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Physical and Optical Properties of CdO B_2O_3 Bi_2O_3 TeO_2 Glass System

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THE PHYSICAL and optical properties of xCdO (35-x) B_2O_3 $60Bi_2O_3$ $5TeO_2$ glass system (where, x=10, 20, 30) has been investigated. Thermal stability , density , optical transmittance and the refractive index of these glasses have been studied. It was found that the values of density increase but the values of molar volume and oxygen packing density decrease by increasing CdO content. Also, the thermal stability of all the studied samples increase by increasing CdO content. However, it was found that the values of optical energy gap decrease by increasing CdO content for all the studied samples. While as the values of refractive index, molar polarizability, oxide ion polarizability, optical basicity increase by increasing CdO content. Also, all the studied samples exhibit insulating behavior and become more basic and more polarized by increasing CdO content. The high values of third order nonlinear optical susceptibility for all the studied samples, were found to be in the range (1.408-2.307)x 10^{-12}esu, which is larger than that of pure silica glass. Finally, it has been suggested that all the studied samples are promising materials for nonlinear optical requests.

Keywords: Density, Molar volume, Optical energy gap, Refractive index, Third order nonlinear optical susceptibility.

Introduction

The materials of high optical nonlinearity have been given attention in science and technology of materials. Tellurium oxide glasses have attracted much care because of their optical requests due to their high linear and nonlinear refractive indices and high nonlinear optical susceptibility [1]. The structural, optical and electrical properties of these glasses have been studied [2-5]. Borate glasses have been given attention due to their wide range of applications in the fields of linear and nonlinear optics and related techniques [6]. Boron oxide can form the vitreous structures with other oxides [7]. Addition of cadmium oxide to boron oxide modifies the properties of these glasses [7]. Also, it was found that Bismuth oxide glasses have been studied because of their potential applications in optoelectronics and photonics [8]. It has been showed [9] that TeO_2-Bi_2O_3-B_2O_3 glasses are promising optical glasses due to their high refractive index and high third order nonlinear susceptibility. In the present article, the physical and the optical properties of xCdO (35-x) B_2O_3 $60Bi_2O_3$ $5TeO_2$ glass system (where, x=10, 20, 30) have been studied.

Experimental

Glasses having a composition xCdO (35-x) B_2O_3 $60Bi_2O_3$ $5TeO_2$, where (x = 10, 20, 30) were prepared by the conventional melt quench technique. Proper weights of CdO , B_2O_3 ,Bi_2O_3, TeO_2 in accurate molar ratio were mixed to obtain uniform acceptable fine powder and then, placed in a porcelain crucible and heated in an electric furnace whose temperature was elevated in steps to 1100^0C for half an hour. Then, the molten samples were rapidly cooled to room temperature by pouring it onto a cooper plate and successively pressing it with another to get glasses. The studied samples have been characterized by the X-ray diffraction (XRD). All the samples reveal non-crystalline nature as no noticeable peaks were detected in their (XRD) spectra. The transmission of all the samples in the

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wave length (400-1100nm) was measured using a computerized recording spectrophotometer (type Jasco, V-570).

Discussion and Results

The density

The glass density was determined by Archimedes principle .The values of density for all the studied samples are listed in Table 1.

The molar volume V_m can be calculated as follows:

The molar volume = (Total molecular weight)/ (density)

The values of molar volume for all the studied samples are listed in Table 1. Oxygen packing density is the arrangement of the oxygen atoms in the glass system and can be calculated as follows,

Oxygen packing density =(1000xO)/ V_m

where O denotes the sum of oxygen in the oxide glass element. It is clear that the values of the density increase because the values of molecular weight increase by increasing CdO content for all the studied samples. Also, the values of molar volume decrease for all the studied samples. *i.e.* it follows the normal behavior. The reduction in oxygen packing density for all the studied samples is most likely due to the decrease in number of the oxygen atoms in the glass network.

The optical basicity

Consideration of optical basicity would be useful for the design of the novel optical functional materials with higher optical performances. The high optical basicity means high electron donating power of the oxygen in the oxide glass [10]. The optical basicity can be calculated [11] as follows:

$$\text{Optical basicity}=x(CdO)\Lambda(CdO)+ x(B_2O_3)\ \Lambda\ (B_2O_3)+ x(Bi_2O_3)\ \Lambda\ (Bi_2O_3) + x(TeO_2)\ \Lambda\ (TeO_2)$$

Where x (CdO) x (B_2O_3), x (Bi_2O_3) and x (TeO_2) are the corresponding portion of the different oxides. And Λ (CdO), Λ (B_2O_3), Λ (Bi_2O_3) and Λ (TeO_2), are the optical basicity values of the principal oxides.. It is clear from Table 2 that the values of theoretical optical basicity increase by increasing CdO content which means that the studied glasses became more basic.

Polarizability of oxide ions

The relation between electronic polarizability of oxide ions and optical basicity of oxide is calculated as follows [10], polarizability of oxide ion =1.67/(1.67-optical basicity)

From Table 2, it is clear that, by increasing CdO, the values of the electronic polarizability of oxide ions increase which means that the glasses become more polarized.

The molar refraction and the molar polarizability

The molar refraction R_m for all the studied samples with the common molar formula $xCdO(0.35-x)B_2o_30.\ 60Bi_2O_30.\ 05TeO_2$ can be expressed as a function of molar polarizability, α_m, which can be calculated as follows [12]:

$$R_m = 2.52\alpha_m = 2.52(xCdO\alpha_{Cd}^{2+} + xB_2O_3\alpha_B^{3+} + x\ Bi_2O_3\ \alpha_{Bi}^{3+} + xTeO_2\alpha_{Te}^{+4})$$

Where, α_{Cd}^{2+} , α_B^{3+} , α_{Bi}^{3+}, α_{Te}^{+4} ,are cation polarizability of CdO, B_2O_3 ,Bi_2O_3 and TeO_2, respectively. From Table 2, it is clear that the values of molar polarizability and molar refraction increase by increasing CdO content.

Differential scanning calorimetry (DSC) analysis

Typical DSC traces of xCdO (35-x) B_2O_3 $60Bi_2O_3$ $5TeO_2$ powder glasses recorded at heating rate 10 deg./min. are shown in Fig. 1. Table 3, represents the values of the glass transition temperature, T_g, the crystallization temperature T_p , and the melting temperature T_m for all the compositions under investigations. From the table, it is clear that the transition temperatures (T_g,T_p,T_m) decrease by increasing CdO content. The difference ($\Delta T=T_p-T_g$) increases by increasing CdO content as shown in Table 3 so, the thermal stability increases by increasing CdO content. This is in fair agreement with the above arguments. The density increases by increasing CdO content *i.e.,* the bond strength increases, this along with the polarizability data suggest the increase of thermal stability.

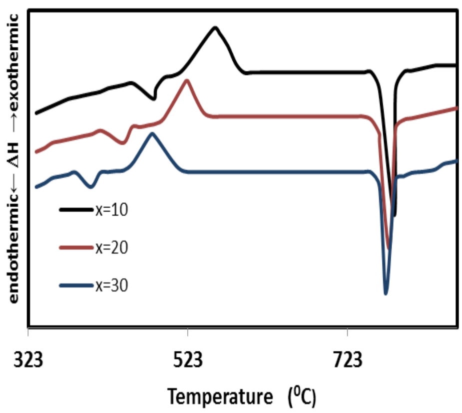

Fig. 1. DSC spectra for all the studied samples.

TABLE 1. The values of density, molecular weight, molar volume and oxygen packing density for all the studied samples.

Sample	Density (g/cm^3)	Molar volume (cm^3/mol)	Molecular weight (g/mol)	Oxygen packing density
$10CdO25B_2O_360Bi_2O_35TeO_2$	6.742	47.138	317.802	58.339
$20CdO15B_2O_360Bi_2O_35TeO_2$	7.310	44.279	323.681	57.589
$30CdO5B_2O_360Bi_2O_35TeO_2$	7.891	41.764	329.560	56.269

TABLE 2. The values of optical basicity , polarizability of oxide ions, molar polarizability and molar refraction for all the studied samples.

Sample	Optical basicity	Polarizability of oxide ions	Molar polarizability ($^0A^3$)	Molar refraction (cm^3/mol)
$10CdO25B_2O_360Bi_2O_35TeO_2$	0.980	2.420	8.651	21.800
$20CdO15B_2O_360Bi_2O_35TeO_2$	1.051	2.698	9.085	22.894
$30CdO5B_2O_360Bi_2O_35TeO_2$	1.122	3.047	9.366	23.603

TABLE 3. Transition temperatures and thermal stability for all the studied samples.

Sample	$T_g(^0C)$	$T_c(^0C)$	$T_m(^0C)$	ΔT
$10CdO25B_2O_360Bi_2O_35TeO_2$	478.3	553.3	781.2	75
$20CdO15B_2O_360Bi_2O_35TeO_2$	440.2	518.2	775.0	78
$30CdO5B_2O_360Bi_2O_35TeO_2$	400.8	480.8	769.8	80

Optical energy gap

Figure 2 shows the optical transmission spectra for all the studied samples. The absorption coefficient α of each sample was calculated using the relation [13].

$$\alpha=(1/d)\ln(I_0/I_t)$$

Where I_0 and I_t are the intensity of the incident and transmitted radiation, respectively and d is the thickness of the sample. Mott and Davis [13] proposed the relation between the absorption coefficient α(ω) and the photon energy ħω of the incident radiation, for indirect transitions this relation can be written as follows,

$$\alpha\hbar\omega=\beta(\hbar\omega-E_{opt})^2$$

Where ω is the angular frequency of radiation, β is constant called band parameter, E_{opt} is the optical energy gap. The values of E_{opt} can be determined as the intersection between $(\alpha\hbar\omega)^{1/2}$ and ħω as shown in Fig. 3. The obtained values of E_{opt} for all the studied glasses are given in Table 4. It is clear that, the value of optical band gap energy decreases by increasing CdO content for all the studied samples. Increasing CdO content increases the number of non-bridging oxygen atoms. The reduction in optical energy gap is most likely due to the increase in amount of electrons localization and as a result these cause increase in the donor centers in the glass system [14].

The linear refractive index

The calculation of the refractive index is very important to determine the ability of glass material to be optical devices [14]. The refractive index, n, can be calculated from the value of E_{opt} using the formula proposed by Dimitro and Sakka [15] as follows :

$$(n^2-1)/(n^2+1)=1-(E_{opt}/20)^{1/2}$$

The values of refractive index for all the studied samples are listed in Table 4. It is clear, that by increasing CdO content , the values of the refractive index increase because the polarizability of oxide ions increase for all the studied samples.

Third order nonlinear susceptibility

The glasses with higher nonlinear optical properties, especially third order nonlinear susceptibility, are appropriate to produce nonlinear waveguide devices useful for optical signal processing [10]. The third order nonlinear susceptibility in esu units is calculated by the following relation [12],

$$\chi^{(3)} = ((n^2 - 1)/ 4\pi)^4 \times 10^{-10}$$

From Table 4, it was found that the values of third order nonlinear optical susceptibility increase by increasing CdO content .This due to increasing values of the refractive index for all the studied samples.

Metallization criterion of the glasses

According to the Herzfeld theory of metallization [16] the following simple criterion appears to be the necessary but sufficient condition to predict the metallic or insulating behavior of the condensed state [10] (R_m/V_m) > 1 (metal) and (R_m/V_m) < 1 (insulator).

$$\text{The metallization criterion} = 1-(R_m/V_m)$$

The values of metallization criterion for all the studied samples are listed in Table 4. It is clear that the metallization criterion values of the present glasses are found to be less than one and thus all the studied samples exhibit insulating behavior .

Conclusion

From all the above arguments, it was found that the values of density, refractive index, increase by increasing CdO content. On the other hand, the values of optical energy gap, decrease by increasing CdO content. Also, all the studied samples exhibit insulating behavior and become more basic and more polarized by increasing CdO content. The high values of third order nonlinear optical susceptibility for all the studied samples were found to be in the range (1.0408-2.307) x 10^{-12}esu. Finally, all samples are promising materials for nonlinear optical devices.

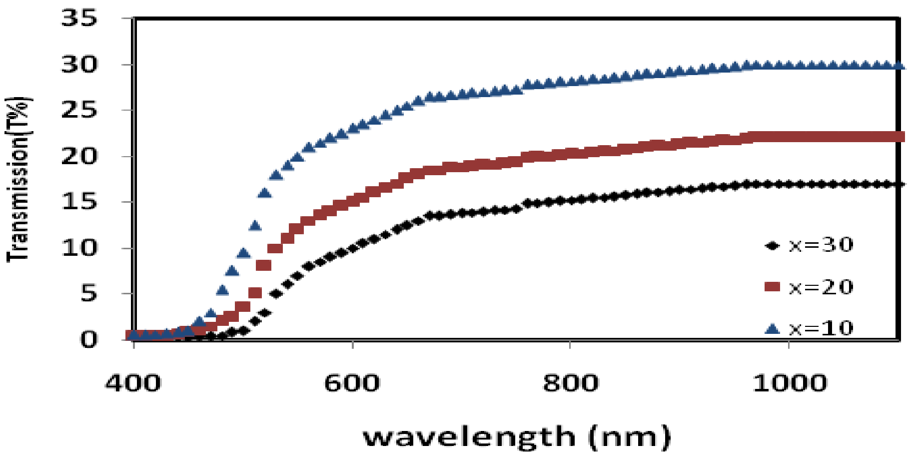

Fig. 2. The transmission spectra for all the studied samples

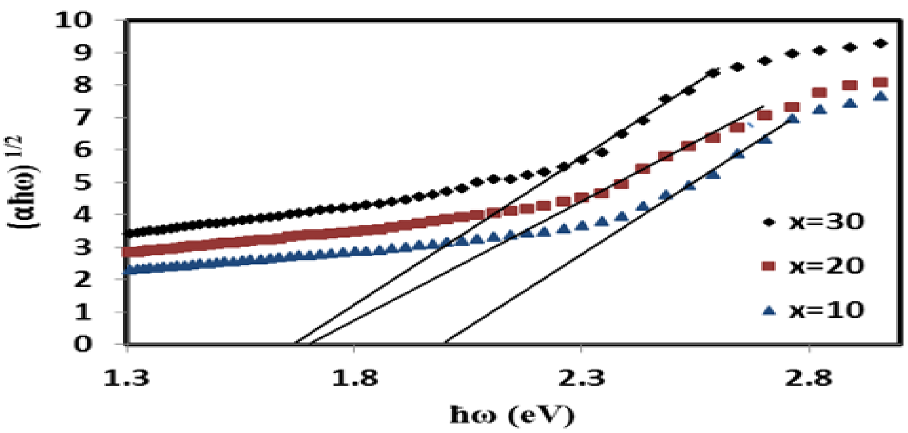

Fig. 3. The relation between $(\alpha\hbar\omega)^{1/2}$ and ħω for all the studied samples

TABLE 4. The values of optical energy gap, refractive index ,third order nonlinear susceptibility for all the studied samples.

Sample	Optical energy gap (eV)	Refractive index	Third order nonlinear susceptibility (e.s.u)	Metallization
$10CdO25B_2O_360Bi_2O_35TeO_2$	2.00	2.308	$1.408x10^{-12}$	0.538
$20CdO15B_2O_360Bi_2O_35TeO_2$.	1.72	2.414	$2.182x10^{-12}$	0.483
$30CdO5B_2O_360Bi_2O_35TeO_2$	1.68	2.428	$2.307x10^{-12}$	0.435

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الخواص الفيزيائية والضوئية للنظام الزجاجى $CdO_2B_2O_3Bi_2O_3TeO_2$

غادة عادل

قسم الفيزياء - كلية العلوم - جمعة الأزهر (بنات) - القاهرة - مصر

تمت دراسة الخصائص الفيزيائية والبصرية للنظام الزجاجي $xCdO\ (35\text{-}X)\ B_2O_3 60Bi_2O_3\ 5TeO_2$ حيث $x = 10,20,30$ وجد أن الكثافة تزداد بزيادة محتوى CdO. من ناحية أخرى ، فإن الحجم المولي وكثافة تعبئة الأكسجين تتبع الاتجاه المعاكس بزيادة محتوى CdO. يزداد الثبات الحراري للعينات المدروسة بزيادة محتوى CdO. ومع ذلك ، فقد وجد أن قيم فجوة الطاقة الضوئية تقل بزيادة محتوى CdO. في الوقت نفسه ، تزداد قيم معامل الانكسار ، الاستقطاب المولي ، الاستقطاب الأيوني للأكسدة ، والأساسية البصرية بزيادة محتوى CdO. تم العثور على قيم عالية من الحساسية البصرية غير الخطية من الدرجة الثالثة لجميع العينات المدروسة ، في النطاق $(1.408\text{-}2.307) \times 10^{-12}$، وهو أكبر من ذلك من زجاج السيليكا النقي، وأخيرًا تم اقتراح أن جميع العينات المدروسة هي مواد واعدة للطلبات البصرية غير الخطية.