alpha(E,T) = \alpha_0 exp\left[\frac{\sigma(E-E_0)}{kT}\right] \tag{1}$$

Or

$$\alpha(E,T) = \alpha_0 exp\left[\frac{(E-E_0)}{E_U(T)}\right]$$
(2)

Where α_0 and E_0 are constant determined by extrapolated linearly a curve between $ln(\alpha)$ and E at a given temperature, σ is the steepness parameter of the absorption edge, $E_U = \frac{kT}{\sigma}$ is the urbach energy which is equal to the width of the absorption band edge and reverse to the slope of the absorption edge[9].

$$E_U^{-1} = \frac{\Delta(\ln \alpha)}{\Delta(E)} \tag{3}$$

According to Urbach, the exponential behavior of the absorption coefficient is in the following form:

$$S = \frac{\partial (ln(K))}{\partial (hv)} = -\frac{1}{kT}$$
(4)

Where S is slope of the exponent, K is the absorption coefficient, hu is the photon energy and k is Boltzmann coefficient. From this equation it was clear that slope S depends only on the temperature not on the material properties but experimentally it was found that slope depends on temperature as well as material properties.

Hence Martinssen redefined the exponential behavior of absorption coefficient. This is shown in equation 1.

The form of σ as a function of temperature is given by Mahr and is as follows:

$$\sigma(T) = \sigma_0 \left(\frac{2kT}{E_P}\right) tanh\left(\frac{E_P}{2kT}\right)$$
(5)

Where $E_P = \hbar \omega$ is the energy of phonon which contributes to the urbach tails. σ_0 is a constant and can be considered as the inversely proportional to the electron-phonon interaction[10].

Origin of the urbach energy:

Urbach tail appears due to the various kind of disordered, present in the sample. These disordered may occur due to the change in temperature,

chemical composition and various kind of structural disordered present in the sample.

Band theory of the solids proposed that electron is moving in the periodic varying potential having time period equal to the lattice constant which is responsible for the observed well defined band structure[11]. If any fluctuation in the periodicity due to temperature variation, and incorporation of the impurity of different ionic radii then the arrangements of the atom get distributed and electron feels the potential differ from place to place. So due to this, the conduction band and valance band do not have sharp cut off. As a result, optical band edge does not have sharp fall but have an exponential fall in the absorption edge.



Figure 1. 3: The localized states formation between the valance band and conduction band.

When a photon of the band gap energy is incident on the crystal then the electron will excite from valance band to conduction band. So there should be a sharp transition in the absorption curve at the band edge. But as it is known that "nothing is perfect" according to Mosaic effect. Due to some kind of disorder, there is an exponential part in the absorption curve at the band edge. The exponential behavior of absorption coefficient is shown in figure 1.4.



Figure 1. 4: An exponential variation in the absorption curve near the band edge.

1.4 Structure of LGO perovskite:

Perovskite structure is adopted by many oxides that have the chemical formula ABO_3 . LaGaO₃ has the ABO_3 type perovskite structure, in which, A and B are cations and O⁻ is an anion. Cations A are present on the corners and B are present on the center and all these anions (O⁻) are presented at mid of each faces of the cube and all of them are equidistant from the B atom which forms a Centro- symmetric octahedron (BO₆) around B atom. Due to this, net dipole moment of the system is zero.



Figure 1. 5: The structure of the LGO perovskite

CHAPTER 2 Experimental methods and characterization techniques

In this chapter, some experimental methods and characterization techniques are discussed.

2.1 Experimental methods:

2.1.1 Solid state reaction route

- 2.1.2 Sol-gel route
- 2.2 Characterization techniques:
 - 2.2.1 X-ray diffraction (XRD)
 - 2.2.2 Diffuse reflectance spectroscopy (DRS)
 - 2.2.3 Temperature dependent DRS
 - 2.2.4 Raman spectroscopy

2.1 Experimental methods:

2.1.1 Solid state reaction method:

Solid state reaction route is the most commonly used method for preparation of polycrystalline samples from a mixture of solid starting materials. In this method, very fine powders which do not react at the room temperature, are used as the starting materials. Hence these fine powders were heated at very high temperature (800° C to 1300° C).

The process of the solid state reaction method is as following:

In this method, at first starting (raw) materials are taken and weighed in stichromatic ratio. After that all the materials are mixed in homogenous medium. Isopropyl alcohol is used as the medium to make homogenous mixture. This mixture is grinded very properly yields a fine powder obtains. Grinding is done to increase the surface area and reaction rate. Calcinations have been done in high temperature programmable furnace at constant heating and cooling means a heat treatment is given to that fine powder at different-different temperatures[12]. After that pellet preparation has been done by mixing one or two drops of PVA binder in that calcinated powder and pressed by using hydraulic press machine. Sintering of the pellet has been done in the presence-of air.



Figure 2. 1: Methodology of the preparation of sample by solid state reaction method

2.1.2 Sol- gel method:

Sol gel is one of the well-established methods to prepare novel metal oxides nanoparticles. This method has potential control over the textural and surface properties of the materials.

This method depends on the transformation of the relevant precursors into sol and then finally to a network called gel.

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 sol gel method can be classified into two routes. 1) aqueous sol gel, if water is used as reaction medium.2) nonaqueous sol gel method, if organic solvent is used as reaction medium. The aqueous sol gel method is more popular method than the nonaqueous sol gel method.

The process of the sample preparation by aqueous sol gel method is as follows:

Polycrystalline powder of LaGaO₃ samples were prepared by using modified wet chemical route. In this method, La (NO₃)₃.6H₂O and Ga metal were used as the starting materials or precursors. Ga metal was dissolved in the nitric acid to make gallium nitrate. Instead of Ga metal, Ga $(NO_3)_3$.xH₂O may be used but the value of x is unknown in this nitrate. The value of x can be determined by performing very sophisticated experiments such as Thermogravimetry analysis (TGA). Hence in presented report Gallium metal was used instead of Ga (NO₃)₃.xH₂O. So Ga metal was used as the starting material or precursor. The stoichiometric amounts of nitrates were dissolved in the distilled water for forming a solution. A small amount of citric acid as well as ethylene glycol were added in solution[13]. The resulting solution was stirred 2h at 80^oC until gel was formed. Gel was dried 2h at 200° C and grinded by using mortar pestle and calcined. The calcinations were performed in a high temperature programmable furnace at 1000°C for 12h and 1300°C for 12h with constant heating and cooling rate $(5^0 \text{ per min})[14]$. The fine and homogenous powder was cold pressed in to pellets (10 mm diameter and 1-2 thickness) under uniaxial pressure by hydraulic press. The polyvinyl alcohol (PVA) was used as a binder during preparation of pellets. The pellets were sintered at 1300⁰ K temperature for 12 h in a programmable furnace.



Figure 2. 2: Methodology of preparation of sample by sol-gel method

2.2 Characterization techniques:

Here all the experimental techniques which are used in the sample analysis are discussed.

2.2.1 X ray diffraction:

X ray diffraction technique is the most important non-destructive tools to analyze all kind of materials ranging from fluids, to powders and crystals. X-ray diffraction is used to get information of crystal structure, crystal size, lattice parameters, lattice strain, chemical composition, state of ordering, spacing between two crystal planes structure of the sample etc.

The working principal of X-ray diffraction is as follows:

The filament inside the cathode tube is heated by applying the voltage between the electrodes. As filament gets heated then free electrons which have a very high velocity, collides with the water cooled anode. This results the formation of X-rays in the X-ray tube. These X-rays originated from the tube falls on the surface of the sample. As wavelength of these originated X-rays has wavelength is order of the lattice parameter

which results the diffraction of X-rays in the different directions by continuous change in the intensity with the incident angle. The intensity of these diffracted peaks depends on the electron density across the miller plane. So the intensity distribution varies with the angle between incidence and diffracted beam[15]. By knowing those planes the structure of materials, composition of sample, spacing between two planes and lattice constants can be calculated X-ray diffraction is totally based on the principal of Bragg's law.

According to Bragg's law of X-ray diffraction,

A certain wavelength of X-ray will constructively interfere if they are reflected between crystal planes with the path difference is equal to an integral number of wavelength.

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



Figure 2. 3: X-ray diffraction from a crystal

This is the condition of Bragg's law. Where d is the interplaner distance, θ is the angle between incident X-rays and planes of reflection, λ is the X-rays wavelength and n is the integer.

Whenever this Braggs condition is satisfied, a peak, across the θ value corresponding to 2θ curve appears.

In this work, the primary structural phase purity of the samples has been done by using X-ray experiment on the Rigaku smart lab work.

2.2.2 Diffuse reflectance spectroscopy:

Diffuse reflectance spectroscopy is the effective tool to investigate the optical properties like optical band gap and disorder of any materials near the band edge[16]. Diffuse reflectance spectroscopy is commonly used in the visible, UV regions and near and mid infrared regions. The main advantage of DRS is that there is no need of difficult sample preparation, only power samples could be used for this purpose. The principal of this spectroscopy is based on the diffuse reflection. Two types of reflection can occur:

Specular or regular reflection usually associated with the reflection from smooth and polished surfaces like mirrors. Diffuse reflection usually associated with the reflection from dull or mat surfaces textured like powder. When light falls on the surface of powered sample, it is reflected in specular and diffuse directions through multiple scattering. Some part of the light undergoes multiple scattering inside the sample and fraction of this part emitted back to dictator. As known that light cannot penetrate solid materials, it is reflected back to samples. When UV-Visible falls on the surface of the samples, this incident light get absorbed or reflected. This diffuse reflected light is detected by the dictator and analyzed and give the DRS spectrum.



Figure 2. 4: The specular reflection and diffuse reflection

In order to calculate the optical band gap of any sample, the obtained DRS spectra have been converted into equivalent absorption spectra using Kubelka–Munk equation shown in Eq. 1

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$
(6)

Where, $F(R_{\infty})$ is Kubelka- Munk function, K and S are the Kubelka–Munk absorption and scattering functions respectively and $R_{\infty} = R_{(Sample)}/R_{(Standard)}$. R $_{(Sample)}$ and R $_{(Standard)}$ are the diffuse reflectance of the sample and standard white reference respectively[3].E_g can be calculated by fitting straight line of $[F(R_{\infty})hv]^n$ after converting the Kubelka- Munk function into tauc equation. Here 'n' can take two values i.e. n = 2 for direct band gap transition and n = ½ for indirect band gap transition.

The Tauc plot shows the quantity $h\mathbf{v}$ on the abscissa and the quantity $(\alpha h\mathbf{v})^{1/n}$ on the ordinate. Here α is the absorption coefficient of the material and n represent the nature of transition[17]. The Kubelka- munk function can be related to the absorption coefficient as:

$$F(R\infty) \propto \alpha \propto \left(hv - E_g\right)^{1/n} \tag{7}$$

Thus, A plot between $(\alpha h \mathbf{v})^{1/n}$ and $h \mathbf{v}$ (energy) produce straight line and intercept on the energy axis gives the value of the band gap of the sample.

Set up of Carry 60 UV-VIS Spectroscopy:

Set up of the carry 60 UV-VIS Spectroscopy is as follows:



Figure 2. 5: Experimental set up for diffuse reflectance measurements (a) carry 60 UV-Vis spectrometer (b) an integrating sphere attachment to the diffuse reflectance spectrometer (c) internal system of the carry 60 UV-Vis spectrometer.

Working of the carry 60 DRS spectroscopy:

In this set up, diffuse reflectance has been measured by the carry 60 DRS spectroscopy. Xenon flash lamp source produces UV-VIS spectrum. This UV-VIS spectrum passes to the different filters and monochromator and after doing some optical arrangement, light incident on the sample then diffuse reflectance of the light happens. This diffuse reflectance can be measured by the detector.

2.2.3Temperature dependent carry 60 DRS set up:

Temperature dependent DRS set up shown below in the figure-2.6.

This set up consist some components 1) heater 2) temperature controller 3) detector 4) DRS set up 5) data analyzer. In this set up a sensor is connected to the heater (which heats the sample) and this heater further is connected to the temperature controller to measure the sample temperature. When UV –VIS light incident on the sample through the optical fiber then diffuse reflectance is detected by the detector at the different- 2 temperatures[18].



Figure 2. 6: Temperature dependent diffuse reflectance set up

2.2.4 Raman spectroscopy:

Raman spectroscopy is a non destructive chemical analysis technique which gives detailed information about phase, crystallinity, chemical structure and molecular interactions. This spectroscopy is basically based upon the interaction of light with chemical bonds within the materials. So it is used to observe the vibrational, rotational and other low frequency modes presented in the system. The discovery of the Raman Effect is done by C.V. Raman and K.S. Krishna in 1928.

When light is incident on the sample then most photons are elastically scattered. The elastically scattered photons have the same energy and frequency. This is called the Rayleigh scattering. However a small amount of light is scattered from the sample at different optical frequency from the frequency of the incident photons. This is called the inelastic scattering. The process of this scattering is named as the Raman Effect. If frequency of the scattered photons are less than to the frequency of the incident light then this is the stokes Raman scattering and if frequency of the scattered photons are more than to the frequency of the incident light then this is the anti-stokes Raman scattering[19].



Figure 2. 7: Energy level diagram of Raman spectroscopy

Instrumentation of the Raman spectrometer:

A Raman system mostly consists four major components.

- 1) Source (Laser light)
- 2) Sample illumination system (optical arrangement)
- 3) Filters and spectrophotometer (wavelength selector)
- 4) Detector (CCD, photodiode)

Mercury was used as the light source in Raman spectrometer in early days but now a day's argon ion laser, krypton ion laser and helium neon ion laser are used as the light source in Raman spectrophotometer. These laser sources provide very intense and balanced beam of light.

Band pass filters are used to isolate the single laser beam. Filters and gratings are used to separate the weak intense Raman lines from the highly intense Rayleigh radiation.

Detectors are used to detect the Raman spectra obtained from the Raman spectrophotometer. In early days thermoelectrically cooled photomultiplier tubes and photodiodes were used in Raman spectrometer but now a day's more sensitive charge devices (CCD) are used as a detector due to new technology.

Working of the Raman spectroscopy:

Figure-2.8 shows Schematic diagram of Raman spectrometer. In Raman instrument a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through interference filter or spectrometer to obtain Raman spectrum of a sample. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector. By changing the laser light you can confirm if a peak is a true Raman peak and not a peak just associated with the wavelength of the laser light that was used. Spontaneous Raman scattering signal is very weak because most of the incident photons undergo elastic Rayleigh scattering. Therefore special measures should be taken to distinguish it from the predominant Rayleigh scattering. Instruments such as notch filters, tunable filters, laser stop apertures, double and mono spectrometric system are used to reduce Rayleigh scattering and obtain high quality Raman spectra.



Figure 2. 8: Schematic diagram of Raman spectrometer

Chapter 3

Results and discussions

In this chapter the results obtained by various experiments are discussed here:

3.1 Structural phase analysis

3.2 Optical properties

3.3 Structural phase transition by using diffuse reflectance spectroscopy and Raman spectroscopy.

3.4 Various band gap fitting models.

3.5 Urbach energy variation with temperature.

3.1 Structural phase analysis:

In order to estimate the structural phase purity, XRD has been carried out to confirm the structural phase. All the experiments have been done using lab source XRD on Rigaku smart lab, diffractometer, with Cu K_{α} radiation was employed and operated at applied voltage of 45 KV and current of 40 mA[20]. Figure-3.1 shows the representative x-ray diffraction patterns of the polycrystalline sample LaGaO₃. In this figure xx, XRD has been refined considering orthorhombic structure having space group Pnma[21].



Figure 3. 1: Experimental XRD Patterns of prepared LGO sample through Sol-Gel method calcinated at (a) 1000° C (b) 1300° C

In this figure, all the peaks totally match with the corresponding JCPDS file no.241102.

A comparison of experimental calculated diffraction data and the absence of any extra peak in the diffraction data confirm the structural phase purity of the prepared samples. So it can be say that the prepared sample is in single phase.

Here the calculation of lattice parameters has been done using following procedure.

As it is known that the relation between interplanar and miller indices are given by[22]:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
(8)

And from Bragg's law

$$2d\sin\theta = n\lambda\tag{9}$$

Taking square of equation 9,

$$4d^2 \sin^2 \theta = \lambda^2 \tag{10}$$

Comparing equation x and y,

$$4\sin^2\theta = \lambda^2 \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)$$
(11)

To compute the value of c, taking plane (004) from the XRD patterns, value of λ is 1.54 Å and value of θ correspond to this plane is 23.33 degree,

$$4\sin^2 23.33 = (1.54)^2 \left[\frac{0^2}{a^2} + \frac{0^2}{b^2} + \frac{4^2}{c^2}\right]$$
(12)

So after solving this, the value of c will be

$$c^2 = \frac{4(1.54)^{2}}{\sin^2 23.33} \tag{13}$$

Doing same calculation with (044) and (420) planes, the value of lattice parameters a, b and c are 5.480 Å, 5.530 Å and 7.764 Å respectably.

| Lattice parameter a | 5.480 Å |
|---------------------|---------|
| Lattice parameter b | 5.530 Å |
| Lattice parameter c | 7.764 Å |

Table1. 1: Values of lattice parameters of a prepared sample

3.2 optical properties:

Band gap calculation using DRS:

In order to calculate the band gap of LaGaO₃, DRS experiments have been carried out. These experiments have been performed in wavelength range (200 nm to 800 nm) using carry 60 UV NIR VIS spectroscopy. 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.

Here figure-3.2(a) shows a spectra obtained by DRS experiments at room temperature. Figure-3.2(b) shows the Tauc plot which is obtained by converting wavelength in to energy and Kubeka-munk Function is converted in to Tauc plot[23]. After doing the linear fitting of this linear portion, where the extrapolated cuts on the energy axis that gives the value of band gap. Using Tauc fitting, the obtained experimental band gap of the LGO sample is 4.6 eV at room temperature.



Figure 3. 2: (*a*) *A DRS spectra obtained from DRS* (*a*) *A graph between Kubelkamunk function and wavelength*). (*b*) *The Tauc plot to calculate the band gap*.

3.3 Temperature dependent band gap measurements:

In order to estimate the variation in band gap with temperature, the temperature dependent DRS experiments have been carried out. The variation in optical band gap as a function of temperature of LGO sample is shown in figure-3.3. This figure shows that with increase in temperature the value of optical band gap decreases. The possible reason of this could be if one considers that when the value of temperature increases then interatomic spacing increases because amplitude of the atomic vibration increases due to the increased thermal energy. An increased interatomic spacing decreases the potential seen by the electrons in the materials which in turn reduce the size of the energy band gap.



Figure 3. 3: The variation of band gap as a function of temperature. In inset an anomaly observed at 420 K temperature and the derivative of band gap with respect to temperature and change in rate of band gap with temperature.

From the figure-3.3, it is clear that the electronic disorder near band edge systematically increases with temperature, however an anomaly has been observed closed to 420K, which could be due to change in structure from orthorhombic (*Pnma*) to rhombohedral (*R3c*).that is reported in the many literatures.

3.4 Various band gap fitting models:

Amongst the various band gap models some popular models have been evaluated in this study (1) Varshni model (2) Bose- Einstein model. These models suggest that the variation in band gap as a function of temperature is mainly due to the electron phonon interactions and thermal expansion. Using these models, many thermal quantities can be measured.

Varshni model:

The effects on the band gap energy loss of the temperature has been quantified through many empirical and semi empirical models. Amongst the various empirical models, Varshni model is the very much used for numerical fitting of temperature dependent band gap[24].

The Varshni relation for the temperature dependence of semiconductor band gaps is[25]

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T}$$
(14)

Where α and β are fitting parameters characteristic of a LaGaO₃. Eg(0) is the band gap of the semiconductor at 0 K. α tells us about the change in band gap per Kelvin and β indicates the nearly value of Debye temperature[26]. The theoretical basis of this much-used relation is unfortunately rather weak, since β which is supposed to be related to the Debye temperature, may in certain important cases be negative. Moreover, at low temperature, this equation predicts quadratic temperature dependence, whereas experiment finds (an approximate) temperature independence at very low temperatures and in the high temperature limit, this equation predicts a linear fit both due to the cumulative effects of the lattice expansion and the electrons-phonon contribution. Using above equation, the linear fitting has been done of the temperature dependent optical band gap of the both phases.



Figure 3. 4: The Varshni fitting of temperature dependent optical band gap (a) orthorhombic phase and inset shows the values of fitting parameters. (b) Rhombohedral phase and inset shows the values of fitting parameters.

It can be seen that the Varshni relation fits very well for low temperatures (up to 417 K); however, it shows deviation from experimental values, above 417 K.

It is observed from the figures that in both phases the values of the fitting parameters (band gap energy at 0K temperature and value of β) are little bit different.

It is proposed that value of the β is related to the Debye temperature. The relation between Debye temperature and β is as follows

$$\theta_D = \left(\frac{8}{3}\right) \boldsymbol{\beta} \tag{15}$$

so the value the Debye temperature is approximate 380 K which is similar to the reported Debye temperature[27].

Bose- Einstein model:

Temperature dependent band gap also has been fitted by Bose-Einstein model which accounts for the coupling of bands with the temperature dependent phonon population. Bose-Einstein model, considers electron interaction within crystals, also relates energy shift and temperature with the Debye energy. According to this model, the band gap energy can be determined from[25,28]

$$E_g(T) = E_g(0) - a_B \left(1 + \frac{2}{exp\left(\frac{E_{ph}}{k_b T}\right) - 1} \right)$$
(16)

Where, $E_g(T)$ band gap as a function of temperature which may be direct or indirect, $E_g(0)$ is the energy gap at 0K (unperturbed value), a_B represents strength of electron phonon interaction and E_{ph} represents average energy of phonon most strongly coupled with electron[29,30].

The optical band gap data of temperature dependence has been fitted linearly using the equation-(16).



Figure 3. 5: The Bose-Einstein fitting of temperature dependent optical band gap (a) orthorhombic phase and inset shows the values of fitting parameters. (b) Rhombohedral phase and inset shows the values of fitting parameters.

It is observed from the figure that the band gap data of temperature dependence has been fitted very well using Bose-Einstein equation.

3.5 Temperature dependent urbach energy:

Urbach energy:

The Urbach energy E_U has been estimated by plotting optical absorption α as a function of energy E. This optical absorption coefficient α is related to energy as[31]:

$$\alpha(E,T,X) = \alpha_0 \exp\left[\sigma\left(\frac{E-E_{00}}{kT}\right)\right]$$
(17)

Here, α_0 and E_{00} are the constants can be determined by inverse of slope of linear region from $ln(\alpha)$ vs E curves at given temperature T. The term $E_U = \frac{kT}{\sigma}$ is known as Urbach energy.

So the equation-(17) can be written as:

$$\alpha(E,T,X) = \alpha_0 exp\left[\frac{E-E_{00}}{E_U}\right]$$
(18)

After taking the logarithm of the both sides of the equation-(18) one can get a straight line equation[32].

$$\ln(\alpha) = \ln(\alpha_0) + \left[\frac{E - E_{00}}{E_U}\right]$$
(19)

Or

$$\ln(\alpha) = \ln(\alpha_0) + \frac{hv}{E_U}$$
(20)

From equation-(20), it is observed that plotting a curve between $\ln(\alpha)$ and $h\mathbf{v}$ and doing the linear fit of the linear portion of the obtained curve and inversing the slope will give the value of urbach energy.

Variation in Urbach energy with temperature:

The variation of urbach energy as a function of temperature is shown in the figure-3.6. As figure 3.6 shows that urbach energy increases systemically with the increases in the temperature but at around 417 K temperature urbach energy shows a anomaly which could be due to the well known structural phase transition from orthorhombic to rhombohedral phase. Here it is observed that band gap and urbach energy both are opposite to each other. Figure-3.3 and 3.6 show that with increases in temperature band gap decreases but urbach energy increases. Means it can be say that due to increase in temperature disorder increases in sample LGO.



Figure 3. 6: The variation in urbach energy as a function of temperature. Inset shows an anomaly at 417 K temperature which is due to structural phase transition and change in rate of Urbach energy.

3.6 Structural phase transition using Raman spectroscopy:

Raman spectroscopy is a versatile and non-destructive technique to probe the local structure especially for detection of structural distortion in perovskite materials. In order to confirm the structural phase transition in LGO sample, Raman spectroscopy of the LGO has been carried out. Raman measurements were done using LABRAM HR dispersive spectrometer equipped with a 633 nm excitation laser source and a CCD detector in backscattered mode. For TD Raman measurements THMS600 stage from linkam having accuracy 0.1 K was used. In case of LGO which possess orthorhombic structure with space group *Pbnm* at room temperature (RT). It is well known that a system having *Pbnm* space group have 24 Raman active vibrational modes. Temperature dependent (TD) Raman spectra obtained at various temperatures through the phase transition temperature for LaGaO₃ ceramic is illustrated in Fig. xx. The observed Raman spectra for LGO shows a profile having 17 bands at RT, namely, $55(A_g)$, $92(B_{1g})$, $101(B_{3g})$, $117(B_{2g})$, $137(B_{1g})$, $147(A_g)$, $173(B_{3g})$, $255(A_g)$, $277(A_g)$, $335(B_{3g})$, $357(B_{1g})$, $404(B_{3g})$, $417(B_{2g})$, $433(A_g)$, $451(B_{3g})$, 584(overtone), 708(overtone) cm⁻¹. It is clear from the figure that with increase in temperature Raman spectrum changes drastically above 420 K, which is closed to reported structural phase transition from *Pnma* to *R3c* at 418 K.[33] The irreducible representations for *Pnma* and *R3c* space group for optical as well as acoustic vibrational modes are given below.

For *Pnma* space group:

$$T_{op} = 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g} + 8A_g + 7B_{1u} + 9B_{2u} + 9B_{3u}$$
$$T_{ac} = B_{1u} + B_{2u} + B_{3u}$$

For R3c space group:

$$T_{op} = A_g + 3A_{2g} + 4_{Eg} + 2A_{1u} + 3A_{2u} + 5E_u$$
$$T_{ac} = A_{2u} + E_u$$



Figure 3. 7: The Raman spectra of LGO at (a) 30°*C (b)* 90°*C (c)* 145°*C (d)* 150°*C (e)* 300°*C temperature.*

Additionally, the shifting of Raman modes to lower wave numbers is observed with increasing the temperature, which could be due to expansion in the structure[34]. The systematic shifting of bands with temperature is illustrated in Figure-3.8. Raman is a powerful technique to probe the thermal/structural disorders and possible signature of such disorders is essentially lies in spectral width of Raman line shapes.



Figure 3. 8: The systematic shifting of band positions with increase in temperature through the phase transition of LGO.

Chapter 4

Summary and conclusion:

In this chapter summary and conclusion of the thesis are discussed. First of all, summary is going to discuss here below.

Summary:

Polycrystalline sample of LaGaO₃ has been prepared by modified wet chemical route method. The structural phase purity of the prepared samples is confirmed by powder X-ray diffraction (PXRD) measurements followed by the JCPDS file. The optical properties such as band gap and urbach energy etc, of the prepared sample have been studied using diffuse reflectance spectroscopy (DRS). Temperature dependent (TD) optical absorption spectroscopy and TD Raman spectroscopy experiments has been performed in order to determine the exact structural phase transition temperature. An anomaly observed at 420 K in optical band gap and electronic disorder variation has been observed and understood in terms of change in structure from orthorhombic (*Pnma*) to rhombohedral (R3c), which is well conformance with Raman structural phase transition temperature. Temperature dependent band gap measurements shows that band gap decreases as the temperature increases. Our results clearly suggest that optical absorption spectroscopy could be an economical and non-destructive temperature dependent optical absorption spectroscopy and TD Raman spectroscopy.

Conclusion:

In conclusion, a single phase sample LGO has been prepared by wet chemical route. Structural phase transition in LaGaO₃ from orthorhombic (*Pnma*) to rhombohedral (*R3c*) is probed by economical and non-destructive temperature dependent optical absorption spectroscopy and TD Raman spectroscopy. An anomaly observed at 420 K in optical band gap and electronic disorder (urbach energy) variation has been understood in terms of change in structure from orthorhombic (*Pnma*) to rhombohedral (R3c), which is well conformance with Raman structural phase transition temperature.

Outcomes of this thesis work:

- Some experimental synthesis methods such as solid state method and sol-gel route are learned.
- Some sample characterization techniques such as X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), temperature dependent (TD) DRS, Raman spectroscopy and TD Raman spectroscopy are studied.
- Variation of band gap as a function of temperature is studied.
- Variation of Urbach energy as a function of temperature is studied.

Future research plans:

- Temperature dependent (TD) X-ray diffraction (XRD) measurements to confirm the structural phase transition.
- Temperature dependent (TD) dielectric measurements also to confirm the structural phase transition.
- Doping of Nickel in pure prepared LGO sample to further study the other properties like magneto-dielectric effect and other effects.

References:

- R. Aleksiyko, M. Berkowski, J. Fink-Finowicki, P. Byszewski, R. Diduszko, E. Kowalska, Growth and structure of strontium-doped LaGaO3, in: A. Rogalski, K. Adamiec, P. Madejczyk (Eds.), Zakopane, Poland, 2001: pp. 50–54. doi:10.1117/12.435870.
- [2] N.V. Chezhina, É.V. Bodritskaya, N.A. Zhuk, V.V. Bannikov, I.R. Shein, A.L. Ivanovskiĭ, Magnetic properties and electronic structure of the LaGaO3 perovskite doped with nickel, Phys. Solid State. 50 (2008) 2121–2126. doi:10.1134/S106378340811019X.
- [3] V. Mishra, M.K. Warshi, A. Sati, A. Kumar, V. Mishra, R. Kumar, P.R. Sagdeo, Investigation of temperature-dependent optical properties of TiO2 using diffuse reflectance spectroscopy, SN Appl. Sci. 1 (2019) 241. doi:10.1007/s42452-019-0253-6.
- [4] Y. Q. Tang,a C. López-Cartes,a M. A. Avilésb and J. M. Córdoba, Isosymmetric structural phase transition of the orthorhombic lanthanum gallate structure as a function of temperature determined by Rietveld analysis - CrystEngComm (RSC Publishing), (2018). https://pubs.rsc.org/en/content/articlelanding/2018/ce/c8ce00726h#!d ivAbstract (accessed June 18, 2019).
- [5] W Marti, P Fischer, F Altorfer, H J Scheel and M Tadin, Crystal structures and phase transitions of orthorhombic and rhombohedral RGaO3 (R=La,Pr,Nd) investigated by neutron powder diffraction -IOPscience, (n.d.). https://iopscience.iop.org/article/10.1088/0953-8984/6/1/014/meta (accessed June 18, 2019).
- [6] D.C. Dube, H.J. Scheel, I. Reaney, M. Daglish, N. Setter, Dielectric properties of lanthanum gallate (LaGaO 3) crystal, J. Appl. Phys. 75 (1994) 4126–4130. doi:10.1063/1.355993.
- [7] Wei-Lin Wangw and Hong-Yang Lu, Phase-Transformation-Induced Twinning in Orthorhombic LaGaO3: {121} and [010] Twins, (2006).
- [8] M.V. Kurik, Urbach rule, Phys. Status Solidi A. 8 (1971) 9–45. doi:10.1002/pssa.2210080102.
- [9] I. Bonalde, E. Medina, S.M. Wasim, Temperature dependence of the Urbach energy in ordered defect compounds Cu-III3-VI5 and Cu-III5-VI8, J. Phys. Chem. Solids. 66 (2005) 1865–1867. doi:10.1016/j.jpcs.2005.10.002.
- [10] I. Bonalde, E. Medina, M. Rodríguez, S.M. Wasim, G. Marín, C. Rincón, A. Rincón, C. Torres, Urbach tail, disorder, and localized modes in ternary semiconductors, Phys. Rev. B. 69 (2004) 195201. doi:10.1103/PhysRevB.69.195201.
- [11] S. John, C. Soukoulis, M.H. Cohen, E.N. Economou, Theory of Electron Band Tails and the Urbach Optical-Absorption Edge, Phys. Rev. Lett. 57 (1986) 1777–1780. doi:10.1103/PhysRevLett.57.1777.
- [12] A. Ecija, K. Vidal, A. Larrañaga, L. Ortega-San-Martín, M.I. Arriortua, Synthetic Methods for Perovskite Materials; Structure and Morphology, Adv. Cryst. Process. (2012). doi:10.5772/36540.
- [13] I. Stijepović, A.J. Darbandi, V.V. Srdic, Conductivity of doped LaGaO3 prepared by citrate sol-gel method, J. Optoelectron. Adv. Mater. 12 (2010) 1098–1104.

- [14] K. Huang, J.B. Goodenough, Wet Chemical Synthesis of Sr- and Mg-Doped LaGaO3, a Perovskite-Type Oxide-Ion Conductor, J. Solid State Chem. 136 (1998) 274–283. doi:10.1006/jssc.1997.7706.
- [15] C. Suryanarayana, M.G. Norton, X-Ray Diffraction: A Practical Approach, Springer US, 1998. https://www.springer.com/in/book/9780306457449 (accessed March 25, 2019).
- [16] R.W. Frei, H. Zeitlin, Diffuse Reflectance Spectroscopy, C R C Crit. Rev. Anal. Chem. 2 (1971) 179–246. doi:10.1080/10408347108542764.
- [17] V. Mishra, M.K. Warshi, A. Sati, A. Kumar, V. Mishra, A. Sagdeo, R. Kumar, P.R. Sagdeo, Diffuse reflectance spectroscopy: An effective tool to probe the defect states in wide band gap semiconducting materials, Mater. Sci. Semicond. Process. 86 (2018) 151–156. doi:10.1016/j.mssp.2018.06.025.
- [18] V. Mishra, M.K. Warshi, R. Kumar, P.R. Sagdeo, Design and development of in-situ temperature dependent diffuse reflectance spectroscopy setup, J. Instrum. 13 (2018) T11003. doi:10.1088/1748-0221/13/11/T11003.
- [19] J.R. Ferraro, K. Nakamoto, C.W. Brown, Introductory Raman spectroscopy, 2. ed, Academic Press, Amsterdam, 2003.
- [20] A. Kaabi, M. Tliha, A. Dhahri, C. Khaldi, J. Lamloumi, Electrochemical properties of the LaGaO3 perovskite-type oxide used as negative electrode in Ni/MH accumulators, in: 2016 7th Int. Renew. Energy Congr. IREC, 2016: pp. 1–5. doi:10.1109/IREC.2016.7478911.
- [21] H.M. Rai, R. Late, S.K. Saxena, V. Mishra, R. Kumar, P.R. Sagdeo, Archna Sagdeo, Room temperature magnetodielectric studies on Mndoped LaGaO 3, Mater. Res. Express. 2 (2015) 096105. doi:10.1088/2053-1591/2/9/096105.
- [22] C. Kittel, Introduction to Solid State Physics, Wiley, 2004.
- [23] P.R. Sagdeo, P. Singh, H.M. Rai, R. Kumar, A. Sagdeo, P. Rajput, Optical bandgap and bowing parameter for Fe doped LaGaO3, ArXiv160304961 Cond-Mat. (2016). http://arxiv.org/abs/1603.04961 (accessed June 12, 2019).
- [24] L. Gupta, S. Rath, S.C. Abbi, F.C. Jain, Temperature dependence of the fundamental band gap parameters in cadmium-rich ZnxCd1-xSe using photoluminescence spectroscopy, Pramana. 61 (2003) 729– 737. doi:10.1007/BF02706122.
- [25] P.K. Sarswat, M.L. Free, A Study of Energy Band Gap Temperature Relationships for Cu2ZnSnS4 Thin Films, (n.d.) 8.
- [26] J. Wu, W. Walukiewicz, W. Shan, K.M. Yu, J.W.A. Iii, S.X. Li, E.E. Haller, H. Lu, W.J. Schaff, Temperature dependence of the fundamental band gap of InN, J. Appl. Phys. 94 (2003) 4457–4460. doi:10.1063/1.1605815.
- [27] H. Hayashi, M. Suzuki, H. Inaba, Thermal expansion of Sr- and Mgdoped LaGaO3, Solid State Ion. 128 (2000) 131–139. doi:10.1016/S0167-2738(99)00346-X.

- [28] L.F. Jiang, W.Z. Shen, Q.X. Guo, Temperature dependence of the optical properties of AlInN, J. Appl. Phys. 106 (2009) 013515. doi:10.1063/1.3160299.
- [29] J. Bhosale, A.K. Ramdas, A. Burger, A. Muñoz, A.H. Romero, M. Cardona, R. Lauck, R.K. Kremer, Temperature dependence of band gaps in semiconductors: Electron-phonon interaction, Phys. Rev. B. 86 (2012) 195208. doi:10.1103/PhysRevB.86.195208.
- [30] R. Pässler, Semi-empirical descriptions of temperature dependences of band gaps in semiconductors, Phys. Status Solidi B. 236 (2003) 710–728. doi:10.1002/pssb.200301752.
- [31] B. Abay, H.S. Güder, H. Efeoğlu, Y.K. Yoğurtçu, Temperature dependence of the optical energy gap and Urbach–Martienssen's tail in the absorption spectra of the layered semiconductor Tl2GaInSe4, J. Phys. Chem. Solids. 62 (2001) 747–752. doi:10.1016/S0022-3697(00)00236-5.
- [32] A. Kumar, M.K. Warshi, V. Mishra, S.K. Saxena, R. Kumar, P.R. Sagdeo, Strain control of Urbach energy in Cr-doped PrFeO3, Appl. Phys. A. 123 (2017) 576. doi:10.1007/s00339-017-1186-9.
- [33] G.A. Tompsett, N.M. Sammes, R.J. Phillips, Raman spectroscopy of the LaGaO3 phase transition, J. Raman Spectrosc. 30 (1999) 497– 500. doi:10.1002/(SICI)1097-4555(199907)30:7<497::AID-JRS409>3.0.CO;2-V.
- [34] T. Inagaki, Raman studies of LaGaO3 and doped LaGaO3, Solid State Ion. 118 (1999) 265–269. doi:10.1016/S0167-2738(98)00350-6.