STUDY OF BAND GAP ENERGY AND REFRACTIVE INDEX OF SUPERCONDUCTING CERAMIC $GdBa_2Ca_3Cu_4O_{10.5}$

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Abstract : Superconducting ceramic $GdBa_2Ca_3Cu_4O_{10.5}$ is a perovskite with orthorhombic crystal system in nanometer range. To prepare the ceramic we followed conventional steps of solid state reaction route using a special furnace. The ceramic is calcined at 30, 500, 850 and 900 degree Celsius. After each calcination UV-VIS analysis is done. Absorbance and reflectance spectra at different wavelengths are obtained. Optical band gaps at different temperatures are determined with the help of Tauc plots. Effect of temperature and particle size on band gap energy is studied. Band gaps are tunable with respect to temperature. Refractive index of the ceramic is calculated and its variations with different parameters such as wavelength and photon energy are noted. Dispersion of refractive index is studied using Wemple- Di Domenico single-oscillator model. Band gap energy, oscillator energy and dispersion energy of refractive index at different temperatures are calculated. They are found to be decreasing with increasing temperature.

IndexTerms - **$GdBa_2Ca_3Cu_4O_{10.5}$, UV-VIS analysis, Absorbance, Reflectance, Optical band gap, Tauc plot, Refractive index, Oscillator energy, Dispersion energy, Wemple-DiDomenico model**

I. INTRODUCTION

Ceramics are inorganic solids made up of metallic, non-metallic or metalloid atoms. It may contain one or more crystalline structures. By heating we can increase the mechanical strength of ceramics. Conventionally ceramics are considered as insulators. But last few decades have seen the growth of ceramics as superconductors, especially after the mind boggling discoveries in the field of perovskites with ABO_3 structure. Because of so many desirable dielectric, diamagnetic, optical, thermal and superconducting properties superconducting ceramics are, now a days, a very hot research topic. Superconducting ceramics have so many technological applications in magnetic levitation, magnetic separation, manufacturing of powerful electromagnets, particle accelerators, beam steering accelerators and Josephson junctions.

Gadolinium Barium Calcium Copper Oxide ($GdBa_2Ca_3Cu_4O_{10.5}$ /GBCCO) is a type 2 high-TC superconductor. Type 2 superconductors are superconductors having very high critical fields. Since the discovery of metastable superconductors stabilized at high pressure by Takano, numerous new series of superconductive cuprates have been confirmed by the high-pressure method and one of them is oxycarbonate cuprates $(Sr/Ba)CaCuO(CO_3)$ [1]. $Ba_2Ca_{(n-1)}Cu_nO_{(2n+4-\delta)}$ where n=2,3,4 etc. is an eminent superconducting phase in the high temperature super conducting family[2].

In this paper the author is presenting the optical properties of $GdBa_2Ca_3Cu_4O_{10.5}$ in terms of band gap and refractive index. Variation of band gap with temperature and particle size as well as variation of refractive index with wave length and photon energy is analyzed in this section. The effect of wavelength on absorption spectra and reflectance spectra are noted. Oscillator energy and dispersion energy are calculated. The energy band gap values of the sample are analyzed for different temperatures and they are fundamentally important to the design of practical devices [3]. The study of the optical parameters, like the refractive indices or absorption properties, is most desirable for usage in optic devices [4]**.**

II. THEORY OF THE OPTICAL PROPERTIES

2.1. Band Gap

Band gap or energy gap is an energy range in a solid where no electron states can exist [5]. According to band theory in solids, band gap is defined as the forbidden energy gap existing between the conduction band and the valence band. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material [6]. Insulators usually possess very large band gaps greater than or equal to ten electron Volts. Band gap of semiconductors are approximately one electron Volt. In the case of conductors, there exist overlapping levels of valence band and conduction band. When temperature of semiconductors is increased electrons from valence band jump to conduction band and they act as conductors.

- ***Tauc Plot***

One of the important methods to find out the optical band gap of a material is by constructing Tauc plot. Tauc plot is drawn, according to Tauc equation. Tauc equation is given as follows.

$\alpha = A(h\nu - E_g)n$ --------[1]

where, α = absorbance coefficient, E_g= optical band gap energy, $(h\nu)$ = photon energy, A = constant (depends on transition) n=1/2, 3/2, 2 or 3. The value of n depends on the nature of the electronic transition causing reflection.

For direct allowed transition············· n = 1/2

For direct forbidden transition·········· n = 3/2

For indirect allowed transition··········n = 2

For indirect forbidden transition·······n = 3   [7]

A Tauc plot is drawn by marking the values of $h\nu$ on x axis against $(h\nu\alpha)^2$ on y axis. An extrapolation of this linear region to $(h\nu\alpha)^2 = 0$, gives the band gap energy of the material under study[8].
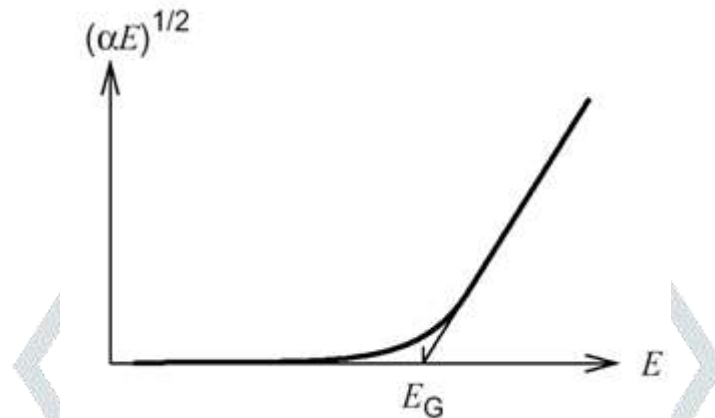

Fig.1. Schematic representation of calculation of band gap from Tauc plot

- **Urbach Energy**

Urbach energy is obtained commonly for amorphous materials. Lack of order in the arrangement of atoms gives rise to Urbach energy. In amorphous or poor crystalline materials valence band and conduction band do not end sharply. They do not show sharp cut offs but show tails of localized states. In a Tauc plot these band tails are visible as deviation from straight line. These deviations are often at lower energies.

Urbach energy is calculated by plotting, photon energy $h\nu$ at x axis against $\ln \alpha$ at y axis. A schematic representation is given below in figure 2. Urbach energy is obtained using the empirical equation given by

$\alpha = \alpha_o \exp (h\nu/E_U)$ -------------------[2]   where, α_o= constant and E_U = Urbach energy.

In the figure 2 region B denotes Urbach energy. Sometimes Urbach energy is also called Urbach tail. It represents localised energy states near the band edge.

Taking log on both sides of the equation 2, we get

$\ln \alpha = \ln \alpha_o + (h\nu/E_U)$ -------------------[3]

or $\ln \alpha = (h\nu/E_U) + \ln \alpha_o$

Equation 3 is a straight line equation similar to " y=mx+c ". with slope representing Urbach energy (E_U). The absorption edge called the Urbach energy depends on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds and on average photon energies [9]. The edge arises due to a radiative recombination between trapped electrons and trapped holes in tail and gap states as shown in Fig.2, and is dependent on the degree of structural and thermal disorder [10].
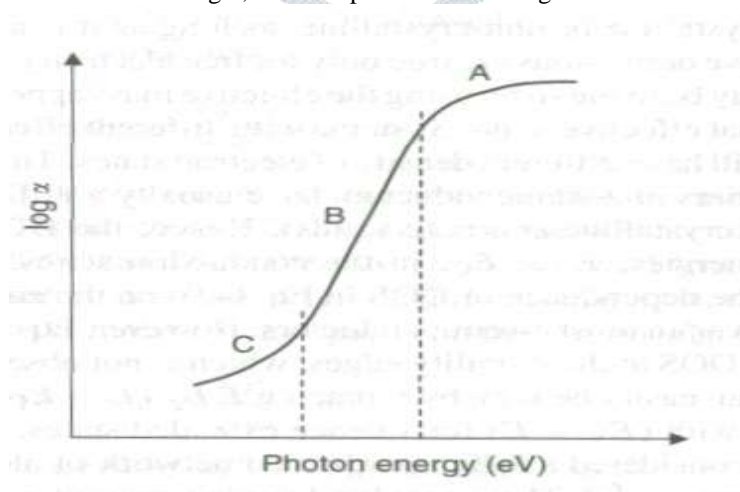

Fig.2. Schematic representation of Urbach energy (Region B is Urbach energy)

Region C represents optical absorption due to defects present in the sample and this region is related to the structural properties of materials[11]. Intrinsic defects present in the crystal provide to the temperature-independent portion of Urbach energy. To reduce the intrinsic defects we have to use high purity raw materials while growing the crystal. Optimization of growing conditions is also necessary.

2.2. Refractive Index

Refractive index, index of refraction, mutual refractive index or refractive constant is the extent of bending of light when it traverses from one medium to another medium. It is usually denoted by "n". It is also defined as the ratio of sin of angle of incidence to the sine of angle of refraction, i.e, sin i/sin r. It is also calculated as the ratio of velocity of light in empty space (c) to the velocity of light in the material (v), for a given wavelength. It is an indication of propagation of light in a particular medium. Yet another equation of refractive index is

$n = c/v$ ---------------------[4]

But we know that

$v = \nu\lambda$--------------------[5],so

$n = c/\nu\lambda$ ------------------[6].

Here c represents the velocity of light in free space, ν represents the frequency of light and λ denotes the wavelength of light.

- **Dispersion of Refractive Index**

A slight variation of refractive index is notable with changing wavelength. This change in the value of refractive index according to change in wavelength is called dispersion. The dispersion of refractive index is studied using Wemple-DiDomenico (W-D) model [12]. According to Wemple-DiDomenico (W-D) model

$n^2 - 1 = E_d E_0 / (E_d^2 - E^2)$ ---------- [7]

where E, E_o and Ed represent photon energy, oscillator energy and dispersion energy respectively.In order to calculate oscillator energy and dispersion energy we plot a graph with values of $(h\nu)^2$ on x axis against values of $(n^2-1)^{-1}$ on y axis. Oscillator energy is calculated from the slope of the graph and dispersion energy is calculated from the intercept (Eo/Ed) on the vertical axis of the straight line portion of the graph. The static refractive index n(0) i.e. the refractive index when photon energy is zero is given by[13].

$n^2(0)=1+E_d/E_o$------------[8]

III. MATERIALS AND EXPERIMENTAL METHODS

- **Preparation of the Sample**

$GdBa_2Ca_3Cu_4O_{10.5}$ is a newly designed polycrystalline ceramic following conventional steps of solid state reaction route. Ingredients used in the preparation are of high quality and purity. Gadolinium Oxide, Barium carbonate, Calcium Oxide and Cupric Oxide are the ingredients. Stoichiometric formula of the ceramic is determined as

$\frac{1}{2} Gd_2O_3 + 2 BaCo_3 + 3 CaO + 4 CuO = GdBa_2Ca_3Cu_4O_{10.5} + 2 CO_2$ --------------- [9]

The ingredients in the form of powder are weighed correctly. Then they are mixed and milled. Manual milling is done in an agate mortar for a couple of weeks. Mechanical milling is done in a ball mill with suitable zirconium beads for three months followed by attrition milling for three hours. The ceramic is calcined at 30, 500, 850 and 900 degree Celsius in a special furnace followed by oxygenation especially on cooling. After each calcination UV-VIS analysis is done. Control of temperature is often necessary to ensure that the desired crystalline phase is formed with optimum particle size [14].

- **UV-VIS ANALYSIS**

After each calcination of the sample, UV-VIS-Near IR analysis is done. Analysis is done in a Varian, Cary 5000 spectrophotometer having a spectral range of175-3300nm with an accuracy ±0.1nm(UV-Vis). Absorption spectra and reflectance spectra at different wavelengths are obtained by UV-VIS-Near IR analysis.

IV. RESULTS AND DISCUSSIONS

4.1. Absorption and reflectance

Absorption spectra and reflectance spectra are obtained for $GdBa_2Ca_3Cu_4O_{10.5}$ by UV analysis. Absorption and reflection of the sample at wavelength range of 250 nm -3000 nm is given in the figures 3(a) & (b).
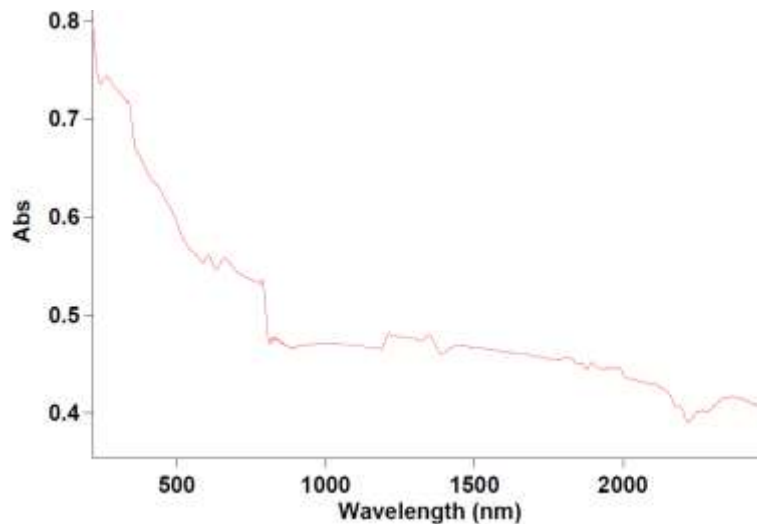
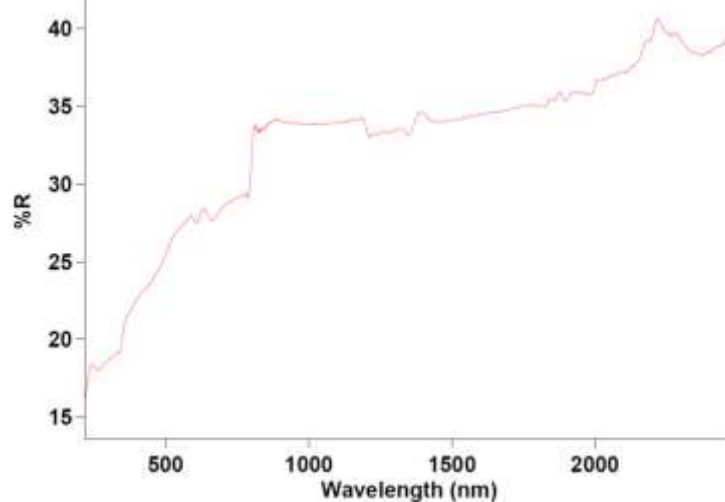Fig.3.a.UV-VIS spectrum of absorbance of $GdBa_2Ca_3Cu_4O_{10.5}$

Fig.3.b.UV-VIS spectrum of reflectance of $GdBa_2Ca_3Cu_4O_{10.5}$

The reflectance spectra is translated into absorption spectra using Kubelka-Munk equation which is written as given below
α =2(1-R)/2R------------[10] where α is the absorption coefficient and R the reflectivity at a particular wavelength[15].

1. As wavelength increases absorption decreases. In the absorption spectra we can see peaks. These peaks denote direct transmissions. Absorption decreases suddenly at lower values of wavelength. This denotes the presence of optical band gap.
 2. As wavelength increases reflection also increases. This is a predictable result because absorption decreases with increasing wavelength. Absorption coefficient of a material (α) is inversely proportional to reflectance as

$\alpha \propto ln\ \frac{(Rmax-Rmin)}{(R-Rmin)}$-----------[11]

R max = maximum value of reflection

R min=minimum value of reflection

R   = reflectance from any intermediate energy photon.

As absorption decreases reflectance increases from R min to R max.

4.2. BAND GAP

Even though there are so many methods to calculate band gap energy we use Tauc plot here. As stated earlier we draw a Tauc plot by marking the values of hv on x axis against $(hv\alpha)^2$on y axis. By extrapolating the linear portion of the graph to y axis, we obtain the value of band gap energy of the ceramic. Tauc plot drawn of the sample at the final calcining temperature at 900^0C is shown in figure 4 given below. While constructing Tauc plot we consider the transitions which are direct.
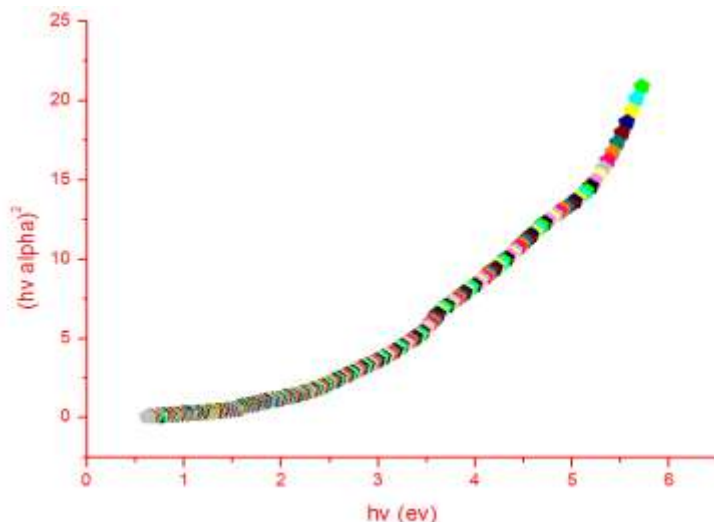
Fig.4.The Tauc plot of GdBa$_2$Ca$_3$Cu$_4$O$_{10.5}$ at 900^{0}C.

Drawing a tangent at the straight line region to the y axis in the Tauc plot, gives the value of optical band gap. The value of band gap energies of the ceramic at different temperatures are given in table 1

Table 1: Band gap energy at different temperatures

Number	Temperature(^{0}C)	Band gap(ev)
1	30	4.55
2	500	4.53
3	850	4.48
4	900	4.42

From the table, a graph connecting band gap energy and temperature is constructed as follows (Fig.5).
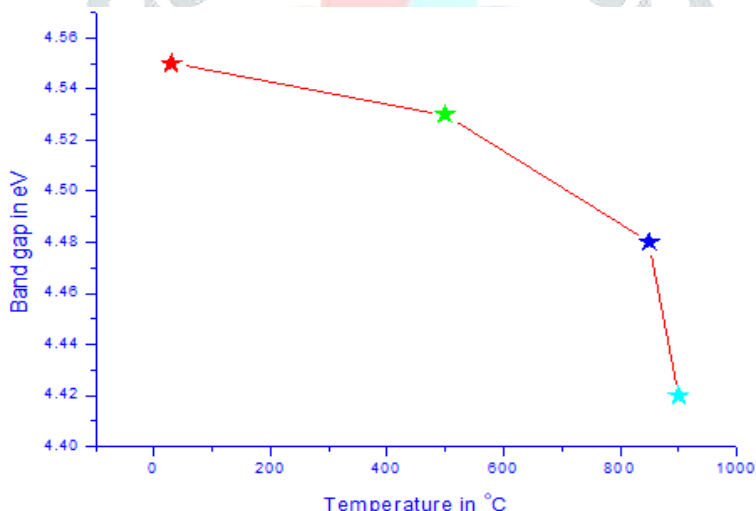

Fig.5. Band gap energy variation of GdBa$_2$Ca$_3$Cu$_4$O$_{10.5}$ with temperature

From the table and graph it is very clear that band gap energy decreases as temperature increases.

Particle size of the prepared ceramic sample is calculated at different temperatures using Debye Scherrer formula. The Debye Scherrer equation for calculating particle size is given by

$$D = K\lambda / \beta\cos\Theta \text{ --------------------[12]}$$

where K is the Scherrer constant, λ is the wave length of the X ray beam used in the diffractometer, β is the FWHM (Full Width at Half Maximum) of the peak and ϴ is the Bragg angle of diffraction [16-17].

The change in band gap energy with change in particle size at different temperatures is given below

Table 2: Band gap energy at different particle sizes at different temperatures.

Temperature of (^{0}C)	Particle size (nm)	Band gap(ev)
30	15.60	4.55
500	19.55	4.53

| 850 | 22.03 | 4.48 |
| 900 | 22.72 | 4.42 |

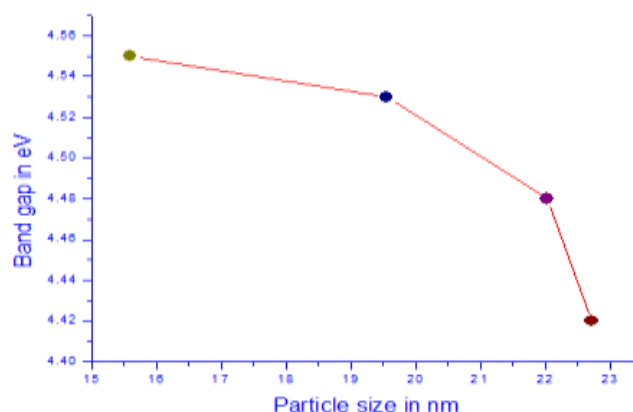From the table a graph connecting particle size and band gap energy is drawn (fig. 6).

Fig. 6. Band gap energy variation of $GdBa_2Ca_3Cu_4O_{10.5}$ with particle size

It is very clear that band gap energy increases with decrease in particle size. From fig.5 and fig.6 and from table 1 and table 2 it can be concluded that band gap energy decreases as temperature increases and band gap energy decreases as particle size increases.

1. As temperature increases band gap energy of the ceramic decreases. This is because of the change in atomic vibrations within the crystal. With increase in temperature, vibrations of atoms in the crystal lattice increases. Then spacing between the atoms (d-spacing) decreases and the potential felt by the electrons to overcome the energy barrier decreases. This results in the reduction of size of band gap and hence optical band gap decreases. Temperature and band gap are related as given in the equation given below.

$$Eg(T) = Eg(0) - \frac{\alpha T^2}{T+\beta}$$ -------------- [13]

Here Eg(T) represents the band gap at any particular temperature T. Eg(0) is the band gap at 0 K, α and β are fitting parameters. Fitting parameters depend on the material.

2. Particle size decreases when temperature decreases. But when particle size decreases band gap energy of the ceramic material increases.This is called quantum size effect or quantum confinement. This happens in materials with nano sized particles. Actually valence band and conduction band is a result of merging and overlapping of different energy levels of large number of atoms present in the atom. As particle size decreases, total number of atoms in the particle decreases. So the available orbitals or energy levels for merging and overlapping decreases. So the width of valence band and conduction band becomes smaller. This means increase in the energy difference between valence band and conduction band. Hence increase in band gap energy.

4.3. REFRACTIVE INDEX

Refractive index of the ceramic is calculated from the equation connecting frequency of radiation, wavelength of radiation and speed of light in vacuum (eqn. 6). Dispersion of refractive index with wavelength of radiation (200-2000 nm) is given in figure 7(a) and dispersion of refractive index with photon energy (0.55 eV -5.8 eV) is given in figure7(b).
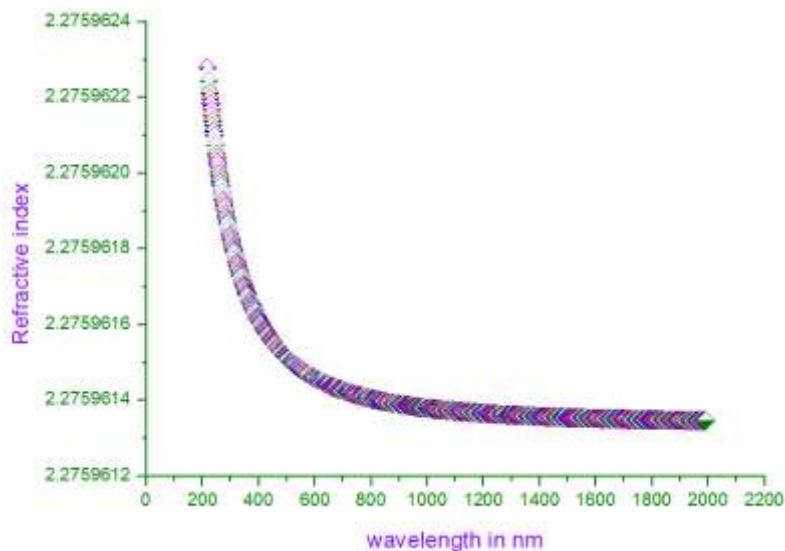
Fig. 7.a. Variation of refractive index (n) with wavelength

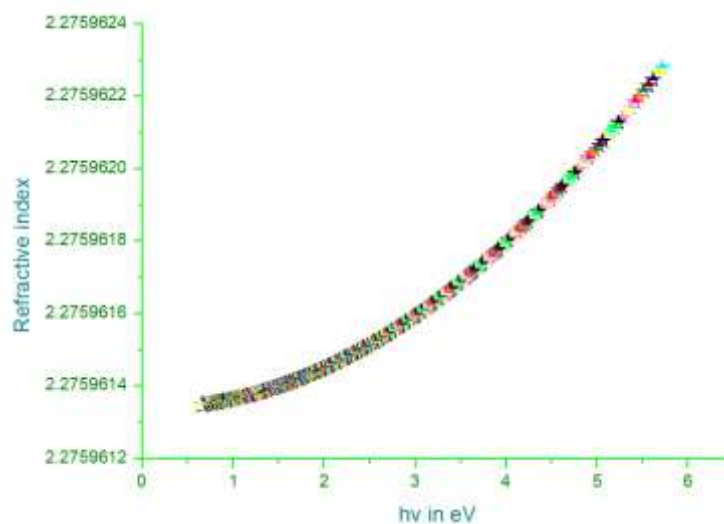*Fig. 7.b.   Variation of refractive index (n) with photon energy*

Refractive index decreases suddenly with increasing wavelength till 500 nm. After that it decreases very slowly and can be considered almost constant. Peak value of refractive index obtained is 2.2759623. At 500 nm it attains a value of 2.2759614. The constant value obtained after 500 nm is approximately 2.2759613. When wavelength rises from 200 nm to 2000 nm, refractive index falls from 2.2759623 to 2.2759613. Change in refractive index is very slight, only .000001. So refractive index can be considered as a constant.

Refractive index increases with increase in photon energy. Minimum value of refractive index is obtained when the photon energy is 0.55 eV and its value is 2.2759613. Maximum value of refractive index is obtained when the photon energy is 5.8 eV and its value is 2.2759623. So when photon energy rises from 0.55 eV to 5.8 eV, refractive index falls from 2.2759613 to 2.2759623. Change in refractive index is very slight, only 0.000001. So refractive index can be considered as a constant.

1. Refractive index decreases as wavelength of radiation increases because of its dependence on light energy. Interstitial layers in the crystal structure disperse light energy. This dispersion of light decreases with increasing wavelength, as a result the values of refractive index fall.

2. Refractive index increases as photon energy increases. This is because of the increase in particle size with increasing photon energy. As the particle size increases spacing in the atomic lattice decreases and this favours polarization process within the crystal. For perovskites, refractive index is proportional to electronic polarization per unit volume. So as polarization rate increases refraction rate also increases.

- ### *DISPERSION PARAMETERS*

Some optical parameters such as band gap energy (E_g), oscillator energy(E_o) and dispersion energy(E_d) can be determined with Wemple-DiDomenico (WD)model. Slope of the graph with $(n^2-1)^{-1}$ at y axis against $(hv)^2$ at x axis (Fig.8) gives oscillator energy E_o and the intercept (E_o/E_d) on y axis gives the dispersion energy E_d.
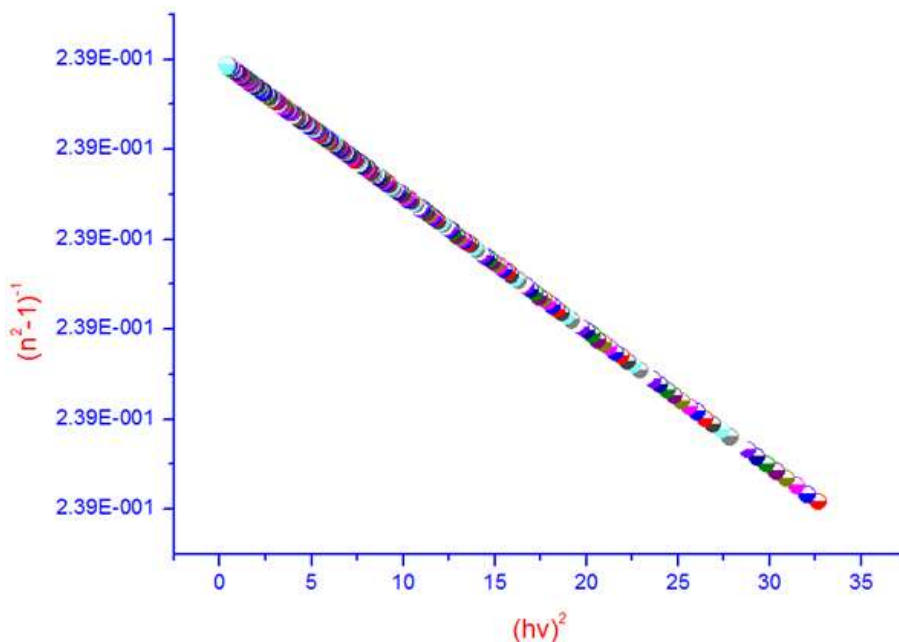
Fig. 8. $(n^2-1)^{-1}$ against $(hv)^2$

An alternative method to determine optical parameters is Sell Meier's dispersion model. Here we plot a graph with $(n^2 - 1)^{-1}$ on y axis against $(1/\lambda^2)$ (Fig.9) on x axis given by

$n^2-1=S_0 \lambda_0^2 /[1-(\lambda o / \lambda)^2]$ --- [14]

S_o denotes the average oscillator strength and λ_o denotes the average oscillator wavelength. S_o and (λ_o) are determined from the slope and intercept of the straight line graph obtained [18].
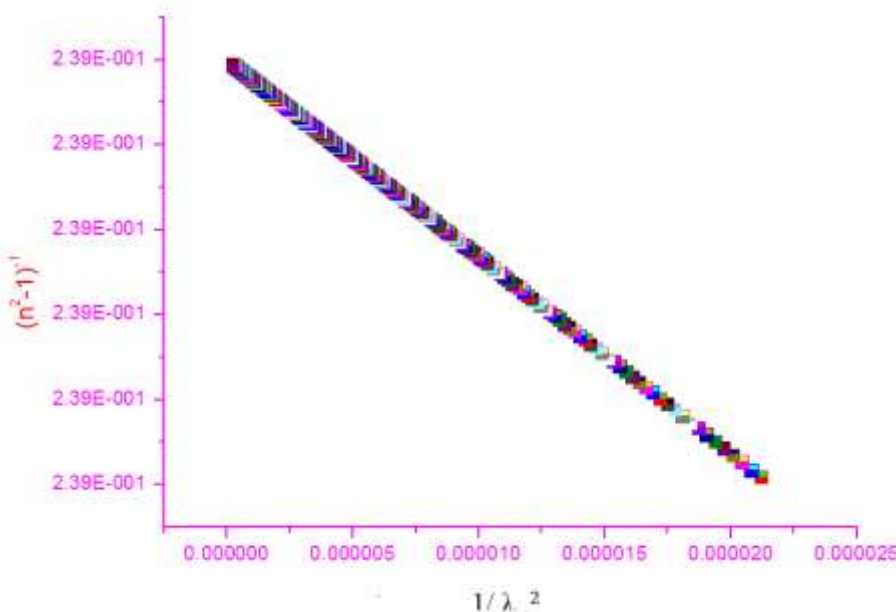

Fig. 9 . $(n^2-1)^{-1}$ against $1/\lambda^2$

Various optical parameters calculated at different temperatures are given in the table 3 below.

Table 3:The optical parameters of $GdBa_2Ca_3Cu_4O_{10.5}$

Temperature (^0C)	E_g (eV)	E_o(eV)	E_d (eV)
30	4.55	6.37	13.031
500	4.53	6.341	12.99
850	4.48	6.3	11.51
900	4.42	6.188	11.08

Band gap energy, oscillator energy and dispersion energy decreases as temperature increases.

V. CONCLUSIONS

1. Absorption rate of superconducting ceramic $GdBa_2Ca_3Cu_4O_{10.5}$ decreases as wavelength of radiation increases where as reflectance increases. Peaks obtained in the absorption spectra represent direct transmissions. At lower wavelengths a sudden decrease of absorption is noted and it corresponds to optical band gap.

2. Band gap energy of the ceramic shows decrease with increasing temperature as well as increasing particle size. This is because of the change in atomic vibrations within the crystal. With increase in temperature, vibrations of atoms in the crystal lattice increases. Then spacing between atoms (d-spacing) decreases and potential felt by the electrons to overcome the energy barrier decreases. This results in the reduction of size of band gap and hence optical band gap decreases. Similarly when particle size decreases band gap energy of the ceramic material increases due to quantum size effect or quantum confinement in materials with nano sized particles. As particle size decreases, total number of atoms in the particle decreases. So for valence band and conduction band the available orbitals or energy levels for merging and overlapping decreases. So the width of valence band and conduction band becomes smaller. This means increase in the energy difference between valence band and conduction band. Hence increase in band gap energy.

3. Refractive index decreases as wavelength of radiation increases and increases as photon energy increases. Refractive index depends on light energy. Interstitial layers in the crystal structure disperse light. This dispersion of light decreased with increasing wavelength. As a result the values of refractive index fall. Refractive index increases as photon energy increases because of the increase in particle size with increasing photon energy. As particle size increases d spacing in the atomic lattice decreases. This favours polarization process within the crystal. For perovskites, refractive index is proportional to electronic polarization per unit volume. So as polarization rate increases refraction rate also increases.

4. Band gap energy, oscillator energy and dispersion energy decreases as temperature increases.

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