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OPTICAL PROPERTIES OF TITANIUM SUBSTITUTED MANGANESE -ZINC FERRITE SYSTEM- $MN_{0.8+X}\,ZN_{0.2}TI_XFE_{2-2X}O_4$ WITH X=0.10

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ABSTRACT: *Titanium substituted Manganese-Zinc ferrite ($Mn_{0.8+x}\,Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10) was synthesized thermo chemically by solid state method at different treating temperatures. Basically, the substitution cause a rearrangement of Fe^{+3} ions into the two preexisting octahedral and tetrahedral sites. The X-ray analysis confirms the formation of single phase cubic spinel structure. The lattice constant decreases slightly and porosity increases with increase in sintering temperature. They can be disrupted into smaller particles by shear forces generating mechanical stress gradients. A characteristic feature of all solid-state reactions is that they involve the formation of product phase(s) at the interfaces of the reactants. UV-VIS analysis of the sample was carried out. Tunable band gaps can be obtained by varying annealing temperatures. The optical constants of refractive index, extinction coefficient, normal-incidence reflectivity, and absorption coefficient showed systematic variation with temperature. The dispersion of refractive index was analyzed by the Wemple-DiDomenico single-oscillator model.*

KEYWORDS: MnZnTiFeO, band gap energy, Dispersion, Wemple-DiDomenico model, refractive index.

INTRODUCTION

Ferrite crystals are interesting materials due to their rich physical properties. Spinel ferrites, with common formula of MFe2O4 (M: a divalent metal ion), have wide technological applications, e.g., in multilayer chip inductor (MLCI), ferrofluids, high-speed digital tape or recording disks, rod antenna, and humidity sensor. The effects of Ti^{4+} ions substitution on the magnetic, electric and dielectric properties of ferrites were reported by many authors [1–6]. Many different optical properties of ceramic products are of concern in different applications [7]. The optical properties of dielectric materials are generally of interest because of their good transmission in the optical part of the spectrum as compared with other classes of materials. At short wavelengths this good transmission is terminated at the ultraviolet absorption edge, which corresponds to radiation energies and frequencies ($E=hv=hc/\lambda$) where absorption of energy arises from electronic transitions between levels in the valence band to unfilled states in the conduction band. Both the index of absorption and refractive index are necessary to describe the optical properties of a ceramics. The absorption index is a function of wavelength and is mostly related to the absorption coefficient $\beta=4\pi k/\lambda$. For a single-phase material, the fraction of light transmitted is given by the absorption coefficient and sample thickness; $dI/I0=-\beta dx$ and $T=I/I0=\exp(-\beta x)$, $LnI/I0=-\beta x$ where I0 is the initial density, I is the transmitted intensity, x is the optical path length and T is the fraction transmitted. This overall transmission is given for normal incidence by $T^1=I_{in}/I_{out}=(1-R)^2\exp(-\beta x)$ Where R is the reflectivity[8]. In solid state physics a band gap, is an energy range in an ideal solid where no electron states can exist. In

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the present work the authors describes the optical behavior and band gap energy of $Mn_{0.8+x}$ $Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10 crystalline material. The energy band gap values of the sample were analyzed for different temperatures and they are fundamentally important to the design of practical devices. In the case of insulators the band gap energy is large (>4eV), but is lower for semiconductors (<3eV). Measuring the band gap is an important factor determining the electrical conductivity.

The band gap energy values obtained using Tauc plot showed a direct relation with temperature. The optical constants of absorption coefficient, extinction coefficient, and refractive index showed a systematic variation with temperature. The dispersion of refractive index was analyzed by the Wemple-DiDomenico single-oscillator model and such optical behaviour is rarely reported. The dispersion of the refractive index results from the fact that the visible spectrum is adjacent to the natural frequency of electronic oscillators in the ultraviolet. The index increases with decreasing wavelength in the visible range, and is referred to as normal dispersion [8].Refractive index of material determines the speed of light in the material. It is an important constant for optoelectronic devises as it would responsible for the nature of interaction of the material with the optical energy incident on it. The absorption coefficient, α, is a property of a material which defines the amount of light absorbed by it. The extinction coefficient denoted by K was calculated according to the equation: $K = \alpha\lambda/4\pi$[9].

EXPERIMENTAL

Titanium substituted Manganese-Zinc ferrite ($Mn_{0.8+x}$ $Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10) was synthesized by the conventional solid state reaction technique according to their molecular formula using a high-energy ball milling process through mechanically assisted synthesis. The initial ingredients MnO, ZnO, TiO_2, Fe_2O_3 were weighed and mixed in correct Stoichiometric ratio and grounded for ten hours using an agate mortar. The resulting mixture was air dried and presintered in air for 10 hours. Temperature is controlled by a platinum-Rhodium thermocouple within the furnace. The presintered ferrites were then again grounded for two to three hours. The granulated powder was then pressed into pellets and toroids at a pressure of 1N/M2 with the help of hydraulic press. The binder used was polyvinyl alcohol solution. After milling, the material was calcined at four different temperatures, 30˚C, 500˚C, 800˚C & 950˚C in a special furnace with oxygen flow arrangements. The temperature of the furnace was increased in steps. After each step the ceramics was grinded well before heating. High temperature is needed for metal oxide phase transformations [10]. The optical transmission characteristics were measured using a double beam ultraviolet–visible (UV–Vis.) spectrophotometer.

UV-VIS. Analysis

Photoluminescence spectroscopy is measured at room temperature to detect the optical properties. The optical absorption and reflectance 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 ferrites. The optical absorption data were analyzed using the classical relation for near edge optical absorption of semiconductors [11-12]. The sample obtained after calcinations 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 ±0.1nm (UV-Vis.).The optical band gap of the system has been estimated from these absorption spectra. This type of sample has high mechanical hardness, high thermal conductivity, large

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dielectric constant, and high resistance to harsh environment. Figure.1 shows the UV-VIS behaviour of the sample at 950^0C.UV-Visible spectrum give information about the excitonic and inter transition[13]. The transmittance of a sample is defined as the fraction of photons that pass through the sample over the incident number of photons, i.e., T = I/I0. In a typical UV/Vis spectroscopy measurement, we are measuring those photons that are not absorbed or scattered by the sample. It is common to report the absorbance (A) of the sample, which is related to the transmittance by $A = -\log_{10}(T)$[14]. Figure 1 illustrates the variation of optical band gap with the increase of Ti concentration. In the near IR, where the sample does not absorb strongly, the transmittance is close to 100%. In the UV portion of the spectrum, where the sample absorbs strongly, the transmittance drops to around 10% or less.

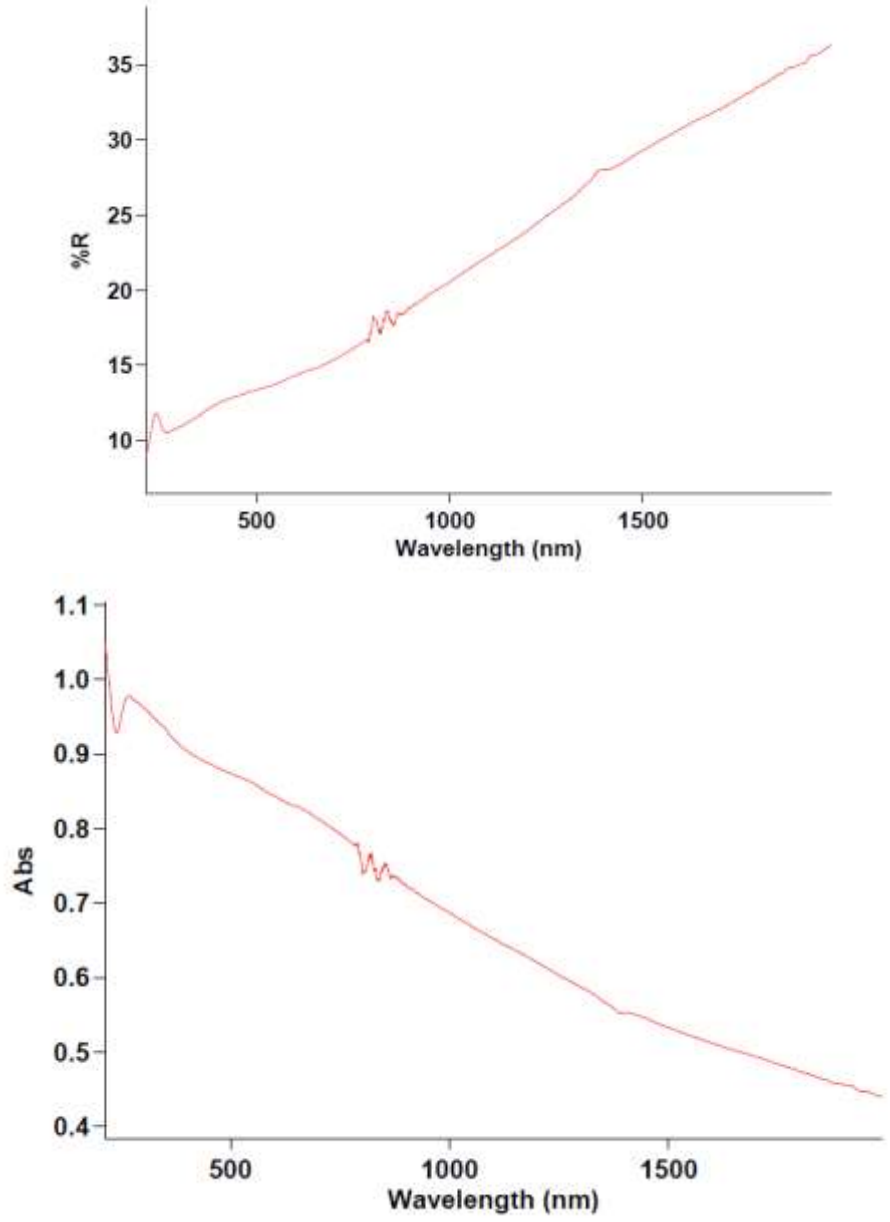

Figure.1 UV-VIS spectrum of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10 (reflectance and absorbance)

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The Kubelka-Munk method is used to translate the diffuse reflectance spectra into the absorption spectra. Kubelka-Munk's equation is described as follows: $\alpha = (1-R)^2/2R$--- (1), α where is the absorption coefficient and R the reflectivity at a particular wavelength[13].

To calculate the band gap of the synthesized material using Tauc's relation the absorption spectra is used as $(\alpha h\nu)^{1/n} = A(h\nu - Eg)$, where A is a constant and Eg is the band gap of the materials and exponent n depends on the type of transition. For direct allowed transition n=1/2, indirect allowed transition n=2, direct forbidden transition n=3/2 and forbidden indirect transition n=3 [14]. To determine the possible transitions, $(\alpha h\nu)^2$ versus hν is plotted and corresponding band gap were obtained from extrapolating the straight portion of the graph on hν axis[15].

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 energy of photon in eV and n denotes the nature of the sample transition[16]. The band gap energy can be determined using the Tauc relation. The region A of the TAUC plot defines the optical band gap of a sample as in fig.2.The tauc plot of the above sample is traced in Fig 3. It is noted that the optical gap energy of nano – sized crystal depends on its crystallite size, it increases with decreasing crystallite size in the nano size range [17,18].

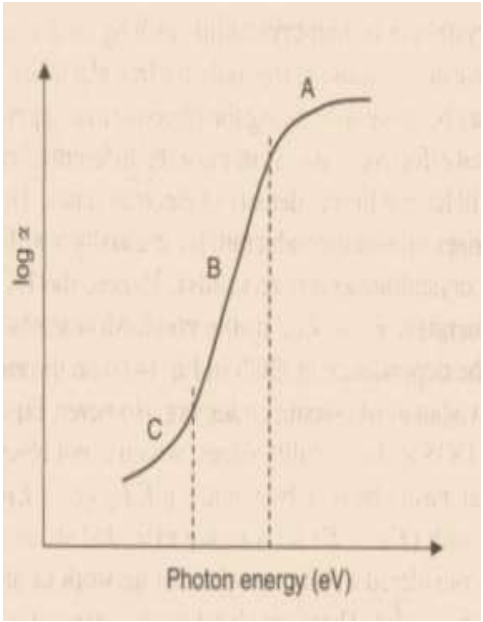

Fig.2- Photon energy versus log of absorption coeft.

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 Urbach energy is less than the band gap energy.The region B in the fig.2 represents the Urbach energy. The absorption edge called the Urbach energy, depends on, induced disorder, static disorder, temperature, thermal vibrations in the lattice, strong ionic bonds and on average photon energies [18]. 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

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on the degree of thermal disorder and structural [19]. It is noted in manycases that optical absorption by defects also appears at (region C of fig.2) energy lower than optical gap. This region is related to the structural properties of materials[20].

Dispersion and Refractive Index

It is found that with the increase in wavelength refractive index decreases linearly. The variation of the dispersion curve with annealing temperatures is shown in Fig.7. Refractive index increases with increase in annealing temperature and attains a constant value after a certain wavelength value. In figure (6), a graph with wavelength along X axis and refractive index along Y axis is plotted. Here refractive index values showed a linear decrease with increase in wavelength.

Using the Wemple-DiDomenico(W-D) model the dispersion of refractive index below the inter band absorption edge is studied[22]. In this W-D model, the refractive index n can be written as $\mathbf{n^2 - 1 = E_d E_0 / (E_d^2 - E^2)}$ -- (5),where E is the photon energy, E_o 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 [22]. The oscillator energy E_o and dispersion energy E_d are obtained from the slope $(E_o E_d)^{-1}$ and intercept E_o/E_d on the vertical axis of the straight line portion of $(n^2-1)^{-1}$ versus E^2plot. By evaluating equation(5) we get the equation as $n^2_{(0)}=1+E_d/E_o$— (6) [23].Thus the static refractive index $n_{(0)}$ at zero photon energy is noted.

RESULTS AND DISCUSSION

The UV-VIS analysis revealed that band gap energy of the prepared sample increases as the annealing temperature is increased. The optical analysis of the sample prepared by solid state reaction technique and treated at different temperatures is successfully done using UV-VIS Spectrophotometer. Here the direct allowed transitions are considered. In table-1 the calculated values of the band gap energies of the sample at different values of temperatures is tabulated.

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.3.

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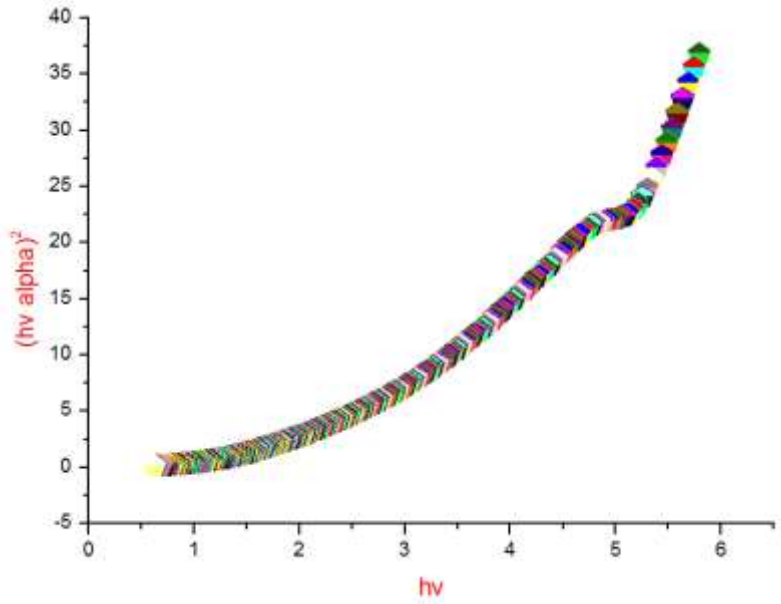

Fig.3.The Tauc plot of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10

Table-1. Band gap energy values of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10 at different temperatures

Temperature	Band gap energy in eV
30˚C	4.14
500˚C	4.21
800˚C	4.30
950˚C	4.35

From the table it is observed that band gap energy increases 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 crystalline phase is formed which proves the quantum confinement also decreasing its dislocation density [24].

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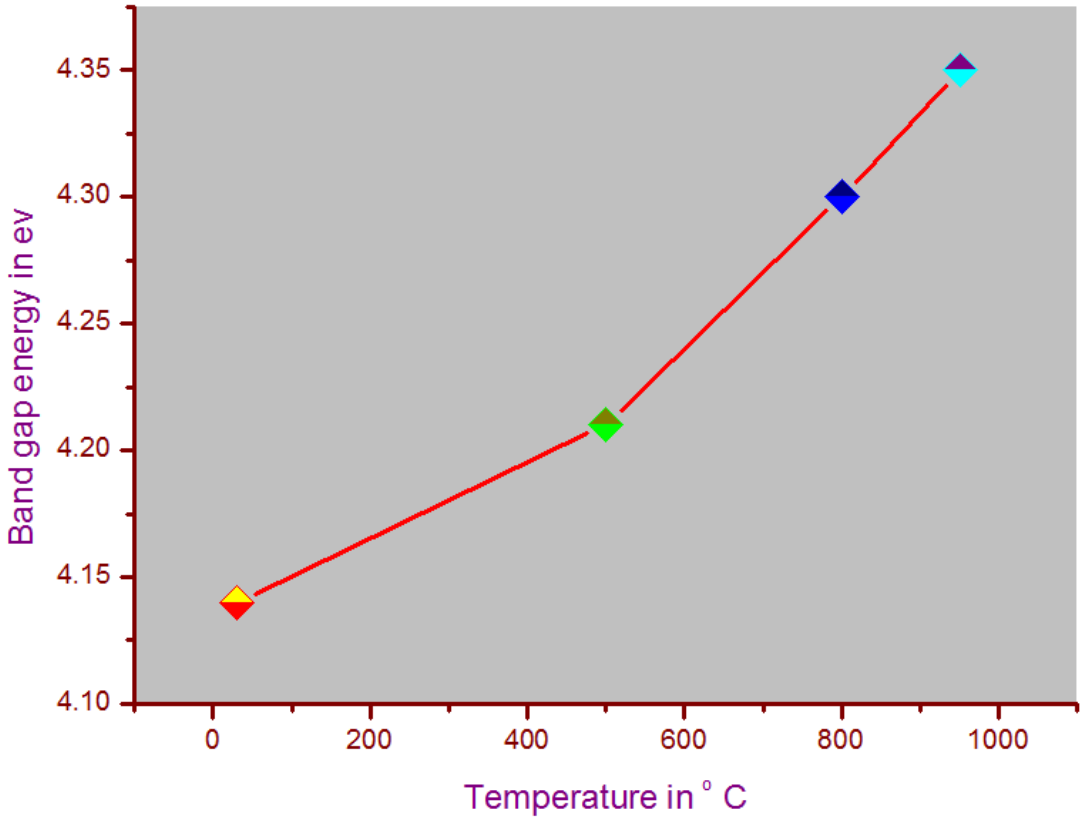

Fig.4.Variation of Band gap energy of the sample at varied annealing temperatures of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ *with x=0.10*

Due to an increase in temperature the crystallite size also increases which shows an increase in band gap energy[24].From theTauc plot data it is confirmed 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. The band gap energy E_g consequently increases.

By plotting the natural logarithm of the absorption coefficient with hv in eV, Urbach energy is calculated (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.

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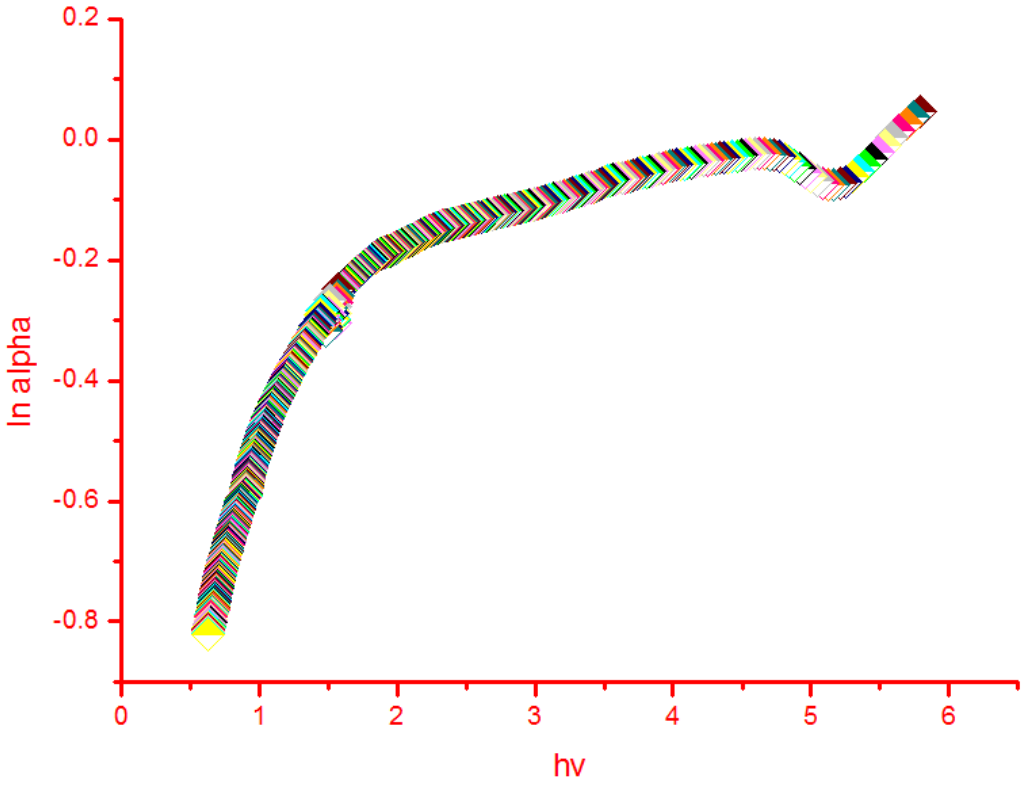

Fig.5. Absorption variation with photon energy of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10

The refractive index of the sample at different values of temperature was also studied. From the analysis it is observed clearly 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 phase. The refractive index is known to be proportional to their electronic polarization per unit volume which is inversely proportional to distance between atomic planes. The above result can also be explained by an increase in crystallite size.

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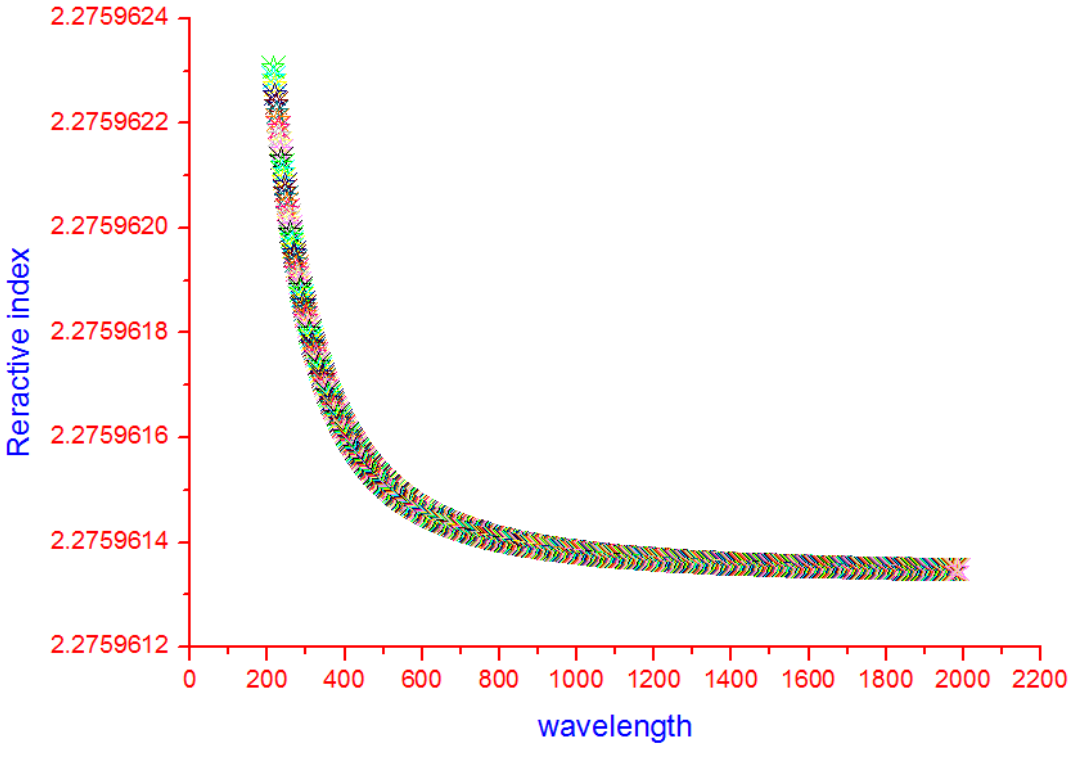
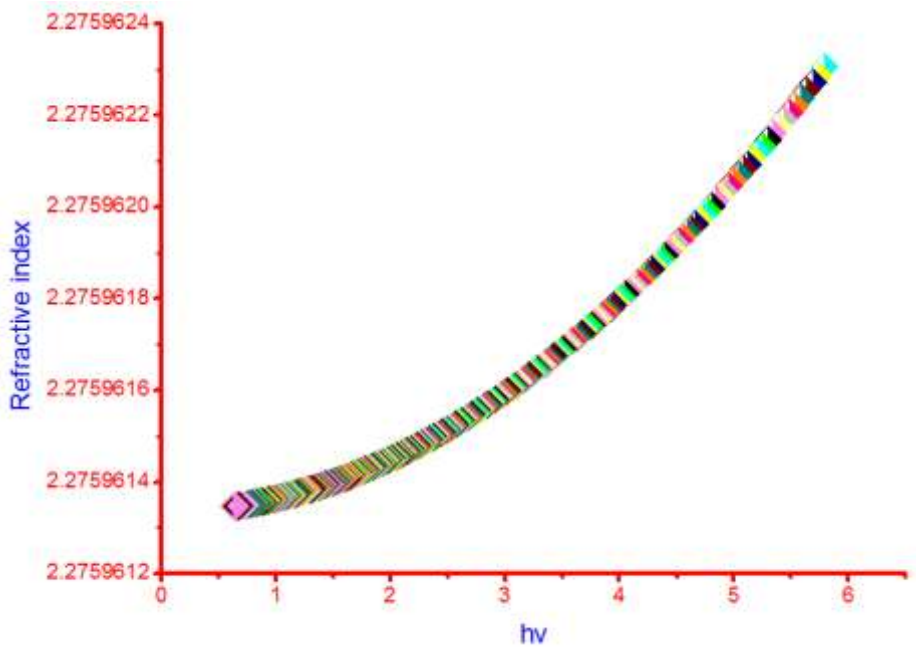


(a)



(b)

*Fig.6. Variation **of** Refractive index **(n)** with (a) wavelength and (b) photon energy of* $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ *with x=0.10*

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Using Sellmeir dispersion formula[24] refractive index of the sample annealed at different temperatures can be calculated. Using the Wemple-DiDomenico (WD) model the dispersion energy of the sample is calculated. Figure[7] shows the graphical representation of this.

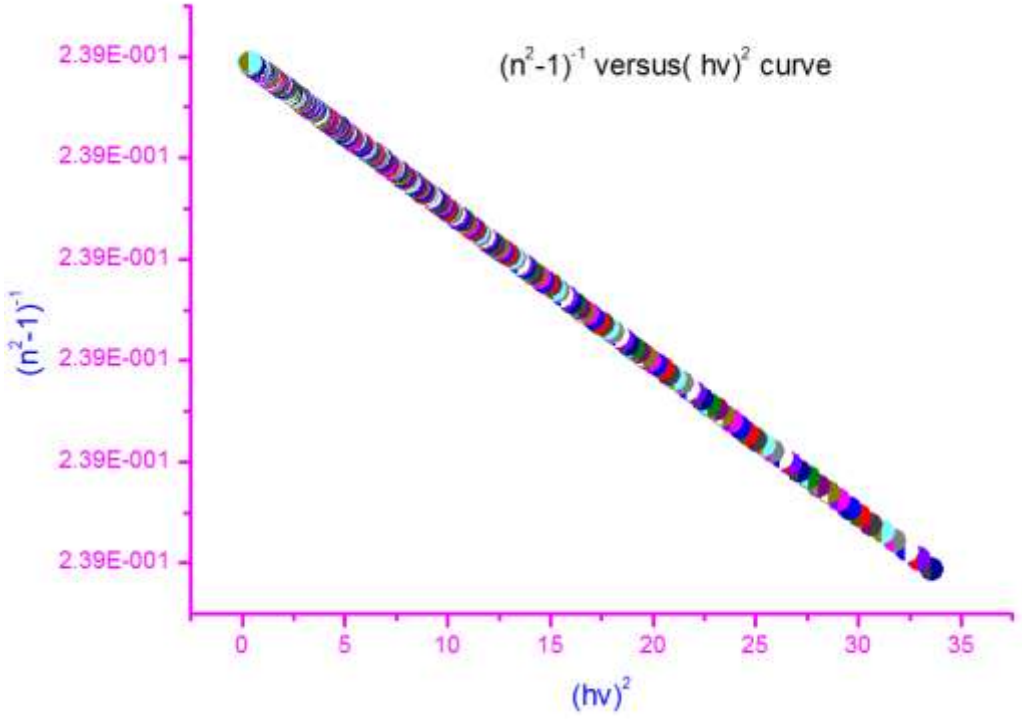

Fig.7. $(n^2-1)^{-1}$ versus(hv)^2 curve.

According to the single oscillator model proposed by wimple and DiDomenico the data of the dispersion of the refractive index [n] were evaluated using the equation, $n^2 = 1 + (E_dE_0)/(E_0^2-hv^2)$----(7), Where E_o is the oscillator energy and E_d is the oscillator strength or dispersion energy. A graph is drawn with $(n^2-1)^{-1}$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_0varies in proportion to the Tau c gapE_o~2E_g, where E_0 is considered as an average energy gap. (WD) oscillator model can be also written as $n^2-1=S_0\ \lambda_0^2\ /[1-(\ \lambda_o\ /\ \lambda)^2\ ]$ --- (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 curves with straight line graph confirm the Sell Meiers dispersion formula. The value of S_o and (λ_o) are estimated from the slope $(1/S_o)$ and the infinite wavelength intercept $(1/S_0\lambda_o)^2$. In table 2 the calculated values of the optical parameters of the sample were tabulated.

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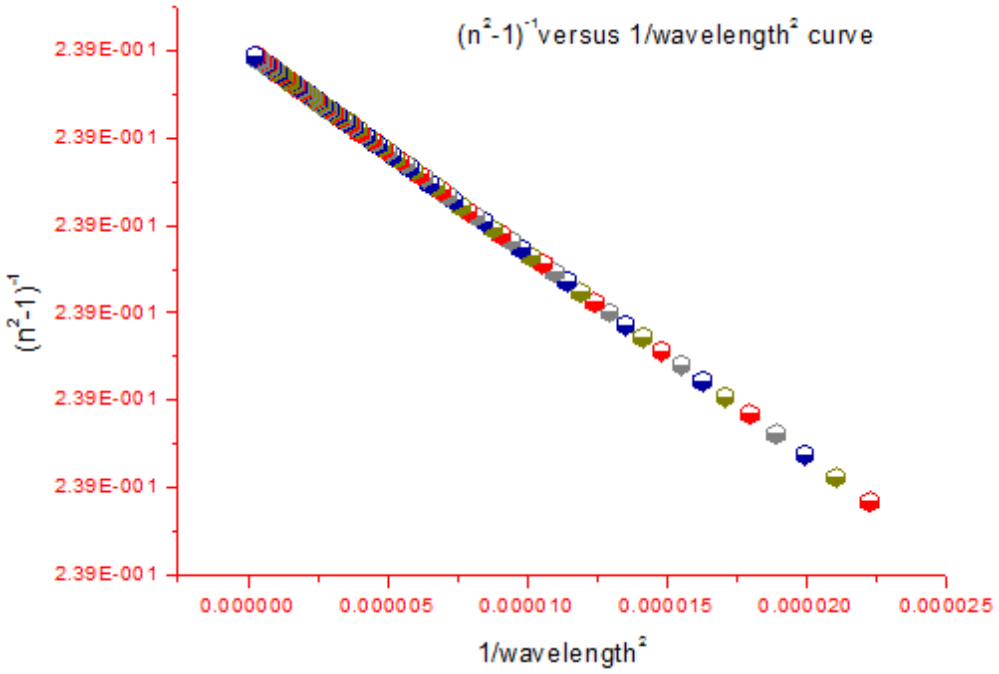

Fig.8. $(n^2-1)^{-1}$ versus $1/\lambda^2$ curve

Table 2.The optical parameters of $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10 calculated.

sample	E_g(eV)	E_O(eV)
at 30˚C	4.14	8.28
at 500˚C	4.21	8.42
at 800˚C	4.30	8.60
At 950˚C	4.35	8.70

As the temperature is increased, band gap energy $E_{g\,also}$ increases. But the dispersion energy E_d also shows a decline as the temperature rises and the sample attains its perosvkite phase. Further the mechano chemical process has an advantage due to low-costs and widely available materials, leading to a simplified process.The curves with straight line graphs confirms the sell Meier's dispersion formula.

Doping effect of titanium can be explained as: Experiments on titanium dioxide show that it is an electronic semi-conductor in which the current carriers are actually free electrons, as contrasted with the hole conduction of the other type of semi-conductor. It is found that the variation with oxygen pressure is that which would be expected if the titanium dioxide decomposes in the following manner: TiO2-->Ti++O2+e-. The deviation of the curves at low pressures is probably due to the presence of small impurities in the samples used. It is found that the variation of conductivity with temperature is represented by the formula $\sigma=Ae^{-\varepsilon kT}$. The activation energy ε is about 1.7 electron volts. Transport measurements show that the ionic conductivity is less than that which can be measured in these experiments[25]. Measurements of the Hall effect, although not very quantitative, show that the mean free path for the conduction electrons is very small.

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CONCLUSION

With the increase in annealing temperature, the UV emission peak shifts significantly to higher wavelengths. The increase in the band gap energy E_g 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 material $Mn_{0.8+x}Zn_{0.2}Ti_xFe_{2-2x}O_4$ with x=0.10 can be taken as a better candidate for UV_VIS shielding applications. Optical measurements confirmed that absorbance and reflectance increases with temperature. According to Wemple-DiDomenico single-oscillator model the dispersion energy decreases as the sample attains its cubic spinel structure. For new generation electronic equipments this will prove as a future component. As higher the band gap energy more the material becomes dielectric at higher temperature

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