

## Study the Optical properties of Amorphous Structure (Glassy) of $B_2O_3$ -CdO Binary System

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### ABSTRACT

Using optical absorption and studying the edge – absorption of either crystalline or amorphous structures, is an efficacious and useful method for better realizing the electronic structure of these materials. In this paper, firstly, we prepared the bulk specimens of different percentages of  $B_2O_3$  and CdO in form of binary systems, and then we studied UV- Visible spectrums of specimens in the range of 200–800 nm. After determination of absorption coefficient  $\alpha(\omega)$ , then we traced out  $(\alpha\hbar\omega)^{1/n}$  against  $(\hbar\omega)$  diagrams for obtaining the value of  $n$ . In this research, by considering  $n=2$ , we have obtained a linear diagram with exponential tail. Therefore, according to Mott and Davis's statement, it was established that, the type of transition is indirect allowed. By extrapolating the linear part of  $(\alpha\hbar\omega)^{1/2}$  against  $(\hbar\omega)$  diagram, we determined the optical gap energy ( $E_{opt}$ ) at  $(\alpha\hbar\omega)^{1/2} = 0$ . The obtained amounts of  $E_{opt}$  (2.505 to 2.965 eV) show that,  $E_{opt}$  decreases with increasing in CdO percentage. By tracing the plot of variation of  $\ln \alpha(\omega)$  against  $(\hbar\omega)$ , we have determined the slope of the linear part of diagram, which is equal to width of localized states  $\Delta E$  (about 0.469 to 0.811 eV).

**Keywords:** Amorphous structure, edge–absorption, binary system, optical gap, localized states.

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### INTRODUCTION

Studying optical absorption, in particular, shapes and modifications of edge – absorption are a significant method for understanding essential mechanism and behavior of optical displacements in crystalline and none crystalline materials, with useful information relevant to their related structures [1]. This method is based on absorption of photons by energy and also by relating them to transition from the states engaged in bonds capacity to states non-engaged in their conduction bond. Two types of optical transitions may be occurring for basic edges of these materials, a) direct transition, and b) indirect transition [2]. In direct transition, either vector or electron's wave direction remains constant, but in indirect transition, photon applying is necessary for retaining the amount of kinetic energy and, electron's wave direction changes.

Optical edge – absorption of the most amorphous semi conductors is defined by an absorption coefficient  $\alpha(\omega)$ , which varies exponentially with energy,  $\hbar\omega$ .

The variation of absorption coefficient with energy, takes an exponential tail at high temperatures. Edge – absorptions of none crystalline an amorphous material has a slope less than its crystalline form. Determination and interpretation of edge - adsorption had significantly helped to understand electronic structure theory of amorphous materials.

In many of amorphous materials the edge – absorption is classified in two categories:

1) High absorption zone [ $\alpha(\omega) > 10^4 \text{ cm}^{-1}$ ]; in this zone, absorption coefficient is obtained from relation as:

$$\alpha(\omega) = B \left[ (\hbar\omega - E_{\text{opt}})^n / \hbar\omega \right] \quad (1)$$

where B is the proportion coefficient,  $E_{\text{opt}}$  is optical gap energy,  $\omega$  is angular frequency of transmitted ray, and n may be equal to 1/2, 1, 2 or 3/2, which is depend to the type of electronic transition in K space, and to the case whereas the transition is allowed or none allowed. Firstly, this equation was proposed by Tauk, et al in 1966 as  $n = 2$  [3], then in 1970 by Mott and Davis, as  $n = 3/2$  [4].

2) Low absorption zone [ $\alpha(\omega) < 10^4 \text{ cm}^{-1}$ ]; in this zone, absorption coefficient varies exponentially with the energy of descent photon ( $\hbar\omega$ ). The best relation, which explain optical behavior of these materials in this zone have given by Urbach in 1953 [5]:

$$\alpha(\omega) = C \exp(\hbar\omega / \Delta E) \quad (2)$$

where C is a constant,  $\Delta E$  is the width of localized states in the energy of bonds, and ( $\omega$ ) is angular frequency of descent photon. The general formula for the optical absorption coefficient  $\alpha(\omega)$  is given as:

$$\alpha(\omega) = 1/L \ln(I_0/I) \quad (3)$$

Where  $\alpha(\omega)$  is the absorption coefficient ( $\text{cm}^{-1}$ ),  $I_0$  and I, are the intensity of incident and transmitted light respectively, and L is the thickness of the sample (cm).

In this investigation, we have characterized the type of transmission vectors and have calculated the optical gap energy for  $\text{B}_2\text{O}_3$  – CdO binary system as amorphous structure.

Amorphous structures have specific characteristics including semi-conductivity. The electrical properties of glassy materials have been investigated and reported in literature [6]. It has been suggested that the presence of interstitials or dangling bonds give rise to a number of localized states or traps near the band edges of glassy materials. These localized states are responsible for the transport of charge carriers. At low electric field the small polaron hopping has a dominant role [4 and 7] and at high field this is attributed to either Schottky (electrode-limited) [8] or Poole-Frankle effect (bulk-limited) [9]. The band structure of amorphous solids can be described by the C.F.O model [10], which was further improved by Mott and Davis [4]. These models provide a clear picture of density distribution of states in the energy gap of amorphous semiconductors. Boron trioxide can form the vitreous structures with other oxides. Addition of certain oxides to boron trioxide modifies the properties of these glasses. In our investigation  $\text{B}_2\text{O}_3$  - CdO binary system has been studied. For better understanding the electronic structure and study on the edge-absorption, we could use optical absorption. By using a UV-Visible spectrophotometer the absorption spectrums were obtained. Studying these spectrums by using Urbach [5] and Mott-Davis [2] approaches, the absorption coefficient,  $\alpha(\omega)$ , have calculated according to Bir-Lambert relation. By tracing  $(\alpha\hbar\omega)^{1/n}$  against  $(\hbar\omega)$  plot, the amount of n was determined. For  $\text{B}_2\text{O}_3$ -CdO binary system  $n = 2$  was achieved.

By extrapolating the plot of  $(\alpha\hbar\omega)^{1/2}$  against  $(\hbar\omega)$ , we could determine optical gap energy,  $E_{\text{opt}}$ , at  $(\alpha\hbar\omega)^{1/2} = 0$ . Obtained results show that,  $E_{\text{opt}}$  decreases with the increase of CdO percentage.

By determining the slop of  $\ln\alpha(\omega)$  versus  $(\hbar\omega)$  diagram, the width of localized states in the energy of bonds was concluded. In this research we were investigated these properties for amorphous samples of binary system of boron and cadmium oxides,  $\text{B}_2\text{O}_3$  – CdO, with different amounts of percentages, and we have concluded that the obtained results in this research has the best consistency with the theories indicated in literature [11, 12, and 13].

## MATERIALS AND METHODS

Firstly we have prepared the samples of required binary system  $\text{B}_2\text{O}_3$  – CdO having the amounts of 75–25, 70–30, 65–35, 60–40, 55–45, 50 – 50, 45 – 55, and 40 – 60 percents of  $\text{B}_2\text{O}_3$  and CdO respectively, in bulk form. Further step was preparation the samples by fast cooling of melted binary systems. Then we have studied optical properties of these samples.

### 2.1. Preparation the samples

An electrical furnace with maximum temperature of 1450 °C is used for preparation the samples. Firstly, we have prepared the fine powder of each oxide by well milling them individually in an agate mortar. Afterwards, we have

prepared the samples of B<sub>2</sub>O<sub>3</sub> – CdO binary system by well mixing B<sub>2</sub>O<sub>3</sub> and CdO oxides powders with percentages as indicated in table 2. Then we have placed all samples, after milling, precise weighing and well homogenizing, about 2 hours in desiccators for eliminating any eventually moisture. Afterward, we have put the prepared samples about 2 hours in an oven at 250° C, for eliminating probable internal stresses and temporary bonds. At that time the samples completely homogenized for second of time. These accurately prepared homogenous samples were placed within a furnace for melting. Down to 600° C we increase temperature step by step to 100, 200, 300, 400, 500, and 600 °C, and allow them to remain for 10 minutes at each of these staging temperatures, before any further temperature increase. As achieving 600° C we have mixed well, once more, every sample for obtaining better homogeneity. Then, up to 600° C we do the same above treatment after every 50 °C of temperature increasing up to softening temperature, and allow the samples to remain for 5 minutes at this temperature. Then we perform an increase of 50 °C above softening temperature, and allow remaining about 15 minutes at achieved temperature. Then we have unloaded the melted material on a ceramic surface at ambient temperature. For obtaining the best required results, unloading of melted material must perform as quickly as possible, and very rapidly we put another ceramic plate above it for obtaining a thin and plate uniform sample. All samples support 2 hours annealing for eliminating any internal stresses and break down eventual provisional boundaries formed during melting process. Finally, the thicknesses of samples were measured precisely by a micrometer.

## RESULTS AND DISCUSSION

### 3.1 UV-Visible and XRD Spectra and Calculation method

Absorption spectra of samples were obtained by an UV-Visible spectrophotometer (G.B.C. Cintra20 model) within a range of 200 to 800 nm.

The shape of spectrums show that the edge – absorption of them is not sharp, which is the characteristic of vitreous structures (Fig. 1). As the spectrum (shows, there is not any sharp edges of absorption. This characteristic is specific for vitreous structures, and not for crystalline structures.

When an electromagnetic wave having intensity  $I_0$  radiate the surface of a solid with the thickness  $L$ , the intensity of incident photon decreases exponentially as passing through it.

Intensity of transmit radiation may obtain by following equations (A. A. Hosseini, and C. A. Hogarth, 1983),

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

$$\ln I / I_0 = -\alpha(\omega)L \quad (5)$$

$$\alpha(\omega) = 1/L \ln I_0 / I \quad (6)$$

Finally, rearrangement of equation (6) gives the following equation as:

$$\alpha(\omega) = 1/L \times 2.303 \log I_0 / I = 1/L \times 2.303 \times A \quad (7)$$

Where  $A$  is  $\log I_0 / I$ .

Therefore, for calculating  $\alpha(\omega)$ , we need to measure the thickness of sample,  $L$ , and calculate  $\log I_0/I$ . We have measured  $L$  by means of a micrometer, in cm, and determined  $\log I_0/I$  from absorption plot of corresponding spectrum of each sample. Consequently, we could obtain the value of  $\alpha(\omega)$  ( $\text{cm}^{-1}$ ). Thus, we can study the variation of  $(a\hbar\omega)^{1/n}$  versus  $(\hbar\omega)$ . Thereafter, angular frequencies of incident photon have been determined for any point selected on absorption spectrum, and  $\omega$  may be obtained from following relation as:

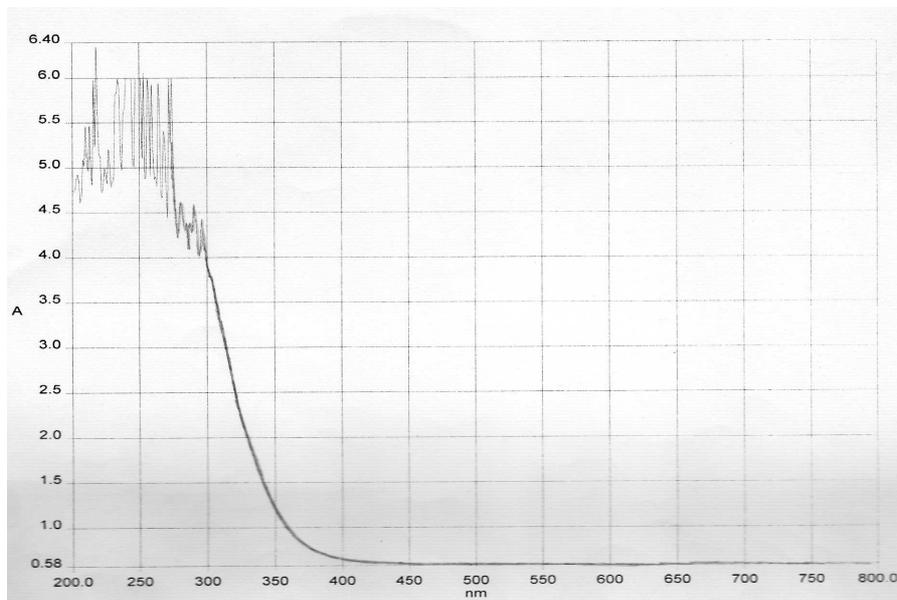
$$\omega = 2\pi\nu = 2\pi c / \lambda \quad (8)$$

Where  $c$  is the velocity of light in vacuum, and  $\lambda$  is the wave length of incident photon which may be obtain from selected points on absorption spectrum. Determining  $n$  for binary system B<sub>2</sub>O<sub>3</sub> – CdO, we traced the plot of variation of  $(a\hbar\omega)^{1/n}$  with different  $n$  amounts (i.e., 1, 2, 1/2 and 3/2), in relation with emitted photon energy  $(\hbar\omega)$ , according to the obtained data that was shown for a typically sample on table 1 (for example, No. 1). So, we plot the diagrams of  $(a\hbar\omega)$ ,  $(a\hbar\omega)^{1/2}$ ,  $(a\hbar\omega)^2$  and  $(a\hbar\omega)^{2/3}$  versus  $(\hbar\omega)$ . The obtained diagrams show that the plot of  $(a\hbar\omega)^{1/2}$  versus  $(\hbar\omega)$  has most linear tail in comparison with the other ones. Thus, for this binary system,  $n$  is considered as 2, and this shows that, absorption process is indirect and allowed. Then we have obtained  $E_{\text{opt}}$  for the samples by extrapolating the linear part of plot of  $(a\hbar\omega)^{1/2}$  versus  $\hbar\omega$ . Thus, we have calculated  $(\hbar\omega)$ ,  $\alpha(\omega)$  and  $(a\hbar\omega)^{1/2}$  for all

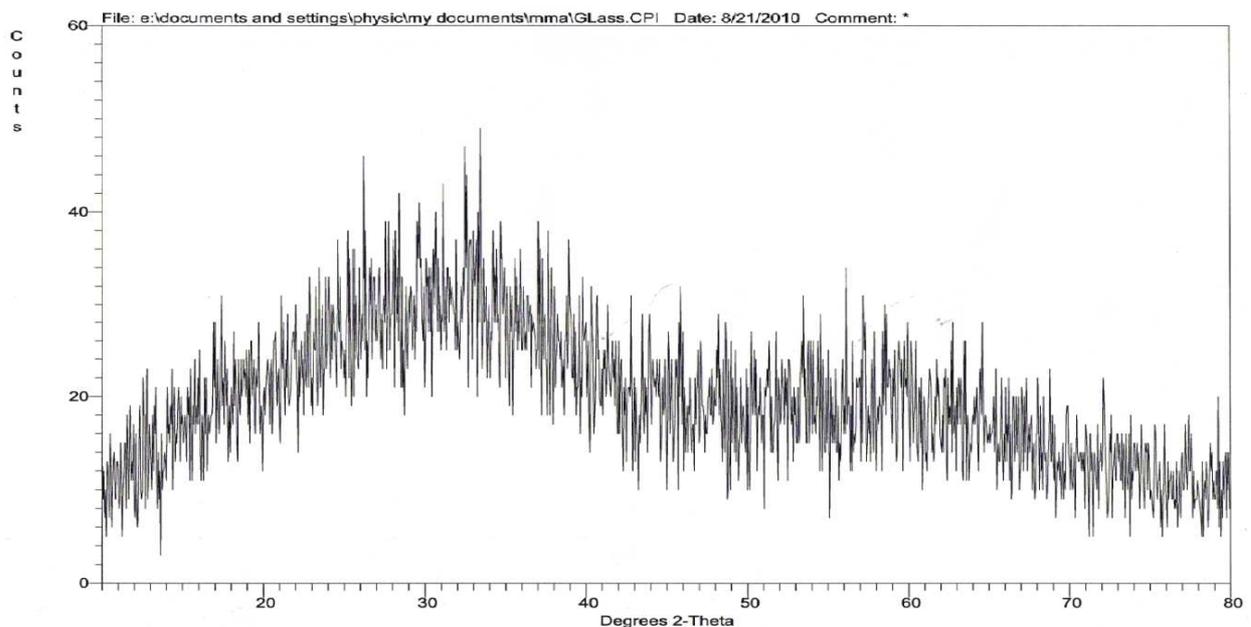
points on the spectrum of figure 1 [14]. The results of such calculations were carrying out for a typical sample on table 1 (for example, No. 1).

Calculating the width of localized states ( $\Delta E$ ), we have plotted the variation of  $\ln \alpha (\omega)$  against  $(\hbar\omega)$  and determined the slope of the linear part of diagram. The XRD spectrum of this typical sample (for example, No. 1), also, confirms the vitreous structure of prepared samples (Fig. 2). Figure 3 and 4 shows the diagrams of variation of  $(\alpha\hbar\omega)^{1/2}$  and  $\ln \alpha (\omega)$  versus  $(\hbar\omega)$  for the typically sample (for example, No. 1).

Then, by the same method described above, we have plotted  $(\alpha\hbar\omega)^{1/2}$  and  $\ln \alpha (\omega)$  versus  $(\hbar\omega)$  for the rest prepared samples. The results obtained from this proceeding for the rest prepared samples have reported in table 2. Just, the XRD spectra of these samples, also confirms the vitreous structure of them. In addition, for showing dependence of  $E_{opt}$  on thickness of samples we have prepared two samples with the same percentages of components, but different in thickness. The results of this experiment have shown on table 2. Note that the melting point (softness) of samples increases with increasing of CdO percentage, and vitreous characteristics decrease inversely.



**Fig.1. Absorption spectrum of  $B_2O_3$ – CdO binary system, for a typical sample (No. 1)**



**Fig. 2. XRD spectrum obtained for a typical sample (No.1)**

Table1. Typical results obtained from the plot shown in figure1, for a typical sample (No. 1)

$\lambda$ (nm)	A	$\omega$ $\times 10^{15}$ (s <sup>-1</sup> )	$h\omega$ (eV)	L $\times 10^{-1}$ (cm)	$\alpha(\omega)$ (cm <sup>-1</sup> )	$(\alpha h\omega)^{1/2}$ (cm <sup>-1/2</sup> eV <sup>1/2</sup> )	$\ln \alpha(\omega)$
475.47	0.59493	3.962	2.608	1.38	9.928	5.088	2.295
450.50	0.60266	4.182	2.753	1.38	10.057	5.262	2.308
441.03	0.60668	4.272	2.812	1.38	10.125	5.336	2.315
434.15	0.60821	4.340	2.857	1.38	10.150	5.385	2.317
422.96	0.61499	4.454	2.932	1.38	10.263	5.485	2.328
412.63	0.62482	4.566	3.005	1.38	10.427	5.597	2.344
400.57	0.64617	4.703	3.095	1.38	10.783	5.777	2.378
391.10	0.67395	4.817	3.170	1.38	11.247	5.971	2.420
383.36	0.71272	4.914	3.234	1.38	11.894	6.202	2.476
369.58	0.82135	5.098	3.355	1.38	13.707	6.781	2.618
355.81	1.0477	5.295	3.485	1.38	17.484	7.806	2.861
350.65	1.1727	5.373	3.536	1.38	19.570	8.318	2.974
342.90	1.4162	5.494	3.616	1.38	23.634	9.244	3.163
333.43	1.8119	5.650	3.719	1.38	30.238	10.604	3.409
328.26	2.0883	5.739	3.777	1.38	34.850	11.473	3.351
319.66	2.5470	5.894	3.879	1.38	42.505	12.840	3.750
310.44	3.1847	6.069	3.995	1.38	53.147	14.571	3.973

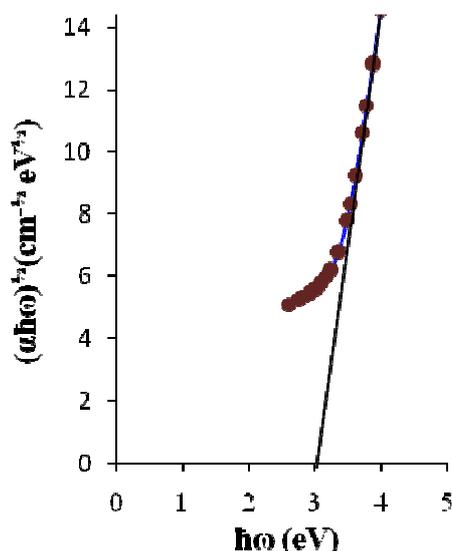
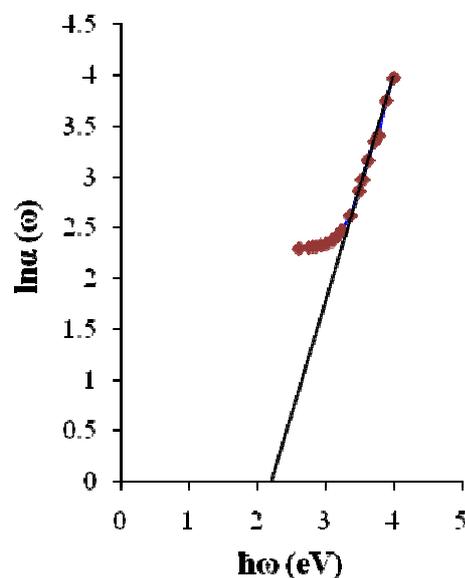
Figure 3 – Variation of  $(\alpha h\omega)^{1/2}$  in relation with  $h\omega$  for sample No. 101 with 25 % CdO and 1.38 mm thickness and  $E_{opt} = 2.965$  eV.Figure 4 – Variation of  $\ln \alpha(\omega)$  in relation with  $h\omega$  for sample No. 101 with 25 % CdO and 1.38 mm thickness and  $\Delta E = 0.469$  eV.

Table 2 – Experimental and calculated results for all samples

No. of Sample	B <sub>2</sub> O <sub>3</sub> wt%	CdO wt%	Thickness (mm)	E <sub>opt</sub> (eV)	ΔE (eV)
1	75	25	1.38	2.965	0.469
2	70	30	1.12	2.505	0.584
3-A	65	35	1.11	2.660	0.734
3-B	65	35	1.16	2.650	0.745
4-A	60	40	1.12	2.670	0.784
4-B	60	40	1.42	2.644	0.811
5-A	55	45	1.02	2.810	0.619
5-B	55	45	1.22	2.610	0.716
6-A	50	50	1.07	2.930	0.564
6-B	50	50	1.09	2.920	0.596
7	45	55	0.91	2.755	0.652
8	40	60	1.09	2.780	0.563

## CONCLUSION

Studying the spectra, and accomplished data lead us to conclude the following results:

The edge – absorption of these spectra is not sharp, in comparison with the spectra of crystalline, and this is specifying characteristic of amorphous (vitreous) structures.

The obtained experimental data show that, the edge – absorption tends towards long waves (low energies), when CdO percentage increases and B<sub>2</sub>O<sub>3</sub> percentage decreases. This effect may be interpreted by optical gap energy ( $E_{opt}$ ) decreasing. In fact, this may be due to certain structural changes of materials with changing in composition.

Increasing of contents of CdO may more localize some of the localized states present in deep energy levels. Of course, an ESR spectrum will show more acceptable interpretations.

Studying spectra we observe that, the edge – absorption, when the thickness of a determined specimen with the same percentages increases, tends towards long waves; which may be explicate by optical gap energy decreasing.

The same reasoning which has described above, also, explicates increasing in the width of localized states ( $\Delta E$ ). Interpretation is the same. As a matter of fact, we may interpret these latter phenomena, more probably, by increasing of electron wave functions overlap, due to increasing of specimen thickness, the width of localized states increases and the optical gap energy decreases. The same explication has reported for MoO<sub>3</sub> –In<sub>2</sub>O<sub>3</sub> binary system [15].

The variation in optical gap energy with variation in the width of localized states tail, reinforce Mott and Davis's theories for localized states within energy gap of amorphous semiconductors [4, 14]. The XRD spectrum does not show any peak so that it is a proof for (amorphous) vitreous structure of these samples.

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