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BANDGAP ANALYSIS OF NANO CRYSTALLINE L0.1ZY0.9BCCO CERAMICS

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ABSTRACT

Crystalline Ceramic Lanthanum Zirconium Yttrium barium Calcium Copper oxide($L_{0.1}ZY_{0.9}BCCO$) was prepared by a high-energy ball milling process through mechanically assisted synthesis at a high temperature to acquire the desired homogeneity and phase formation. Inorder to study the optical properties like reflectivity, absorptivity, refractive index, the UV-VIS analysis of the above nonstochiometric sample was carried out. The dispersion of refractive index was analyzed by the Wemple-DiDomenico single-oscillator model.The band gap energy of the sample was elucidated from the Tauc plot. The refractive index n was calculated and the results obtained are plotted with the wavelength.

Indexing terms/Keywords

L0.1ZY0.9BCCO; Dispersion; Wemple-DiDomenico model; band gap energy; refractive index; Urbach energy.

Academic Discipline And Sub-Disciplines

Faculty of Science, Physics.

SUBJECT CLASSIFICATION

Condensed Matter Physics, Nano ceramics.

TYPE (METHOD/APPROACH)

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1.Introduction

The semiconductor nanoparticles have properties between molecules and bulk solid semiconductors. Their physicochemical properties are found to be strongly size dependent. It is well known that the nanoscale systems show interesting physical properties such as increasing semiconductor band gap due to electron confinement. Surface atoms play an important role in governing the electronic and optical properties in nano materials. The estimation of energy band gap in nano structural semiconductors is somewhat difficult because surface atoms edges of the valence and conduction bands are not abrupt and the tail states complicate the definition of the true optical gap. The aim of this paper is to explain how one can determine the energy band gap in nano crystalline ceramics that only requires the measurement of the absorbance spectrum and without the need of additional information, such as the film thickness or reflectance spectra[1]. Optical characterisation is considered to be a good quality check for nano crystalline ceramics. Nano crystalline materials have attracted considerable interest in recent years because of the possibility of improving macroscopic properties of materials by varying the crystallite sizes [2]. Due to chemical and physical properties arising from the large surface–volume ratios and also the quantum size effect, compared with those of bulk counterparts [3-8].

Another way to improve the absorption by reorganizing the intermolecular packing, therefore changing the properties of the material, is through the annealing process. The maximum absorption increases and broadens to a longer wavelength for corresponding transitions. This means that because the optical absorption corresponds to differences in energy states, it can be considered an indirect measure of the electronic structure. The optical band gap E_{opt}, expressed in electron volts, depends on the incident photon wavelength by means of a Planck relation

$E_{opt}=hv=hc/\lambda$

where h is the Planck constant, v is the wave frequency and c light speed in vacuum. Experimentally, the optical band gap E_{opt} is estimated by linear extrapolation from the absorption feature edge to A=0 and subsequent conversion of the wavelength (nm) into energy value versus vacuum (eV)(9,10).

In the present work the authors describes the optical behavior of Lanthanum Zirconium Yttrium barium Calcium Copper oxide($L_{0.1}ZY_{0.9}BCCO$), nano crystalline superconductor material. The energy band gap values of the sample were analyzed and they are fundamentally important to the design of practical devices [11]. In solid state physics a band gap, is an energy range in an ideal solid where no electron states can exist. 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 [12]. The band gap energy of insulators is large (>4eV), but lower for semiconductors (<3eV). Measuring the band gap is an important factor determining the electrical conductivity in nano material industries.

The band gap energy values is obtained using Tauc plot as a direct relation. The Urbach energy of the sample was also studied. The optical constants of refractive index, extinction coefficient, and absorption coefficient showed a systematic variation. The dispersion of refractive index was analyzed by the Wemple-DiDomenico single-oscillator model and such optical behaviour is rarely reported.

2. Experimental

Crystalline Ceramic Lanthanum Zirconium Yttrium barium Calcium Copper oxide ($L_{0.1}ZY_{0.9}BCCO$) sample was prepared by the solid state thermo chemical reaction technique using a high-energy ball milling process through mechanically assisted synthesis. Mechanical mixing, ball milling and attrition milling were utilized to insure homogeneity. Then the material was calcined at a temperature of 950^0C. Control of temperature is often necessary to ensure that the desired crystalline phase is formed with optimum particle size [13]. Then UV-Vis spectrum of these materials was taken. The optical constants of refractive index, extinction coefficient, and absorption coefficient, normal-incidence reflectivity showed systematic variation. The dispersion of refractive index was analyzed by the Wemple- Di Domenico single-oscillator model.

2.1. UV-VIS. Analysis

UV-Vis. spectroscopy is based on the principle of electronic transition in atoms or molecules upon absorbing suitable energy from an incident light that allows electrons to excite from a lower energy state to higher excited energy state. While interaction with infrared light causes molecules to undergo vibrational transitions, the shorter wavelength with higher energy radiations in the UV (200-400 nm) and visible (400-700 nm) range of the electromagnetic spectrum causes many atoms/molecules to undergo electronic transitions.

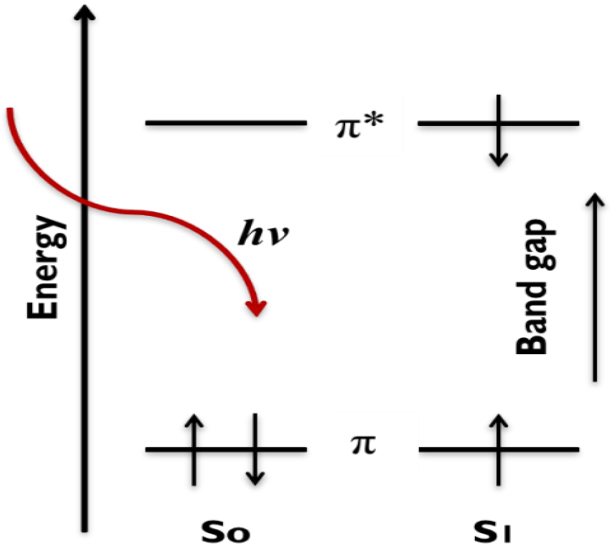

Figure 1. : schematic representation of electronic transition from the ground state (S_0) to an excited state (S1)

The sample obtained after calcination was subjected to UV-VIS-Near IR analysis (Fig.1) using Varian, Cary 5000 Spectrophotometer over a spectral range of 175-3300nm with an accuracy of ±0.1nm (UV-Vis.). This type of sample has high mechanical hardness, high thermal conductivity, large dielectric constant, and high resistance to harsh environment. UV-Visible spectrum give information about the excitonic and inter transition of nano materials[14]. Figure.1 shows the UV-VIS behaviour of the sample $L_{0.1}ZY_{0.9}BCCO$ at 950^0C.The optical absorption spectrum of the sample were studied at room temperature. The UV analysis can be thought as a good quality check for the optical behaviour of the ceramic materials. The optical absorption data was analyzed using the classical relation for near edge optical absorption of semiconductors [15-16].

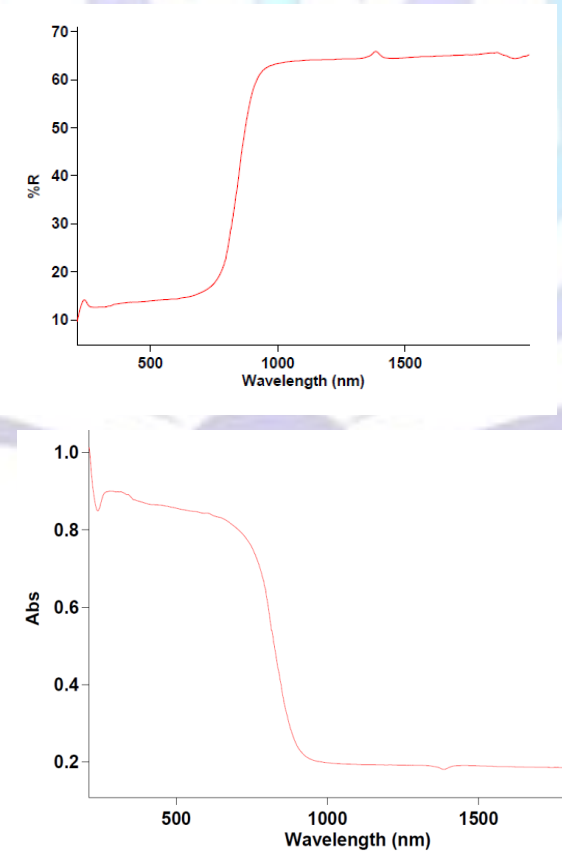

Figure.2: UV-VIS spectrum of $L_{0.1}ZY_{0.9}BCCO$ (reflectance & absorbance)

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The diffuse reflectance spectra were translated into the absorption spectra by the Kubelka-Munk method. Kubelka-Munk's equation is described as follows:

$\alpha = (1-R)^2/2R$-(1), where α is the absorption coefficient and R the reflectivity at a particular wavelength[17].

According to the Tauc relation, the absorption coefficient α for a material is given by $\alpha = A(h\nu - Eg)n$--(2), Where Eg the band gap, constant A is different for different transitions, (hv) is photon energy in eV and n denotes the nature of the sample transition[18].The 'n' in the equation has values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions [19-21] respectively. The TAUC plot of a sample defines the optical band gap as the region A in fig.3.The tauc plot of the sample is given in Fig 3. It is reported that optical gap energy of nano –sized crystal depends on its crystallite size, it increases with decreasing crystallite size in the nano size range [22-23].

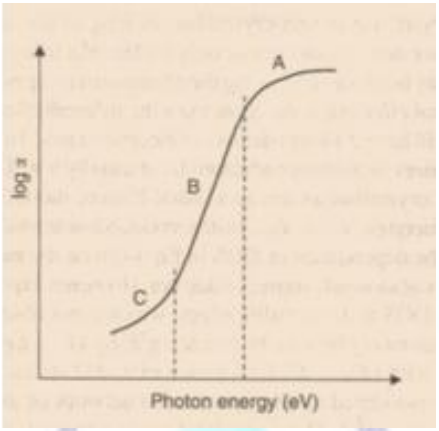

Fig.3-optical band gap energy variation with absorption.

The absorption coefficient at the photon energy below the optical gap (tail absorption) depends exponentially on the photon energy: $\alpha(\hbar\nu) \sim \exp(\hbar\nu/Eu)$--(4) where Eu is called Urbach energy.The region B in the fig.3 represents the Urbach energy. 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 [24]. The edge arises due to a radiative recombination between trapped electrons and trapped holes in tail and gap states as shown in Fig.3, and is dependent on the degree of structural and thermal disorder [25]. It is observed in many cases that optical absorption by defects also appears at energy lower than optical gap (region C of fig.3). This region is related to the structural properties of materials[26].

The extinction coefficient and the absorption coefficient are related as $\alpha(E) = 4\pi/\lambda\ (k(E))$—(3).

The natural logarithm of the absorption coefficient, α(v), was plotted as a function of the photon energy, hv (Fig.5). The value of Eu was calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of curves.The measurement of temperature-dependent Urbach tails distinguishes a temperature-dependent tail and a temperature-independent part, which mainly are due to intrinsic defects.The latter can be controlled by improving the crystal growth and the purity of the ingradients. The temperature-dependent part of the Urbach tail, is purely of intrinsic reasons[27].

2.2. Refractive Index and Dispersion

Variation of refractive index with wavelength was also studied. The refractive index values show a linear decrease with the increase in wavelength,Fig.7 shows the variation of the dispersion curve with annealing temperatures. Refractive index value shows a slight increase with increasing annealing temperature and attains a fixed value after a particular wavelength.The refractive index values showed a linear decrease with the increase in wavelength when plotted with refractive index along the Y-axis & wavelength along the X axis(figure 6).

The dispersion of refractive index below the interband absorption edge is analyzed using the Wemple-DiDomenico (W-D)model [28]. In the W-D model, the refractive index n can be written as $n^2 - 1 = E_d E_o/(E_d^2 - E^2)$-- (5),

Where E is the photon energy, Eo is the oscillator energy, and E_d is the dispersion energy. Wemple and DiDomenico reported that the dispersion energy may depend upon the charge distribution within each unit cell, and that it would be closely related to chemical bonding [28]. The oscillator energy E_o and dispersion energy E_d are obtained from the slope $(E_oE_d)^{-1}$ and intercept E_o/E_d on the vertical axis of the straight line portion of $(n^2-1)^{-1}$ versus E^2 plot. The static refractive index n(0) at zero photon energy is evaluated from Equation (5), i.e. $n^2(0) = 1 + E_d/E_o$—(6) [29].

3.Resultsand Discussion

UV-VIS analysis, clearly confirms that band gap energy of the nano ceramic material increases as the annealing temperature of the sample is increased. The optical analysis of the ceramic material prepared by solid state reaction technique is successfully done using UV-Vis Spectro photometer. Here the direct allowed transitions are considered.

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The Tauc plot is plotted with hv along the X-axis and $(h\nu\alpha)^2$along the Y-axis. The band gap at a particular temperature is found by extrapolating the X axis. The Tauc plot of the sample at temperatures 950˚C is given in Fig.4. The band gap energy value of $L_{0.1}ZY_{0.9}BCCO$ at the calcined temperature 950˚C is calculated as 4.9 ev.

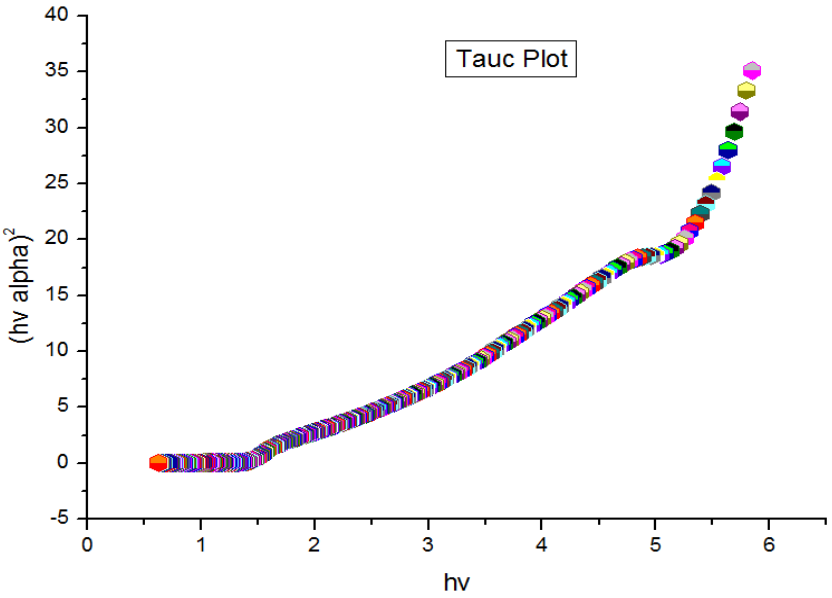

Fig.4. The Tauc plot of $L_{0.1}ZY_{0.9}BCCO$.

It is observed that band gap energy rises with increase in annealing temperature of the sample(fig.4). The energy levels are dependent on the degree of structural order–disorder in the lattice. The band gap increases with the crystallite size but decreases as the perosvkite phase is formed which proves the quantum confinement also decreasing its dislocation density.

As the temperature is increased the crystallite size also increases which shows an increase in band gap energy[12]. Tauc plot data well confirms that the band gap energy of the sample increases slightly when the temperature is increased. The energy levels are dependent on the degree of structural order–disorder in the lattice. Therefore, the increase of structural organization in nano ceramic leads to a reduction of the intermeditary energy levels and consequently increases the Eg values.

Urbach energy is calculated by plotting the natural logarithm of the absorption coefficient with the energy in eV (Figure 5). This energy value is found to be lower than the band gap energy and hence Sumi-Toyozawa(ST) model theory can be well applied to this material.

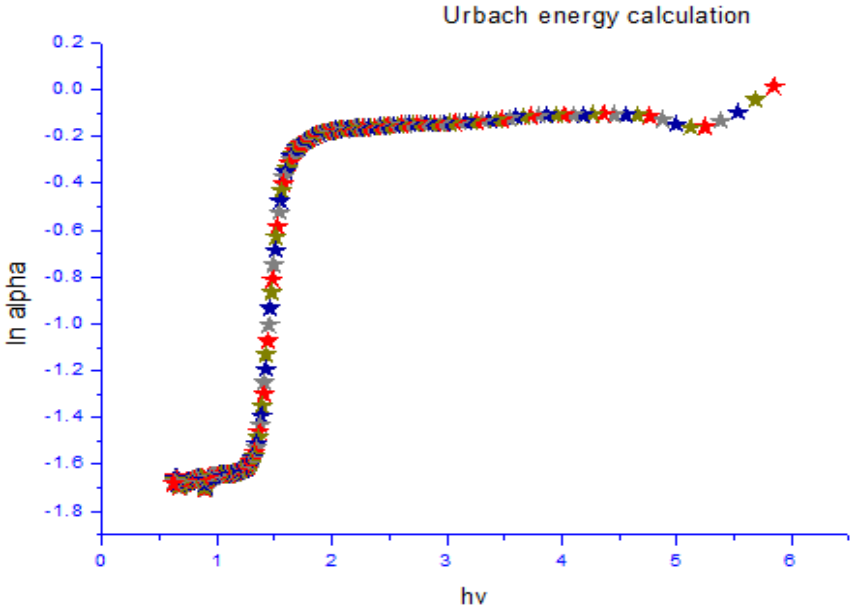

Fig.5. Absorption variation with photon energy of $L_{0.1}ZY_{0.9}BCCO$

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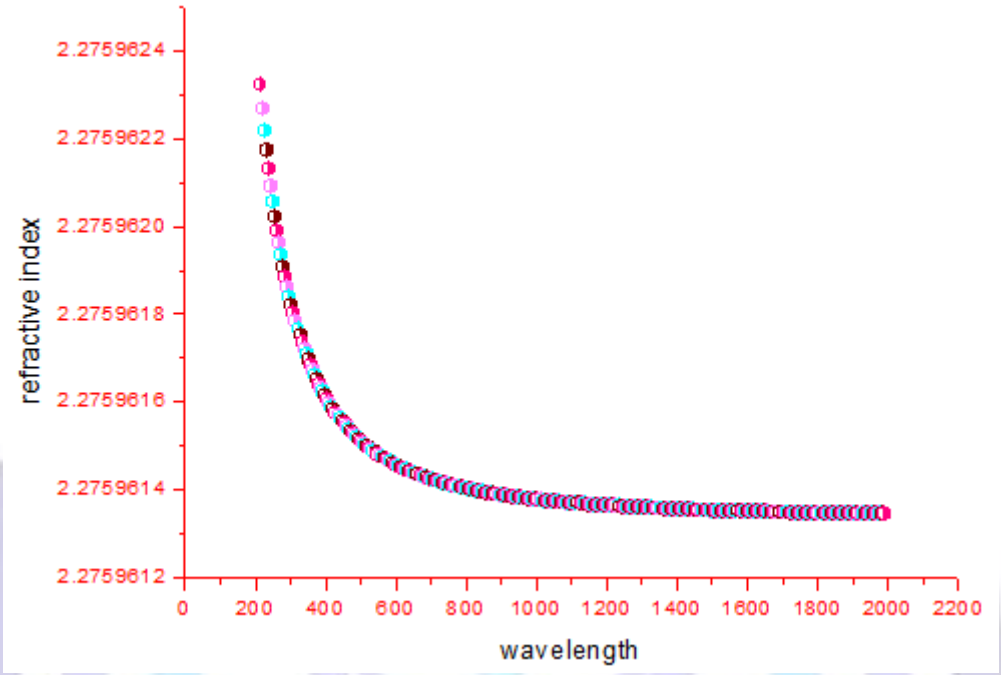
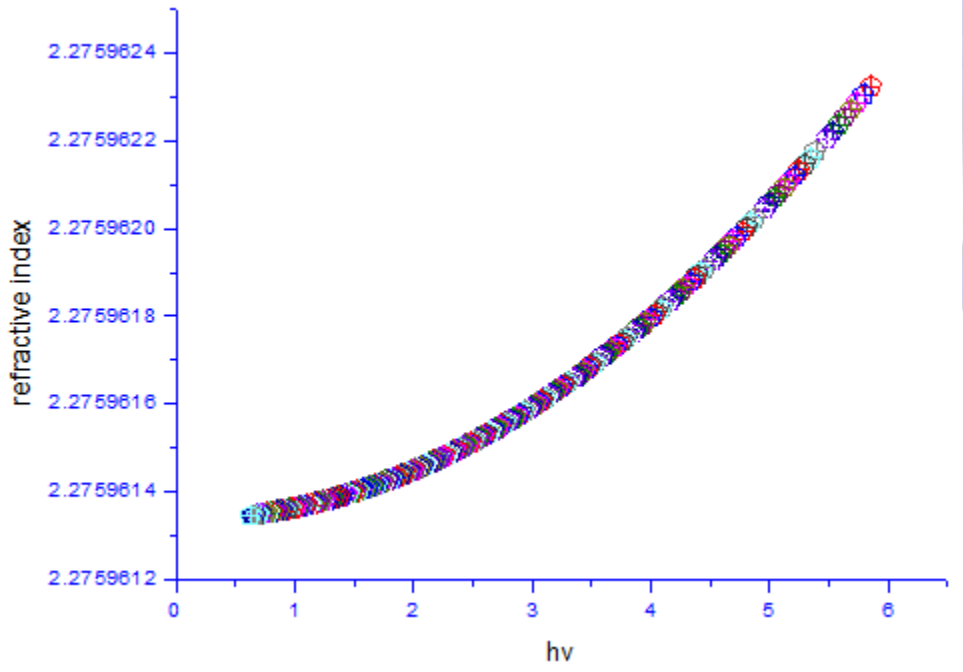
Variation of refractive index of the sample with wavelength was also studied. Analysis clearly shows that refractive index of the sample decreases as the wavelength increases and attains a definite value at all temperatures. This linear variation of the refractive index with the wavelength is due to dispersion of light energy at the different interstitial layers. The refractive index also shows a linear relation with the photon energy (fig.6).The increase in refractive index is due to crystallization of the perovskite phase. The refractive index of perovskites is known to be proportional to their electronic polarization per unit volume which is inversely proportional to distance between atomic planes.This result can also be explained by an increase in crystallite size.



(a)



(b)

Fig.6. Variation of Refractive index (n) with (a) wavelength and (b) photon energy of $L_{0.1}ZY_{0.9}BCCO$

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Refractive index of the sample annealed at a temperatures can be calculated using Sellmeir dispersion formula[30]. The dispersion energy of the sample was calculated using the Wemple-DiDomenico (WD) model. Results are plotted graphically in(Fig.7).

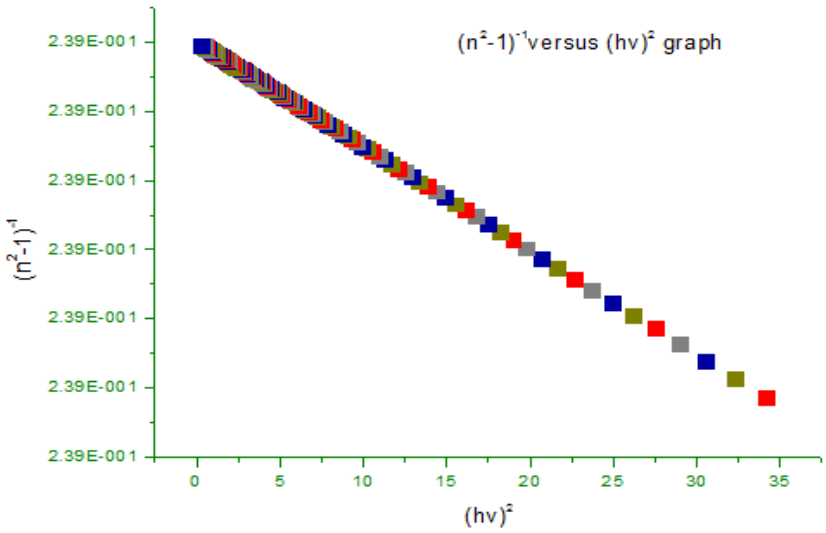

Fig.7. $(n^2\text{-}1^{)\text{-}1}$ versus(hv)^2 curve.

The data of the dispersion of the refractive index (n) were evaluated according to the single oscillator model proposed by wimple and DiDomenico as, $n^2 = 1 + (E_dE_0)/(E_0^2\text{-}hv^2)$----(7).

whereEo is the oscillator energy and Ed is the oscillator strength or dispersion energy.

Plotting of $(n^2\text{-}1)^{-1}$against $(h\ v)^2$ allows to determine, the oscillator parameters, by fitting a linear function to the smaller energy data, E_o and E_d can be determined from the intercept, (E_o/E_d) and the slope $(1/E_oE_d)$. E_o is considered as an average energy gap to, it varies in proportion to the Tauc gap E_o~$2E_g$.

The oscillator model can be also written as $n^2\text{-}1=S_0\ \lambda_0^2\ /[1\text{-}(\ \lambda_o\ /\ \lambda)^2\ ]$--- (8) where λ is the wavelength of the incident radiation , S_o is the average oscillator strength and λ_o is an average oscillator wavelength.

The curves of $(n^2 – 1)^{-1}$ against $(1/\lambda^2)$ (Fig.8) are fitted into straight lines following the sell Meier's dispersion formula . The value of S_o and (λ_o) are estimated from the slope $(1/S_o)$ and the infinite wavelength intercept $(1/S_0\lambda_o)^{\ 2}$.

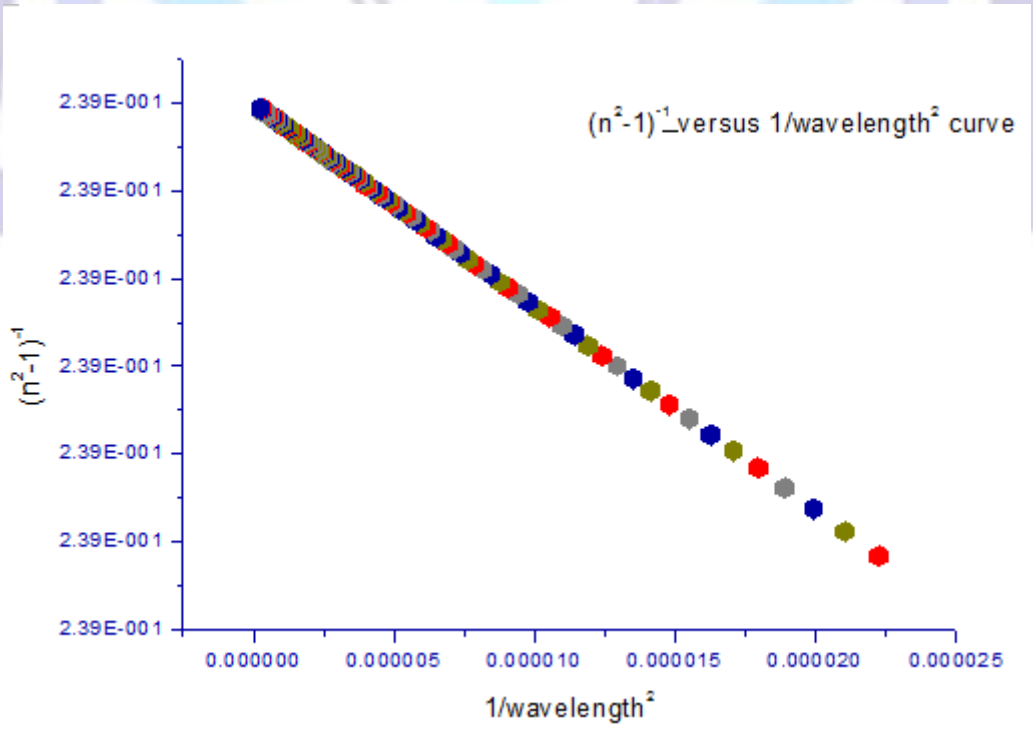

Fig.8. (n2-1)-1 versus 1/ λ ^{2} curve

The dispersion energy also shows a decline as the temperature rises and the sample attains its perosvkite phase.The curves with straight line graphs confirms the sell Meier's dispersion formula. Further the mechano chemical process has an advantage due to low-costs and widely available materials, leading to a simplified process.

4.Conclusion

Studies confirmed high band gap energy showing high dielectricity. The UV emission peak shifts significantly to higher wavelengths with increasing annealing temperatures. As the binding energy increases the dielectric properties of the materials also increases. It is confirmed that tunable band gaps are obtained by varying annealing temperatures. Band gap energy and The optical properties of the nano ceramic material $L_{0.1}ZY_{0.9}BCCO$ can be utilized for UV_VIS shielding applications. Optical measurements confirmed that absorbance and reflectance varies with temperature. According to Wemple- DiDomenico single-oscillator model the dispersion energy decreases as the sample attains its perosvkite phase. As the band gap energy increases at high temperature the material becomes more dielectric. For new generation capacitors nano crystalline ceramics $L_{0.1}ZY_{0.9}BCCO$ materials will prove as a future substitute.

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