# OPTICAL AND ELECTRICAL PROPERTIES OF SiO<sub>2</sub> AND CaSiO<sub>3</sub>

M.Sc. Thesis By RITU YADAV



## DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

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# OPTICAL AND ELECTRICAL PROPERTIES OF SiO<sub>2</sub> AND CaSiO<sub>3</sub>

## A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by RITU YADAV



## DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2018

Dedicated To

My Parents

And Teachers

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Ritu Yadav Master of Science Department of Physics Indian Institute of Technology Indore

#### Abstract

Wide band gap materials are of very high research interest due to their wide applications in semiconductor industry.  $SiO_2$  and  $CaSiO_3$ , both can be used as the topmost layer of the solar cell because it is observed in literature survey that their optical properties can be modified by the action of temperature and these modified samples may exhibit some interesting properties by doping suitable material. Keeping all these in view, in present work, samples of  $SiO_2$  and  $CaSiO_3$  has been prepared by sol gel method and hydrothermal method respectively. Purity of these samples has been confirmed by analyzing their XRD pattern and indexing was done for miller planes corresponding to each peak. The band gap for all presently studied samples has been determined through diffuse reflectance spectroscopy (DRS) based on the formalism of Kubelka-Munk function and Tauc relation.

The band gap of SiO<sub>2</sub> Samples was observed to be decreasing with increase in Annealing temperature making it suitable to use as the top most layer of solar cell if band gap can further be decreased by doping/defects or other means. The band gap of CaSiO<sub>3</sub> has been observed to be increasing with increase in Annealing temperature; it proves that we will need some other method such as doping/defects to make it suitable so that it can be used in increasing the efficiency of solar cell. Defect states (extra state at lower energy) are clearly visible in DRS absorption plot, by comparing this plot with theoretical calculations; one can find the exact amount (percentage) of oxygen defects produced by annealing at different temperatures. Keeping this in view, we have performed Density functional to generate Density of states (DOS) and optical spectra using WIEN2k code. A first-principle calculation has been carried out using local density Approximations (LDA). To validate our experimental results, we have performed first principle calculations and the results are found to be in accordance with the experimental data.

**Key Words:** Wide band gap semiconductors, sol gel method, hydrothermal method, diffused reflectance spectroscopy, First-principle calculations.

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	oxygen vacancy			

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## Abbreviations

X-ray Diffraction	XRD
Diffused reflectance spectroscopy	DRS
Density of States	DOS
Local density Approximation	LDA
Density functional Theory	DFT
Urbach Energy	$E_U$
Indium Tin Oxide	ITO
Florine doped tin oxide	FTO
Wide band gap semiconductors	WBGS
Metal-oxide semiconducting field effect transistor	MOSFET
Kohn Sham	KS
Iso-propyl Alcohol	IPA

#### **CHAPTER 1**

#### **Introduction and Motivation**

During last six decades the nature of electronic devices has witnessed huge changes. Discovery of solar cell has revolutionized the industry of renewable sources of energy[1,2]. The top electrode used in solar cell (marked in blue in figure 1.1) needs to be optically transparent i.e. a material which transmit not only visible but even UV part of the solar spectrum with minimum optical absorption coefficient as well as it should be electrically conducting. Indium tin oxide (ITO), Florine doped tin oxide (FTO), Tin oxide, Titanium oxide etc are presently being used. All present transparent conducting oxides are having band gap ranging from 2.8 eV to 3.3 eV, which blocks significant part of solar spectrum to enter to the active solar cell material [3,4]<sup>-</sup>

The Idea is to improve the efficiency of the solar cell by replacing this top most electrode, for which we need a wide band gap semiconducting material as top layer which is cheap as well as easily available.



(http://www.alternative-energy-tutorials.com/solar-power.html)

Figure-1.1: Components of solar cell



Figure-1.2: spectrum of solar radiation

Optical properties have significant effect on the efficiency of solar cell. A wide research has been done on the modification of optical properties of Silicon dioxide and Calcium Silicates by the action of temperature [5,6]<sup>,</sup> self or external doping by suitable material [7]. Which suggests that the band gap of these materials can be modified by the action of heat and same has been investigated in this project work? Suitable wide band gap materials which are studied here include SiO<sub>2</sub> and CaSiO<sub>3</sub>. We have tried to make them to absorb the photons near visible region (moderate band gap). These materials have been discussed in detail.

#### **1.1 Wide Band Gap materials**

On the basis of band gap we can classify the solids in three different categories; insulator, conductor and semi-conductor. Wide-band gap semiconductors (WBG or WBGS) are semiconducting materials which have a relatively large band gap compared to typical semiconductors. Typical semiconductors like silicon have a bandgap in the range of 1 to 1.5 eV, whereas wide-bandgap materials have bandgaps in the range of 2 - 4 eV [8,9].Generally, wide-bandgap semiconductors have electronic properties which fall in between those of typical semiconductors and insulators.

Wide band gap semiconductors find applications in optoelectronics and in the fabrication of high-power and high-frequency microelectronic devices[9,10]. Wide bandgap semiconductors permit devices to operate at much higher voltages, frequencies and temperatures than conventional semiconductor materials like silicon and gallium arsenide. They are the key component used to make green and blue LEDs and lasers, and are also used in certain radio frequency applications, notably military radars. Their inherent qualities make them suitable for a wide range of roles, and they are one of the leading contenders for next-generation devices for general semiconductor use.



Figure-1.3: classification on the basis of band gap

#### **1.2 Quartz (SiO<sub>2</sub>)**

The word "Quarz" ("t" missing) came into existence from 14th century; Quartz is a crystalline form of  $SiO_2$  and known to crystallize at very high pressure inside the earth crust. In pure form, quartz is a colorless crystalline material having glass-like appearance.

#### Structure

It is a compound of silicon and oxygen (silicon dioxide SiO<sub>2</sub>), the Si atom shows tetrahedral coordination, with four oxygen atoms surrounding a central Si atom. In the unit cell of  $\alpha$ -quartz, there is a tetrahedral arrangement with one silicon bonded to four oxygen atoms, the central tetrahedron shares all four of its corner O atoms, the two face-centered tetrahedra share two of their corner O atoms, and the four edge-centered tetrahedra share just one of their O atoms with other SiO<sub>4</sub> tetrahedra. Most oxygen atoms will be bonded to two silicon atoms, so that two tetrahedra are joined at a corner (bridging atoms). If all oxygen atoms are bridging, then a regular crystal structure results – quartz. Literature survey reveal that crystalline SiO<sub>2</sub> (Quartz) shows Hexagonal structure [11].



Figure-1.4: Structure of SiO<sub>2</sub>

#### **Industrial Applications**

Silicon dioxide, also known as silica, has wide industrial applications due to its exceptional electronic and optical properties. It is found mainly in Amorphous and crystalline form.

 $\alpha$  – Quartz is used in time measurements purpose i.e. clocks because its crystal oscillations are very precise.

Amorphous silicon dioxide ( $\alpha$ -SiO<sub>2</sub>) is a key element in silicon integrated circuits and optical glass fibers [12–15]

Amorphous form of  $SiO_2$  is used as an insulation layer between the gate and the conducting channel of the metal-oxide-semiconductor-field effect transistor (MOSFET)[16]. It is also used in optical fibers due to its good optical transmission over a range of wavelengths[17]

#### **1.3 Wollastonite (CaSiO<sub>3</sub>)**

#### Structure

 $CaSiO_3$  have a ABO<sub>3</sub> Perovskite structure in which A atoms are present on the corners, B atoms are present on the centre and O atoms are present on the centre of each face of the cube. This arrangement of atoms depending on the symmetry of the system may form a centro-symmetric or noncentrosymmetric octahedron which may lead to net dipole moment of the system.



Figure-1.5: Structure of CaSiO<sub>3</sub>

#### **Industrial applications**

CaSiO<sub>3</sub> has wide application in sensors, LEDs, solar cell etc. silicates show outstanding chemical and thermal stability, visible-light transparency, high yield and multicolor phosphorescence[18] and depending on calcinations temperatures, CaSiO<sub>3</sub> shows various kind of phases including triclinic and monoclinic crystal structure i.e  $\alpha$ -CaSiO<sub>3</sub> and  $\beta$ -CaSiO<sub>3</sub> [19]. So Wollastonite material is very significant material for research purpose to investigate the effect of crystallographic structure on electronic and optical properties and also from application point of view. It has low thermal conductivity, moderate melting point ( $1540^{\circ}$ C), high crystallization capacity and a low viscosity at high temperatures [20,21].

Study shows that the electrical conductivity of SiO<sub>2</sub> increases with increase in defect states which may arises from various reasons. These defect states may arise from temperature variation (self-doping) and can be easily seen from optical spectra measured form Diffused reflectance spectroscopy. DRS is explained in detail in chapter-2 Experimental techniques. These optical spectra are highly affected by urbach tail. Literature survey shows that urbach energy increase with increase in temperature for most of the substances[8].

#### **1.4 The Urbach Energy**

It is also termed as Urbach width and Urbach tail states. Localized states are present in between the valance band and conduction band in optical spectroscopy for disordered semiconductors is a problem of research from fifties. It is well known that band tail states in amorphous semiconductors and imperfect crystalline solids arise due to the thermal variation, change in the chemical composition and presence of any dislocation or vacancy. This tail varies exponentially. This can easily be seen as exponential variation in absorption coefficient along the absorption band edge.

Absorption coefficient ( $\alpha$ ) for Urbach tails can be written as[2]:

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

Where E' and  $\alpha'$  are constants determined by extrapolated linearly from  $\ln(\alpha)$  Versus E curves at a given temperature T and  $\frac{kT}{\sigma}$  is Urbach energy (E<sub>u</sub>). Behavior of  $\alpha$  is referred in literature as **Urbach-Martienssen's rule**[21,22].

#### Origin of urbach tail

Urbach tail appears due to various kinds of disorders present in crystals, these disorders may occur due to change in temperature, chemical composition or various structural defects present in the crystal[23–25].

Band theory of solids suggests that electron is moving in periodically varying potential having period equal to lattice constant is responsible for the observed well defined band structure, any fluctuation in the value of periodicity possibly due to temperature variation or incorporation of impurities of different ionic radii arrangement of atoms gets disturbed (periodicity gets disturbed) and electron feels a potential which differ from place to place. Due to this, the valence band and conduction band do not have sharp cut off but have localized tails states. As a result, optical absorption edge is not fall sharp and has tail at lower energies. This tail may also arise from various kinds of defects, structural coherency, chemical in-homogeneity etc.



*Figure-1.6: localized state formation in between the valance band and Conduction band.* 

Many studies has been done on the theoretical calculation of various properties of materials for which it is difficult to carry out experiments and also some literature compares the results obtained from theoretical calculations and experimental data. In this regard, Density functional theory has been discussed here:

#### **1.5 Density functional theory**

Impurities and defects present in a material play a crucial role in determining the properties of a device. Hence it is essential to understand these defects and impurities to improve their properties. In this field, first principle proves to be very useful tool when combined with experimental studies. It can provide strong support to experimental data and can help in understanding the results on the basis of theoretical results. We can use first principle calculations to predict the properties for which experimental data is not available or it is not easy to carry out experiment. Large numbers of experimental and theoretical researches focused on the defects and their effects on dielectric properties in quartz [26,27].

#### Hartree - Fock and Density Functional Theory Analysis

The accuracy of the results depends mainly on the Hamiltonian and variational basis set we adopted in calculation.

#### **The Hartree–Fock Method**

<u>Electronic Hamiltonian in the Born–Oppenheimer approximation:</u> it includes three terms, the kinetic-energy operator, the Columbic repulsive energy between the electrons and the Columbic attractive energy between electrons and fixed nuclei.

$$H = -\sum_{i}^{N} \nabla_{i}^{2} + \frac{1}{2} \sum_{i} \sum_{j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i} \frac{z_{o}}{|\mathbf{r}_{o} - \mathbf{r}_{i}|},$$
(2)

The N -electron problem is reduced to a system of coupled one-electron equations, the HF equations[26], for the orbital of the Slater determinant

to minimize the total energy of the system. To impose the correct spin symmetry of the state, we can use the restricted version of the HF method (RHF), in which the same spatial orbital is used for describing electrons of opposite spin. In this way, the computational effort gets reduced with respect to the unrestricted version of the HF method, but the correlation between electrons of different spin is neglected. Indeed, the minimum energy calculated by RHF is overestimated with respect to the experimental one by a quantity called "correlation energy". This method, however, provides an appreciable description of the band structure and band shape.

#### **Density functional theory (DFT)**

It is based on the Hohenberg–Kohn theorem [26,28,29] according to which the ground-state energy per unit cell are functional of the electron density. Here, the density is considered to be the fundamental quantity for studying any electronic system, Kohn and Sham (KS)[28-30] proposed the use of a model made of non interacting electrons having the same density as the real one. In this model, one can define, as in the HF method, a system of coupled one-electron equations, the KS equations, allow us to obtain the exact solution of the problem, i.e., the exact density of the ground state of the interacting -electron system[29]. The difficulty of this method, now only reduces to the determination of the energy functional that gives the exact charge density. As the theory does not indicate an explicit and general form for the exchange- and correlation-energy functional, a number of approximate expressions have been proposed in relation to specific density classes. Some of them include: the local density approximation (LDA) model, it based on the assumption of a locally homogeneous electron gas [29]. In recent years, gradient-corrected schemes for the density functional have been worked out, which provide results in agreement with experiments.

#### First Principle Calculations using density functional theory:

Hamiltonian of a system can be written as

$$H = -\sum_{i}^{m} \nabla_{i}^{2} - \sum_{n=1}^{n} \nabla_{n}^{2} + \frac{1}{2} \sum_{i} \sum_{j} \frac{1}{|r_{i} - r_{j}|} - \sum_{i} \frac{Z_{o}}{|r_{j} - r_{i}|} + \sum_{m} \sum_{n} \frac{Z_{m} Z_{n}}{|R_{m} - R_{n}|}, \qquad (3)$$

Here, first term is kinetic energy operator of e, second term is for Nucleus, third term stands for e-e repulsion, fourth term represents e- nucleus interaction and last term represents Nucleus- Nucleus interaction. Appliying Born-oppenhiemer approximation, it is reduced to the form,

$$H = -\sum_{i}^{N} \nabla_{i}^{2} + \frac{1}{2} \sum_{i} \sum_{j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i} \frac{Z_{o}}{|\mathbf{r}_{o} - \mathbf{r}_{i}|},$$
(4)

Using Hartree fock approximation, we get expression as shown in equation(5)

$$H = -\sum_{i=1}^{N} \nabla_{i}^{2} + \frac{1}{2} \sum_{i=1}^{N} \frac{1}{|r_{i} - r_{j}|} + \sum_{i=1}^{N} \nu(r_{i}),$$
(5)

Within this scheme, this quantity is minimized over the class of wavefunctions given by single slater determinant of one particle orthonormal orbitals,

Resultant ground state energy is minimized to the following form:

$$E = \sum_{i} \langle \phi_{i} | \mathbf{h}_{i} | \phi_{i} \rangle + \frac{1}{2} \sum_{i,j} [\langle \phi_{i} \phi_{j} | \frac{\mathbf{e}^{2}}{|\mathbf{r}-\mathbf{r}'|} | \phi_{i} \phi_{j} \rangle - \delta_{i,j} \langle \phi_{i} \phi_{j} | \frac{\mathbf{e}^{2}}{|\mathbf{r}-\mathbf{r}'|} | \phi_{j} \phi_{i} \rangle],$$

$$(6)$$

#### Kohn- sham approximation

It employs Iterative Self- Consistency scheme which satisfies following Schrödinger equation

$$\left[\frac{-h}{2m}\nabla^2 + V(r) + V_N(r) + V_{XC}(r)\right]\Psi(r) = E\Psi(r),\tag{7}$$

Here, first term indicates the kinetic energy of the electrons, second term V(r) represents electron- electron interaction,  $V_N(r)$  represents electron-

nucleus interaction and  $V_{XC}(r)$  is exchange potential which represents the assymetric distribution of electrons in different orbitals due to their assymetric shape. This exchange potential has been introduced so as to get the exact values of energy as that of experimental results.

It employs Iterative Self- Consistency[31] scheme which satisfies Schrödinger equation as shown in equation(7). In each cycle, the exchange correlation potential has been varied. This cycle goes on untill total energy is minimum.

#### **CHAPTER 2**

#### **Experimental Techniques**

In this chapter some of the experimental techniques are discussed which proved to be useful in this project work. It includes following techniques:

#### 2.1 Sample Preparation Method

- 2.1.1 Solid State Reaction Method
- 2.1.2 Sol-Gel Method
- 2.1.3 Hydrothermal Method
- **2.2 Characterization Techniques**
- 2.2.1 X- Ray Diffraction (XRD)
- 2.2.2 Diffuse reflectance spectroscopy (DRS)
- 2.2.3 Theoretical calculations: A first principle study

#### 2.1 Sample Preparation Methods

#### 2.1.1 Solid State Reaction Method:

In conventional solid state reaction method, powder oxides of constituents are mixed in their proper stoichiometric ratio. It 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 higher temperatures (800°C to 1600°C). The reaction may be written in the following form.

$$CaCO_3 + Si + O_2 + Heat \rightarrow CaSiO_3 + CO_2, \tag{8}$$

$$CaCO_3 + SiO_2 + Heat \rightarrow CaSiO_3 + CO_2, \tag{9}$$

Atomic weight of  $CaSiO_3 = 116.1617 \text{ g}$ Atomic weight of  $CaCO_3 = 100.0872 \text{ g}$ Atomic weight of  $SiO_2 = 60.0843 \text{ g}$  116.1617 g of  $CaSiO_3 = 1 \text{ mole}$  5 g CaSiO3 = 5/116.1617 moles = 0.043043 molesWeight of  $CaCO_3$  needed  $1 \text{ mole of } CaCO_3 = 100.0872 \text{ g}$   $0.043043 \text{ moles of } CaCO_3 = 0.043043 \times 100.0872 \text{ g}$  = 4.308093 gWeight of  $SiO_2$  needed  $1 \text{ mole of } SiO_2 = 60.0843 \text{ g}$ 

0.043043 moles of  $CaCO_3$  = 0.043043  $\times$  60.0843 g

$$= 2.58623$$
 g

After weighing these oxides, following steps were followed:

- a) Corresponding oxides were mixed and grinded with the help of Agate mortar and pestle in Iso-Propyl Alcohol (IPA) for 4-5 hours.
- b) The sample was then heated in furnace at 1000°C for 24 hours with a controlled heating rate of 5° per minute.
- c) Resulting sample was cooled up to 300°C with a cooling rate of 1° per minute, after that, it was allowed to cool naturally to room temperature by switching off the furnace.
- d) Repeat the steps (a) to (c) for second heating at  $1250^{\circ}$ C.
- e) Circular pellets of 1 mm thickness and about 13 mm diameter (by using almost half quantity of corresponding powder sample) were prepared by applying a high pressure by hydraulic pressure pelletizer.
- f) These prepared pellets and powdered samples were sintered separately in air at 1350°C for 24 hours.

CaSiO<sub>3</sub> (CaSiO<sub>3</sub>-I and CaSiO<sub>3</sub>-II) powders are conventionally prepared by solid-state reaction between CaCO<sub>3</sub> and Si powder.

This method requires a high calcination temperature for a long period of time because of the limited diffusion during calcinations [32].

#### 2.1.2 Sol-Gel Method:

#### Why sol gel method??

<u>Homogeneity</u>: since it is a liquid suspension of solid particles, it causes the precursors to mix in homogenous manner and hence increasing the tendency to react.

<u>Less temperature needed</u>: we need to heat the sample upto  $1600^{\circ}$ C in case of solid state method, sol gel method has the advantage that it needs a temperature less than that of solid state.

$$Si + O_2 + Heat \rightarrow SiO_2,$$
 (10)

Atomic weight of  $SiO_2 = 60.0843$  g

60.08430g of SiO<sub>2</sub> = 1 mole 5 g SiO<sub>2</sub> = 5/ 60.0843 moles = 0.08321 moles

Weight of Si powder needed

1 mole of Si = 28.0855 g  
0.08321 moles of Si = 0.08321 × 28.0855 g  
= 2.3369 g  

$$Si(NO_3)_3.9H_2O + C_6H_8O_7.H_2O + C_2H_6O \rightarrow SiO_2 + 10H_2O + 8CO_2 + \frac{3}{2}N_2,$$
(11)

a) Proper amount of Si powder was dissolved in HNO<sub>3</sub> to form water soluble nitrates and were dissolved in excess of water to form stable metal chelate complex.

b) 1 mole of citric acid per mole of metal ions is used which acts as a chelating agent.

c) Small amount of ethylene glycol was added to the solution, which helps in hydrolysis process.

d) The resulting sol was heated at constant temperature 70°C with a constant stirring rate until a gel is formed.

e) This gel was dried in furnaces at  $100^{\circ}$ C and then grinded in agate mortar and heated in the air at  $400^{\circ}$ C for 4 hours with constant heating rate of  $5^{\circ}$ C/min and constant cooling rate  $1^{\circ}$ C/min.

 f) Then again grinding in agate mortar the powder was heated to 700°C for 12 hours at constant heating and cooling rates.

#### 2.1.3 Hydrothermal Method:

We switched to Hydrothermal method because it is difficult to prepare the single-phase CaSiO<sub>3</sub> by calcinations in air [32,33].

a) Powders of  $CaCO_3$  (0.86161gm) and  $SiO_2$  (0.51724 gm) were dissolved in HNO<sub>3</sub> in proper ratio (calculations same as done before for sol gel method).

b) KOH was added as reagent in proper ratio.

c) The solution was kept in Teflon liner (50ml) and this setup was kept in furnace at 120°C for 24 hours.

d) 1gm of sample was extracted from the resulting solution.

## 2.2 Characterization techniques:

#### 2.2.1 X-Ray diffraction (XRD)

XRD is the most common and most important technique to characterize polycrystalline samples. It gives information regarding lattice parameters, phase purity, crystalline nature, crystal structure and strain. X-rays are produced by the interaction of electron beam and the electrons in atomic shells. In our lab source, electron beam is bombarded on Cu target, producing the x-rays.

Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles. X-rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter. The condition that needs to fulfill for x-ray diffraction to take place is:

Bragg's law is given by, 
$$2d_{hkl}sin\theta = n\lambda$$
, (11)

Here,  $\lambda$  is wavelength of incident x rays, which must be comparable to the interplanar spacing,  $d_{hkl}$  and  $\theta$  is the angle made by x-ray beam with that of planes.



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

From figure 2.1,

$$\sin(\theta) = \frac{x}{d_{hkl}}$$
$$\Rightarrow x = d_{hkl} \sin(\theta)$$

Path difference  $\Delta = 2x$ ; Condition for Constructive interference is:  $\Delta = n\lambda$ Hence,  $2d_{hkl}\sin(\theta) = n\lambda$ , (12)

#### Instrumentation:

X-ray diffractometer consists of three parts: X-ray source, sample holder and an X-ray detector as shown in fig.(2.2). The X-rays are produced in cathode ray tube, filament is heated to produce electrons, these electrons are accelerated towards the target by applying an electric field and the target material is bombarded with electrons.



Figure-2.2: Schematic diagram of X-ray diffractometer

When electrons have sufficient energy to knock out inner shell electrons of the target material, characteristic spectra of X-rays are produced when the outer electron fill the empty vacancy created by the knock out. The total spectra of X-rays consist of several components; the most common are K $\alpha$  and K $\beta$  line. K $\alpha$  consists of K $\alpha_1$  and K $\alpha_2$ . K $\alpha_1$  has a slightly shorter wavelength and much more intensity than K $\alpha_2$ . These wavelengths are characteristic of the target material (Cu, Fe, Mo,Cr). There also exists a continuous spectrum called *Bremsstrahlung*. X-rays which are produced due to the de-acceleration of incoming electron beam by atomic electron.



(www.doitpoms.ac.uk)

Figure-2.3: Continuous (Bremsstrahlung) X-rays and characteristic X-rays

The produced X-rays are then passed through filters (generally Ni) to get monochromatic X-rays.  $K_{\alpha 1}$  and  $K_{\alpha 2}$  are sufficiently close in wavelength such that a weighted average of the two is used. These X-rays are collimated and directed onto the sample. When the geometry of the incident X-rays satisfies the Bragg Equation with the sample plane, constructive interference occurs and it represents a peak of high intensity. These peak intensities are different for different planes because electron density varies in different planes. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded.

#### 2.2.2 UV Visible Diffuse reflectance spectroscopy (DRS):

UV visible spectroscopy is electronic spectroscopy in which we study the light absorbed in UV and visible regions of electromagnetic spectrum (200nm-800nm).

It is also called electronic spectroscopy because the transition occurs between two electronic levels.



(web.phys.ksu.edu)

Figure-2.4: Electromagnetic spectra

We can find Band gap of powder and thin films, Temperature dependent band gap, Refractive index of thin films, Thickness of thin films using this spectroscopy.

#### **Explanation**:

When an electromagnetic of proper frequency (optical range) falls on a sample, some part may gets; transmitted, reflected or absorbed.

Transmittance (T), Reflectance(R) and Absorbance (A) for any material may follows as:

$$T + R + A = 1,$$
 (13)

When a light wave gets transmitted through a sample, it follows Beer-Lambert's law[34],





Figure-2.5: Transmission of incident beam from a sample of thickness t

Here,  $I_o$  is intensity of incident beam, I is the intensity of transmitted wave,  $\alpha$  is Absorption coefficient and t is the thickness of the sample.

The expression for absorption coefficient:

$$\alpha = \frac{-1}{t} ln \frac{l}{l_0},\tag{15}$$

For  $\alpha$  to be maximum it is required to measure transmitted intensity (I) accurately.

For reflecting surfaces, it is necessary to find the reflectance(R) using refractive index

$$R = \left(\frac{n-1}{n+1}\right)^2,\tag{16}$$

Here, n is the refreactive index of the sample

Reflectance can be measured accurately when the sample surface is perfectly smooth (follow law of reflection).

For powdered samples, it is very difficult to calculate reflectance because of its rough surface, in which the light rays, gets reflected in all directions at different angles. These reflected rays are needed to be converged to the detector by using spherical mirrors.

For diffused reflectance, Kubelka-munk gave an expression for calculating absorption coefficient using following expression: [35,36]

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} , \qquad (17)$$

 $F(R_{\infty})$  is the Kubelka–Munk function ( $R_{\infty} = R_{sample}/R_{stan\,dard}$ ). The Kubelka– Munk function is proportional to the absorption coefficient ( $\alpha$ ) and can be written as-

$$F(R_{\infty}) \propto \alpha \propto \frac{(h\nu - E_g)^{\frac{1}{n}}}{h\nu}$$
, (18)

$$(\alpha h \nu)^n = A(h\nu - E_g), \qquad (19)$$

for direct transition , n= 2 and indirect transition [6], n = 1/2 We will get a straight line when  $[F(R_{\infty}) \times hv]^n$  is plotted against *hv*, the intercept of this straight line on energy axis gives band gap. **Working:** Xenon flash lamp is used to produce electromagnetic waves; these waves are then passes through various filters so as to filter the radiations lying between UV-visible spectrums. Light is incident on the sample by using optical fiber (for powder samples) and the reflected light in diffused form is detected by a special attachment. The instrumentation of DRS is shown below



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

#### **2.2.3 Theoretical Calculations**

The *WIEN2k* code is used to study crystal properties on the atomic scale by using LAPW method within DFT, the most precise approach to solve the Kohn-Sham equations. The advantage of first principle method is that they can be carried out without knowing any experimental data. WIEN2k is one of the most reliable simulation codes among computational methods. *WIEN2k* is a full-potential all-electron code developed by *Blaha et al.*[37–39]at the Institut fur Materialchemie, Technical Universitat at Wien, Austria. *WIEN2k* consists of many independent F90/intel programs, which are linked together via C-shell scripts. The code is based on the Kohn-sham formalism of DFT[28,40–43]. To solve the complex Schrodinger wave equation of many interacting particles we need to construct the effective Hamiltonian operator which depends only on the electron density of the electronic system. The schematic diagram of solving Schrodinger wave equation within Code *WIEN2k* is represented by *Figure 2.7*.



Figure-2.7: schematic diagram of solving Schrodinger wave equation within Code WIEN2k

#### Self Consistent Field

Here, we are solving Kohn-Sham equations to obtain the ground state electron density by iterative method; this method is called *Self consistent Field (SCF)*. We set Hamiltonian operator by using the atomic densities at position of the atoms in the system. We solve the Kohn-Sham equations[26], to calculate the electron density of the system. We can calculate new potential and hence new Hamiltonian operator by using this electron density.

These steps are repeated until we get predefined convergence criteria *i.e.* total energy of the material. This converged result is self- consistent i.e. independent of starting potential.

#### **Basis Function**

We need to use a set of basic functions to represent the electronic wave function in order to solve Kohn-Sham equations. The electronic structure calculations done by first principles methods are employed by expanding in basis sets of atomic orbitals.

#### Linearized Augmented Plane Wave Method (LAPW)

In LAPW method[44] the valence electrons (*weakly bonded*) can easily be described by Plane Wave which is the solutions of the Hamiltonian with a zero potential. In case of a core electron (deep in energy) bonded strongly to the nucleus and hence it can be described by spherical harmonics (solutions for a single free atom). The LAPW method combines these two cases by setting up a muffin-tin (MT) sphere[45–47] on each atom. The rest of the space is the interstitial region.

The core and valence electrons are divided on the basis of whether or not electrons in an atom participate in the chemical bonding with other atoms. Core electrons, bound to their nucleus and are thus entirely localized in the MT sphere. The corresponding states are called core states. Valence electrons which are leaking out of the MT-sphere and bond with other atoms. However, we cannot clearly distinguish on this basis for many elements.

#### Steps involved in WIEN2k calculation:-

Following are the steps that needs to be followed to carry our various calculations theoretically

#### Generation of Structure file

- Space group selection of the chosen material.
- Lattice coordinates.
- Selection of appropriately fitted Rmt's of atoms in unit cell structure.
- To import the cif file.

#### Initialization

- Detection of the symmetry.
- Generation of automatic input.
- Selection of k-points generated in irreducible wedge first Brillion Zone.
- Minimum separation energy required to stabilize the unit cell structure.

#### **SCF Calculations**

During self consistent functional, we have to make the appropriate selection regarding the nature of chosen materials. For, a non-magnetic material there is no Need to chosen the spin polarised option. In case the material is magnetic then Following steps are necessarily been considered

- Spin-polarization
- Spin –orbit coupling (strongly localized electronic system).
- Choice of diagonal matrix in strongly correlated systems.
- Electron and charge convergence limit.

After the successful completion of SCF, different properties of selected problems are analyzed like equilibrium lattice constants, bulk modulus, cohesive energy, electronic structures, density of states, optical response etc.

#### **CHAPTER-3**

#### **Results and Discussions**

 $SiO_2$  and  $CaSiO_3$  has been prepared by sol gel and hydrothermal method respectively, the samples are Annealed at different temperatures has been characterized by using the experimental techniques discussed in chapter-2 and results are discussed in this chapter.

#### 3.1 Result discussion for SiO<sub>2</sub>

#### 3.1.1 Structural Study:

Powder X-ray diffraction (XRD) experiments were carried out at BL-12 ADXRD beamline of Indus 2, Indian synchrotron radiation source at Raja Ramanna Centre for advanced Technology Indore [30, 31] to confirm the phase purity of the samples. The wavelength of the x-ray beam was 0.82Å and the diffraction pattern was recorded in the 20 range of 10-50° with a step size of 0.01° using Huber six-circle diffractometer (model: 5020). Figure 3.1 shows the powder XRD pattern of all prepared samples.



Figure 3.1: XRD pattern of SiO<sub>2</sub> annealed at different temperature

It is confirmed from X-rd pattern that the  $SiO_2$  is in single phase. There is a systematic shift in  $SiO_2$  peak towards higher 2 $\theta$  values. This shift shows that the lattice parameters are decreasing with the increase in Annealing temperature. The decrease in lattice parameters is may be due to lattice shrinking. This effect can be explained by creating oxygen vacancy inside the sample.

#### Indexing



Figure 3.2: XRD pattern of SiO<sub>2</sub> indicating miller planes corresponding to each peak

Indexing of XRD pattern has been done by adopting following procedure: Since  $SiO_2$  has hexagonal structure, the relation between interplanar distance d and miller indices is given by:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \,, \tag{20}$$

Using bragg's law,  $2dsin\theta = n\lambda$ 

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} = \frac{4sin^2\theta}{\lambda^2},$$
(21)

Rearranging this,

$$\sin^2\theta = \frac{\lambda^2}{4} \left[\frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}\right],\tag{22}$$

We know the value of c/a for hexagonal system

$$\sin^2\theta = \frac{\lambda^2}{4a^2} \left[\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{(\frac{c}{a})^2}\right],\tag{23}$$

h	K	0	1	2	3
0		0	1.3333	5.3333	12.0000
1		1.3333	4.0000	9.3333	17.3333
2		5.3333	9.3333	16.0000	25.3333
3		12.0000	17.3333	25.3333	36.0000

**Table 3.1:** Values for 
$$\frac{4}{3}(h^2 + hk + k^2)$$

**Table 3.2:** Values of 
$$l^2 / (\frac{c}{a})^2$$
, c/a= 1.8563

l	l <sup>2</sup>	$\frac{l^2}{(c/a)^2}$
0	0	0.0000
1	1	0.2902
2	4	1.1608
3	9	2.6118
4	16	4.6432

From *tables 3.1* and *3.2*, try different combinations of *h*, *k* and *l* for which satisfy the equation (4),

Reject the combinations for which *l* is odd and h+2k is a multiple of 3 (from structure factor calculations). Here, the value of  $\theta$ ,  $\lambda$  and a/c is known for hexagonal crystal system.

#### **Calculation for lattice parameters**

We can also calculate the lattice parameters by following procedure: Look for the indices for which l=0,

$$\sin^2\theta = \frac{\lambda^2}{4a^2} \left[ \frac{4}{3} (h^2 + hk + k^2) \right],$$
(24)

Equation (4) becomes,

$$a^{2} = \frac{\lambda^{2}}{3sin^{2}\theta} \left(h^{2} + hk + k^{2}\right), \qquad (25)$$

Here,  $\lambda, \theta, h$  and k are known

Look for (00l) type of combination,

$$\sin^2\theta = \frac{\lambda^2}{4a^2} \left[ \left( \frac{l^2}{\left(\frac{c}{a}\right)^2} \right) \right] = \frac{\lambda^2}{4c^2} l^2, \tag{26}$$

$$c^2 = \frac{\lambda^2}{4sin^2\theta} l^2$$
 Here,  $\lambda$ ,  $\theta$  and  $l$  are known

#### **3.1.2 Optical properties Analysis:**

#### Band gap by using UV-VIS Spectroscopy

The optical band gap of  $SiO_2$  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[8,35]. 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 calculate the optical band gap, the diffuse reflectance spectra has been converted to equivalent absorption spectra using Kubelka–Munk equation[35,48]:

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

 $R_{\infty} = R_{(Sample)}/R_{(Standard)}$ .  $R_{(Sample)}$  is the diffuse reflectance of the sample and  $R_{(Standard)}$  is that of the standard (BaSO<sub>4</sub> in present case). K and S are the Kubelka–Munk [36]absorption and scattering functions, respectively. Tauc plot[49,50] shows the quantity hv (the energy of the light) on the abscissa and the quantity ( $\alpha$ hv)<sup>1/n</sup> on the ordinate, where  $\alpha$  is the absorption coefficient of the material. The value of the exponent n denotes the nature of the transition:

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

Where n=2 (indirect allowed transition), n=1/2 (direct allowed transition)[35,48].

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 direct band gap fitting for SiO<sub>2</sub> annealed at 700°C, 800°C, 900°C, 1000°C and 1100°C.



**Figure 3.3:** *Band gap plot of sio*<sub>2</sub> *Annealed at (a)* 700°*C (b)* 800°*C (c)* 900 °*C(d)*1000°*C and (e)* 1100°*C* 

The extra energy state (defect states) at low energy values (approx. 5eV) shown in *figure 3.3. Mishra et. al.*[51] shows that the origin of defect states may be due to oxygen deficiency in the sample. In our case these extra states arises with annealing temperature shows clear evidance of oxygen vacancy in sample. It is clearly visible from *figure 3.3* that these

defect states are decreasing systmatically with increase in annealling temperature.



Effect of Annealing temperature on Band gap

Table 3.3

**Figure 3.4:** Band gap variation of  $SiO_2$  sample with annealing temperature and same has been shown in table 3.2.1

From *figure 3.4*, we can say that the band gap of given sample is decreasing with increase in Annealing temperature. This is due to dominating effect of increase in disorderness within sample with temperature as the effect of defect state is not considerable. This can be explained by increase in urbach energy (disorderdness), which has been described from *figure 3.5*.

#### **3.1.3 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. Urbach tail is related to localized states at band edges. 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.

Exponential variation in absorption coefficient along the absorption band edge is a well-known universal feature in optical properties. This exponential tail appears in disordered materials, because these materials have localized states which extended in the band gap. The same phenomenon has been observed in all imperfect crystalline solids and amorphous solids known as Urbach-Martienssen's rule [52,53]or simply Urbach rule given by[22]:

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

Where  $E_u$  is Urbach energy,  $\alpha_o$  is a constant,  $\alpha$  is absorption co-efficient, E' is material-dependent constant and  $\sigma$  is steepness parameter which basically tells us about electron phonon interaction in material. Urbach energy is a measure of how disorder varies with temperature or chemical composition. We know that with increase in temperature periodicity in crystal gets disturbed or we can say atoms will oscillates with higher and higher amplitudes i.e. uncertainty in spatial arrangement of atoms increases so disorder in crystals increases on increasing the temperature which contributes in increase of urbach energy that directly reveals from Figure 3.5. For a disorder free crystal (ideal crystal) the valence band and conduction band have sharp cut off and do not have localized tail states. Due to this, optical absorption edge fall is sharp and there is nothing like urbach tail, this kind of crystal is impossible to synthesize in the lab. So this phenomenon is universal phenomena, observed in all crystalline and amorphous solids. The width of Urbach tail is not only defined by temperature but also defined by two additional temperature independent parameter's so called structural disorder and compositional disorder[23,25,54]. So Urbach energy can be expressed as temperature dependent and temperature independent parameter's which is as following:

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

Where  $E_u(T)$  is contribution due to temperature[8] in Urbach energy,  $E_u(S)$  is contribution due to structural disorders[22]. 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.

 $E_u$  (C) is compositional disordering[55] arises due to non homogeneous chemical composition. So we can conclude that urbach energy gives us idea about various kind of disorder present in Real crystals.





**Figure 3.5:** Urbach energy fitting of SiO<sub>2</sub> annealed at different temperatures (a) 700°C (b) 800°C (c) 900°C (d) 1000°C (e) 1100°C

#### Variation of Urbach energy with Annealling Temperature:



**Figure 3.6:** Variation of Urbach energy of  $SiO_2$  with annealing temperature and same has been shown in table 3.3.1

It can easily be seen from *figure 3.6* that the urbach energy is increasing systematically with the increase in Annealing temperature since disorderedness increases with increase in temperature[8].

#### 3.1.5 Resistivity measurement

Resistivity measurement of  $SiO_2$  pallets has been done using four probe method. The results of which have beens shown in *figure 3.7* 



**Figure 3.7:** Variation of Resistivity of  $SiO_2$  pallets with annealing temperature

It shows that although the resistivity of  $SiO_2$  pallet is decreasing with the increase in annealing temperature, the resistivity is still very height to be used as top electrode of solar cell.

#### **3.1.4 Theoretical calculations**

#### First Principle Calculations using density functional theory

First principle calculation has been done for  $\beta$ -Quartz (SiO<sub>2</sub>) super cell. The structure of this unit cell is Hexagonal with space group P3<sub>2</sub>21. Local Density Approximation (LDA) has been applied for computation, taking lattice parameters a=b=4.9082A°, c=5.3992A°,  $\alpha$ = $\beta$ =90° and  $\gamma$ =120°.The supercell (221) is of 36 atoms, 12 Si atoms and 24 O atoms. The data that I got from computation is as follows: Band gap = 5.725 eV Total energy = -2632.9382 (Ry) Fermi energy = 0.079251 (Ry) or 1.07826 eV

Density of states of SiO<sub>2</sub>



**Figure 3.8:** Partial Density of states (PDOS) of  $SiO_2$  in  $2 \times 2 \times 1$  super cell in (a) without defect (b) with 2.7% oxygen vacancy (c) with 5.5% oxygen vacancy (d) with 8.3% oxygen vacancy

We can see from *figure 3.7* that some extra energy states (defect states) are created in between the valence band and conduction band. Thes extra states are increasing with increasing oxygen vacancy. In this case, these defect states are more dominating since percentage of oxygen vacancy is very high as compared to practical sample.

#### **Optical spectra**



**Figure 3.9:** Optical spectra of of  $SiO_2$  in  $2 \times 2 \times 1$  supercell in (a) without defect, band gap= 5.72 eV (b) with 2.7% oxygen vacancy, band gap= 3.666 eV (c) with 5.5% oxygen vacancy, band gap= 2.243 eV (d) with 8.3% oxygen vacancy, band gap= 1.387 eV

There is a systematic decrease in band gap with increase in oxygen vacancy as shown in *figure 3.8*. the theoretical optical spectra is similar to the spectra obtained by DRS. The extra energy states at lower energy values are dominating in this case as percentage of oxygen vacancy created is very high in practical.

#### Band structure of SiO<sub>2</sub>

Band structure generated from *WIEN2k* code is shown in *figure 3.9*. This figure shows that  $SiO_2$  is an indirect band gap material.



Figure 3.10: Band structure of SiO<sub>2</sub>

#### Comparison between experimental and theoretical results:

Experimentally, it is seen that the band gap of  $SiO_2$  is decreasing with increasing the annealing temperature; this annealing causes oxygen defects due to which defect state. The variation of experimental results is in accordance with the theoretical results. The defect states can be clearly seen from theoretical results.

## 3.2 Result discussion for CaSiO<sub>3</sub>

Following are the results for CaSiO<sub>3</sub> sample

#### 3.2.1 Structural study



Figure 3.11: XRD pattern of CaSiO<sub>3</sub> annealed at different temperatures

It is not recommended to go for indexing of  $CaSiO_3$  as it has a lot of peaks. The XRD pattern shows that  $CaSiO_3$  is formed in single phase.

#### 3.2.2 Optical properties Analysis:

#### Band gap by using UV-VIS Spectroscopy

The data obtained from DRS has been fitted linearly so as to calculate the band gap of  $CaSiO_3$ . Fitting is done by considering that  $CaSiO_3$  shows indirect band gap as this was specified in some studies.



**Figure 3.12:** Band gap plot of  $CaSiO_3$  annealed at different temperatures i.e. (a)  $600^{\circ}C$  (b)  $700^{\circ}C$  (c)  $800^{\circ}C$  (d)  $900^{\circ}C$  (e)  $1000^{\circ}C$ 



Effect of Annealing temperature on band gap

**Figure 3.13:** *Band gap variation of CaSiO<sub>3</sub> with annealing temperature* 

From *figure 3.13*, It can easily be concluded that the band gap of  $CaSiO_3$  is increasing with the increase in annealing temperature. This is due to decrease in urbach energy, *i.e.* disorderness decreases with increase in annealing temperature in case of  $CaSiO_3$  samples.

We can also observe the systematic decrease in band gap of  $CaSiO_3$  form the optical spectra shown in *figure 3.14*.



Figure 3.14: optical spectra plot of CaSiO<sub>3</sub> at different annealing temperature

## 3.2.3 Urbach energy



**Figure 3.15:** Urbach energy plot of CaSiO<sub>3</sub> at different annealing temperatures (a) 600°C (b) 700°C (c) 800°C (d) 900°C (e) 1000°C

**Table 3.6:** 220 Temperature **Urbach energy** 215 (°C) (meV) 210 600 215.58 205 700 213.06 E<sub>u</sub>(meV) 200 800 205.77 195 900 191.98 190 1000 185.66 185 600 700 800 900 1000 Temperature(°C)

#### Variation of Urbach energy with temperature

**Figure 3.16:** Urbach energy variation of CaSiO<sub>3</sub> samples with annealing temperature

From *figure 3.16*, we can easily observe that the values of Urbach energy is decreasing systematically with the increase in annealing temperature. We can conclude that the disorderness is decreasing. Hence the lattices are now arranged in more ordered manner. This variation can be seen from *figure 3.14* also which depicts that the increase in band gap of CaSiO3 is due to urbach energy only since change in urbach energy (30 meV), which equal to change in band gap.

## **CHAPTER 4**

#### **Summary and Conclusion**

XRD pattern shows that the samples has been prepared in single phase and are in pure form (free from any kind of impurities). DRS data of  $SiO_2$  reveal that the band gap of  $SiO_2$  decreases when its Annealing temperature is increased; this is due to dominating effect of disorderness as compared to the decrease in defect states. This defect state is due to disturbance in Silicon and Oxygen stoichiometry, i.e. probably due to oxygen deficiency, which is verified by theoretical calculations also. In case of CaSiO<sub>3</sub>, band gap is increasing with increase in Annealing temperature; this can be explained on the basis of Urbach tail. Since urbach energy is decreasing with temperature, causing more ordered arrangement of sample atoms.

Since the band gap of  $SiO_2$  is decreasing in a pattern, this sample can be further studied to increase the efficiency of solar cell if we can further reduce its band gap by using other methods of annealing. There is no significant effect of temperature on CaSiO<sub>3</sub> the band gap of this sample may be varied by proper doping or by adopting some other methods.

#### What I have learned from this project work

- Literature survey.
- Various sample preparation techniques.
- Understanding of various Optical properties.
- Different characterization techniques.
- Understanding of how to handle sophisticated instruments.

## **Future Scope**

Present work deals with synthesis of solid samples and their characterization using XRD, DRS and DFT measurements at room temperature. Following are the possible scopes to extend this work further in future as:

- Photoluminescence studies need to confirm the nature of the band gap in the prepared samples
- Electrical properties can be studied by temperature dependent dielectric, magneto-dielectric and magnetization measurements.
- Variation of optical and electrical properties with doping.
- Super cell can be extended to get more accurate results.

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