

Analysis of Bandgap Energy and Refractive Index of Ferroelectric Perovskite PbBaTiO_3

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Abstract: Lead barium titanate (PbBaTiO_3) is a newly designed ferroelectric, nanocrystalline ceramic with perovskite structure prepared by solid state reaction method. In order to study the band gap energy, refractive index and other optical properties of this ceramic, UV-VIS analysis is done at different annealing temperatures. Absorbance and reflectance spectra are obtained from analysis. Band gap energy at different temperatures is determined using Tauc plots and is found to be decreasing with temperature. Absorption edge is studied in terms of Urbach energy. Refractive index is calculated and their variations with wavelength and photon energy are noted. Dispersion of refractive index is studied and band gap energy, oscillator energy and dispersion energy is calculated using Wemple- Di Domenico single-oscillator model.

Keywords: PbBaTiO_3 , UV-VIS analysis, Band gap energy, Tauc plot, Refractive index, Oscillator energy, Dispersion energy, Wemple-DiDomenico model

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I. Introduction

Barium titanate is one of the most important ferroelectric ceramic materials with Ba_2^+ ions occupying the corners, O_2^- ions occupying the phase centers and Ti_4^+ ions occupying the body center. It is polycrystalline with nano sized particles and has perovskite crystal structure. It shows very good dielectric, thermal and optical properties. Barium titanate is considered as very attractive in optical research field because of spontaneous polarization. Barium titanate is used in the manufacturing of high capacitance capacitors, piezo electric sensors and electro optical devices. Studies about its optical properties and optical characterization techniques are abundant in literature. Barium titanate compounds are well suited for optical applications because of its high optical transparency and its large linear and non-linear electro-optic coefficients [1].

PbBaTiO_3 is a new ceramic synthesized, which belongs to barium titanate family. In this paper optical behavior of PbBaTiO_3 is described in terms of effect of certain parameters such as temperature, wave length, photon energy on optical band gap and refractive index. Absorption spectra, reflectance spectra, Urbach energy, oscillator energy, dispersion energy etc. are also studied. The energy band gap values of the sample are analyzed for different temperatures and they are fundamentally important to the design of practical devices [2]. The study of the optical parameters, like the refractive indices or absorption properties, is most desirable for usage in optic devices and to have knowledge about the physical nature of this class of ferroelectrics [3].

II. Theory Of Optical Properties

2.1. Band Gap

Band gap or energy gap is an energy range in a solid where no electron states can exist [4]. It is the forbidden energy gap between conduction band and 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 [5]. Insulators have large band gaps (approximately 10 eV) and for semiconductors, gaps are small (approximately 1 eV), while for conductors, valence band and conduction band overlap each other.

- **Tauc Plot**

An important tool used to determine band gap energy is Tauc plot, which is drawn, making use of the Tauc equation given by

$$\alpha = A(h\nu - E_g)^n \text{-----[1]}$$

where α is the absorbance, E_g is the band gap energy, $(h\nu)$ is the photon energy (h is the Planck's constant), A is a constant (varies from transition to transition) and n is an index. n takes the values $1/2$, $3/2$, 2 and 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..... $n = 3$ [6]

The Tauc plot is constructed with $h\nu$ on x axis and $(h\nu\alpha)^2$ 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[7].

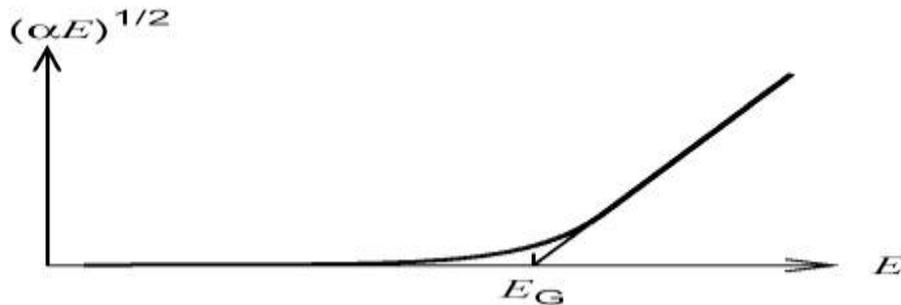


Fig.1. Schematic representation of calculation of band gap from Tauc plot

• Urbach Energy

Urbach energy is present only in amorphous or poor crystalline materials. This happens because of the absence orderly arrangement of atoms. In such materials valence conduction bands do not have sharp cut offs. Instead they have tails which represent localized states. Because of these band tails we do not get straight line at lower energies while constructing Tauc plot. Urbach tail represents localized states at band edges. If we plot a graph with $\ln \alpha$ at y axis against photon energy $h\nu$ on x axis, we obtain a curve as given in figure.2 below. When photon energy is low, the relation between the absorption coefficient (α) and photon energy ($h\nu$) is given by Urbach empirical rule which is as follows

$$\alpha = \alpha_0 \exp (h\nu/E_U) \text{ -----[2]}$$

where α_0 is a constant and E_U is called Urbach energy. Region B in fig.2 represents Urbach energy. The exponential part is also called Urbach tail and it gives the energy of the band tail. It depends very weakly on temperature.

Taking log on both sides of the equation, a straight line equation is obtained as.

$$\ln \alpha = \ln \alpha_0 + (h\nu/E_U) \text{ -----[3]}$$

So Urbach energy (E_U) is obtained from the slope of the straight line with $\ln (\alpha)$ against photon energy ($h\nu$) of the incident radiation. 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 [8]. 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[9].

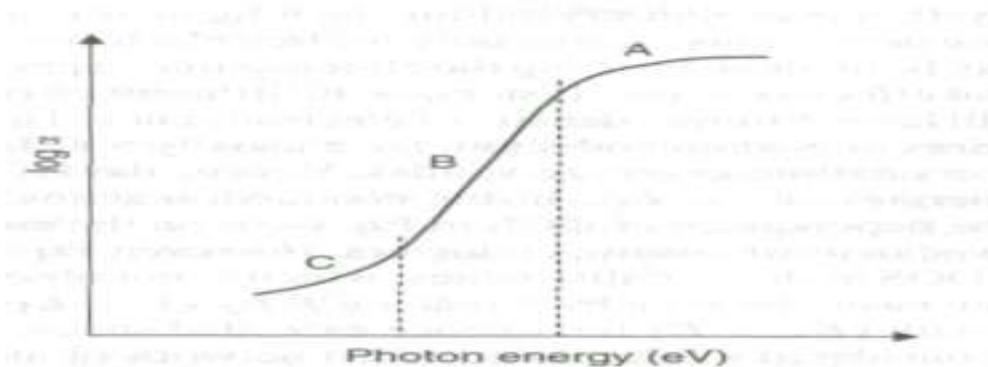


Fig.2. Schematic representation of Urbach energy (Region B is Urbach energy)

Region C represents optical absorption due to defects present in the sample. This region is related to the structural properties of materials[10]. The temperature-independent part, of Urbach energy is due to intrinsic defects and these defects can be minimized by improving purity of raw materials used and crystal growth in optimized conditions.

2.2. REFRACTIVE INDEX

Refractive index of a medium is the ratio of velocity of light in vacuum(c) to velocity of light in a medium(v). It indicates how light propagates through a medium.

$$n = c/v \text{ -----[4]}$$

Since in a medium

$$v = v\lambda \text{-----[5],}$$

refractive index can be calculated as

$$n = c/v\lambda \text{ -----[6] where c is the velocity of light in vacuum, v is the frequency of radiation used and } \lambda \text{ is the wavelength of radiation.}$$

• **DISPERSION OF REFRACTIVE INDEX**

Refractive index varies with wavelength. The change in refractive index with wavelength is called dispersion of refractive index. The dispersion of refractive index is studied using Wemple-DiDomenico (W-D) model [11]. Accordingly the refractive index *n* is given by

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

where *E* represents photon energy(*hν*), *E₀* represents oscillator energy, and *E_d* represents dispersion energy. A graph is plotted with $(n^2 - 1)^{-1}$ on y axis against $(h\nu)^2$. The slope of the graph gives oscillator energy *E₀* and the intercept (*E₀/E_d*) on y axis of the straight line portion gives dispersion energy *E_d*. The static refractive index *n*(0) i.e. the refractive index when photon energy is zero is given by the following formula[12].

$$n^2(0) = 1 + E_d/E_0 \text{-----[8]}$$

III. Materials And Experimental Methods

• **PREPERATION OF THE SAMPLE**

PbBaTiO₃ is a new ceramic material prepared by solid state reaction method from very pure raw materials of fine quality in a specially designed furnace. The raw materials are BaCO₃, TiO₂ and PbO₂. The molecular formula used is



The raw materials are mixed in an agate mortar for a few hours to ensure homogeneity. Then the sample in the form of powder is ball milled with zirconium beads for three weeks followed by 1 hour attrition milling. The fine powder is calcined at different annealing temperatures 30⁰C, 500⁰C, 850⁰C and 900⁰C. Control of temperature is often necessary to ensure that the desired crystalline phase is formed with optimum particle size [13].

• **UV-VIS ANALYSIS**

The sample in the form of powder, after each calcination is subjected to UV-VIS-Near IR analysis in a Varian, Cary 5000 Spectrophotometer. Its spectral range is 175-3300nm with an accuracy of ±0.1nm (UV-Vis). By UV-Visible spectrum analysis we get data of absorption and reflectance at different wavelengths.

IV. Results And Discussions

4.1. Absorption and reflectance

Absorption and reflectance spectra of the sample at different wavelengths are given fig.3.

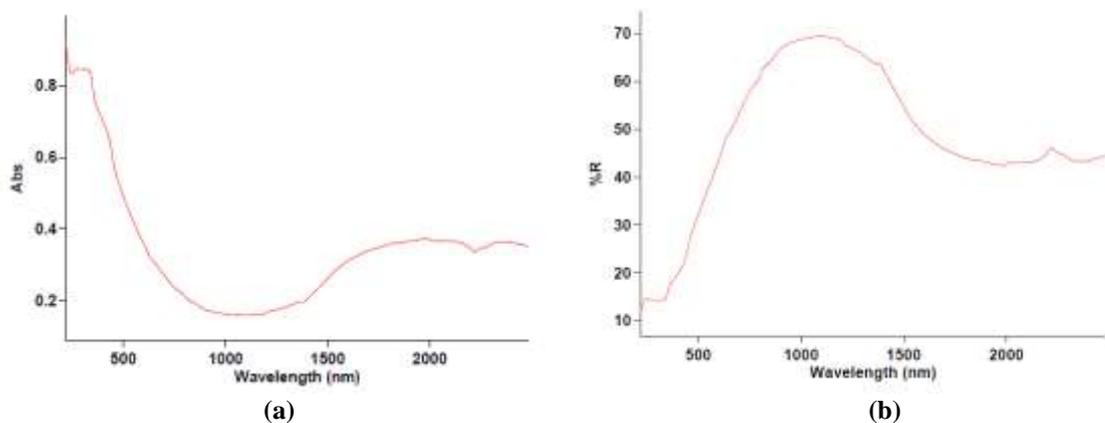


Figure. 3. UV-VIS spectrum of PbBaTiO₃ (a) Absorbance (b) reflectance

The reflectance spectra is translated into absorption spectra using Kubelka-Munk equation which is written as follows

$$\alpha = 2(1-R)/2R \text{-----}[10]$$

where α is the absorption coefficient and R the reflectivity at a particular wavelength[14]. Absorption is found to be decreasing with wavelength whereas reflectance is found to be increasing with wavelength.

1. We can see that absorption decreases with increasing wavelength. The peaks in the graph represent direct transmissions. A sudden decrease in absorption in the lower wavelength region corresponds to band gap.

2. Reflection is found to be increasing with increasing wavelength. This is an obvious result because absorption coefficient of the material, i.e, α is proportional to reflectance as given below

$$\alpha \propto \ln \frac{(R_{max} - R_{min})}{(R - R_{min})} \text{-----}[11]$$

Where R max is the maximum value of reflection, R min is the minimum value of reflection and R is the reflectance from any intermediate energy photon. Reflectance decreases from R max. to R min. due to absorption.

4.2. Band Gap

In order to obtain band gap energy we construct a Tauc plot with $h\nu$ (on x axis) against $(h\nu\alpha)^2$ (on y axis) at final calcining temperature at 900°C. Tauc plot at 900°C is given in Fig.4. We take direct allowed transitions only.

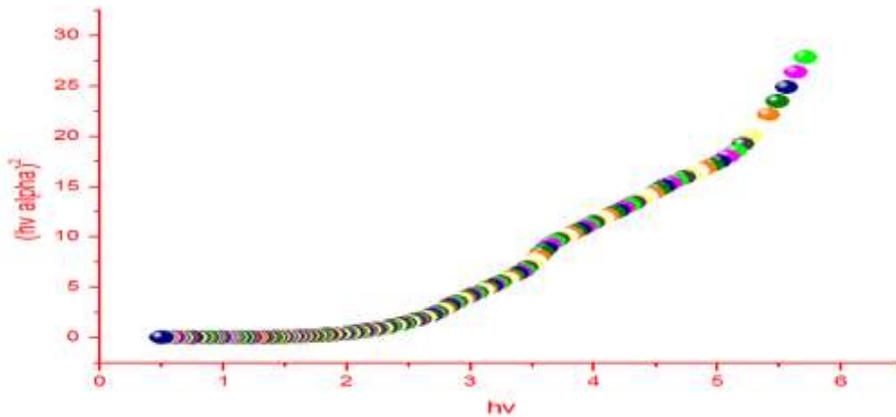


Fig. 4.The Tauc plot of PbBaTiO₃ at 900⁰C.

From the Tauc plot, band gap is determined by fitting a line through the linear portion of the band edge region. The band gaps of the sample determined at different temperatures is given below in table 1.

Table 1. Band gap energy at different temperatures

Number	Temperature(°C)	Band gap(ev)
1	30	4.55
2	500	4.483
3	850	4.38
4	900	4.31

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

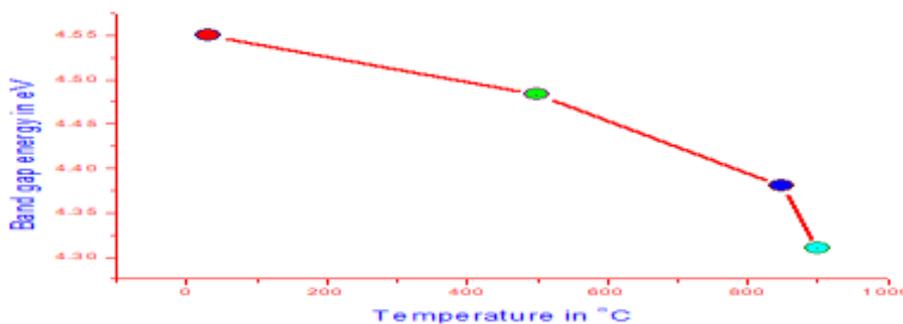


Fig. 5. Band gap energy variation with temperature of PbBaTiO₃

It is very clear that band gap energy of the sample decreases with increase in temperature. Particle size of the sample at different temperatures is calculated 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[15-16]. The variation of band gap with particle size is given below in the table.

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

Temperature of (^o C)	Particle size (nm)	Band gap(ev)
30	19.55	4.55
500	20.00	4.483
850	22.97	4.38
900	25.99	4.31

From the table a graph is plotted with particle size on x axis and temperature on y axis. The graph is given below in fig. 6.

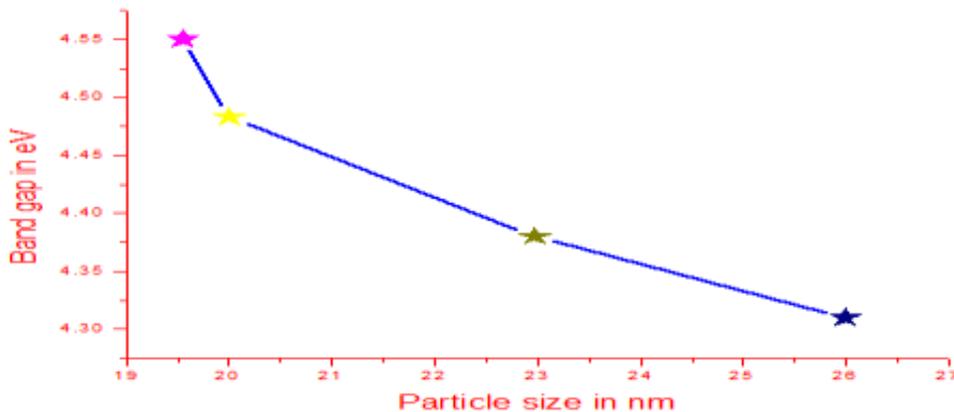


Fig. 6. Band gap energy variation with particle size of PbBaTiO₃

It is very clear that band gap energy increases with decrease in particle size. So from the graphs given in fig. 5a and fig. 6 it is found that band gap energy decreases with increase in temperature and increases with decrease in particle size.

1. In dielectric materials band gap energy falls with the rise in temperature. Rise in temperature causes increased vibrations of atoms within the crystal which reduces inter atomic spacing or d-spacing. This result a fall in the potential felt by the electrons. Hence band gap energy decreases. Temperature and band gap energy are related as given below according to Varshni's Equation

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

Eg(T) denotes the band gap energy at a temperature T. Eg(0) is the band gap at 0 K, α and β are fitting parameters.

2. The band gap energy of the ceramic increases as particle size decreases. Quantum size effect is responsible for this. It is common in crystalline ceramics with nano sized particles. Actually valence band and conduction band consists of so many energy levels merged together, corresponding to a large number of atoms. As particle size decreases the number of available atoms in the particle also decreases. So number of energy levels decreases. So width of valence band and conduction band get thinner and forbidden energy gap increases.

4.3. Refractive Index

Refractive index of the ceramic is calculated using eqn. 6. Variation of refractive index with wavelength is given in (a) of fig. 7 and variation of refractive index with photon energy is given in (b) of fig. 7.

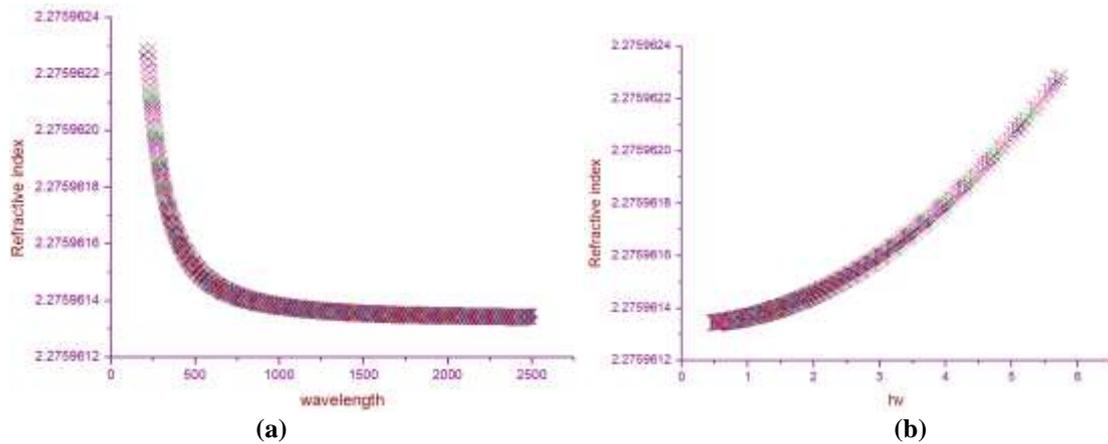


Fig. 7. Variation of Refractive index (n) with (a) wavelength and (b) photon energy of PbBaTiO₃

From fig.7(a) it is clear that refractive index decreases abruptly with wavelength up to 500 nm. Maximum value of refractive index is 2.2759623. At 500 nm its value is 2.2759614. After that the refractive index is almost constant with an approximate value of 2.2759613. So it is clear that when wavelength increases from 250 nm to 2500 nm, refractive index decreases from 2.2759623 to 2.2759613. So there is only a slight change of 0.000001. Hence refractive index is almost a constant at all wavelengths.

From fig.7(b) it is clear that refractive index increases with photon energy. When energy is 0.45 eV minimum value of refractive index is obtained and its value is 2.2759613. When energy is 5.8 eV maximum value of refractive index is obtained and its value is 2.2759623. So it is clear that when photon energy increases from 0.45 eV to 5.8 eV, refractive index increases from 2.2759613 to 2.2759623. So there is only a slight change of 0.000001. Hence refractive index is almost a constant at all photon energies.

1. Refractive index decreases with increase in wavelength because of the dependence of the refractive index on light energy. Dispersion of light energy at various interstitial layers present in the polycrystalline ceramic increases with increasing wavelength and this causes fall in the values refractive index.
2. Refractive index increases with photon energy as a result of increasing crystallite size with increasing photon energy. When crystallite size or particle size increases inter atomic spacing decreases and as a result polarization increases. The refractive index of perovskites is proportional to electronic polarization per unit volume.

• **Dispersion Parameters**

Various dispersion parameters such as band gap energy(E_g), oscillator energy(E_o) and dispersion energy(E_d) can be calculated using Wemple-DiDomenico (WD)model. Accordingly a graph (fig.8) is constructed with $(n^2-1)^{-1}$ against $(hv)^2$. Oscillator energy E_o is calculated from the slope $(1/E_oE_d)$ and dispersion energy E_d is calculated from the intercept (E_o/E_d) on y axis.

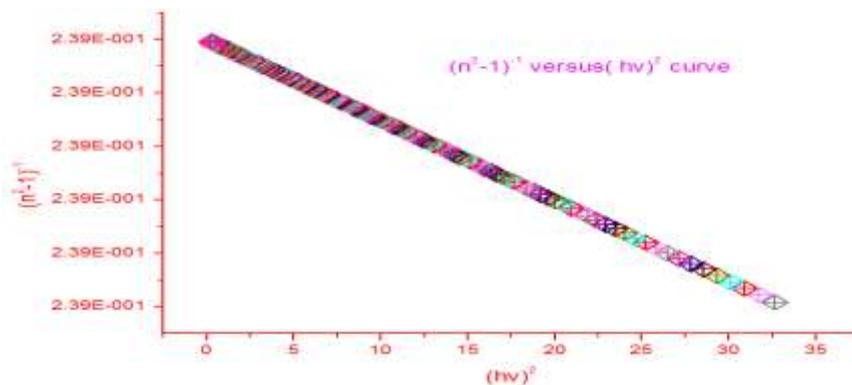


Fig. 8 $(n^2-1)^{-1}$ against $(hv)^2$

Another representation of the oscillator model is given by sell Meier's dispersion formula as

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

Here S_o represents is the average oscillator strength and λ_o represents the average oscillator wavelength. $(n^2 - 1)^{-1}$ is taken on y axis and $(1/\lambda^2)$ is taken on x axis (Fig.9). S_o and (λ_o) are determined from the slope and intercept of the straight line graph obtained [17].

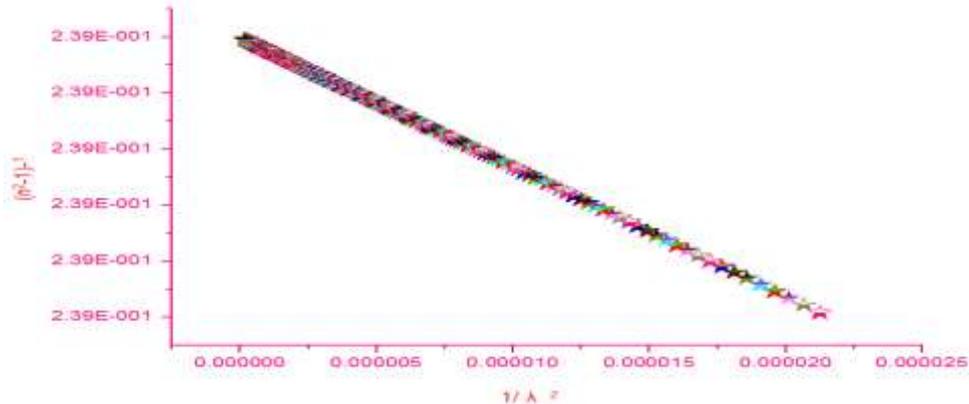


Fig.9 $(n^2-1)^{-1}$ against $1/\lambda^2$

Dispersion parameters such as band gap energy (E_g), oscillator energy (E_o) and dispersion energy (E_d) are calculated at different temperatures and given in the table below

Table 3. The dispersion parameters of $PbBaTiO_3$

Temperature ($^{\circ}C$)	E_g (eV)	E_o (eV)	E_d (eV)
30	4.55	6.37	12.8
500	4.483	6.2788	12.42
850	4.38	6.12	12.187
900	4.31	6.041	12.15

Band gap energy, oscillator energy and dispersion energy decreases with increase in temperature.

V. Conclusions

1. Absorption of the polycrystalline perovskite ceramic $PbBaTiO_3$ decreases with increasing wavelength. Peaks representing direct transmissions are obtained. A sudden decrease in absorption in the lower wavelength region corresponding to band gap is also obtained.
2. Band gap energy is found to be decreasing with increase in both temperature and particle size. It is observed that as the temperature increases atomic vibrations in the crystal increases and the d-spacing decreases. Hence potential felt by the electrons decreases. As a result, size of the band gap and band gap energy decreases. The band gap energy increases with decrease in particle size due to quantum size effect in the nano crystalline ceramics. When particle size decreases the number of atoms present in the particle also decreases and hence the number of overlapping orbitals or energy levels decreases and as a result the width of both valence band and conduction band narrows. Hence band gap increases.
3. Refractive index decreases with increase in wavelength and increases with photon energy. Dispersion of light energy at various interstitial layers present in the polycrystalline ceramic increases with increasing wavelength and this causes fall in the values refractive index. Refractive index increases with photon energy as a result of increasing crystallite size with increasing photon energy. When crystallite size or particle size increases inter atomic spacing decreases and as a result polarization increases. The refractive index of perovskites materials is proportional to electronic polarization per unit volume.
4. Band gap energy, oscillator energy and dispersion energy decreases with increase in temperature.

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