

Effect of Ag⁺ Ions on the Properties of Some Calcium Niobium Bismuth Borate Glasses

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Abstract: Silver oxide was introduced, by weight addition, to the chemical mixtures of some calcium bismuth niobium Borate glasses. The following formula was considered for preparation series of five samples (100-x) wt% [0.6 mol B₂O₃ – 0.2 mol CaO – 1.75 mol Bi₂O₃ – 0.25 mol Nb₂O₅] – x wt% Ag₂O, where x = 0, 1, 2, 3 and 4 wt%. For characterization process some spectra like XRD, DSC and UV-Vis have been used. Where both X-ray and DSC measurements indicated the amorphous state formation, for all compositions. UV-vis spectra exhibited two indirect ($\gamma=1/2$) and direct ($\gamma=2$) electronic transitions, for each sample. For direct transitions, the optical band gap was perturbed by the addition of Ag⁺ cations.

Keyword: XRD, DSC, UV-Vis., Borate Glass, Optical Properties

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I. Introduction

Glassy fast ion conductors are characterized by a selective ion mobility, which takes place in an otherwise frozen amorphous matrix. There is a very large decoupling of the dynamical timescale for the ion motion from that for the structural relaxation of the host network forming glass [1]. As well as the scientific interest in understanding the origin of the remarkable conductivity of these materials there is now a wide interest in studying fast ionic conductors for possible application to batteries, sensors, and fuel-cell technology. Borate glasses belong to valuable and interesting systems which find extensive applications for optical, thermal, electrical and biological purposes [2–3]. Silver ion conductive super ionic glasses have been studied extensively among many glass families. [4-5] Among these glasses, silver iodide–silver meta borate glasses which are characterized by the relatively simple glass network structure have a high room temperature ionic conductivity with Ag⁺ as the mobile ions [6-7]. This simple work aims to review the effect of addition of Ag₂O on the optical and thermal properties of some calcium bismuth niobium Borate glasses.

II. Experimental Work

For each sample, the chemical components were mixed according to their ratio and then they were grinded well. All samples putted at the same time within the melting chamber of an electric muffle at 1000 °C, for more than 90 min. and then quenched onto in air at room temperature. The formation of glasses was checked by X-ray diffraction (XRD) technique using X-ray powder diffractometer (Rigaku Miniflex, Japan, Cu K α radiation). Thermal measurements were carried out using Shimadzu 50-DSC Analyzer with heating rate 20 °C/min in the temperature ranged from 30 to 820 °C. Optical UV–vis. absorption measurements were obtained by Genway 6405-UV-Vis. Spectrophotometer, in the range from 200 to 2500 nm.

III. Results And Dissection:

3.1 XRD analysis

XRD is a nondestructive technique to identify crystalline phases, determination of the structural properties and order-disorder transformation, in addition to many useful applications. So XRD charts were obtained for all samples, to check if their internal structures are of long or short range orders. In other word, to monitor the internal structure of each sample. Figure 1 exhibits XRD pattern for the sample contains 3 wt% of Ag₂O for representative, where all sample showed the same behavior. The careful examination of such figure lead to observation of two broad peaks have different intensities. By reviewing of X-ray databases it can be stated that the high intense peak centered approximately at $2\theta = 27^\circ$ may due to XRD by some Bi³⁺ cations, while the other peak at $2\theta = 48^\circ$ may due to XRD by Ag⁺. This result may give an impression of the existence of some/few crystallization agents inside the structure, these agents may enclosed within the interstitial vacancies, the thing which may be confirmed or not by DSC measurements. On the other side, the absence of

any sharp peak in addition to the broad of the observed peaks may refer to the short range order nature of the internal structure of the studied samples.

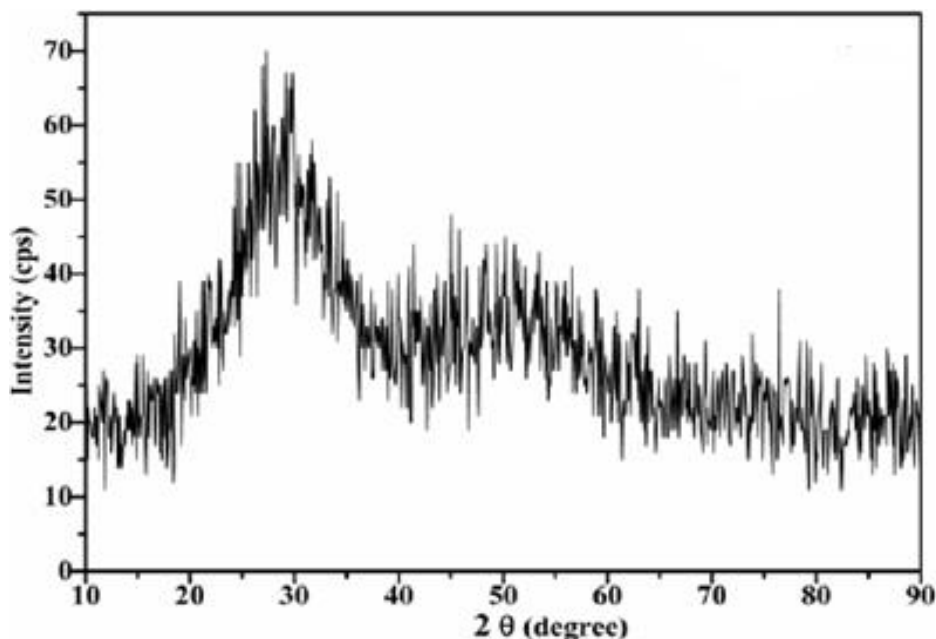


Figure (1): XRD for the sample contains of 3 wt% of Ag

3.2 DSC Thermal analysis

Differential scanning calorimetric DSC have been used to evaluate the stability level of the studied glass samples. Where some thermal parameters such as the glass transition temperature T_g and crystallization temperature T_c were obtained during heating Process. Figure 2 is a representative figure shows the DSC chart of the sample contains 3 wt% of Ag_2O . The chart in such figure appear the presence of an endothermic and exothermic peaks. Where the endothermic peaks refers to sort of heat absorption due to glass transition and/or melting, while the exothermic peaks indicates to some sort of heat release due to crystallization [8]. By checking figure 2 carefully, one glass transition temperature can be detected in addition to two crystallization peaks, this result was observed in all studied samples. The presence of two crystallization peaks is a strong indication that there are two different phases appeared during the crystallization process, this means that there are two crystallization agents [9-10-11]. Therefore, by correlate this result with XRD it can be stated that both Bi^{3+} and Ag^+ act as nucleating agents. The appearance of one glass transition temperature, for each sample, May indicates good homogeneity glass network formation [12]. Table (1) shows the glass transition temperatures for all samples, it is clear that T_g value increase with increasing Ag_2O content, Such behavior may means that the thermal stability of the studied glasses increase as Ag_2O content increased [13-14].

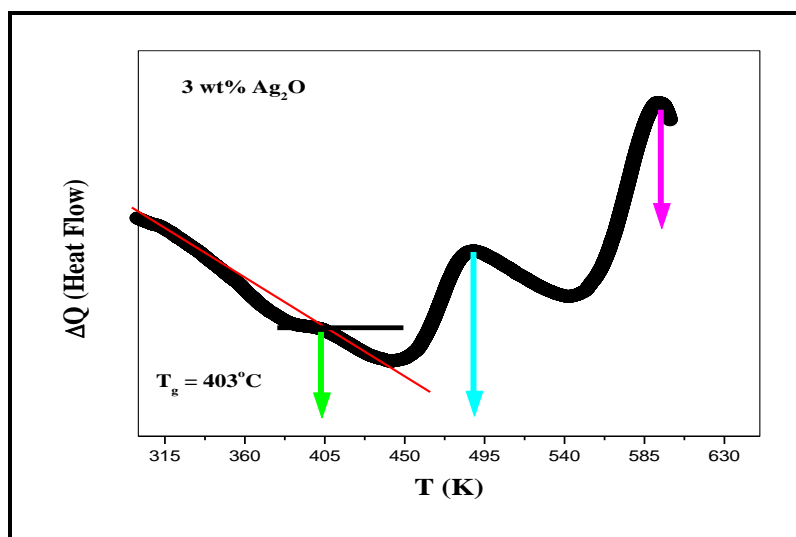


Figure (2): DSC charts for the sample contain 3 wt% of Ag_2O

Table (1): Glass transition temp. T_g, optical band gap E_{opt} and refractive index n

Ag ₂ O wt%	T _g C ⁰	E _{opt}		n
		Direct transition	Indirect transition	
0	301	1.26	0.125	2.94
1	304	1.355	0.708	3.43
2	305	1.358	0.711	3.43
3	404	1.375	0.721	3.42
4	428	1.396	0.726	3.41

3.3 UV-vis. spectroscopy

The absorption spectra of all prepared glasses were carried out as a function of wave length in the range from 190 to 1100 nm. Then the optical absorption coefficient α has been calculated using the following formula [15];

$$\alpha = \frac{A}{t}$$

Where A is the absorbance while t is thickness of the sample. Where the optical energy band gap E_{opt} was obtained from the intersection between Ln(α) ~ Ln(hc/ λ) curve tangent with x-axis. Figure 3 has a representative curve describes Ln(α) versus Ln(hc/ λ) for the sample contains 3 wt% of Ag₂O, Where two tangents were observed, all samples showed same behavior. The slopes of the two tangent (γ values) were found to be about 1/2 (red side) and 2 (blue side) corresponding to both the indirect and the direct transitions, respectively. The optical band gap values were detected then recorded in table (1). The value of the optical band gap showed slightly increase as Ag₂O content increased. E_{opt} values were used to calculate refractive index n, by considering the following relations [16-17-18];

$$n = 0.73 \text{ Ln } [0.102\chi] + 0.5511 \quad \& \quad \chi = 0.2688 E_{\text{opt}}$$

Where n and χ are the refractive index and the optical electronegativity, respectively. The values n that recorded in table (1), tell that the refractive index increase by increasing of Ag₂O content. The large values of the refractive index may due to the nonlinear optical properties of Bi₂O₃ glasses.

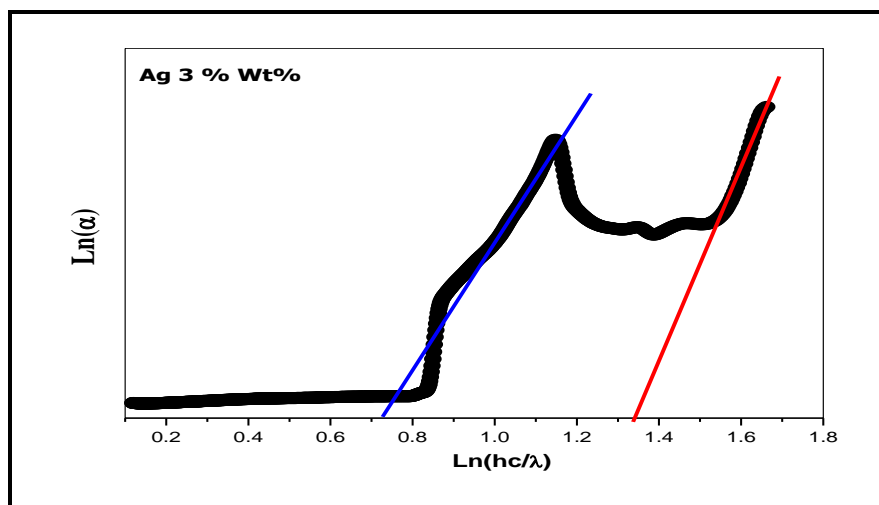


Figure (3): UV-vis. for the sample of 3 wt% Ag₂O

IV. Conclusion

The addition of Ag₂O to calcium bismuth niobium Borate glasses of the following chemical composition [0.6 mol B₂O₃ – 0.2 mol CaO – 1.75 mol Bi₂O₃ – 0.25 mol Nb₂O₅] causes an increase in both refractive index values and the glass matrix stability.

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