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Band gap studies on *Cu*-doped borate-based semiconducting glassy thin films

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In this paper, optical properties of $B_2O_3.Na_2O.MgO.V_2O_5$(*:Cu*) semiconducting glassy thin films (GTFs) were reported. The glassy thin films are produced with argon gas plasma under vacuum with RF sputtering technique. Obtained glassy thin films were observed to have amorphous structure as a result of XRD analysis. The fundamental absorption edge for the present glasses has been analyzed using the theory proposed by Davis and Mott. It has been observed that the fundamental absorption edge and cut-off wavelength shift towards red with the increase in V_2O_5 content.

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1. Introduction

Semiconducting glasses can be generally divided into two groups, chalcogenide glasses and oxide glasses containing transition metal ions [1]. Oxide glasses containing transition metals such as vanadium, copper, etc. exhibit semiconducting properties [2-8]. These glasses are potential candidates for electrical memory and optical switching devices [9-11], cathode materials for making solid devices and optical fiber [12-14]. Very few studies have been carried out on glasses containing both B_2O_3 and V_2O_5 [15]. Glasses containing high concentration of transition metal ions are electronic conductors [16-18]. This classifies them as a form of amorphous semiconductors.

In this study, optical properties of semiconducting glassy thin films prepared from borate-based glasses, that have not been comprehensively investigated are focused on, and the new results are reported.

2. Experimental

Glass samples of compositions, as presented in Table 1, were prepared from reagent grade chemicals. Appropriate amounts of these chemicals were thoroughly mixed. The mixtures were then melted in a platinum crucible placed in an electrical furnace at 1400 ^oC for one hour. The melts were occasionally stirred for homogenization and were finally poured into a graphite mould to yield a cylindrical shape. The samples kept in 350 ^oC for an hour were left to cool at room temperature.

Glassy thin films were formed by using these glass samples with RF sputtering technique in 100% Argon environment. The thicknesses of the glassy thin films, produced under 4.10^2 Torr pressure in approximately 150 minutes were about 400 nm. X-ray diffraction (XRD) patterns of the glassy thin film samples were recorded with an X-ray diffractometer (Shimadzu XRD-6000). The optical absorption and transmission spectra of the glassy thin films were recorded in the wavelength range of 300-1200 nm at room temperature using UV-vis spectrophotometer (Hitachi 150-20).

Table 1. Structures of glassy thin film samples.

Code	Glassy thin film structure
GTF1	*80* B_2O_3+*15* Na_2O+*4* MgO+*1* V_2O_5 : 0,5 Cu
GTF2	*80* B_2O_3+*15* Na_2O+*4,5* MgO+*0,5* V_2O_5 : 0,5 Cu

3. Results and discussion

3.1. X-ray diffraction spectra

X-ray diffraction of each glassy thin film was examined with the help of X-ray diffraction patterns and information related to the structures of these films was obtained. Fig. 1 presents the X-ray diffraction patterns of the glassy thin films. Diffraction patterns of the glassy thin films do not demonstrate any detectable peak. Both of the patterns indicate that samples have amorphous, non-crystalline structures. Two humps at $2\theta=25^o$ and $2\theta=45^o$ were also observed in previous studies of borate glass samples [19].

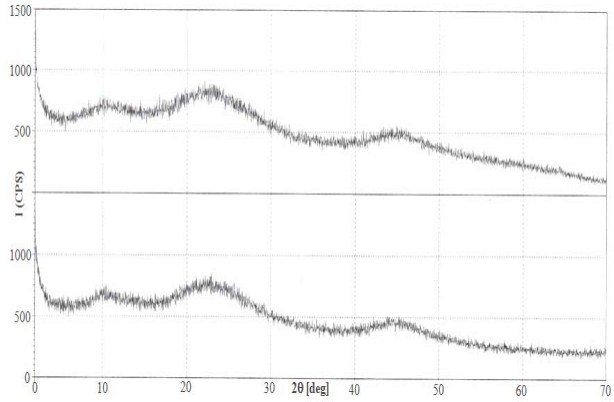

Fig. 1. XRD patterns of glassy thin film samples.

3.2. Optical absorption spectra

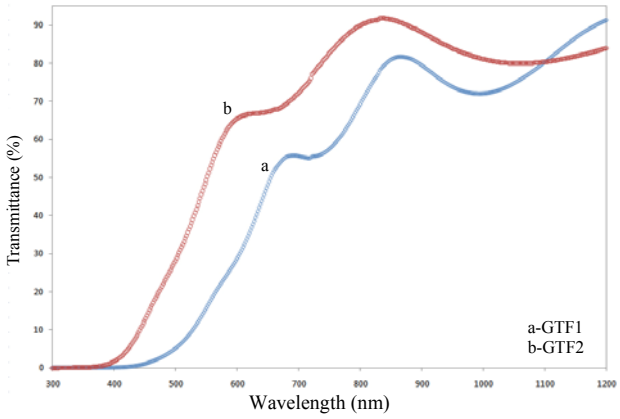

Fig. 2. Transmittance spectra of glassy thin film samples.

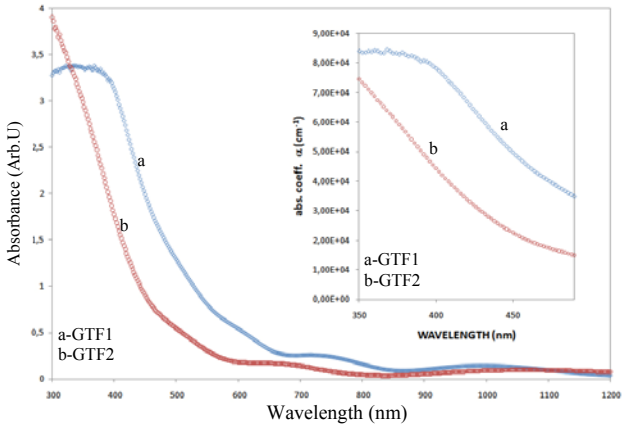

Fig. 3. Absorbance spectra of glassy thin film samples.

The transmission, the absorption and absorption coefficient spectra of both samples are shown in Figs. 2 and 3, respectively. The absorption coefficient, α, near the edge of each spectrum was calculated using the relation [20]

$$\alpha(\nu) = \left(\frac{1}{t}\right) \ln\left(\frac{I_0}{I_t}\right), \quad (1)$$

where t is the thickness of the sample, and I_0 and I_t are, the intensities of the incident and transmitted radiations, respectively. For amorphous materials, the optical absorption at a higher value of $\alpha(\nu)$ ($\geq 10^4 cm^{-1}$) above the exponential tail follows a power law given by Davis and Mott which in the most general form is given by [21]

$$\alpha h\nu = [B(h\nu - E_g)]^r, \quad (2)$$

where r is the index which can have different values; 2, 3, 1/2 and 1/3 corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. B is a constant called band tailing parameter, E_g is the optical band gap energy, and $h\nu$ is the incident photon energy.

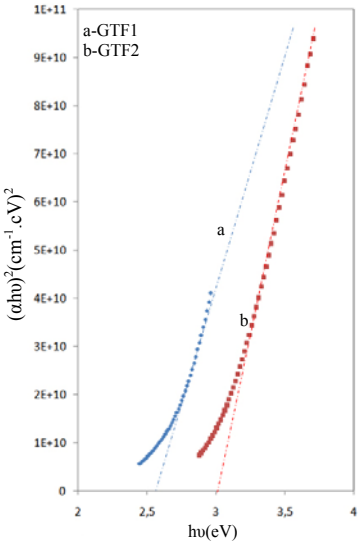

Fig. 4(a). Band gaps for direct transitions of glassy thin film samples.

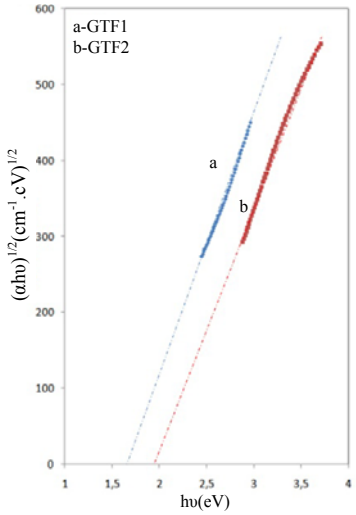

Fig. 4(b). Band gaps for indirect transitions of glassy thin film samples.

In various glass systems, Eq. (2) depicts a straight line for $r = 2$ (Fig. 4(b)). Figs. 4(a) and (b) represents the Tauc's plot $\{(\alpha h\nu)^2 \text{ vs. } h\nu\}$ and $\{(\alpha h\nu)^{1/2} \text{ vs. } h\nu\}$, respectively, for glassy thin film samples. Optical band gaps for direct and indirect transitions obtained according to the linear regions of the curves in Fig. 3 are seen in Table 2. Optical band gaps for direct transitions of the samples are 2.6 eV, 3.0 eV and 1.7 eV, 1.95 eV for indirect transitions. In another similar study of ours, optical band gaps was found to be 2,963-3.228 eV and 2.592-2.807 eV for direct transmissions and indirect transmission, respectively when the samples were in the form of bulk glass. [22].

Table 2. Optical band gaps of glassy thin films.

Code	E_g(direct) (eV)	E_g(indirect) (eV)
GTF1	2,6	1,7
GTF2	3,0	1,95

4. Conclusions

GTF1 and GTF2 glassy thin films are observed to be far from crystalline structure. This situation is consistent with the literature results of borate based bulk glasses. When transmission and absorption spectra of both samples are examined, fluctuations in the high transmission regions, which are the characteristics of thin film characteristics, were observed. However, these fluctuations are not characteristic peaks of vanadium doped glasses which can be found in the literature [23]. While the increase in V_2O_5 ratio carries the transmission margin to the long wavelength, it also narrows the optical band gap as demonstrated by the obtained measurements and performed calculation. While optical band gaps for the direct transitions and optical band gaps for the indirect transitions of GTF1 sample having 1% vanadium ratio were found to be 2.6 eV and 1.7 eV, respectively, it was calculated to be 3.00 eV and 1.95 eV respectively for GTF2 sample having a vanadium ratio of 0.5%. As a result, both of the samples demonstrate the characteristics of an amorphous semiconductor. Our studies on different doping ratios and optical and magnetic works on glassy thin films of various compositions continue.

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