Physico-chemical Study on Amorphous Structure of B₂O₃-PbO₂ Binary System

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Using optical absorption and studying the edge-absorption of either crystalline or amorphous structures, is an useful method for recognizing electronic structure of these materials. In this study, we have prepared the bulk specimens of different percentages from the melt of B_2O_3-PbO_2 binary system and then cooled them rapidly. It was characterized by UV-visible spectrum. In comparison with Mott and Davis's statement, it was established that the type of transition is not allowed. By extrapolating the linear part of $(\alpha \hbar \omega)^{3/2}$ against $(\hbar \omega)$ diagram, the energy of optical gap (E_{opt}) at $(\alpha \hbar \omega)^{3/2} = 0$ was determined. Obtained amounts of optical gap energy ($E_{opt} = 0.2500$ to 3.0735 eV) showed an increased with increasing of PbO_2 mass percentage. Amounts of constant of proportion B is determined by using Mott and Davis relation.

Key Words: Amorphous structure, Edge-absorption, Binary system, Optical gap, Location state.

INTRODUCTION

By studying the optical absorption, in particular, shapes and modifications of edge-absorption are a significant method, for understanding essential mechanism of optical displacements in crystalline and none crystalline materials with useful information in relation with their related structures[1]. This method is based on absorption of photons by energy, by relations related to transition from the states engaged in bonds capacity to states not engaged in their conduction bond. Two types of optical transitions may be occurring for basic edges of these materials, (1) direct transition and (2) indirect transition[2]. In direct transition, either vector or electron's wave direction remains uniform, but in indirect transition, applying of photon is necessary for retaining the amount of kinetic energy and, electron's wave direction is varied.

Optical edge-absorption of most of 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 amorphous layers has a slope less than its crystalline form. After 10 years, the determination and interpretation of edge-adsorption had significantly helped to understand electronic structure and theory of amorphous materials.

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

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

$$\alpha(\omega) = B \frac{(h\omega - E_{opt})^n}{h\omega} \qquad (1)$$

where B is the proportion coefficient, E_{opt} is optical gap energy, ω is angular frequency of transmitted ray and n may be equal to 1, 1/2, 3/2 or 2 which is depending to type of electronic transition in K space and to this fact, whether the transition is allowed or not allowed. At first, this equation proposed by Tauk *et al.*[3] with n = 2, then proposed by Mott and Davis[4] with n = 3/2.

2) **Low absorption zone [$\alpha(\omega) < 10^4$ cm^{-1}]:** In this zone, absorption coefficient is varied exponentially with the energy of descent photon ($\hbar\omega$). The best relation, which explain optical behaviour of these materials in this zone have given by Urback[5]:

$$\alpha(\omega) = C \exp \frac{(h\omega)}{\Delta E} \qquad (2)$$

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

$$\alpha(\omega) = \frac{1}{L} \ln \frac{I_0}{I} \qquad (3)$$

where $\alpha(\omega)$ is the absorption coefficient (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 work, we have investigated on vitreous samples of binary system of boron and lead oxides, B_2O_3-PbO_2, with different percentages and it is suggested that this work has the best concordance with the given theories[6-8].

EXPERIMENTAL

In first stage, the samples of binary system B_2O_3-PbO_2 with 90-10, 80-20, 75-25, 70-30, 65-35, 60-40, 55-50 and 50-50 % of B_2O_3 and PbO_2, respectively in bulk form were prepared.

By fast cooling the melt system, the optical properties of these samples were studied.

Preparing samples contain the following stages: (a) We have placed all samples, after milling, weighing and homogenizing, *ca.* 2 h in desiccators for eliminating the moisture. (b) Then we put samples *ca.* 2 h in 250 ºC, for eliminating probable internal stresses and temporary bonds. Then the samples completely homogenized for second time. (c) The homogenous samples are placed within a furnace for melting. Down to 500 ºC we have increased temperature every 100 ºC and kept them 10 min at received temperature, before another temperature increasing. Up to 500 ºC we have done the same after every 50 ºC temperature. At 400 ºC we have mixed well

once more sample for obtaining better homogeneity. (d) Place the samples for 5 min at softening temperature, then increasing temperature 50 °C, keeping about 15 min at received temperature and unloading the melt matter on a cold ceramic surface. For obtaining best result, unloading must do very rapidly. Then we put another ceramic piece above unloaded matter for obtaining a thin and uniform sample. The thickness of samples is measured with a micrometer.

RESULTS AND DISCUSSION

Absorption spectrum of samples were drawn with a UV-Visible spectrophotometer within a range of 300 to 500 nm. The shape of spectrums shows that the edge-absorption of them is not sharp, which is the characteristic of vitreous structures. Determining the localized states width ΔE, we have obtained the spectrum for the same specimen with different thickness and determined percentage. Specimens number 5 and 6, are typical examples for present subject.
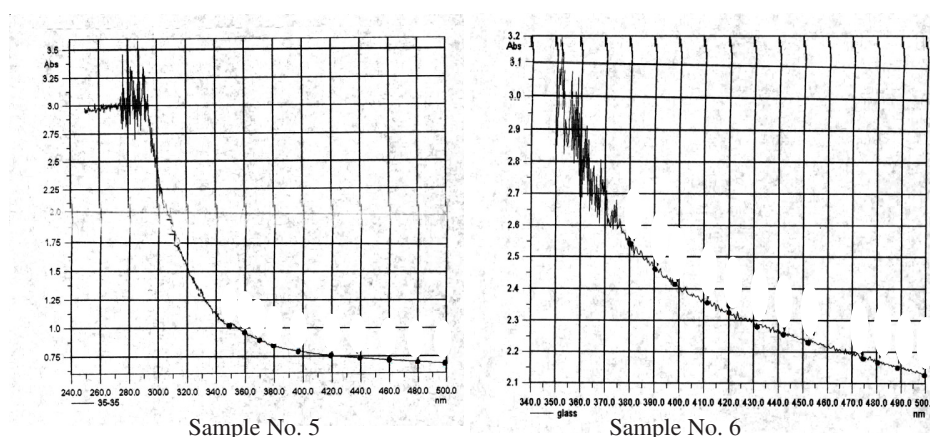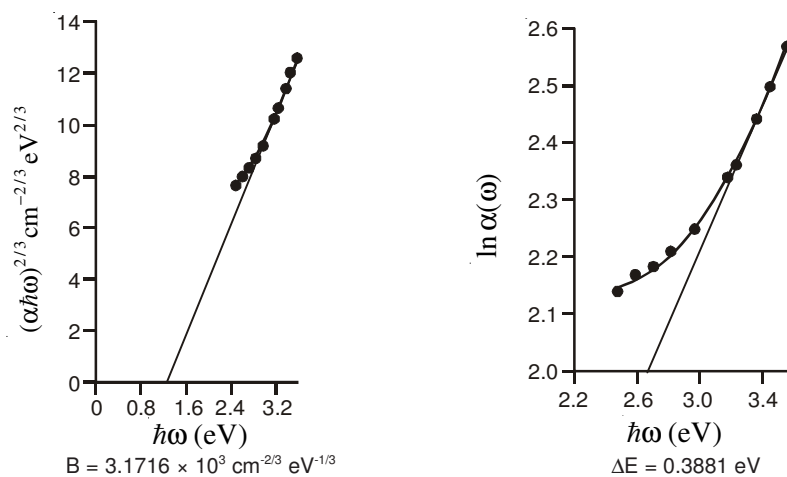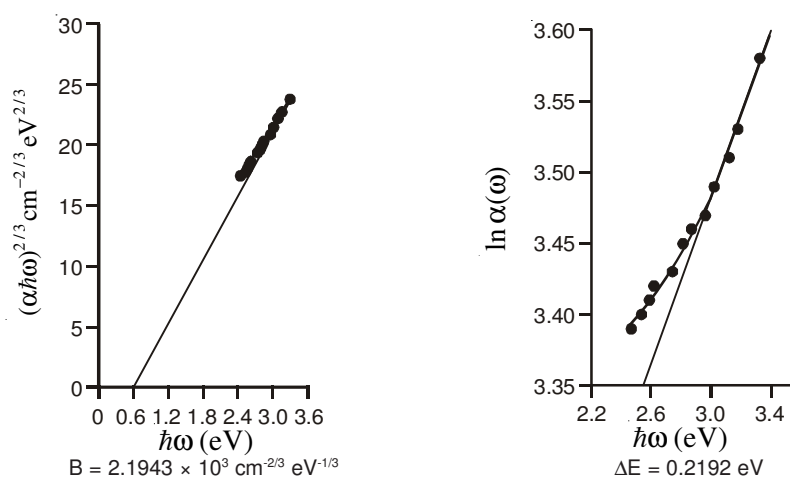

Sample No. 5   Sample No. 6

Fig. 1. UV absorption spectrum of B_2O_3-PbO_2 binary system

By calculating n for binary system B_2O_3-PbO_2, we have traced the diagram of variation of $(\alpha \hbar \omega)^{1/n}$ by different amount n = 1, 1/2, 3/2 and 2, in relation with emitted photon energy ($\hbar \omega$). The amount of n specifies by comparison the diagrams and finding the best linearity. We have obtained n by extrapolating the diagrams and then calculated E_{opt}. Then we obtained the amount of B, from the slope of $(\alpha \hbar \omega)^{2/3}$ diagram *versus* $\hbar \omega$. Figs. 2 and 3 show the diagrams of $(\alpha \hbar \omega)^{2/3}$ and $\ln \alpha(\omega)$ *versus* $\hbar \omega$ for the samples number 5 and 6.

The points 1 to 10 and 1 to 12 on absorption spectrum of B_2O_3-PbO_2 binary system, for samples number 5 and 6, respectively, are the points which our calculations have based on (Tables 1 and 2). The results of calculations for all samples which were the subject of present study are shown in Table-3.

B = 3.1716 × 10³ cm⁻²/³ eV⁻¹/³   ΔE = 0.3881 eV

Fig. 2. Graphs of $(\alpha\hbar\omega)^{2/3}$ and ln $\alpha(\omega)$ *versus* $\hbar\omega$ for sample No. 5

B = 2.1943 × 10³ cm⁻²/³ eV⁻¹/³   ΔE = 0.2192 eV

Fig. 3. Graphs of $(\alpha\hbar\omega)^{2/3}$ and ln $\alpha(\omega)$ *versus* $\hbar\omega$ for sample No. 6

Conclusion

By studying the spectrum and obtained data lead us to conclude the following results: (1) The edge-absorption of these spectrum, comparing with crystallites one, is not sharp and this specification is the characteristic of vitreous structures. (2) The given experimental data show that the edge-absorption tend to short views-high energies-when PbO_2 percentage increases and B_2O_3 percentage decreases. This effect explains by optical gap energy (E_{opt}) increasing. In fact, the same results concerning binary system V_2O_5-CeO_2, have interpreted by V^{4+}/V^{5+} proportion increasing[6]. Therefore, an ESR spectrum will show more acceptable interpretation. (3) By studying spectrum we have observed the edge-absorption tend to high views,

TABLE-1
RESULTS AND DATA FROM UV SPECTRUM OF
SAMPLE NO. 5 WITH 1.82 mm THICKNESS

Points No.	λ (nm)	A	$\hbar\omega$ (eV)	$\alpha(\omega)$ (cm^{-1})	$(\alpha\hbar\omega)$ (cm^{-1}, eV)	$(\alpha\hbar\omega)^{1/2}$ (cm$^{-1/2}$, eV$^{1/2}$)	$(\alpha\hbar\omega)^{2/3}$ (cm$^{-2/3}$, eV$^{2/3}$)	$\ln\alpha(\omega)$
1	350	1	3.5467	12.6538	44.8794	6.6992	12.6289	2.5679
2	360	0.96	3.4482	12.1477	41.8876	6.4721	12.0612	2.4971
3	371	0.91	3.3459	11.5150	38.5280	6.2071	11.4073	2.4436
4	380	0.84	3.2667	10.6292	34.7224	5.8925	10.6432	2.3636
5	390	0.82	3.1829	10.3761	33.0261	5.7468	10.2937	2.3395
6	420	0.75	2.9556	9.4904	28.0498	5.2962	9.2318	2.2503
7	440	0.72	2.8212	9.1107	25.7031	5.0698	8.7094	2.2094
8	460	0.70	2.6987	8.8577	23.9042	4.8892	8.2982	2.1812
9	480	0.69	2.5861	8.7311	22.5795	4.7518	7.9887	2.1669
10	500	0.67	2.4827	8.4781	21.0468	4.5879	7.6234	2.1375

TABLE-2
RESULTS AND DATA FROM UV SPECTRUM OF
SAMPLE NO. 6 WITH 1.65 mm THICKNESS

Points No.	λ (nm)	A	$\hbar\omega$ (eV)	$\alpha(\omega)$ (cm^{-1})	$(\alpha\hbar\omega)$ (cm^{-1}, eV)	$(\alpha\hbar\omega)^{1/2}$ (cm$^{-1/2}$, eV$^{1/2}$)	$(\alpha\hbar\omega)^{2/3}$ (cm$^{-2/3}$, eV$^{2/3}$)	$\ln\alpha(\omega)$
1	380	2.56	3.3167	35.7314	116.7237	10.8039	23.8839	3.5760
2	390	2.45	3.1829	34.1961	108.8427	10.4328	22.7964	3.5321
3	398	2.41	3.1189	33.6377	104.9126	10.2427	22.2443	3.5156
4	411	2.35	3.0203	32.8003	99.0667	9.9532	21.4101	3.4904
5	420	2.31	2.9556	32.2420	95.2944	9.7619	20.8631	3.4733
6	431	2.28	2.8701	31.8233	91.3360	9.5570	20.2812	3.4602
7	442	2.25	2.8085	31.4045	88.1995	9.3914	19.8142	3.4469
8	453	2.22	2.7402	30.9858	84.9073	9.2145	19.3180	3.4335
9	474	2.18	2.6188	30.4275	79.6835	8.9265	18.5173	3.4152
10	480	2.17	2.5861	30.2879	78.3275	8.8503	18.3076	3.4175
11	488	2.14	2.5437	29.8692	75.9783	8.7165	17.9388	3.3968
12	500	2.12	2.4727	29.5900	73.1672	8.5538	17.4935	3.3874

TABLE-3
RESULTS OF CALCULATIONS FOR ALL SAMPLES

Sample No.	B_2O_3 (wt %)	PbO_2 (wt %)	Thickness of sample (mm)	ΔE (eV) $\times$ 10^{-2}	B cm$^{-2/3}$ eV$^{-1/3}$ $\times$ 10^3	E_{opt} (eV)
1	75	25	1.03	6.64	2.4262	0.4545
2	75	25	1.32	9.63	3.7321	1.6184
3	70	30	1.74	5.24	2.5002	0.6136
4	70	30	1.85	8.75	3.1146	1.1579
5	65	35	1.82	13.17	3.1716	1.5000
6	65	35	1.65	11.92	2.1943	0.6818
7	60	40	1.91	3.49	2.1445	0.2500
8	55	45	1.21	6.99	10.9881	3.0735
9	50	50	1.97	3.49	4.0108	1.8158

when the thickness of a determined specimen with the same percentages increases; which defines by optical gap energy decreasing. (4) By the same condition described in above paragraph, also, the localized states width (ΔE) increases. In fact, we may interpret these two latter effects, more probably, by increasing of electron wave functions overlap, due to increasing of specimen's thickness, the localized state width increase and the optical gap energy decrease. The same explication has reported for MoO_2-In_2O_3 binary system[9]. (5) The variation in optical gap energy with variation in location state tail, reinforce Mott and Davis's theories for localized states within energy gap of amorphous semiconductors.

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