

Determination of Physico – Chemical Specifications of Amorphous Structure $B_2O_3 - PbO - ZnO$ Ternary System

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Abstract: Studying optical absorption, in particular, absorption shape and edge is a useful method for understanding the essential mechanism of optical dependent displacements in crystalline and non-crystalline substances. This follows by supplying the data on their correlated structures. The basis of this method depends on absorption of energetic photons by dependence of transmissions from states involved in valance bonds to states none involved in conductivity bonds. Two types of optical transmissions may be occurring in the main states of these substances, either direct transmission or indirect transmission. In direct transmission the vector or wave direction of electron don't change, while in indirect transmission to apply photon for maintaining the value of energy is necessary, and the electron wave direction changes. In this work we characterize the type of transmission vectors and calculate optical gap energy and proportion coefficient B for $B_2O_3 - PbO - ZnO$ ternary system with vitreous structure.

Keywords: Optical absorption, direct transition, electron wave, optical gap energy.

1. Introduction

In many amorphous semiconductors, optical edge of absorption increases exponentially with energy of photon ($\hbar\omega$), by coefficient of absorption, $\alpha(\omega)$. The variation of coefficient of absorption with energy of photon in high energies takes an exponentially tail [1 and 2].

Optical edge of absorption in many amorphous substances divides in two categories.

a) High absorption domain, with $\alpha(\omega) > 10^4 \text{ cm}^{-1}$. In this domain, coefficient of absorption calculates by following equation.

$$\alpha(\omega) = B \frac{(\hbar\omega - E_{\text{opt}})^n}{\hbar\omega} \quad (1)$$

Where B is constant of proportion, E_{opt} is optical gap energy, ω is angular frequency of radiated beam and n may be equal to 1, 2, 3, $\frac{1}{2}$ and $\frac{3}{2}$, which depends to electronic transition in K space, and whether the transition is allowed or none – allowed [2, 3 and 4].

b) Low absorption domain, with $\alpha(\omega) < 10^4 \text{ cm}^{-1}$. In this domain, coefficient of absorption varies exponentially with the energy of incident photon ($\hbar\omega$). In this case, coefficient of absorption calculates by Urbach equation.

$$\alpha(\omega) = C \exp\left(\frac{\hbar\omega}{\Delta E}\right) \quad (2)$$

Where C is constant of proportion, ΔE is the width of localized states in energy bonds [5].

The best values of gap energy obtain by optical absorption. A photon with defined energy may be absorbed by transition metal ions present in glass, and this absorption occurs in two manners.

- 1- Absorption probably is due to internal transmissions between electrons of level.
- 2- Absorption probably is due to the transmission of electron from neighbor atom to transition metal ion, and vice versa [5].

Where the coefficient of absorption in angular frequency and beam width in bond cavity has two electronic transmissions in main absorption edge

(semiconductors), direct and non – crystalline transmissions, and cause interaction between electromagnetic waves with vector in valance band which transmits both them from edge of absorption to conductivity band.

For direct transmission from valance band to conductivity band, it is necessary that, the wave vector of electron remains unchanged. This means that, there is not any photon interaction, and there will be, $E_{\text{gap}} = \hbar\omega$. But for indirect transmissions, interactions occur between vectors and photons. Therefore, the vector of electron wave varies in electronic transmission, and the variation of momentum is due to its exchange between photons and vectors. This means that, if minimum of conductivity band in isolated section of K space, places in maximum of valance band, direct electronic transmission from top of valance band to its bottom will be non – allowed. In this case we have $E_{\text{gap}} = [\omega - \omega(q)]\hbar$, where q is the vector of photon wave [2 and 3].

In this work we study an ion oxide glass, $B_2O_3 - PbO - CuO$, with different percentages of components and lead to a good accord between experimental data and discussed theory.

2. Methods and experiments

a) Instruments: An electrical furnace with maximum temperature 1700°C is used for preparation the samples. An UV- Visible spectrophotometer of G.B.C. Cintra20 model is used for take up related spectra.

b) Preparation of samples: First we have prepared the fine powder of each oxide by well

grinding them individually, in an agate mortar. Then, before mixing these oxides, we kept them in a vacuum desiccator for at least two hours, for removal of any probable moisture. Afterwards, we prepared the samples of $B_2O_3 - PbO - ZnO$ ternary system, by melting well mixed, B_2O_3 , PbO and ZnO oxide mixtures as defined in table 1, and by rapid cooling over a plate of ceramic at ambient temperature. Experiments show that the samples made with more than 10 wt % PbO have not any more the glass structure. All samples support two hours annealing for eliminate internal stresses and break down provisional boundaries formed during melting process. Finally, the thickness of samples determined preciously by a micrometer.

3. Results and discussion

a) The spectra: We have obtained the UV-Visible spectra of these 8 samples between 800 and 200 nm. As the spectra show (Fig. 1), there are not the sharp edges of absorption. This is the characteristic of vitreous structures, and is not the characteristic of crystalline structures. We have provided two samples with the same percentages of components (samples No. 2 and No. 3) for showing dependence of E_{opt} on thickness of samples.

Note that the melting point (softness) of samples increases with increasing of PbO percentage, and vitreous characteristics decrease. UV-Visible spectra of these 8 samples have shown down below

Table 1 – percentages of each component in prepared samples

Oxide	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
B_2O_3 , wt %	96.25	94.75	94.75	92.50	90.25	88.75	87.25	85.00
ZnO , wt %	1.25	1.75	1.75	2.50	3.25	3.75	4.25	5.00
PbO , wt %	2.50	3.50	3.50	5.00	6.50	7.50	8.50	10.00
Thickness, mm	1.23	1.15	1.12	0.71	1.84	0.89	1.02	0.66

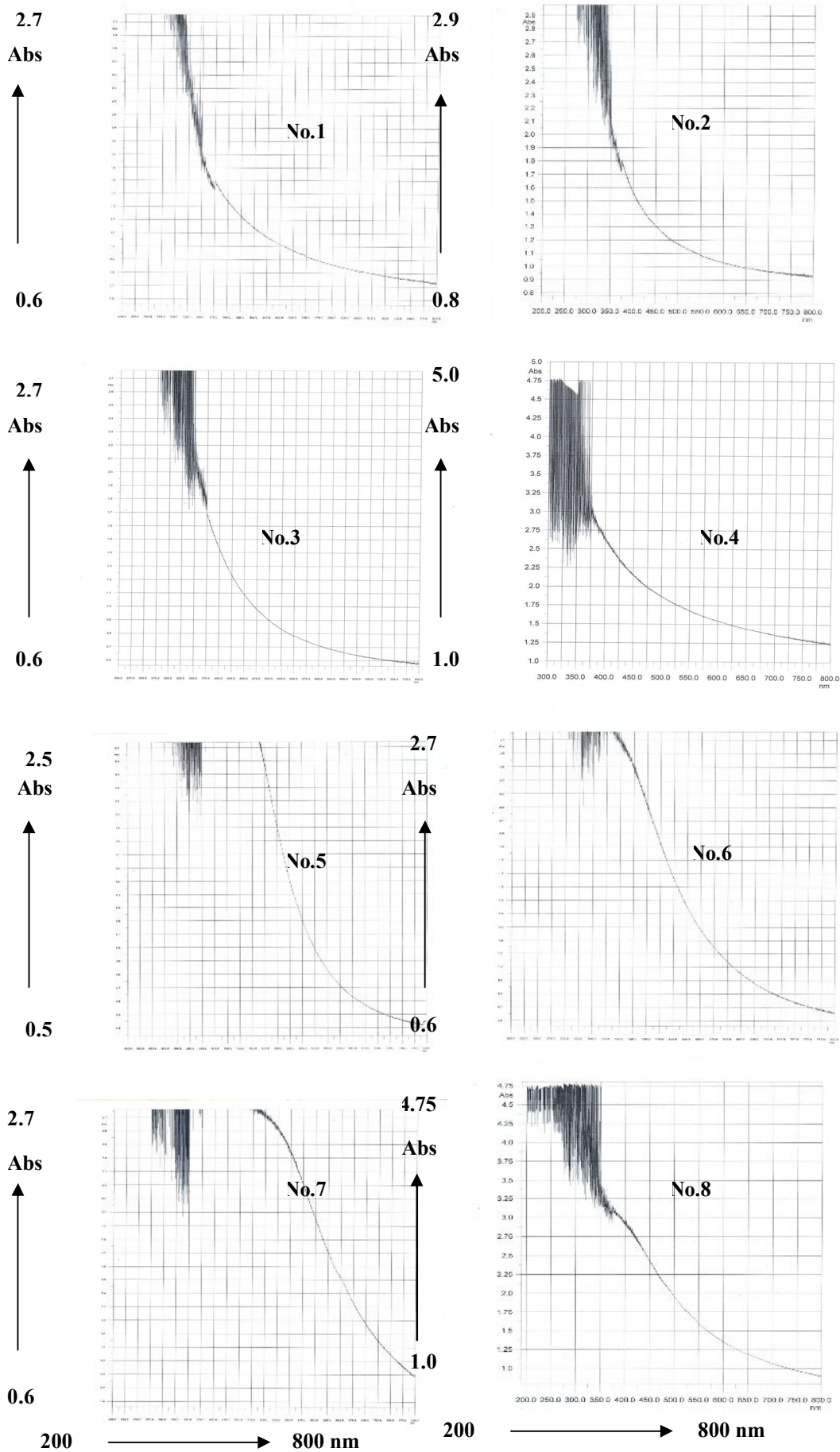


Fig.1. UV-Visible spectra of samples

Table 2. Typical results of calculations by means of the spectrum of sample No. 1
96.25 wt % B₂O₃ – 1.25 wt % ZnO – 2.5 wt % PbO

Point No. on Spectr. No. 1	Thickness (cm)	λ (nm)	$2.303 \log I_0/I$	α (ω) (cm^{-1})	$\hbar\omega$ (eV)	$(\alpha\hbar\omega)^2$ ($\text{cm}^{-2}\text{eV}^2$)
1	1.23×10^{-1}	750	1.737	14.041	1.66	543.263
2		700	1.819	14.789	1.77	685.235
3		675	1.842	14.976	1.84	759.278
4		625	1.935	15.732	1.99	980.128
5		600	1.981	16.106	2.07	1111.489
6		566	2.073	16.854	2.19	1362.348
7		525	2.234	18.163	2.37	1852.958
8		500	2.349	19.098	2.48	2243.254
9		475	2.464	20.033	2.61	2733.826
10		450	2.625	21.342	2.76	3469.682
11		430	2.764	22.472	2.89	4217.723
12		407	2.994	24.342	3.05	5512.023
13		400	3.086	25.089	3.10	6049.106
14		391	3.224	26.211	3.18	6947.556

b) Calculation method: When an electromagnetic wave, with intensity I_0 radiates the surface of a solid with thickness L , the intensity of incident photon decreases exponentially by passing through it. Intensity of transmit radiation obtain by following equations [6],

$$I = I_0 e^{-\alpha(\omega)L} \quad (3)$$

$$\frac{I}{I_0} = e^{-\alpha(\omega)L} \quad (4)$$

$$\ln \frac{I}{I_0} = -\alpha(\omega)L \quad (5)$$

$$\ln \frac{I_0}{I} = \alpha(\omega)L \quad (6)$$

Finally, the following equation obtains by rearrangement of equation (6).

$$\alpha(\omega) = \frac{1}{L} \ln \frac{I_0}{I} = \frac{1}{L} 2.303 \log \frac{I_0}{I} \quad (7)$$

Therefore, for calculating $\alpha(\omega)$, we need measuring the thickness of sample, L , and determining $\ln \frac{I_0}{I}$. We can measure L by a micrometer in cm, and can

determine $\ln \frac{I_0}{I}$ on absorption axe (Abs) of dependant spectrum of each sample. Thus we can obtain $\alpha(\omega)$ in cm^{-1} . Whereas, we must study the variation of $(\alpha\hbar\omega)^{1/n}$ versus $\hbar\omega$. Therefore, angular frequency of incident photon must be determine for each point selected on absorption spectrum, and ω may be obtained from following relation.

$$\omega = 2\pi\nu = 2\frac{c}{\lambda} \quad (8)$$

Where c is the velocity of light in vacuum, and λ is the wave length of incident photon which may be determine from selected points on absorption spectrum. Then we plot the diagrams of $(\alpha\hbar\omega)$, $(\alpha\hbar\omega)^{1/2}$, $(\alpha\hbar\omega)^{1/3}$, $(\alpha\hbar\omega)^2$, and $(\alpha\hbar\omega)^{3/2}$ versus $\hbar\omega$. The diagrams show that the plot of $(\alpha\hbar\omega)^2$ versus $\hbar\omega$ has most linear relation compared with the other diagrams. Thus n for this ternary system is $1/2$, and shows that absorption process is direct and allowed.

We can obtain E_{opt} for each sample by extrapolating the linear part of diagram of $(\alpha\hbar\omega)^2$ versus $\hbar\omega$. Then we have calculated the constant B from slop of above diagram.

For example, we calculate $\hbar\omega$, $\alpha(\omega)$, $(\alpha\hbar\omega)^2$, and B for point no. 1 over the spectrum of sample no. 1 down below.

$$\hbar\omega = \hbar \times 2\pi \times \frac{c}{\lambda} = (1.055 \times 10^{-34} \text{ Js}) \times 2 \times 3.14 \times \frac{3 \times 10^8 \text{ m s}^{-1}}{750 \times 10^{-9} \text{ m}} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} = 1.66 \text{ eV}$$

$$\alpha(\omega) = \frac{1}{L} \ln \frac{I_0}{I} = \frac{1}{L} 2.303 \log \frac{I_0}{I} = \frac{1}{1.23 \times 10^{-1} \text{ cm}} \times 2.303 \times 0.75 = 14.041 \text{ cm}^{-1}$$

$$\alpha \hbar\omega = 14.041 \text{ cm}^{-1} \times 1.66 \text{ eV} = 23.308 \text{ cm}^{-1} \text{ eV}$$

$$(\alpha \hbar\omega)^2 = (23.308 \text{ cm}^{-1} \text{ eV})^2 = 543.263 \text{ cm}^{-2} \text{ eV}^2$$

$$B = \frac{6447.556}{3.18 - 2.532} = 0.860 \times 10^4 \text{ cm}^{-1} \text{ eV}^{\frac{1}{2}}$$

Therefore, we have calculated the same values for all points over the 8 spectra just as the same method, and the plots of $(\alpha \hbar\omega)^2$ versus $\hbar\omega$ for each sample have traced. Below we carry out the typical results of

calculation on table 2. The curves of $(\alpha \hbar\omega)^2$ versus $\hbar\omega$ for these 8 samples have plotted on figures 2 to 9. The specifications of prepared samples have shown in table 3.

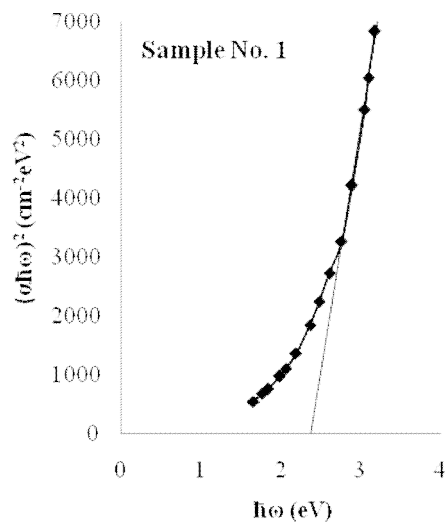


Fig.2. 96.25%B₂O₃ – 1.25%ZnO – 2.5%PbO

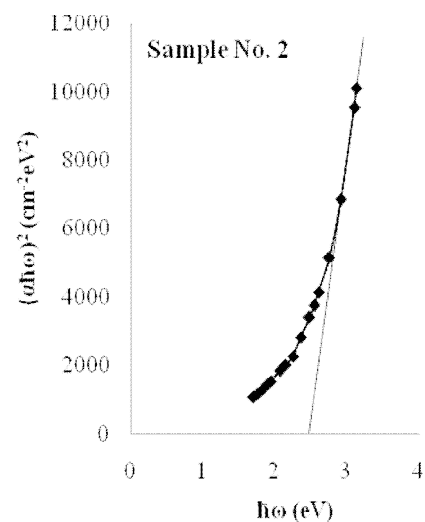


Fig.3. 94.75%B₂O₃ – 1.75%ZnO – 3.5%PbO

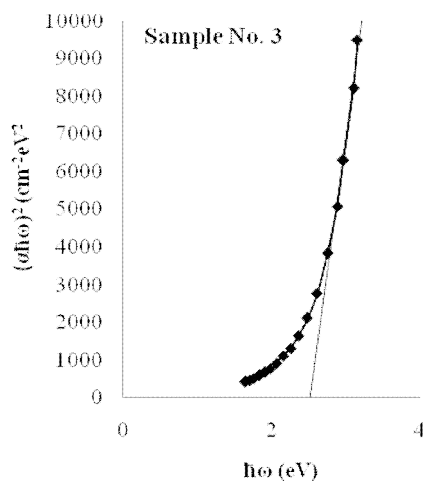


Fig.4. 94.75%B₂O₃ – 1.75%ZnO – 3.5%PbO

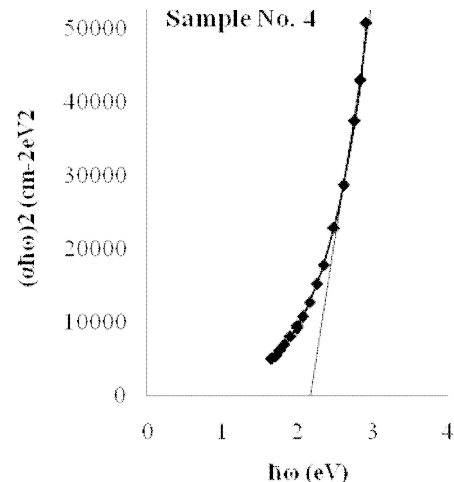


Fig.5. 92.5%B₂O₃ – 2.5%ZnO – 5%PbO

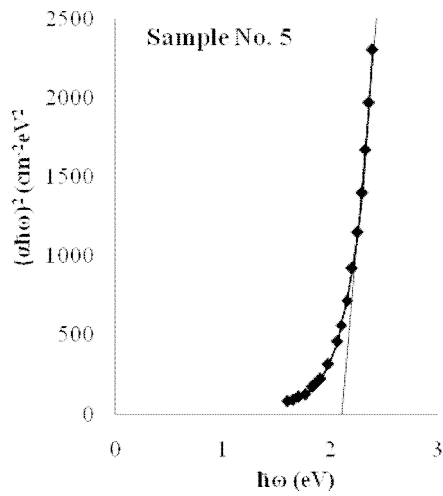
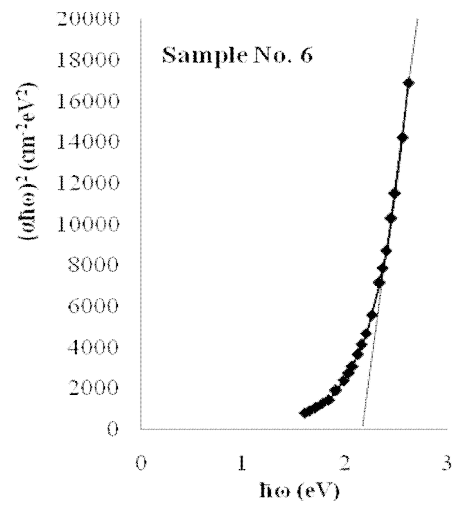
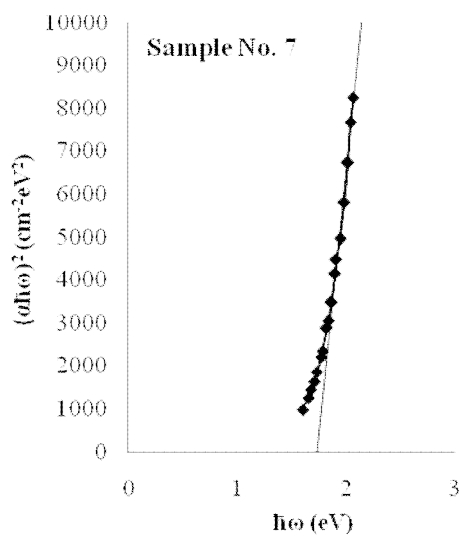
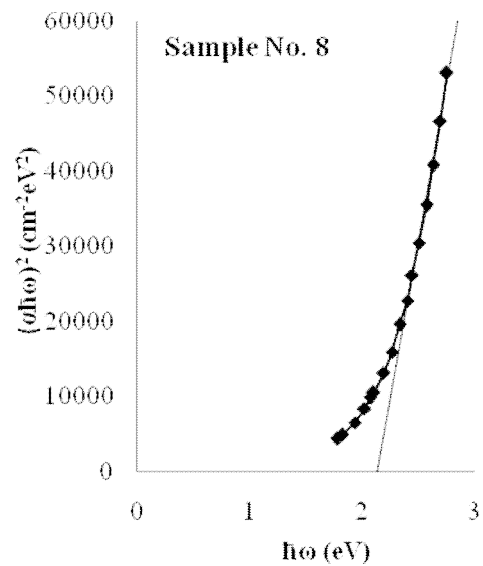
Fig.6. 90.25% B_2O_3 – 3.25% ZnO – 6.5% PbO Fig.7. 88.75% B_2O_3 – 3.75% ZnO – 7.5% PbO Fig.8. 87.25% B_2O_3 – 4.25% ZnO – 8.5% PbO Fig.9. 85% B_2O_3 – 5% ZnO – 10% PbO

Table 3. Specifications of all prepared samples

Sample No	PsO wt%	ZnO wt%	B_2O_3 wt%	E_{opt} eV	B $cm^{-1}eV^{1/2} \times 10^4$	Thickness $cm \times 10^{-1}$
1	2.5	1.25	96.25	2.375	0.863	1.23
2	3.5	1.75	94.75	2.500	1.57	1.15
3	3.5	1.75	94.75	2.532	1.52	1.12
4	5	2.5	92.5	2.140	6.51	0.71
5	6.5	3.25	90.25	2.075	0.716	1.84
6	7.5	3.75	88.75	2.124	3.44	0.89
7	8.5	4.25	87.25	2.174	2.51	1.02
8	10	5	85	2.120	8.42	0.66

Conclusion

Studying spectra, and obtained data which are mentioned in tables we can conclude the followings for $B_2O_3 - PbO - ZnO$ ternary system.

1- Optical absorption edge of UV- Visible spectra of studied samples compared with the crystalline one is not sharp. This is the characteristic of the non crystalline vitreous systems.

2 – The obtained spectra (fig.1) and data (table 3) show that, optical absorption edge tend to lower wave lengths (higher energies) and sharpness with increasing in percentage amount of PbO and decreasing in percentage amount of B_2O_3 for $B_2O_3 - PbO - ZnO$ ternary system. This may interpreted by decreasing in optical gap energy, E_{opt} . This may be

attributing to proportions of positive ions as discussed in [6] and [7].

3 – The obtained and calculated results show that the optical gap energy, E_{opt} , decreases with increasing in thickness of two samples with the same percentages of components. This may be interpreted by overlap of electronic wave functions with increasing in thickness which results in increasing of optical gap energy. The same results have obtained for binary systems [6] and [7].

4 – Variation in optical gap energy with the variation in localized state tails, confirms Mott –Davis theories for localized states in energy gap of amorphous semi – conductors[3].

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