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# Refractive index dispersion and determination of the optical constants of BaTiO3 thin film prepared by sol gel

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The optical properties of the BaTiO3 film deposited on ITO coated glass by sol–gel method using barium acetate and titanium isopropoxide as starting materials have been investigated. The optical constants such as refractive index absorption coefficient and dielectric constant were determined using optical spectra. Type of the optical transition was found to be a direct transition with an Eg value of 3.47 eV. The refractive index dispersion of the film obeys to single oscillator model with dispersion energy of 21.07 eV, oscillator energy of 5.20 eV and dispersion parameter Eo/So of 7.3x10-14 eV.m2. The obtained results indicate that the BaTiO3 film can be a probable candidate for optoelectronic applications as a wide gap material.

***Keywords:*** *BaTiO3 thin film, AFM, Optical constant, Refractive index, Sol gel.*

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## 1. Introduction

C Metal oxide with perovskite structure such as BaTiO3 and Pb(Zr,Ti)O3 are widely used in various electronic applications such as multi-layer ceramic capacitors (MLCC), transducers, actuators and ferroelectric random access memories (FRAM) due to their unique ferroelectric, pyroelectric and piezoelectric properties [1–4]. Barium titanate is one of the most widely studied ferroelectric materials due to its many potential useful properties and it widely applied in electronic devices as high permittivity capacitors, infrared detectors or transducers. It is well known that ferroelectric and optical properties of ferroelectric ceramics depend on the grain size [5]. The properties of BaTiO3 thin films change with various deposition parameters like deposition technique, substrate temperature and substrate type. The function of BaTiO3 thin films in optoelectronic devices depends on structural and optical properties like grain size, lattice distortion, micro-strain, band gap, refractive index and absorption [6]. Thus, it is important to study how optical and structural properties depend on the deposition parameters.

With this aim, we have studied structural properties and the optical characteristics and of BaTiO3 thin film deposited onto indium tin oxide coated glass substrate by sol gel method.

## 2. Experimental

For preparation of BaTiO3 film, the used starting materials are barium acetate and titanium isopropoxide and glacial acetic acid were used as starting materials. Firstly, 1.66 M Ba(CH3COO)2 was dissolved in 70 ml of glacial acetic acid and stirred at 50 oC for 30 min and then, it was cooled down to the room temperature. The stoichiometric amount of titanium isopropoxide was dissolved in 70 ml isopropanol and stirred by magnetic stirrer. After dissolution of two compounds, the precursor solution was mixed with a solution consisting of Ba(CH3COO)2 and titanium isopropoxide and it was stirred for 1 h. After stirring, the solution was refluxing for 2 h. The BaTiO3 solution was coated onto indium tin oxide coated glass with 2000 rpm using a VTC-50 DeskTop Spin Coater.The obtained films were dried at 60 oC for 10 min and it was annealed at 650 oC for 1h. The transmittance, absorbance and reflectance spectra of the film were measured using a Shimadzu UV-VIS-NIR 3600 spectrophotometer.

## 3. Results and Discussion

### *3.1. Determination of optical constants of the $BaTiO_3$ thin film*

The atomic force microscopy image of the $BaTiO_3$ film is shown in Fig.1. The film was not formed from a certain particles. The film has a homogeneous surface with a surface roughness of 16.77 nm.

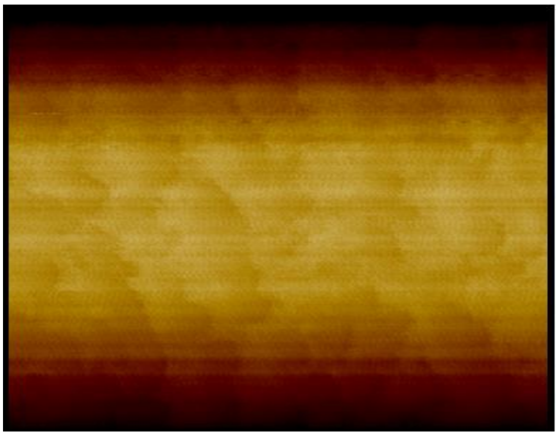

**Fig.1.** AFM image of the BaTiO3 film on ITO glass

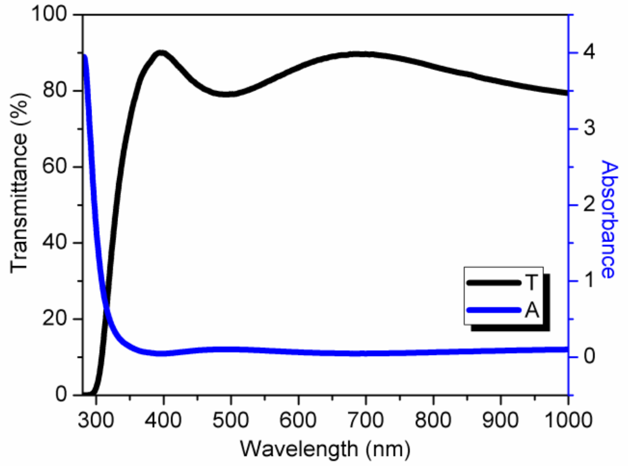

**Fig. 2.** Absorbance and transmittance spectra of the BaTiO3 thin film.

Fig.2 show the absorbance (*A*) and transmittance (*T*) spectra of the $BaTiO_3$ thin film. Transmittance (*T*), absorption coefficient ($\alpha$) and reflectance (*R*) are related through the following relations [7-8]:

$$T(\lambda)=\frac{(1-R(\lambda))^2 e^{-\alpha d}}{1-R(\lambda)^2 e^{-2\alpha d}}, \qquad (1)$$

where *d* is the film thickness, and the reflectance which is described as [7]:

$$R(\lambda)=\frac{(n(\lambda)-1)^2+k(\lambda)^2}{(n(\lambda)+1)^2+k(\lambda)^2}, \qquad (2)$$

The solution of this Eq.2 can be given as:

$$n(\lambda)=\frac{(1+R(\lambda))+\sqrt{4R(\lambda)-(1-R(\lambda))^2 k(\lambda)^2}}{1-R(\lambda)}, \qquad (3)$$

where *k* is the extinction coefficient given by [7]:

$$k=\frac{\alpha\lambda}{4\pi}, \qquad (4)$$

Thus, the refractive index and the extinction coefficient can be calculated by means of these equations. The refractive index of any material is an important parameter for optical communications. It is very important to analyze refractive index dispersion of the investigated materials. The complex refractive index can be described by the following relation:

$$\hat{n}(E)=n(E)+ik(E), \qquad (5)$$

where *n(E)* is the real part of the refractive index and *k(E)* is the imaginary part of the refractive index also called the extinction coefficient. The *n(E)* and *k(E)* constants can be determined from the following relations [9]:

$$n(E)=1+\frac{2}{\pi}\int_0^\infty \frac{E'k(E')}{(E')^2-E^2}dE', \qquad (6)$$

$$k(E)=-\frac{2}{\pi}\int_0^\infty \frac{n(E')-1}{(E')^2-E^2}dE', \qquad (7)$$

The refractive index of the $BaTiO_3$ thin film was calculated using Eq. 3 and the spectral dependence of the refractive index is shown in Fig. 3. It is clear that the refractive index was decreased with increasing the wavelengths, i.e, it exhibits a normal dispersion. The dispersion behavior of the $BaTiO_3$ thin film can be analyzed by Wemple and DiDomenico given by the following relation [10-11],

$$n^2-1=\frac{E_o E_d}{E_o^2-(hc/\lambda)^2}, \qquad (8)$$

where $E_o$ is the single oscillator energy and $E_d$ is the dispersion energy, which is a measure of the intensity of the inter band optical transitions. The plot of $(n^2-1)^{-1}$ vs $E^2$ is shown in Fig.4 and $E_o$ and $E_d$ values were determined from the slope, $(E_oE_d)^{-1}$ and intercept $(E_o/E_d)$, on the vertical axis and were found to be 5.20 eV and 21.07 eV, respectively. The relation between $E_o$ and $E_g$ for the $BaTiO_3$ was found to be $E_o$=1.5 $E_g$. This average gap gives quantitative information on the overall band structure of the $BaTiO_3$. The obtained $E_o$ value is in agreement with the value of melt grown $BaTiO_3$ [12] and it is smaller than that of RF sputtered strontium substituted barium titanate thin films [13]. This difference is due to the substituted strontium into $BaTiO_3$.

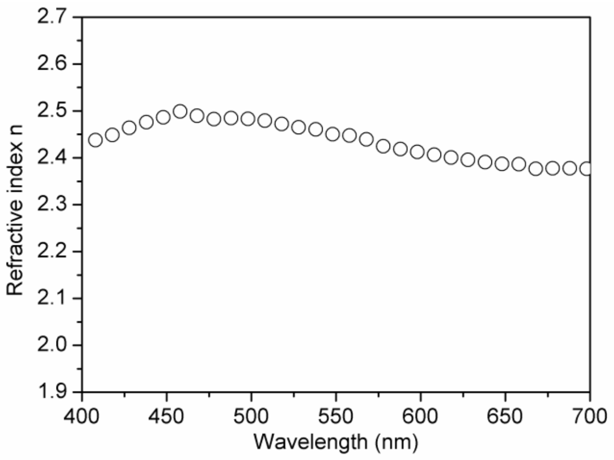

**Fig. 3**. Refractive index as a function of wavelength of the BaTiO3 thin film.

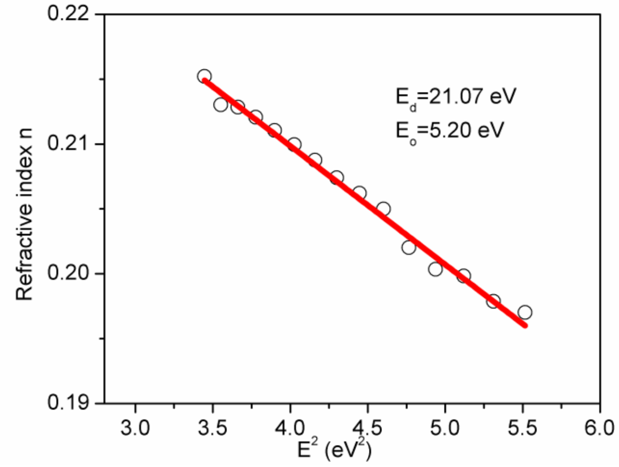

**Fig. 4.** Plot of (n2-1)-1 vs E2 of the BaTiO3 thin film.

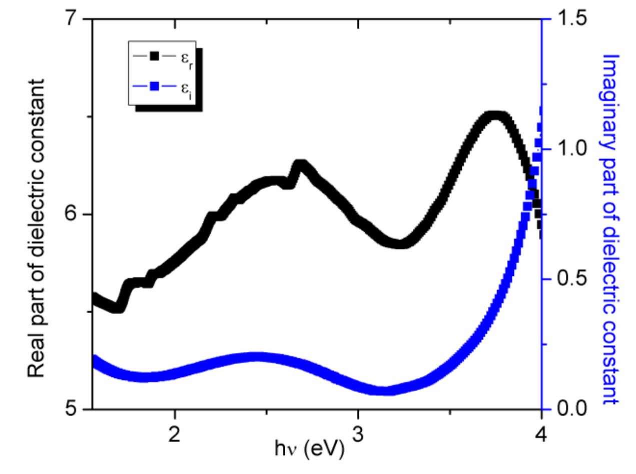

**Fig. 5.** Real and imaginary parts dependence on the photon energy of the BaTiO3 thin film.

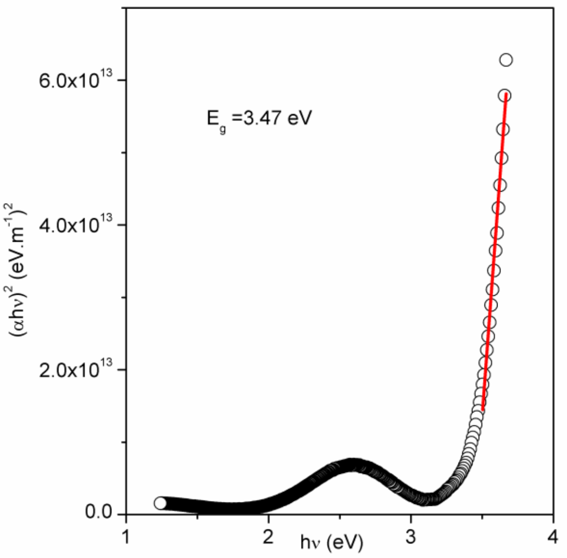

**Fig. 6.** Plot of (αhν)2 v.s hν of the BaTiO3 thin film

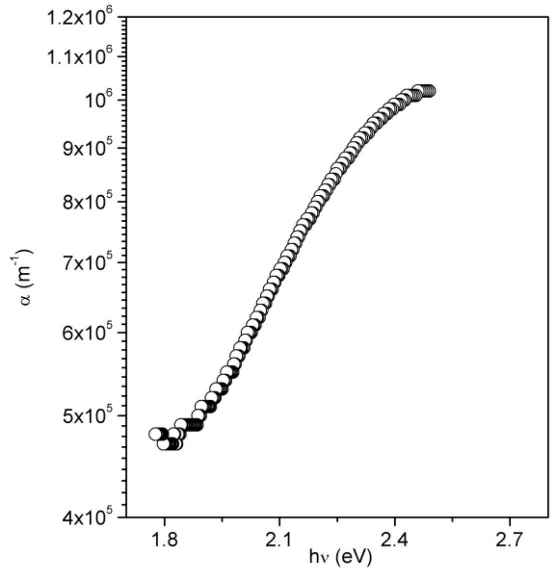

**Fig. 7.** Plot of logα vs h□ of the BaTiO3 thin film

The dispersion energy is related to other physical parameters of the $BaTiO_3$ material and it can be expressed by the following relation [10]:

$$E_d = \beta N_c Z_a N_e, \tag{9}$$

Where $Z_a$ is the formal chemical valency of the anion (2 for $BaTiO_3$), $N_c$ is the effective coordination number of the cation nearest neighbour to the anion (6 for $BaTiO_3$), $N_e$ is the effective number of valence electrons per anion (8 for $BaTiO_3$). The $\beta$ value for the $BaTiO_3$ film was found to be 0.22. This suggests that the $BaTiO_3$ has the ionic bonding. The Sellmeir single oscillator relation can be defined as follows:

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1-(\lambda_o/\lambda)^2}, \tag{10}$$

where $\lambda$ is the wavelength of incident light, $S_o$ is the average oscillator strength and $\lambda_o$ is an average oscillator wavelength. The relation between $S_o$ and $n_\infty$ values can be given by the following relation:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2, \tag{11}$$

Thus, the average oscillator strength can be obtained by the following relation:

$$S_o = \frac{n_\infty^2 - 1}{\lambda_o^2} \tag{12}$$

Where $n_\infty$ is the long wavelength refractive index. In order to obtain $S_o$ , $n_\infty$ and $\lambda_o$ values, we plotted the curve of $n^2$-1 vs $\lambda^{-2}$ and the $S_o$ and $\lambda_o$ values were found to be $7.11 \times 10^{13}$ $m^{-2}$, 2.24 and 238.84 nm, respectively. The dispersion parameter $E_o/S_o$ for the studied $BaTiO_3$ was found to be $7.3 \times 10^{-14}$ $eV.m^2$ and this value is agreement with that of melt grown $BaTiO_3$ sample [12]. This suggests that the dispersion of the refractive index for the perovskite oxides is identical. The $M_{-1}$ and $M_{-3}$ moments of the optical spectra can be expressed as [14]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}}, \qquad E_d^2 = \frac{M_{-1}^3}{M_{-3}}, \tag{13}$$

The $M_{-1}$ and $M_{-3}$ moments were determined using Eq.12 and were obtained to be 4.05 and 0.15 $eV^{-2}$. The complex dielectric constant of the film is expressed as [7]:

$$\varepsilon^* = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = n^2(\omega) - k^2(\omega) + 2in(\omega)k(\omega), \tag{14}$$

where $\varepsilon_1$ is the real part and $\varepsilon_2$ is the imaginary of the dielectric constant. Fig. 5 shows the real and imaginary parts dependence on photon energy. The values of $\varepsilon_1$ and $\varepsilon_2$ increase with increasing the photon energy. The real part of the dielectric constant is higher than imaginary part of the dielectric constant. The real part spectrum of the dielectric constant shows two peaks. One of them at 3.75 eV corresponds to the absorption edge and the presence of this peak is due to electronic transitions between valance and conduction bands. The other peak at 2.68 eV is due electronic transitions taken place in intrabands.

### *3.2. Determination of the optical band gap of $BaTiO_3$ film*

It is well-known that the optical absorption spectrum is an important tool to obtain optical band gap of crystalline and amorphous materials. The band structure of the $BaTiO_3$ obeys the rule of direct transition. The optical transitions occurring in semiconductors can be explained as follows. For indirect optical transitions; the absorption coefficient $\alpha_i$ for indirect transition is expressed by the following relation:

$$\alpha_i = \alpha_e + \alpha_a, \tag{15}$$

where $\alpha_e$ is the contribution of emission and $\alpha_a$ is the contribution of absorption of phonons. Thus, $\alpha_i$ can be written as [15]:

$$(\alpha_i h\nu) = \frac{[h\nu - (E_g - E_p)]^2}{[\exp(E_p/kT) - 1]} + \frac{[h\nu - (E_g + E_p)]^2}{[1 - \exp(-E_p/kT)]}, \tag{16}$$

Absorption coefficient due to phonon absorption and emission is expressed as:

$$\alpha_a = A(T)\frac{[h\nu - (E_g - E_p)]^2}{h\nu}, \quad h\nu > E_g - E_p \tag{17}$$

$$\alpha_e = B(T)\frac{[h\nu - (E_g + E_p)]^2}{h\nu}, \quad h\nu > E_g + E_p \tag{18}$$

where *A(T)* and *B(T)* are constants. For indirect transitions, the plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ at lower photon energies, the straight line corresponds to the phonon absorption and its intercept is equal to $E_g$-$E_p$ and at higher photon energies, the other straight line corresponds to the phonon emission process and its intercept equals to $E_g$+$E_p$. In direct transitions, the absorption coefficient $\alpha_d$ for direct transition is expressed by the following relation:

$$\alpha_d = C(T)\frac{[h\nu - E_p)]^{1/2}}{h\nu}, \tag{19}$$

where *C(T)* is constant. For the direct transitions, the plot of $(\alpha h\nu)^{1/2}$ v.s $h\nu$ indicates a straight line. We have analyzed in detail to determine optical transitions between valance band and conduction bands. It is evaluated that the $BaTiO_3$ has a direct optical band gap. Thus, the curve of $(\alpha h\nu)^2$ v.s $h\nu$ was plotted and is shown in Fig. 6 and this plot shows one straight line. The $E_g$ value of the film was determined from this linear part and was found to be 3.47 eV. The obtained $E_g$ value is in good agreement with the band gap energy of 3.47 eV obtained by Suzuki et al [16] for $BaTiO_3$ thin film prepared by radio-frequency-plasma. The obtained $E_g$ value of the studied $BaTiO_3$ film is close to the data of the films obtained, But it is smaller than that of other films obtained with metallo-organic solution method (3.5 eV) [17], sol–gel technique (3.53 eV) [18], RF sputtering (3.53–3.68 eV), $BaTiO_3$ powders (3.92 eV) and sol–gel derived BaTiO3 films on ITO coated glass [1,19-21]. This suggests that the optical band gap of the $BaTiO_3$ film changes with preparation method and production conditions.

At lower photon energies, the absorption behavior of the $BaTiO_3$ film can be analyzed by following relation:

$$\alpha \propto \exp(E / E_u), \tag{20}$$

Where $E_u$ is Urbach energy, which is interpreted as the width of the tails of localized states in the band gap [22]. In Urbach region, the optical transitions are occurred between extended states in one band and localized states in the exponential tail of the other band. To obtain Urbach energy $E_u$, we plotted the curve of $log\alpha$ vs $h\nu$, as shown in Fig. 7. The $E_u$ value was determined from the slope of Fig. 7 and was found to be 308±2 meV.

## 4. Conclusion

The BaTiO3 film was prepared by sol–gel method. The optical constants such as refractive index absorption coefficient and dielectric constant were determined using optical spectra. The refractive index dispersion behavior was analyzed by single oscillator model and the dispersion and oscillator parameters were determined which in good agreement with other studies. The obtained optical parameters indicate that the BaTiO3 film can be a probable candidate for optoelectronic applications.

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