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Optical properties of lead-bismuth cuprous glasses

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Abstract

The optical transmission and absorption spectra in UV-VIS were recorded in the wavelength range 350-800 nm for different glass compositions in the system: $(CuO)_x$ $(PbO)_{50-x}$ $(Bi_2O_3)_{50}$ (x=2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 20.0). Absorption coefficient {α (λ)}, optical energy gap (E_{opt}), refractive index (n), optical dielectric constant ($\varepsilon`_\infty$), Urbach energy (E_e), constant B and ratio of carrier concentration to the effective mass (N/m^*) have been reported. The effects of compositions of glasses on these parameters have been discussed. It has been indicated that a small compositional modification of the glasses lead to an important change in all the optical properties including non-linear behavior. The optical parameters were found to be almost the same for different glasses in the same family.

Keywords
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الخصائص البصرية لزجاجيات الرصاص- نحاس بزموث

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الخلاصة:

تم قياس أ طياف الامتصاصية البصرية و النفاذية في مدى الاطوال الموجية الفوق بنفسجية-مرئية لنماذج مكونات مختلفة للنظام الزجاجي $(CuO)_x$ $(PbO)_{50-x}$ $(Bi_2O_3)_{50}$ حيث x أخذت القيم: ٢,٥، ٥,٠، ٧,٥، ١٠,٠، ١٢,٥، ١٥,٠، ٢٠,٠. تم حساب معامل الامتصاص {α (λ)}، فجوة الطاقة البصرية(E_{opt})، معامل الانكسار(n)، ثابت العزل البصري($\varepsilon`_\infty$)، عرض ذيول الحالات الموضعية الموجودة داخل فجوة الطاقة (طاقة اورباخ E_e)، الثابتB و نسبة حاملات الشحنة الى الكتلة الفعالة(N/m^*). نوقش تأثير مكونات النماذج الزجاجية على هذه الخصائص البصرية، حيث تبين ان التغير الطفيف في مكونات هذا الزجاج يؤدي الى حصول تغيرات مهمة في الخصائص البصرية تتضمن تغير هذه الخصائص بشكل غير خطي للزجاج المحضر، و قد لوحظ هذا السلوك في أنواع مختلفة من الزجاجيات التي تنتمي الى نفس نوع هذا الزجاج.

Introduction

In recent years, the interest in the study of electrical, optical and structural properties of glassy semiconductors has increased considerably [1]. The frequency dependent dielectric and optical properties of binary semiconducting glasses in the system V_2O_5- TeO_2- PbO have been measured as a function of lead content and the effects of composition on refractive index, dielectric constant and optical phonon frequency have been discussed [2]. The non-linear optical properties of B_2O_3 based glasses have been reported [3]. The effect of iron on the optical, physical and structural properties of several iron phosphate and sodium iron phosphate glasses were investigated by using X-ray photoelectron spectroscopy (XPS), Mossbauer spectroscopy [4].

Optical properties and chemical durability of lead-indium-aluminum phosphate glasses prepared by a wet chemical process have been investigated [5].

Refractive index is an important parameter for the design of optical components such as prism, windows and optical fiber [6]. The electrical and optical studies of chrome ions (Cr^{3+}) doped chlorophosphate and phosphate glasses were carried out at low doping concentration [7].The optical properties of lead- bismuth titanate glasses and lead bismuth glasses have been studied [8]. The effects of composition of glasses on these optical parameters have been discussed.

Linear and non-linear optical properties of chalcogenide glasses were investigated [9]. Very little work appears to have been done on the optical properties of oxide glasses. Therefore, it has been decided to study the optical parameters of these glasses.

The intention to study the optical properties of these glasses by UV-VIS spectra is to investigate the existence of localized states near band edge, and calculating the optical energy gap to evaluate this type of glass in the optical applications like using it in producing the optical machine which have high quality properties, also we can use this type of glass as a semiconducting glass in electronic application.

Experimental

Preparation of samples:

Glass samples under investigation were prepared by mixing appropriate amount of Bi_2O_3, CuO and PbO (mol %). A homogeneous mixture of powders was prepared and fired in a fireclay alumina crucible at 1000 °C for about one hour by using an electric furnace. The glass samples were then formed by quenching the melt on a stainless steel plate and cast into a disc shape. The disc was immediately transferred to another furnace, which was already maintained at 250 °C. The furnace was kept at this temperature for about 2 hour and was switch off to cool down to room temperature. The glass samples were polished using diamond paste down to a minimum grain size of 0.1 μm.

Optical measurements

X-ray diffraction measurements were made using a Philips X-ray diffractometer. The absence of peaks in X-ray diffractometer confirmed the amorphous of the glass samples.

The absorption and transmission spectra of the glass samples were measured in the wavelength range 350-800 nm at normal incidence. The spectral dependence of both absorbance (A) and transmittance (T) on composition of the glass is shown in figure 1.

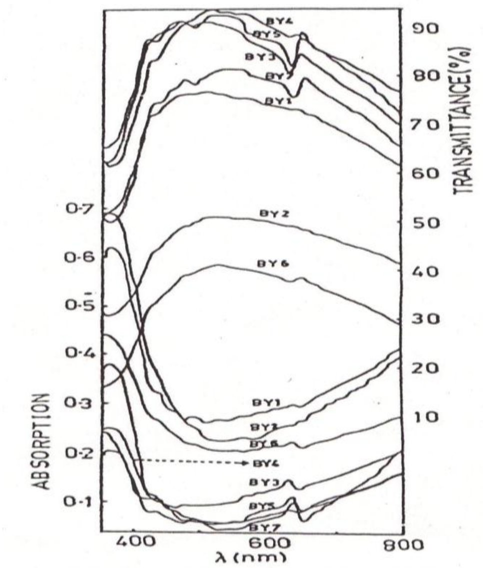

Fig. 1: Spectral dependence of both absorption and transmittance vs. (λ).

The optical absorption coefficient, α(υ), at the given frequency (υ) is given by [10]:

$$\alpha(\upsilon) = 2.303\ A+2\{(\ln(1-R)\}/d \text{ ----- } (1)$$

Where d is the thickness of the sample, and the reflectance R was calculated using the equation [3]:

$T= (1-R)^2 \exp(-A)$ ------------------(2)

The relation between optical dielectric constant, ε`, and the square of the wavelength λ^2 is given by [3]:

$\varepsilon` = n^2 = \{(1+\sqrt{R})/(1-\sqrt{R})\}^2$ --------(3)

$\varepsilon` = \varepsilon`_\infty - \{(e^2N\lambda^2)/(\pi m^*C^2)\}$----(4)

Where $\varepsilon`_\infty$ is the dielectric constant at infinite high frequency, n is the refractive index, e is the electronic charge, C is the velocity of light and N/m^* is the ratio of carrier concentration to the effective mass.

Results and discussion

Figure 2 shows the plots $(\alpha h\upsilon)^{1/2}$ vs. photon energy ($h\upsilon$) for different compositions of glass samples. The most satisfactory representation is obtained by plotting the quantity $(\alpha h\upsilon)^{1/2}$ as a function of $h\upsilon$ (take r =2, is a number depending on the nature of the interband electronic transitions), which given by this equation [10]:

$\alpha h\upsilon = B(h\upsilon - E_{opt.})^r$ -----------(5)

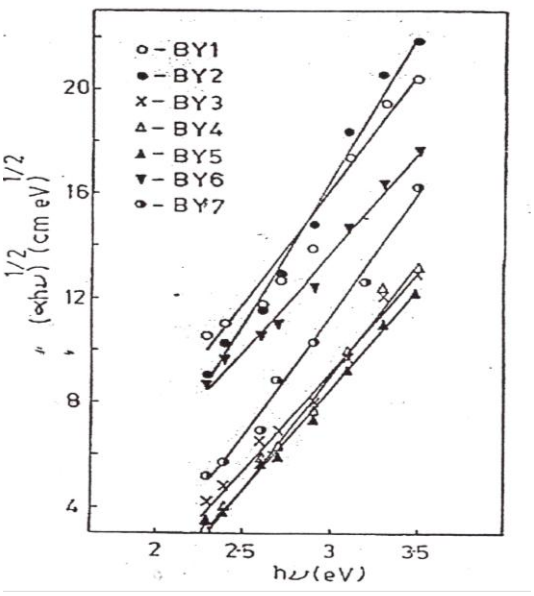

Fig. 2: $(\alpha h\upsilon)^{1/2}$ vs. hυ of glass samples.

The observed behavior suggests forbidden indirect transition for some glassy and amorphous materials. The values of optical energy gap, $E_{opt.}$, obtained from the extrapolation of the linear region and constant, B, from the slopes of the derived curves are shown in table 1.

The dielectric constant ε` vs. $\lambda^2$ plots shown in figure 3 are linear, verifying equation (4). Values of $\varepsilon`_\infty$ and N/m^* is determined from the extrapolation of these plots at $\lambda^2 = 0$ and the values of the ratio of carrier concentration to effective mass calculated by using equation (4) are listed in table 1 as a function of glass composition. The dependence of refractive index and dielectric constant on composition of glasses is rather non-linear and is observed to be similar to other amorphous materials [9]. The values of refractive index, n, are calculated from dielectric constant, ε`, using equation (3), for all the wavelength of λ^2. These values are found to be more or less the same through the wavelength range 350-800 nm. Therefore, average values of, n, are reported in this wavelength range. The average value of, n, shows dependence on PbO composition.

The variation of, E_e, the width of the tail of localized states (Urbach energy) in the normally forbidden gap against PbO (mol %) is shown in figure 4. The optical energy gap, $E_{opt.}$, is found to be minimum for the glass sample having 47.5 mol% of PbO and E_e for 45 and 47.5 mol% of PbO. The decreasing trend of the band tailing energy suggests the presence of sharp localized states in the band gap. The ratio of carrier concentration to the effective mass, (N/m^*), has been calculated from the slope of the plot ε` vs. λ^2 (figure 3). The value of N/m^* for different glass samples (table 1) are found to be of the order of $10^{21} cm^{-3}$ which are in agreement with the reported values for oxide glasses and calculated by other methods [11]

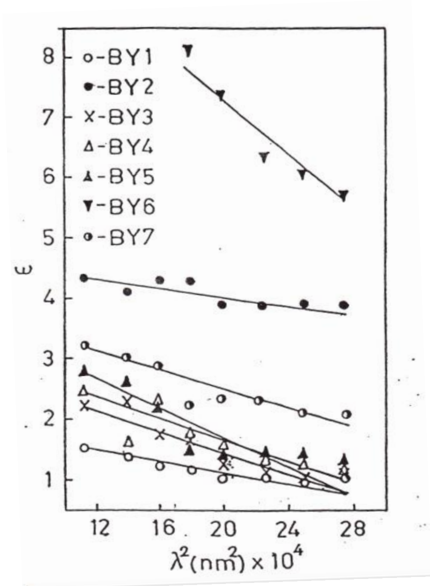

Fig. 3: Dielectric constant vs. λ^2.

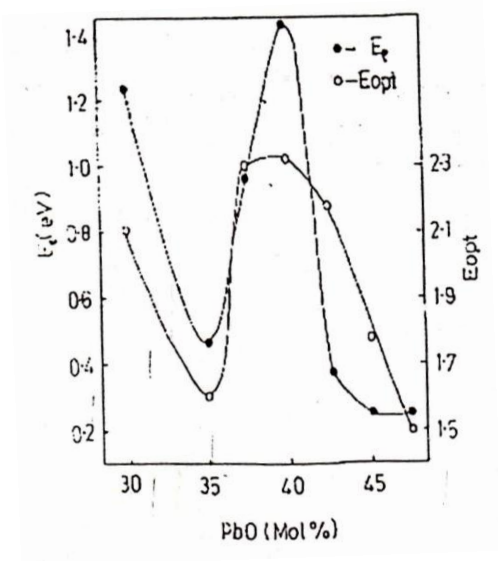

Fig. 4: Optical energy gap, $E_{opt.}$, and band tailing energy, E_e, vs. composition (PbO mol%).

Table 1.The ratio of glass composition and optical measurements.

$N/m^* \times 10^{21}$ cm^{-3}	Constant B ($cm^{-1}eV^{1/2}$)	Refractive index (n)	$\varepsilon`_\infty$	E_e (eV)	$E_{opt.}$ (eV)	Glass Composition (mol %)			Sample no.
						Bi_2O_3	CuO	PbO	
0.64	80.00	1.30	2.15	0.25	1.50	50	2.5	47.5	BY1
0.51	123.00	2.66	4.80	0.25	1.78	50	5.0	45.0	BY2
1.22	73.00	1.39	3.25	0.37	2.18	50	7.5	42.5	BY3
1.19	87.46	1.46	3.50	1.44	2.32	50	10.0	40.0	BY4
1.63	87.89	1.53	4.25	0.95	2.30	50	12.0	37.5	BY5
2.67	56.25	4.03	9.60	0.46	1.60	50	15.0	35.0	BY6
1.06	88.79	1.94	4.15	1.24	2.10	50	20.0	30.0	BY7

PbO consider from modifying lattice glass which consist randomly in the lattice and near from nonbridging ions for glass farmer, also PbO ions can enter instead of some positive ions for glass farmer [12]. So the difference of PbO behavior in the lattice of glass leads to non-linear behavior of optical constants.

Conclusions:

The optical energy gap ($E_{opt.}$) and Urbach energy (E_e) is found to be compositionally dependent on PbO and CuO. The refractive index (n), calculated in the range 350-800 nm, is found to increase with increasing CuO content except for the glass composition, 5 and 15 mol% of CuO. Non-linear behavior is observed in the measure of Urbach energy (E_e) and optical gap ($E_{opt.}$). The straight line behavior in figure 2 suggests forbidden indirect transition.

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