

OPTICAL AND STRUCTURAL PROPERTIES OF PbO-B₂O₃-TeO₂ GLASSES

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ABSTRACT

Optical and structural properties of [TeO₂]_y [(B₂O₃)_{1-x} (PbO)_x]_{1-y} glasses of different composition have been studied using UV-Vis, Raman and XRD spectroscopic techniques. The UV optical absorption was recorded at room temperature in the wavelength range of 200 to 800 nm, while the XRD patterns of as-received samples was verified at 2θ = (5 - 80 deg). Eventually, values of the optical energy gap are calculated and found to be dependent on the glass composition. Furthermore, the XRD diffractograms exhibit a wide smooth halo, which is a fingerprint of amorphous materials and some strong narrow diffraction lines corresponding to crystalline of α-TeO₂. The Raman spectroscopy measurement shows strong existence of Pb group, O-B-O bending and O-Te-O stretching in lattice vibrations.

INTRODUCTION

Glasses have some unique properties such as hardness and transparency at room temperature along with sufficient strength and excellent corrosion resistance. Due to potential application in various engineering and technological fields, the study of the properties of glasses is of great significance. Glassy materials have acknowledged advantages like physical isotropy, the absence of grain boundaries, continuously variable composition and good workability [1]. Tellurite glasses are very promising materials for laser and non-linear application in optics due to some of their important characteristic features such as high refractive index, low phonon maxima and low melting temperature [2]. TeO₂ is known as a conditional glass former, that is it needs a modifier in order to form the glassy state easily. The formation of glass on two glass formers is of both scientific and practical interest; where the structural network will be perturbed. This may lead to the formation of new structural units [3]. The objective of the present work is to study the stability and the optical band gap of the tellurite-borate glass system. To achieve this, a systematic study has been performed to understand the variation of optical band gap as a function TeO₂ composition in borotellurite glasses in addition to density measurement.

Generally, non-silicate glasses raised a lot of significant commercial interest due to their electrical and electronic properties [4, 5], and their transmission of infrared light [6]. Addition of boric oxide, B_2O_3 , which forms a network structure related to the silicates, creates a glass with higher melting point and greater ability to withstand temperature changes. High-density glasses, doped with a rare-earth scintillator, are actively sought for use as detector material in high-energy physics [7]. Radioactive waste disposal, using vitreous solids for containment, is another important application. Hence, radiation damage caused by electrons, alpha particles and gamma rays has been thoroughly investigated [8–10]. The structural and physical properties of PbO glasses are well described by Worrel and Henshell [11]. In previous work, researchers have studied borate glasses containing heavy-metal oxides and shown that they have potential applications in radiation shielding [12–14]. The mass attenuation coefficient, the effective atomic number and the electron density are basic quantities for determining the penetration of X-ray and gamma-ray photons in matter. Tabulations of X-ray mass attenuation coefficients and interaction cross-sections have been published e.g. by Hubbell and Seltzer for the elements and a number of substances of dosimetric and radiological interest, among them also some glasses.

MATERIALS AND METHODS

Preparation of Samples

The binary $(TeO_2)_y [(PbO)_x (B_2O_3)_{1-x}]_{1-y}$ glasses were prepared by mixing together specific weights of Tellurium Dioxide - TeO_2 (Alfa Aesar 99.99%), Lead oxide, Litharge - PbO (99%) and boron oxide - B_2O_3 (Alfa Aesar, 97.5%). The mol fraction $x = 0.00, 0.10, 0.20, 0.30, 0.40, 0.50$ and $y = 0.7$. Appropriate amounts of TeO_2 , PbO and B_2O_3 were weighed by using an electronic balance having an accuracy of 0.0001 g. The chemicals were then thoroughly mixed in an Agate pestle mortar for half an hour. Appropriate amounts of powder chemical were weighed and poured into a crucible. The crucible was covered with a lid and then put inside an electric furnace set at $320^\circ C - 340^\circ C$. The crucible was then transferred to a second furnace at $950^\circ C$ for 120 minutes. The melting process takes a slightly longer time in order to produce a good molten form. Longer heating time will help to reduce the air bubbles that might be produce or captured. The melt was then poured in a stainless steel cylindrical shaped split mould which had been preheated at $320^\circ C - 340^\circ C$. The sample was later annealed at $320^\circ C - 340^\circ C$ for 2 hours. The prepared samples were then cut into required dimension for several measurements using Buhler ISOMET diamond cutter.

Measurements of X-ray Diffraction

The samples were prepared in bulk form for X-ray diffraction measurement, and the data were analyzed using X'pert Pro Panalytical.

Measurements of UV-Visible

Optical absorption measurements in the wavelength range of 190 to 800 nm were performed at room temperature using a Camspec M350 Double Beam UV-Visible Spectrophotometer.

Measurements of Raman Shift

Raman spectra were measured using a Raman spectrometer (RSI 2001 B, Raman system, INC) equipped with a 532 nm solid-state diode green laser as shown in. Grams/32, version 6 software was used to analyse the spectra. All spectra were corrected for base line; smoothed and Fourier Transformed (FT).

RESULTS AND DISCUSSION

The X-ray diffraction experiment in yielded a few distinguishable intensity peaks (Figure 1), indicating that the samples were essentially amorphous but contains a small amount of crystalline structure. Eventually, the optical absorption coefficient $\alpha(\lambda)$ was calculated from the absorbance A , using the following equation:

$$\alpha(\lambda) = 2.303(A/d) \quad (1)$$

Where d is the thickness of the samples. Density measurements were made at room temperature by Archimedes method, involving weighing in air and in acetone as the buoyancy liquid.

The optical absorption spectra of $\text{PbO-B}_2\text{O}_3\text{-TeO}_2$ are shown in Figure 2. Absorption of ultraviolet and visible light by a glass sample excites the outer electrons of the samples to higher energy levels. The amount of energy required for this excitation is equal to the difference in energy between the two electron energy bands. These energy values are quantized for all species in the sample and correspond to the light angular frequencies ω as given by the expression

$$E = \hbar\omega \quad (2)$$

where \hbar is Planck's constant divided by 2π . This method does not take into account the energy tail and is not appropriate for glasses with small band gaps. Therefore, a more accurate model is used in the calculations [15]. The data for Figure 3 (a) and (b) were obtained from the relation:

$$\alpha(\omega) = \frac{\text{const}(\hbar\omega - E_{opt})^n}{\hbar\omega} \quad (3)$$

To calculate the width of the energy tail, ΔE , of the density of states, the model proposed by Urbach and Tauc is followed. According to this model, the following relation is valid:

$$\ln(\alpha) = C + \frac{\hbar\omega}{\Delta E} \quad (4)$$

where C is a constant. The reciprocal of the slope of the plot of the natural logarithm of a versus the photon energy will then yield ΔE .

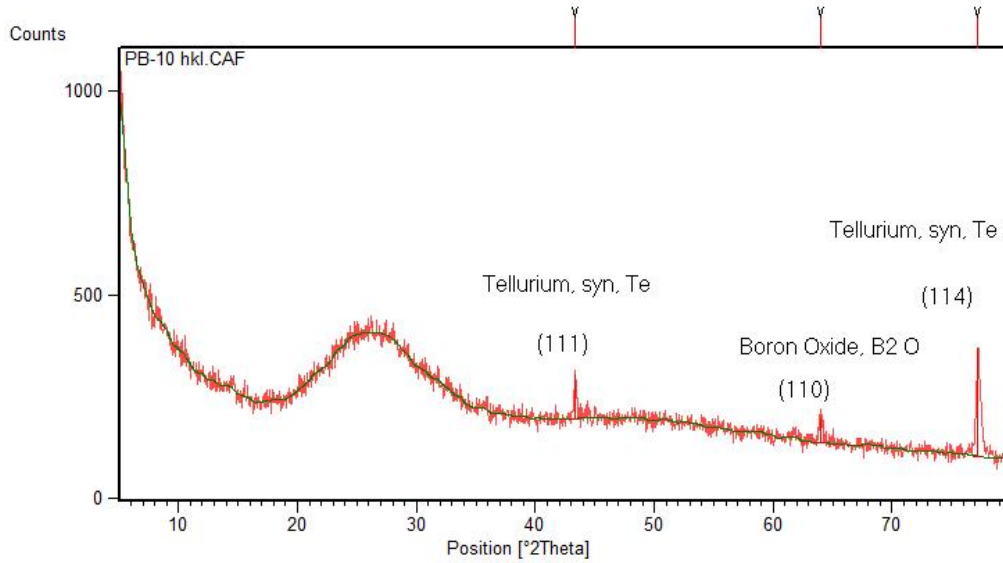


Figure 1: The X-ray diffraction pattern for $\text{PbO-B}_2\text{O}_3\text{-TeO}_2$, ($\text{Pb} = 0.1$)

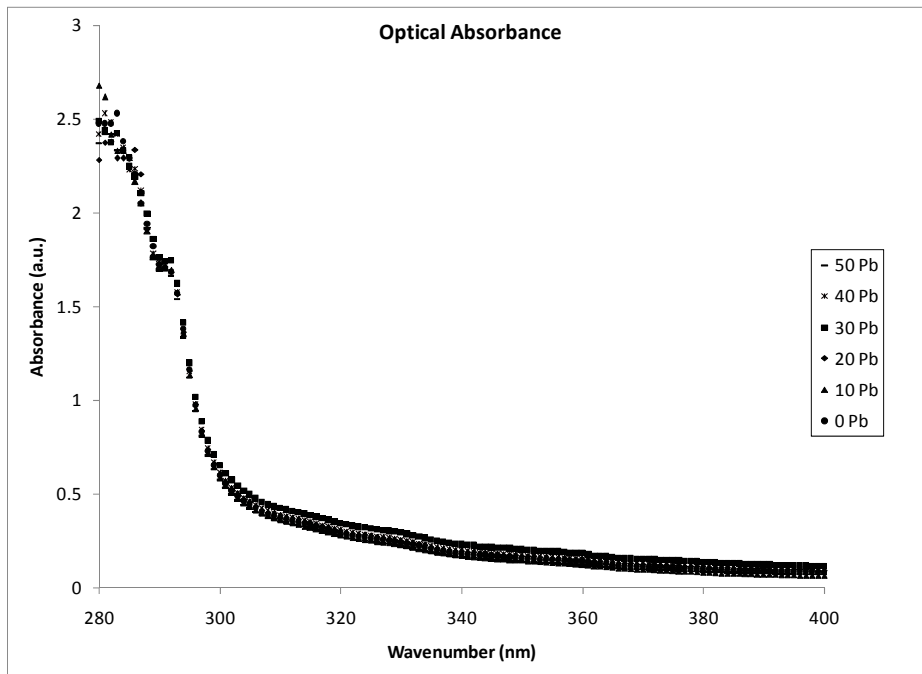
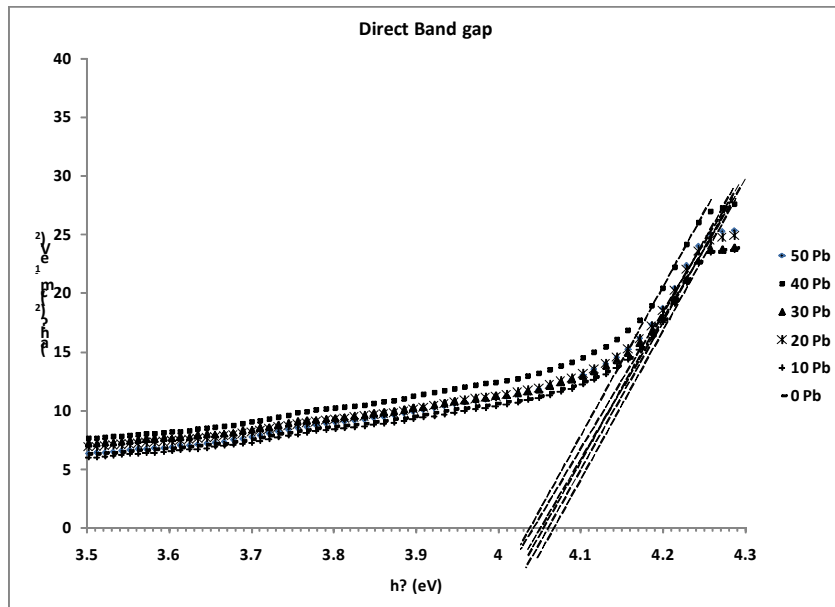
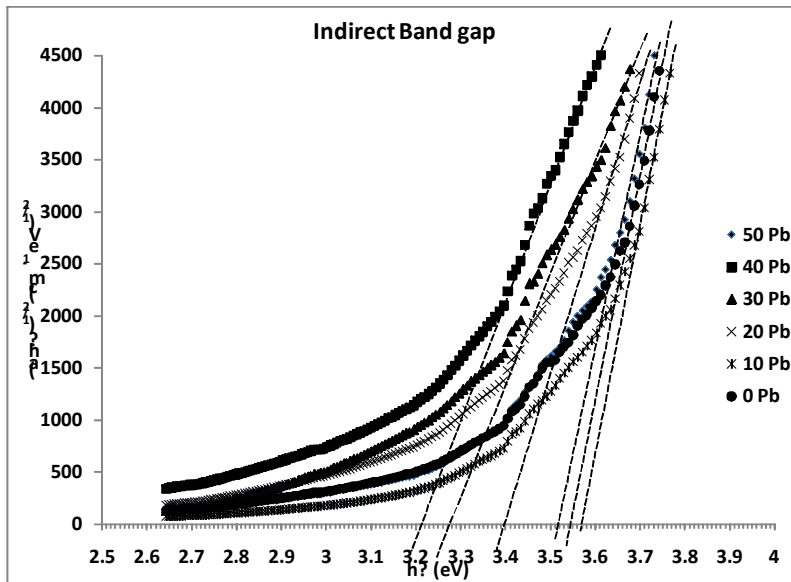


Figure 2: Optical absorbance spectra for $\text{PbO-B}_2\text{O}_3\text{-TeO}_2$ glasses



(a)



(b)

Figure 3: Plot of (a) $(\alpha h\nu)^2$ and (b) $(\alpha h\nu)^{1/2}$ against photon energy $h\nu$ for indirect band gap measurement

Table 1: Density, molar volume, direct band gap, indirect band gap, Urbach energy

Mole fraction (%)	Density (gcm ⁻³)	Molar volume (cm ³ mol ⁻¹)	Direct (eV)	Indirect (eV)	Urbach (eV)
0	4.21	31.44	4.06	3.54	0.69
0.1	4.42	30.98	4.05	3.57	0.72
0.2	4.67	30.34	4.04	3.39	0.90
0.3	4.83	30.30	4.06	3.27	0.82
0.4	5.10	29.58	4.03	3.52	0.95
0.5	5.29	29.37	4.05	3.21	0.86

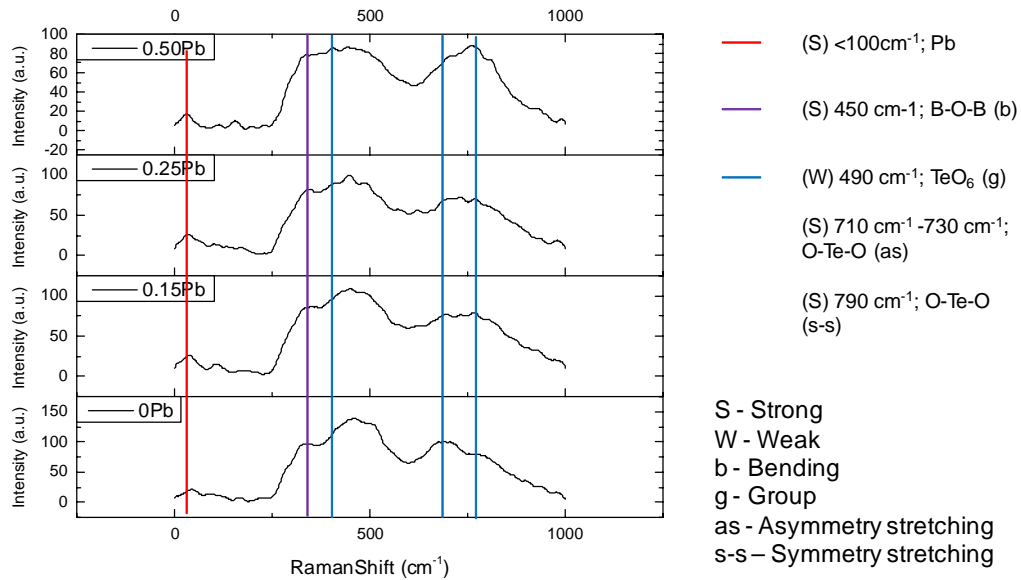


Figure 4: Raman shift spectra for PbO-B₂O₃-TeO₂ glasses at various compositions.

The intensity-normalized Raman spectra of PbO-B₂O₃-TeO₂ glasses with various compositions are shown in Figure 4. It was reported that the Raman spectrum of TeO₂ glass of the frequency range from 420 to 880 cm⁻¹ can be deconvoluted into five peaks at 450, 611, 659, 716 and 773 cm⁻¹ [16]. In the glasses containing B₂O₃, seven peaks are assigned at about 450, 615, 660, 730, 780, 850 and 930 cm⁻¹.

CONCLUSION

It can be concluded that the values of the optical energy gap are calculated and found to be dependent on the glass composition. The decrease of the band gap can be related to the increase of PbO content and to the change in the structure of the glass matrix. It can be attributed to the increasing number of non-bridging oxygen atoms and structural arrangement after breaking the bonds between boron, lead and oxygen atoms during the melting processes. The results attained were indirectly agreed with the publications of certain researchers on elastic properties which contain PbO [17].

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