

# BANDGAP ENERGY AND OPTICAL CONSTANTS OF CERAMIC MATERIAL

## $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with $x=0.20$

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### ABSTRACT

A new crystalline ceramic  $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$  with  $x=0.20$  was prepared by solid state reaction method. Different samples were taken at different temperatures. Much higher temperature is required for Solid-state reactions to take place which involves formation of product phase(s) at the interfaces of the reactants. Product sample undergoes UV-VIS analysis. Tunable band gaps can be obtained by varying annealing temperatures. So many optical constants namely refractive index, extinction coefficient, normal-incidence reflectivity, and absorption coefficient were determined. These parameters show systematic variation with temperature. The variation of refractive index with wavelength was analyzed by the Wemple- Di Domenico single-oscillator model. Urbach energy was also calculated.

**Keywords:**  $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$  with  $x=0.20$ , Band gap energy, Optical Constants, Dispersion of refractive index, Wemple- Di Domenico model, Urbach energy

### 1. INTRODUCTION

In the present work the authors describes the optical behaviour of  $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$  with  $x=0.20$ , a crystalline ceramic, based on its UV analysis. The energy band gap values of the sample were analyzed for different temperatures and they are fundamentally important and to

the design of practical devices [1,2]. 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 [3]. According to band theory insulators have large values of band gap energy. Semiconductors have small values of band gap energy. Measuring of band gap energy is important in micro/nano material industries.

All synthesized samples were subjected to UV-VIS analysis. Tauc method is used for the determination of the band gap or Tauc gap. The band gap energy determined from Tauc plot showed a direct variation with temperature. The Urbach energy of the sample was also determined. Various optical constants were calculated. The optical constants of refractive index, extinction coefficient, and absorption coefficient showed a systematic variation with temperature. The variation of refractive index with wavelength was analyzed by the Wemple-DiDomenico single-oscillator model.

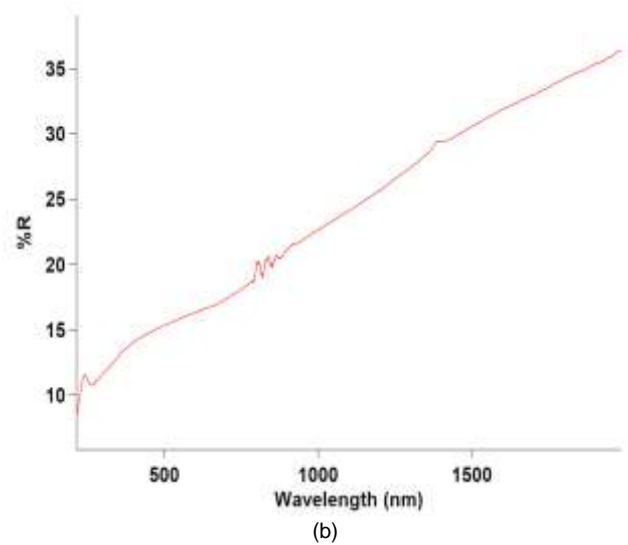
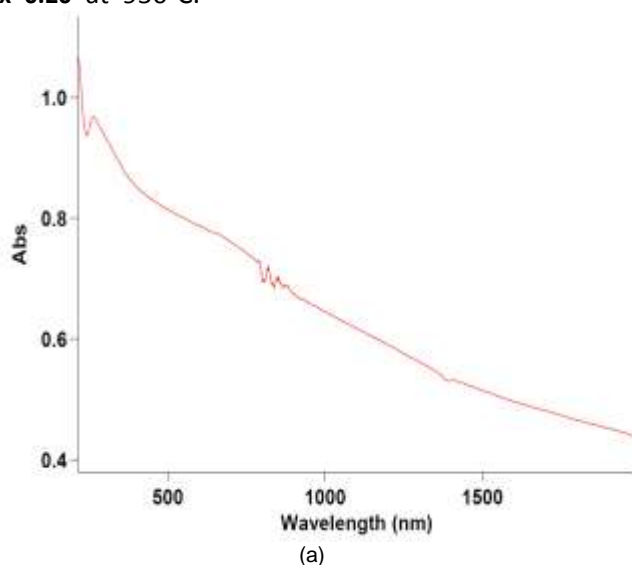
### 2. Experimental

$Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$  with  $x=0.20$  is a new crystalline ceramic synthesized by solid state thermo chemical reaction route. Selection of raw materials was very crucial. The raw materials should be of high purity. They were weighed according to the stoichiometric formula. The particle size of the powders must be in the submicron range for the solid phase reactions to occur by atomic diffusion. The powders were then mixed mechanically, then ball milled for a long time. Attrition milling was utilized to insure homogeneity. The prepared sample was

calcined at different temperatures, 300C, 5000C, 8500C and 9500C. Control of temperature is often necessary to ensure that the desired crystalline phase is formed with optimum particle size [4]. Then UV-Vis spectrum of the prepared ceramic was taken and analyzed. Tauc method is used to determine the optical band gap or Tauc gap. The energy value of band gap determined from Tauc plot has a direct dependence with temperature. The Urbach energy of the sample was also studied. The optical constants such as refractive index, extinction coefficient, and absorption coefficient showed a variation with temperature. The dispersion of refractive index was analyzed by the Wemple-DiDomenico single-oscillator model and such optical behaviour is rarely reported.

## 2.1. UV-VIS. Analysis:

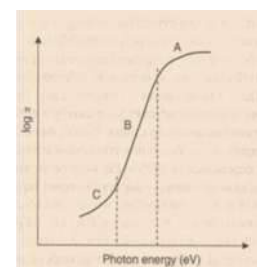
The optical absorption spectrum of the sample was studied at room temperature and optical absorption data was obtained. This data was analyzed using classical relation for near edge optical absorption of semiconductors [5-6]. The UV spectrum analysis is a good quality check for the optical behaviour of the nano crystalline ceramic materials. The sample obtained after calcination at different temperatures 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  $\pm 0.1$ nm (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 [7]. Figure.1 shows the UV-VIS behaviour of the sample  $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$  with  $x=0.20$  at  $950^\circ\text{C}$ .



**Figure.1 UV-VIS spectrum of  $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$  with  $x=0.20$**   
(a) Absorbance (b) reflectance

The diffuse reflectance spectra were translated into the absorption spectra by the Kubelka-Munk method. Kubelka-Munk's equation is described as follows:  $\alpha = 2(1-R)/2R-1$ , where  $\alpha$  is the absorption coefficient and R the reflectivity at a particular wavelength [8].

The band gap energy can be determined using the Tauc relation. According to the Tauc relation, the absorption coefficient  $\alpha$  for a material is given by  $\alpha = A(h\nu - E_g)^n$  (2), Where  $E_g$  the band gap, constant A is different for different transitions, ( $h\nu$ ) is energy of photon in eV and n denotes the nature of the sample transition [9]. 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 [10-12] respectively. The TAUC plot defines the optical band gap (region A in fig.2.) The tauc plot of the sample synthesized is given in Fig 3. It is reported that optical gap energy of nano/micro -sized crystals depends on its crystallite size, it increases with decreasing crystallite size in the nano size range [13-14].



**Fig.2-optical band gap energy variation with absorption.**

The absorption edge called the Urbach energy relies on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds and on average photon energies [15]. 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 (16). The absorption coefficient at the photon energy below the optical gap (tail absorption) depends exponentially on the photon energy:  $\alpha(\hbar\nu) \sim \exp(\hbar\nu/E_u)$  --(4) where  $E_u$  is called Urbach energy. The region B in the fig.2 represents the Urbach energy. It is observed in manycases that optical absorption by defects also appears at energy lower than optical gap (region C of fig.2). This region is related to the structural properties of materials(17).

The extinction coefficient and the absorption coefficient are related as  $\alpha(E) = 4\pi/\lambda (k(E))$ —(3). Variation of band gap energy with samples annealed at different temperatures is shown in figure 4. The natural logarithm of the absorption coefficient,  $\ln(\alpha)$ , was plotted as a function of the photon energy,  $\hbar\nu$  (Fig.5). The value of  $E_u$  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 ingredients. The temperature-dependent part of the Urbach tail, is purely of intrinsic reasons (18)].

## 2.2 Refractive Index and Dispersion

When wavelength increases refractive index values decrease linearly. Refractive index value slightly increases with increase in annealing temperature and reaches a particular value after a fixed wavelength. The refractive index values linearly 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(19). In the W-D model, the refractive index  $n$  can be written as  $n^2 - 1 = E_d E_0 / (E_d^2 - E^2)$  -- (5), where  $E$  is the photon energy,  $E_0$  is the oscillator energy, and  $E_d$  is the dispersion energy.  $E_0$  and  $E_d$  are associated with the crystalline structure and the ionicity of ionic or covalent oxide materials. So the single oscillator model can characterize the optical properties in the visible region for ionic or covalent oxide material, as well as some of its structural properties. The dependence of  $E_d$  on coordination number and valency implies that nearest-neighbor atom-like quantities strongly influence the optical properties of the materials. The oscillator energy  $E_0$  and dispersion energy  $E_d$  are obtained from the slope  $(E_0 E_d)^{-1}$  and intercept  $E_0/E_d$  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.  $n^2(0) = 1 + E_d/E_0$ —(6) (20)

## 3. Results and Discussion

From the studies made on UV-VIS spectrum analysis, it is very clear that band gap energy of the crystalline ceramic increases with the increase in annealing temperature of the sample. During UV-VIS analysis only the direct allowed transitions are considered. The calculated values of the band gap energy of the samples taken at different temperatures are presented in table -1.

The Tauc plot is plotted with  $\hbar\nu$  along the X-axis and  $(\hbar\nu\alpha)^2$  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.3. The band gap energy values of  $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$  with  $x=0.20$  at different temperatures calculated are given in the table 1.

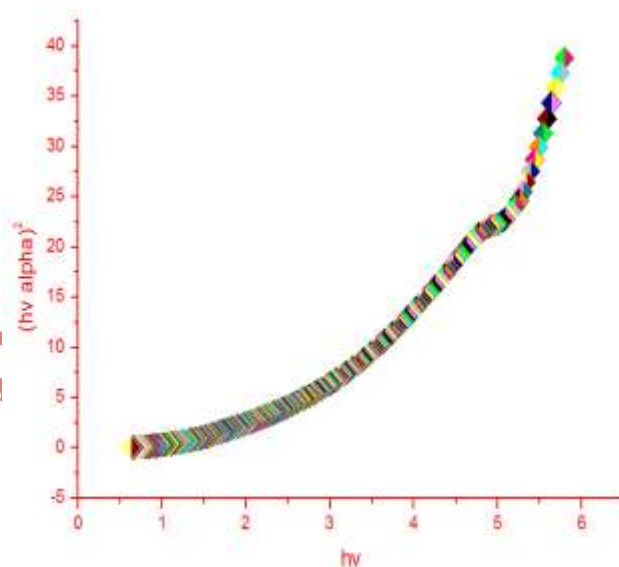


Fig.3. The Tauc plot of  $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$  with  $x=0.20$

Table-1. Band gap energy values of  $\text{Mn}_{0.8+x}\text{Zn}_{0.2}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$  with  $x=0.20$  at different temperatures

Temperature	Band gap energy in eV
30°C	4.28
500°C	4.34
850°C	4.40
950°C	4.45

It is found that band gap energy increases with increase in temperature (fig.4). The energy levels depend on the extent of structural order–disorder in the crystal lattice. Though the band gap increases with crystallite size it

**Mn<sub>0.8+x</sub>Zn<sub>0.2</sub>Ti<sub>x</sub>Fe<sub>2-2x</sub>O<sub>4</sub> with x=0.20**

decreases as the phase is formed which implies the quantum confinement also decreasing its dislocation density.

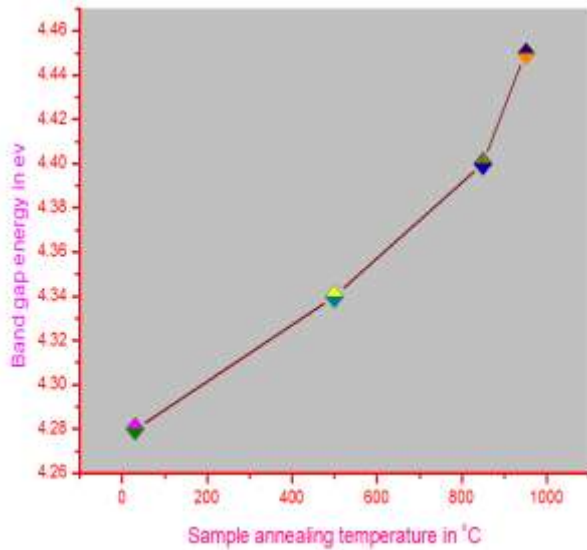


Fig.4. Band gap energy variation with the samples at varied annealing temperature of **Mn<sub>0.8+x</sub>Zn<sub>0.2</sub>Ti<sub>x</sub>Fe<sub>2-2x</sub>O<sub>4</sub> with x=0.20**

The increase in temperature causes an increase in crystallite size makes an increase in band gap energy. It is confirmed from Tauc plot data 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 E<sub>g</sub> values.

Urbach energy is calculated by plotting the natural logarithm of the absorption coefficient with the energy in eV (Figure 5). This 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.

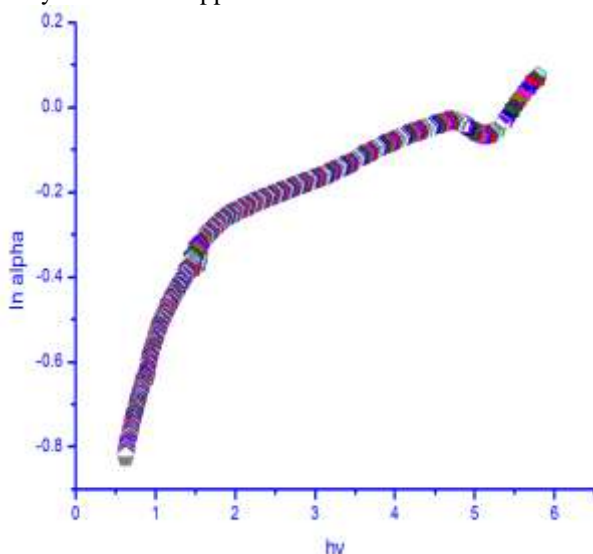


Fig.5. Absorption variation with photon energy of

Variation of refractive index with variation in temperature was also studied. Analysis clearly implies 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 proportionality 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.

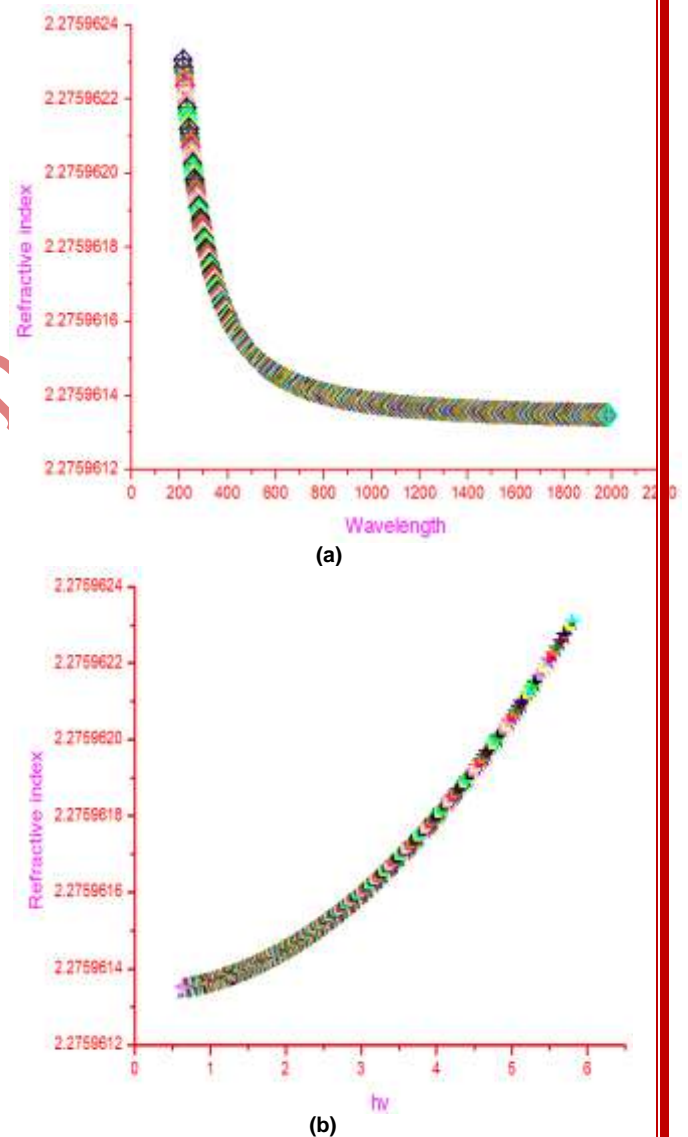


Fig.6. Variation of Refractive index (n) with (a) wavelength and (b) photon energy of **Mn<sub>0.8+x</sub>Zn<sub>0.2</sub>Ti<sub>x</sub>Fe<sub>2-2x</sub>O<sub>4</sub> with x=0.20**

Refractive index of the sample annealed at different temperatures can be calculated using Sellmeir dispersion formula(21).The dispersion energy of the sample is calculated using the Wemple-DiDomenico (WD)model. Results are plotted graphically in (Fig.7).

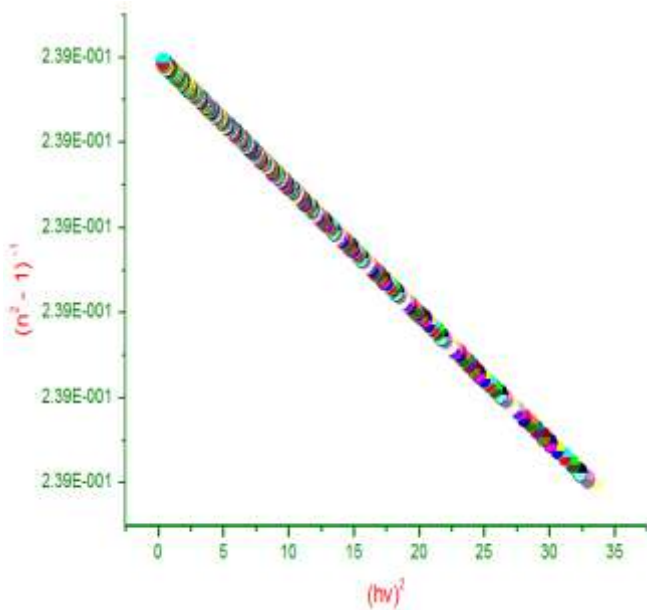


Fig.7.  $(n^2-1)^{-1}$  versus  $(hv)^2$  curve.

The data of the dispersion of the refractive index (n) were evaluated according to the single oscillator model proposed by Wemple and DiDomenico as,  $n^2 = 1 + (E_d E_o) / (E_o^2 - hv^2)$  ---- (7).

where  $E_o$  is the oscillator energy and  $E_d$  is the oscillator strength or dispersion energy. Plotting of  $(n^2-1)^{-1}$  against  $(hv)^2$  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  $(1/E_o E_d)$ .  $E_o$  is considered as an average energy gap to, it varies in proportion to the Tauc gap  $E_o \sim 2E_g$ .

The oscillator model can be also written as  $n^2 - 1 = S_o \lambda_o^2 / [1 - (\lambda_o / \lambda)^2]$  --- (8) where  $\lambda$  is the wavelength of the incident radiation,  $S_o$  is the average oscillator strength and  $\lambda_o$  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 Sellmeier's dispersion formula. The value of  $S_o$  and  $(\lambda_o)$  are estimated from the slope  $(1/S_o)$  and the infinite wavelength intercept  $(1/S_o \lambda_o)^2$ . The optical parameters of the sample were calculated and listed in the table.2 given below.

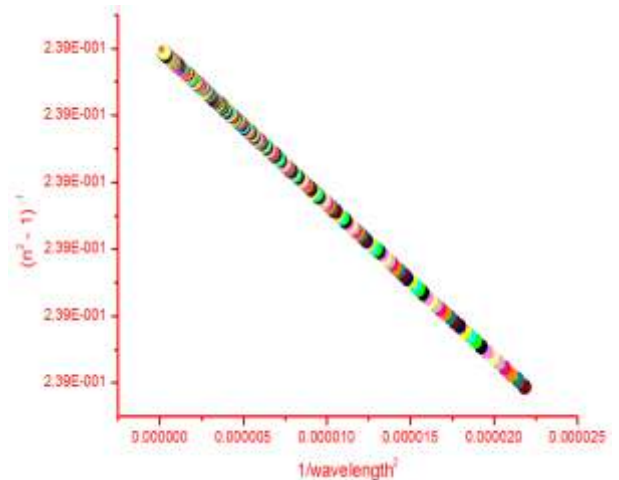


Fig.8.  $(n^2-1)^{-1}$  versus  $1/\lambda^2$  curve

Table 2. The optical parameters of  $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$  with  $x=0.20$  calculated.

sample	$E_g$ (eV)	$E_o$ (eV)
30°C	4.28	8.56
500°C	4.34	8.68
850°C	4.40	8.80
950°C	4.45	8.90

As the temperature is increased, band gap energy or  $E_g$  is increased. The dispersion energy decreases with the rise in temperature and the sample attains its perovskite phase. The curves with straight line graphs confirm the Sellmeier's dispersion formula. The mechano-chemical process has an advantage due to low-costs and wide availability of materials, leading to a simplified process.

#### 4. Conclusion

The UV emission peak shifts significantly to higher wavelengths with increasing annealing temperatures. The increase in the band gap energy increases the dielectric properties of the material. It is confirmed that tunable band gaps are obtained by varying annealing temperatures. Band gap energy and the optical properties of the ceramic material  $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$  with  $x=0.20$  can be taken as a better candidate for UV-VIS shielding applications. Optical measurements confirmed that absorbance and reflectance increase with temperature. According to Wemple-DiDomenico single-oscillator model the dispersion energy decreases as the sample attains its crystalline phase. As the band gap energy increases at high temperature the material becomes more dielectric. For new generation electronic equipments crystalline ceramics  $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$  with  $x=0.20$

materials will prove as a future substitute.

## 5. Acknowledgement

The authors are thankful to SAIF, Kochi for providing the instrumental data, UGC for providing financial assistance and to the Principal, CMS College, Kottayam, Kerala for providing the facilities.

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