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A study on optical characteristics of amorphous structure (Vitreous) including oxides of main and transitional elements in binary system $B_2O_3 - CaO$

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ABSTRACT

Amorphous Structures have specific characteristics including semi-conductivity. Boron trioxide can form the vitreous structure with other oxides. Addition of certain oxides to boron trioxide modifies the properties of these glasses. In our investigation B_2O_3 - CaO binary was studies and it was appeared that the system of (100 - x) B2O3 - x CaO is able to form the vitreous structure and the range of x was determined experimentally. For better understanding the electronic structure and study on the edge-absorption, we can use optical absorption. By using a UV -Visible spectrophotometer the absorption spectrums were obtained. Studying these spectrums and by using Urbach and Mott-Davis theories, 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 B_2O_3 - CaO binary system n = 1/2 was obtained. Extrapolating $(\alpha\hbar\omega)^2$ against $\hbar\omega$ plot, we can determine optical gap energy, E_{opt} , at $(\alpha\hbar\omega)^2 = 0$. Obtaining results show that, E_{opt} increase with CaO percentage increasing. The coefficient B, also, is calculated by using Mott-Davis relation. By determining the slop of $\ln \alpha(\omega)$ against $\hbar\omega$ diagram, the width of localized states in the energy of bonds, ΔE , can be obtain.

Keywords: Amorphous structure, optical edge-absorption, absorption coefficient, E_{opt} , ΔE_{\bullet}

INTRODUCTION

The basis of studying optical edge-absorption of amorphous structures depends on absorption of energetic photons by relations depending the transitions from involved valance band to non involved conductivity band states [1, 2].

Two types of optical transitions may be occur in basic edges of these materials:

a) Direct transition, where the vector or wave direction of electron remains the same.

b) **Indirect transition**, where the gain of photon for conservation of kinetic energy is necessary and the direction of electron wave changes [3].

Optical edge-absorption of the major of amorphous semiconductors identifies by an adsorption coefficient $\alpha(\omega)$ which increases exponentially with increasing of energy $\hbar\omega$. The variation of adsorption coefficient against energy of photon in high energies takes an exponential tail [4]. The edge-absorption of non crystalline and amorphous materials has a smaller slop than crystalline materials. In many much of amorphous materials the edge-absorption classify in two following types.

1) High absorption zone $[a(w) > 10^4 \text{ cm}^{-1}]$: In this zone, absorption coefficient was obtained from following relation [4]:

$$\alpha(\omega) = \mathbf{B} \frac{(\hbar \omega - \mathbf{E}_{opt})^{n}}{\hbar \omega}$$
(1)

Where B is the proportion coefficient, E_{opt} is optical gap energy, ω is angular frequency or transmitted ray and n can be 1/2, 1, 3/2 and 2 which depend to electron transition in K space and to the type of transition [5].

2) Low absorption zone $[a(w) < 10^4 \text{ cm}^{-1}]$: In this zone, absorption coefficient varies exponentially with the energy of descent photon ($\hbar\omega$). The best relations who can interpret the behavior of these materials have proposed by Urbach [6].

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

Where C is the proportion coefficient and ΔE is the width of localized states in the energy of bonds. In amorphous structures formed by B_2O_3 and main or transitional metal oxides, generally, a photon with limited energy can be absorbed by the metal oxide.

Energy absorption may be occurring in two manners [7, 8, 9].

a) Absorption related to internal transition of electrons of layers.

b) Absorption occurs by transition of electron from neighbor atom to metal ion [10].

Study on optical absorption, in particular, on edge-absorption is a convenient method for investigation in optical transitions and for obtaining the data on band structure and energy lacuna in non crystalline semi-conductors and metals.

MATERIALS AND METHODS

2.1. Instruments

a) UV- Visible spectrophotometer GBC Model Cintra 20.
b) XRD – MMA/007/GBC
c) Electrical furnace (Exiton – 1500)

2.2. Sample preparation

The samples were prepared by well mixing of very fine powder of B_2O_3 and CaO oxides in an agate mortar which have weighed accurately by an analytical balance before mixing. The percentages of prepared samples are shown in table 1.

Table	1.	Percentages	of	samples
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B_2O_3	98	95	85	75	60
CaO	2	5	15	25	40

UV spectrums show that the samples which have less than 60 wt % B_2O_3 and more than 40 wt % CaO have not amorphous structure.

Then samples treated as following:

a) Accurately prepared samples have put in a desiccator at least 3 hours, for removal of any probable moisture.

b) The powder samples have supported an annealing at 250°C about 2 hours for removal of all internal stresses and temporary bindings.

c) The samples heated moderately into an alumina crucible, to melting point and preserved about 20 minute at this temperature.

d) Then, temperature increases 50° C above melting point and the samples preserved for 5 minute in this temperature.

e) At last, the samples were evoked rapidly from furnace and decanted the molten material on a cold ceramic plate. By putting another plate of ceramic over the molten material a thin and uniform glassy sample may be obtained.

RESULTS AND ISCUSSION

3.1. UV-Visible and XRD Spectra

12 samples were prepared by above treatment and UV- Visible spectra of all these samples were obtained. The Spectra show that all samples have amorphous structure. Also, XRD spectra confirm the vitreous structure of all prepared samples. The figures 1 to 6 show some UV-Visible and XRD spectra of these samples.







Fig.3. Absorption spectrum of sample with 15 wt % CaO and 2.18 mm of thickness



Fig.2. Absorption spectrum of sample with 25 wt % CaO and 1.62 mm of thickness







3.2. Determinations and Calculations

At least, 15 points on UV-Visible spectrum have selected and $\alpha(\omega)$ can be calculated by general relation of Bir – Lambert.

$$\alpha(\omega) = \frac{1}{L} \times 2.303 \log \frac{I}{I_{\circ}}$$
(3)

Where L is the thickness of sample, I_o and I are intensities of transmitted and absorbed photons. Angular frequency ω may be calculated by following relation.

$$\boldsymbol{\omega} = 2 \, \boldsymbol{\pi} \frac{c}{\lambda} \tag{4}$$

Determining n, plots of $(\alpha \hbar \omega)^{1/n}$ against $\hbar \omega$ have traced for $n = 1, 2, \frac{1}{2}, \frac{3}{2}$ and $\frac{2}{3}$. For $n = \frac{1}{2}$ the obtained plot has more acceptable exponential tail. Thus, the transmission is direct and allowed. By extrapolating the plot $(\alpha \hbar \omega)^2$ against $\hbar \omega$, E_{opt} have determined at $(\alpha \hbar \omega)^2 = 0$. Coefficient B may be obtained from slop of plot. Then the plot of $\ln \alpha(\omega)$ was traced against $\hbar \omega$. Inverse of slop of this plot gives the width of localized states in the energy of bonds, ΔE .

Table 2. Typical determinations and calculations for the plot of sample shown in Fig.1.*

Points	λ	$\omega \times 10^{-15}$	ħω (aV)	$\alpha(\omega)$	$(\alpha\hbar\omega)^2$	Ln α(ω)
on piot	(IIII)	(\$)	(ev)	(cm)	(cm ev)	
1	430	4.377	2.886	6.852	391.129	1.924
2	400	4.710	3.105	7.526	546.063	2.018
3	389	4.841	3.192	8.425	723.179	2.131
4	382	4.929	3.250	9.430	940.464	2.244
5	378	4.980	3.284	10.447	1176.970	2.346
6	373	5.049	3.329	11.234	1398.535	2.418
7	368	5.118	3.376	12.919	1902.180	2.558
8	365	5.155	3.399	14.042	2279.298	2.642
9	363	5.187	3.420	15.727	2892.933	2.755
10	362	5.199	3.428	16.851	3336.795	2.824
11	361	5.218	3.441	18.311	3970.008	2.907
12	360	5.231	3.449	19.659	4597.246	2.978
13	355	5.306	3.499	22.468	6180.318	3.112
14	350	5.381	3.549	25.276	8046.807	3.229
15	348	5.413	3.569	28/085	10047.055	3.335

*The same determinations and calculations have performed for all samples and for $n = 1, 2, \frac{1}{2}, \frac{3}{2}$ and $\frac{2}{3}$.

The plots $(\alpha \hbar \omega)^2$ against $\hbar \omega$ and $\ln \alpha(\omega)$ against $\hbar \omega$ for samples are shown in figures 1 and 2, typically are shown in figures 7, 8, 9 and 10. Data obtained for all samples are shown in table 3. Table 3. Data obtained for all samples

CaO	Thickness	E _{opt}	ΔΕ	B×10 ⁴	Transmission
(wt. %)	(mm)	(eV)	(eV)	$(cm^{-1}eV^{-1/2})$	type
40	2.05	3.50	0.380	3.7329	Direct - allowed
40	1.96	3.76	0.430	22.9818	Direct - allowed
40	2.46	3.40	0.319	4.1708	Direct - allowed
40	2.27	3.40	0.340	14.5471	Direct - allowed
25	1.62	3.78	0.286	9.6581	Direct - allowed
25	1.53	3.80	0.327	10.5418	Direct - allowed
25	1.84	3.77	0.309	4.4203	Direct - allowed
15	2.18	3.60	0.350	3.9988	Direct - allowed
5	1.74	3.57	0.623	11.8769	Direct - allowed
2	1.92	3.85	0.343	6.1220	Direct - allowed
2	5.8	3.63	0.329	1.4074	Direct - allowed
2	5 95	3 60	0.299	1 3011	Direct - allowed



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Fig.7. Variation of $(\alpha h \omega)^2$ against h ω for the sample with 40 % CaO and 2.05 mm thickness. B = 3.7329×10^4 cm⁻¹eV^{1/2} and E_{opt} = 3.50 eV



Fig.9. Variation of $(\alpha h \omega)^2$ against h ω for the sample with 25 % CaO and 2.05 mm thickness. B = 9.6581×10⁴ cm⁻¹eV^{1/2} and E_{opt} = 3.78 eV







CONCLUSION

Studying obtained spectra and the data indicated in tables we can conclude the followings for binary amorphous system B_2O_3 -CaO.

a) The edge – absorption of all prepared samples in the range 2 to 40 % CaO, is not sharp which indicates amorphous structure of them. XRD spectrum confirms this deduction.

b) As CaO percentage increases and B_2O_3 percentage decreases the edge absorption tends towards smaller wave length (higher energies). This fact may be interpreted by increase in optical gap energy, E_{opt} . The similar results have been obtained for other amorphous systems [7, 8, 9].

c) Studies on spectra show that the edge – absorption for the samples with the same composition, tend towards longer wave length with thickness increasing of sample, which show decreasing in optical gap energy. This fact may be interpreted as following: by thickness increasing, overlap of electronic wave functions increase. Thus, the width of localized states decrease and optical gap energy increases.

d) Obtained results show that increasing in thickness of the samples with the same composition, causes decreasing in the width of localized states which may be interpreted as above.

Variation of optical gap energy with variation of the width of localized states, confirm Mott – Davis theories for localized states in the gap energy of amorphous semi – conductors [2, 4].

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