Original Research Paper

Effect of Niobium Oxide Incorporation on Optical Properties of Sodium Bismuth Borate Glasses

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Abstract: Glasses with the chemical compositions 60% B_2O_3–20% Na_2O–(20−x) % Bi_2O_3–x% Nb_2O_5 (where, x = 0, 5, 10 and 15 mol. %), were prepared by fast quenching of their melts. Characteristics of the obtained solids were checked by XRD, FTIR and optical absorption spectroscopy. XRD data confirmed the amorphous nature of the glass samples. FTIR results revealed no changes in the ratio of the structural units BO_3:BO_4 when replacing Bi_2O_3 by Nb_2O_5. Moreover, both Bi^{3+} and Nb^{5+} cations occupied octahedral coordination states and both acted as glass network modifiers. Optical studies affirmed that the lowest value of both direct and indirect optical band gaps was obtained in samples with equal concentration of Nb_2O_5 and Bi_2O_3. All optical absorption bands were elucidated in terms of the terminal oxygen atoms around Nb^{5+} and/or Bi^{3+} cations. The optical nonlinearity of the glass samples was assessed in terms of absorption coefficient and the value of the optical band gap.

Keywords: Sodium Bismuth Niobium Borate Glass, Absorption Coefficient, Direct and Indirect Optical Band Gaps, Optical Nonlinearity

Introduction

Nonlinear optical behavior of amorphous materials has been extensively studied by several researchers because of its promising usage in photonic devices applications (Boyd, 2003; Sutherland, 2003). In this regard, bismuth borate glasses have caught great attention due to their facile and low cost synthesis, enhanced mechanical and chemical stability, in addition to the large range of nonlinear refractive index and nonlinear absorption coefficient (Farouk *et al*., 2013; Shanmugavelu *et al*., 2013). Furthermore, borate glasses doped with heavy metal oxides show interesting nonlinear optical properties and have different application in microscopic lens designing (Ehrt, 2000). Bismuth oxide doesn't play the role of a glass former; it is rather a good modifier that enhances optical, thermal and structural characteristics of the glass (Oo *et al*., 2012). It also increases the ratio of the non-bridging oxygen (NBO) and therefore enhances the glass absorbability (Chen *et al*., 2008; Pal Singh *et al*., 2012). The decrease of the number of NBO is associated to an increase in the optical band gap (Novatski *et al*., 2008). Bismuth is likely occupying octahedral coordination in the Bi_2O_3 oxide inside the glass network, which contributes in the existence of NBO (Rajendran *et al*., 2003). The presence of transition

metal niobium oxide Nb_2O_5 in glasses elevates chemical stability and improves the mechanical properties (Sene *et al*., 2004). It was reported that introducing niobium oxide into the glass matrix increases the activation energy and the glass transition temperature T_g (Sene *et al*., 2004). Optical properties such as optical band gap and optical basicity were strongly improved when Nb_2O_5 was introduced into the glass system containing Bi_2O_3 (Sanghi *et al*., 2010; Swapna *et al*., 2017). The largest value of the non-linear refractive index was reported to glasses containing empty d shell transition metal ions such as Nb^{5+} (Cardinal *et al*., 1997). Furthermore, by incorporating Nb_2O_5 in the glass network, the Nb^{5+} cation acts as a network former and improves the third order nonlinear optical susceptibility (Suhara *et al*., 2012). The usual coordination of Nb^{5+} cation in oxide glasses is octahedral. Therefore, niobium atoms are located in octahedral sites. The non-linear refractive index was reported to increase proportionally to the concentration of Nb^{5+} cation in the glass system (Couzi *et al*., 1996). It was assumed that the polarization of the niobium oxygen bond is the main contribution to the optical non-linearity (Cardinal *et al*., 1997). Recalling that nonlinear optical behavior of glasses is improved by adding lone-pair holder such as Bi^{3+} or cation of empty d shell such as Nb^{5+} (Chen *et al*., 2008).

Table 1: Calculation of the field strength for each oxide in the mixture

	B_2O_2 mol. %	Na_2O mol. %	Bi_2O_3 mol. %	Nb_2O_5 mol. %
Molecular Weight	69.59	61.98	465.99	265.82
Field Strength	1.5	0.19	0.65	0.94
Role of oxide	Former	Modifier	Intermediate	
Nb Composition				
0%			20	0.00
5%	80	20	15	5.00
10%			10	10.00
15%			5	15.00

The aim of the present work is to study the optical characteristics of sodium bismuth niobium borate glasses in relation to the replacement of bismuth oxide by niobium oxide.

Experimental Work

High purity starting materials, not less than 99%, were used to prepare the suggested compositions, as indicated in Table (1). To find out the role of each oxide in the mixture, the field strength was calculated for each oxide using relation (1):

$$F_{C_aO_b} = \frac{z_c}{(r_c + r_o)^2} \qquad (1)$$

where, F is the field strength of oxide C_aO_b, Z_c and r_c are the oxidation state and covalent radius of the cation C and r_o is the covalent radius of oxygen ion (Pye, 2005; Rao, 2002; Shelby and Lopes, 2007).

Oxide precursors were weighted by 4-digits balance, mixed well together in porcelain crucibles and then melted for 2 h at 900±50°C, in an electric furnace. Melts were then solidified by rapid quenching in air onto pre-cooled copper plates. X-ray powder diffractometer (Rigaku Miniflex, Japan), with Cu Kα radiation (1.54 Å), was used for XRD analysis in order to check the formation of glasses. In order to obtain information about structural units for the studied samples, infrared spectra were recorded using Fourier Transform Infrared (FTIR) Jasco 5300 spectrometer. Parts of the solidified glass samples were powdered and diluted in dry KBr, pressed in pellets form and measured at room temperature over the range from 4000 to 400 cm^{-1}. Optical absorption spectra were recorded in the range from 200 to 2500 nm using Genway 6405 UV-VIS spectrophotometer.

Results and Discussion

XRD Data

Figure 1 shows the x-ray diffractograms of all samples, with no observed sharp peaks. Only one broad hump was observed around 2θ = 47°. Such observation refers to the amorphous nature of the prepared solids, with short ordered structure. Each sample, in the studied glasses, contains 60 mol. % of B_2O_3 which is considered as the glass former oxide with two remarkable structural units BO_3 and BO_4. In addition to 20 mol. % of both (Bi_2O_3 + Nb_2O_5), that are considered as intermediate oxides with the ability to act as glass network formers and/or glass network modifiers. From x-ray diffraction tables, the hump observed at 2θ = 47° is a characteristic of the non-crystalline Bi_2O_5 (Junjiang *et al*., 2002). This result affirms that some/all Bi_2O_3 did not participate in the glass matrix as a glass former, but rather as a network modifier.

FTIR Spectra

Figure 2 shows the FTIR spectra for all glass samples and it is clear that the spectrum of each sample can be divided into two spectral zones. The first zone shows the vibrational bands of OH– groups, in the wavenumber from 4000 to 1800 cm^{-1} (El-Maaref *et al*., 2017; Yiannopoulos *et al*., 2001). While the second zone, limited in the range from 1800 to 400 cm^{-1}, contains four broad vibrational bands centered at 1370, 980, 703 and 456 cm^{-1}. Referring to the related previous publications, all observed bands in the second zone were attributed to their structural units or bonds. Whereas, the bands centered at 1370 and 980 cm^{-1} are due to asymmetric stretching vibrations of B–O in BO_3 units (El-Maaref *et al*., 2017; Yiannopoulos *et al*., 2001) and stretching vibrations of B–O in BO_4 units, respectively (Rao *et al*., 2016). Band located around 703 cm^{-1} may be attributed to the bending vibrations of oxygen atoms in B–O–B, in BO_3 units and/or symmetric stretching of the edge-sharing oxygen atoms in Nb–O bond of in NbO_6 groups (Balachander *et al*., 2013; Fragoso *et al*., 2005). Such band may indicate that Nb^{5+} have octahedral coordination numbers, which indicates that these cations did not share in the glass network but occupy the interstitial vacancies. While 456 cm^{-1} band is due to the Bi–O valence band vibrations of BiO_6 structural units and/or the angle modification of the boron oxygen bond linkage (El-Maaref *et al*., 2017; Sutherland, 2003).

Moreover, it is clear that bands of BO_4 became higher and broader than those of BO_3 when B_2O_3 is replaced by Nb_2O_5. In other words, the relative number of compositional group BO_3 decreased while that of BO_4 increased when B_2O_3 replaced by Nb_2O_5, as seen in Fig. 3.
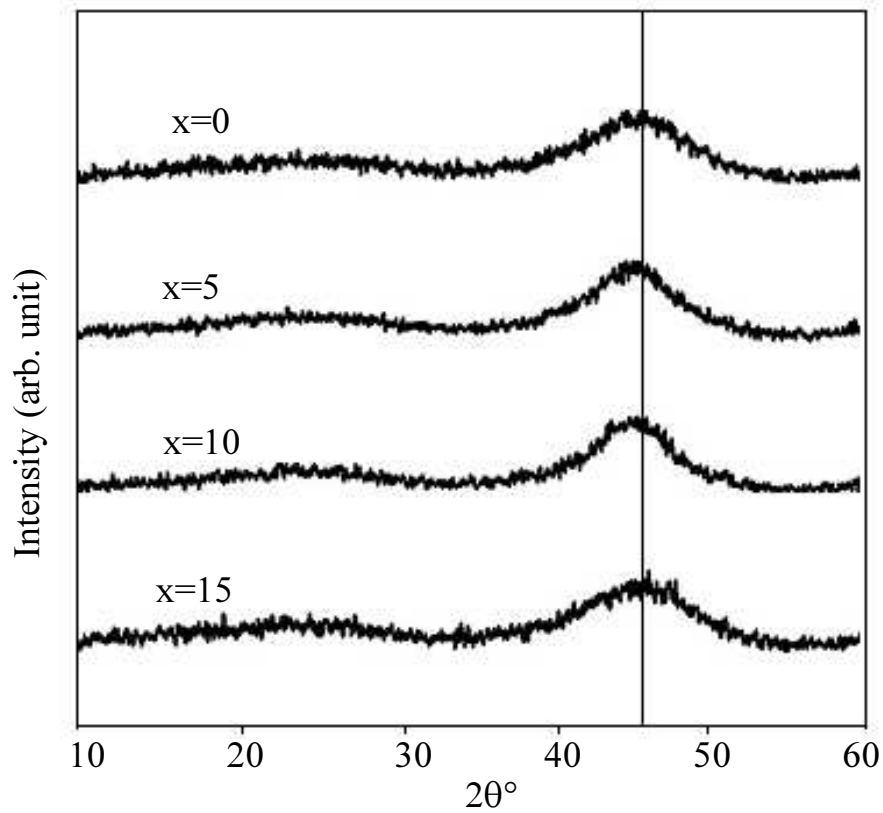
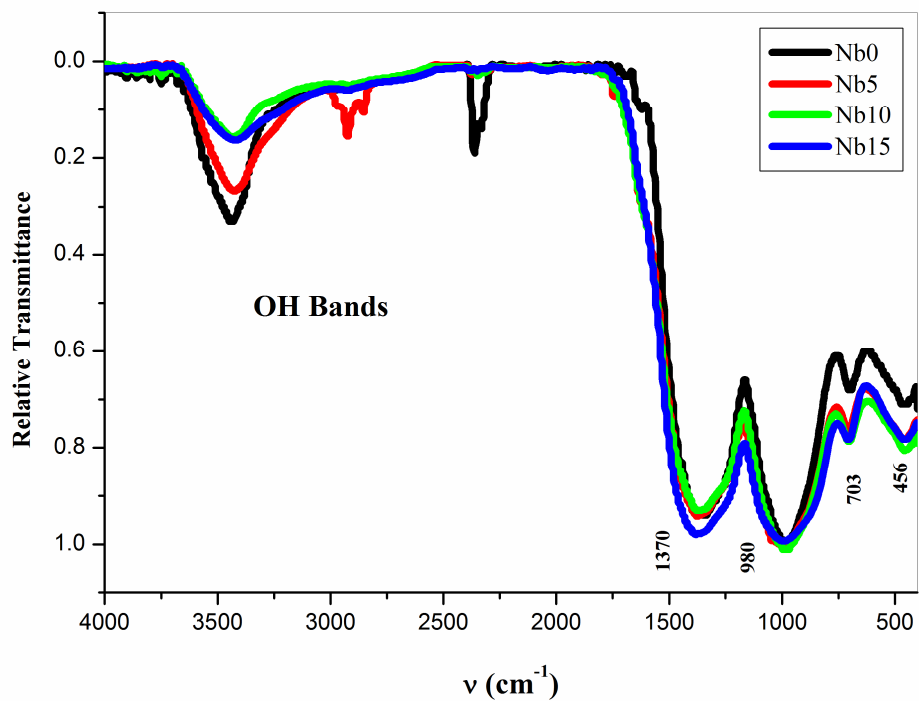**Fig. 1:** X-ray diffraction pattern for all samples

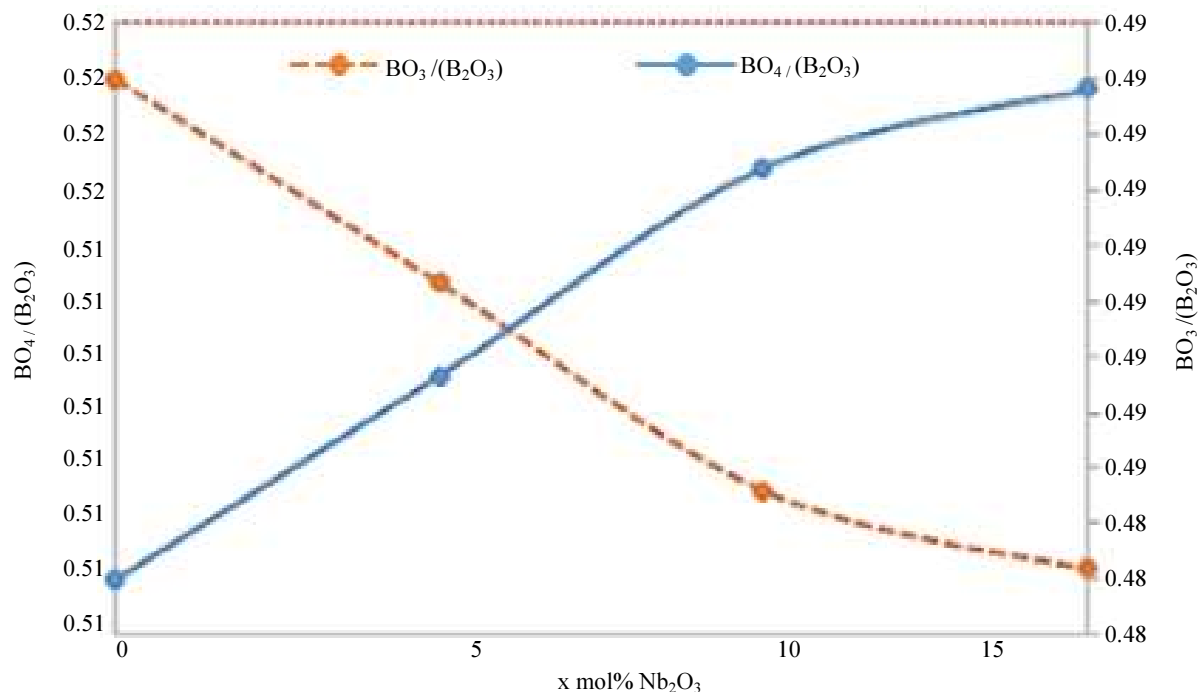**Fig. 2:** FTIR spectra for all samples, with functional groups assigned

Fig. 3: Relative number of compositional groups BO_4 and BO_3 as a function of the concentration of Nb_2O_5 in mol. %

This behavior is due to the richness of Nb_2O_5 in oxygen than B_2O_3. Therefore, it can be concluded that the increase in Nb_2O_5 concentration induces the glass matrix to be more homogenous and open structure, in agreement with the published work (Yiannopoulos *et al.*, 2001).

Optical Absorption Spectra

Figure 4 shows the relative optical absorption spectra of the studied glasses. All samples have the same cutoff wavelength (λ_{cutoff} = 443 nm), with no observed absorption peaks in UV region (200-400 nm). By careful inspection of Fig. 4, two well defined absorption bands can be observed, the first one is a broad band extended from 700 nm to 1000 nm, its center shifted from 810 to 825 nm (red shift) when Bi_2O_3 was exchanged by Nb_2O_5. The second band appeared in region from 1000 to 2500 nm and is peaked at 1745 nm. The red shift noticed from 810 nm to 825 nm may be attributed to the change in the glass optical basicity because of the variations of OH– groups, in addition to presence of niobium oxide and the consequence change in the energy levels (Duffy and Ingram, 1971; Stehle *et al.*, 1998). Also, it is clear that the increase of Nb_2O_5 content increased the intensity and broadness of the absorption peaks. Such behavior may indicate that, the content of OH– in the glass network increased by increasing Nb_2O_5, the thing which mean low density, high molar volume and good amorphous nature for the studied glass system. By surveying previous related publications, it can be stated that the observed optical absorption may be attributed to deformation in the glass networks due to the interstitial impurities in addition to the octahedral forms of both Bi^{3+} and Nb^{5+} cations (Stehle *et al.*, 1998). But, according to ligand field theory the positive transition metal ion is always attached to negatively charged ligands (Figgis, 1987), so the observed absorption may be attributed to the presence of the non-bridging oxygen (NBO) ions that surround each Nb^{5+} cation. It should take into consideration that the increase in NBO may cause the third-order susceptibility to arise and hence improves the nonlinear behavior of the glass (Almeida *et al.*, 2011). Accordingly the broadness of the absorption band may be explained as consequence of the relative increase in the number of NBO in the ligand, by replacement the poor-in-oxygen Bi_2O_3 by the rich-in-oxygen Nb_2O_5. The effect of niobium oxide arises from electronic d-d transitions and the coupling between the d-electrons of Nb^{5+} and the vibrations of the negatively charged O^{2-} in the ligands.

On the other hand, it is well known that the analysis of absorption edges gives precise information about the value of optical band gap (Hodgson, 2012; Meyer *et al.*, 1998). It is also known that the value of absorption coefficient α increase as a consequence of light absorption. This change in α is known as the fundamental absorption edge and is related to the absorbed energy by the relations given (Davis and Mott, 1970; Tauc and Menth, 1972) for direct allowed transitions by $\alpha h\upsilon \propto \left(h\upsilon - E_{opt}\right)^{\frac{1}{2}}$ and for indirect allowed transitions by $\alpha h\upsilon \propto \left(h\upsilon - E_{opt}\right)^{2}$, where $h\upsilon$ is the incident photon energy and E_{opt} is the optical energy gap.

Table 2: Values of cutoff frequency, direct band gap, and indirect band gap for the four samples

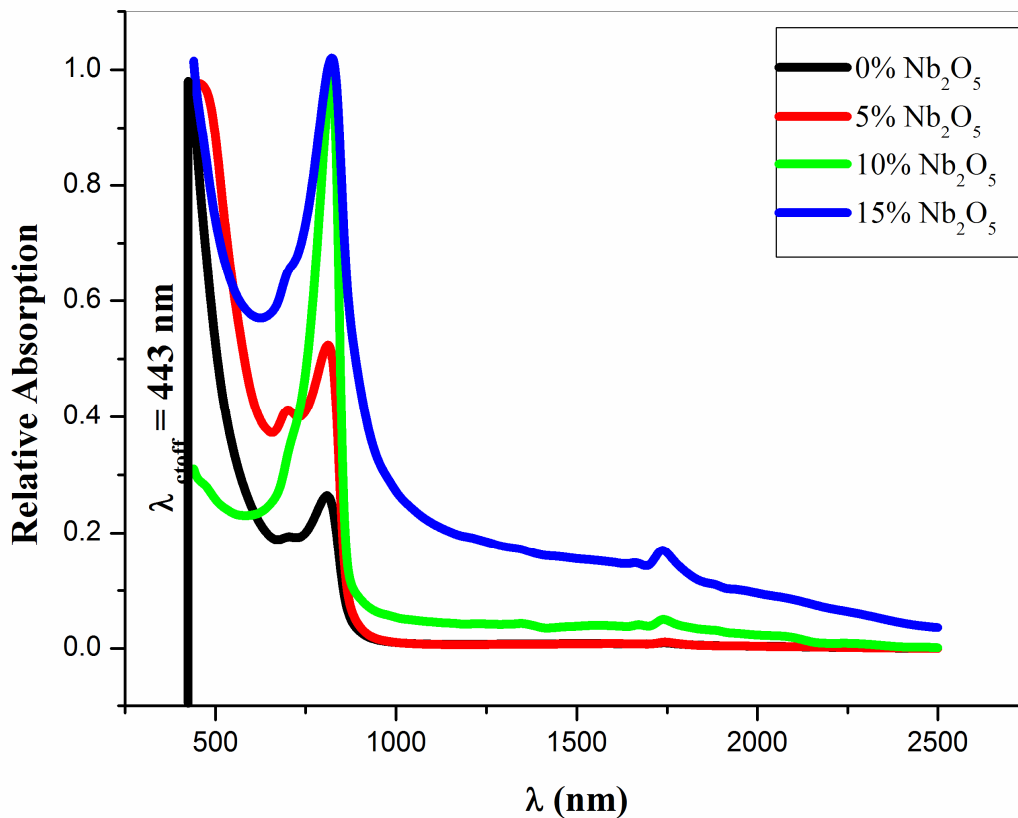| x % Nb_2O_5	λ_{cutoff} (nm)	$(E_{Opt})^d$ (eV)	$(E_{Opt})^i$ (eV)
0		2.43	1.63
5	443	2.06	1.24
10		1.95	0.58
15		2.20	1.04

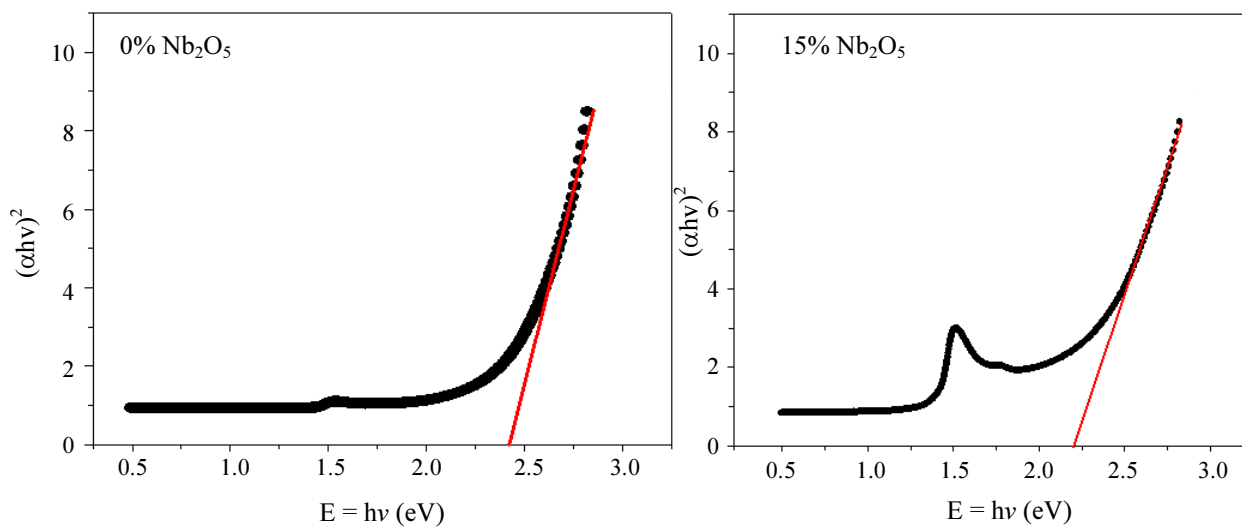**Fig. 4:** Relative absorption spectra for all samples in between 200 and 2500 nm

Fig. 5: $(ahv)^2$ *vs. hv* for direct allowed transition in the niobium free (x=0) and bismuth free (x=15) samples
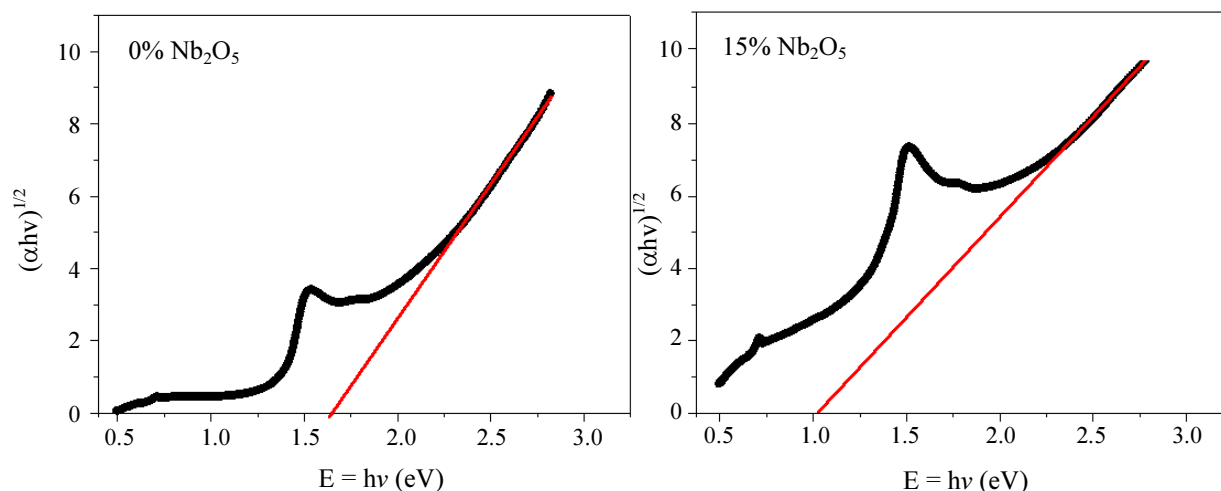
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Fig. 6: $(\alpha h\upsilon)^{\frac{1}{2}}$ vs. *hv* for indirect allowed transition in the niobium free (x=0) and bismuth free (x=15) samples

From this, one can obtain the value of the band gap for direct allowed transitions by plotting the relationship between $(ajv)^2$ on the ordinate axis *vs.* the photon energy *hv* on the abscissa and by extrapolating the linear part of the curve we obtain the value from the interception on the *hv* axis. By a similar way, the indirect allowed transitions can be obtained by plotting the relation between $(ahv)^{\frac{1}{2}}$ and the photon energy *hv*. The values of the direct and indirect allowed transitions of sample with concentration x = 0 and x= 15 mol. % are shown in Fig. 5 and 6, respectively, as representative figures. The values of optical band gaps are tabulated in Table (2) for both direct allowed $(E_{opt})^d$ and indirect $(E_{opt})^i$ allowed transitions. By inspecting Table (2), it can be concluded that both band gaps showed slight decrease as Bi_2O_3 replaced by Nb_2O_5.

Table (2), shows the variation of both direct and indirect optical absorption energy with increasing the niobium contents in glasses. It is clear that, values of both Sand $(E_{opt})^i$ are decreased until reach their lowest values at concentration x=10 mol. % and then increased slightly again until reaching constant values. This result agrees with the literature (Sanghi *et al.*, 2010). This behavior may be attributed to the contributions of two factors, the first one is the increasing of the terminal oxygen atoms number which increased by increasing the concentration of Nb_2O_5 in glass samples. This factor causes the values of both direct and indirect optical absorption energy increased by increasing Nb_2O_5 in glass samples. The second one is the decreasing fraction of Bi_2O_3 which in turn decreases the polarizability and decreases refractive index and finally decreases the values of both direct and indirect optical absorption energy gaps. It is obviously, clear that the second factor is more predominant one in these samples. Lowest values of both $(E_{opt})^d$ and $(E_{opt})^i$ are obtained when x=10 mol. %. This is the case when the concentrations of both

bismuth oxide and niobium oxide are the same, i.e. it is the case, of the highest value of the number of non-bridging oxygen. This result indicates that, the sample with the best nonlinear properties is the one that has concentration x = 10 mol. %, in which the optical band gap has its lowest value. This is because the nonlinearity of the glass system is enhanced by lowering the value of the optical band gap (Meyer *et al.*, 1998).

Conclusion

The present work aimed at studying the effect of replacing bismuth oxide Bi_2O_3 by transition metal oxide Nb_2O_5 in the sodium bismuth borate glass, until the total replacement of Bi_2O_3 by Nb_2O_5. Structural analysis results manifested the amorphous nature of the materials and the correlation between the non-bridging oxygen and the optical absorbance of the glass system. Optical spectroscopic studies showed that the presence of niobium oxides increases the absorption coefficients of the material due to the increased amount of non-bridging oxygen in the negative ligand around the positively charged transition metal cation. It also showed that one of absorption bands is completely affected by the existence of niobium oxide due to the electronic d–d transitions and the coupling between the d–electrons of Nb^{5+} and the vibrations of the negatively charged O^{2-} in the ligands. Results of optical band gap estimation manifested that the sample with lowest value of both optical band gap and subsequently the value of refractive index is the one in which x=10 mol. %. Which is the one in which the concentrations of both bismuth oxide and niobium oxide are the same, which has the highest number of non-bridging oxygen. This indicates that this sample is expected to have best nonlinear behavior, due to the aforementioned results.

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Author's Contributions

All authors equally contributed in this work.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and there are no ethical issues involved.

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