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Structural, spectroscopic correlation of barium bismuth borate glass containing dopant copper oxide

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Abstract: Glasses belonging to the system xCuO-(20-x)BaO-30Bi_2O_3-50B_2O_3 mol% were successfully synthesized via ordinary melt quenching technique. The effect of copper dopant at the expense of the barium oxide was studied via Fourier transform infrared (FTIR) and UV/Vis. spectroscopic techniques. FTIR spectral data point to the presence of both BO_3 triangular and BO_4 tetrahedral structural groups in addition to the linkage of a such group with both heavy metal oxide BaO and transition metal oxide (copper oxide). A minor structural group change was correlated with the values of four coordinated boron and attributed to the dopant level of added transition metal. A change in the optical energy gap was observed with the addition of copper oxide combined with the appearance of a broad band at about 785 nm attributed to the presence of copper ions within the matrix.

Keywords: barium bismuth borate glass; Copper oxide; FTIR; UV/Vis. spectroscopy; DAT analysis.

Introduction

During the last decades, glassy matrices containing transition metal oxides (TMO) attract the attention of scientists due to their unique and interesting optical, electrical, and magnetic characteristics even at the doping level. Such materials are considered suitable for several applications including solid-state lasers, solar energy converters, and plasma display panels in addition to some electronic devices [1-4].

Because of their rich chemistry and their ability to modify their coordination with oxygens in the range of three to four, borate glasses are interesting prospects as effective hosts for transition metal ions. The coordination of the modifying metal cation and subsequent changes to the local habitats around transition metal ions might result from the development of such a broad spectrum of anionic environments with three and four-coordinated borons [5]. The characterization of the anticipated spectrum fluctuations inside borate glasses containing TM ions may be accomplished using optical and infrared spectroscopy, which are both relatively sensitive research techniques [6].

According to recent investigations on the spectroscopic characteristics of 3d-transition metal ions [7,8] and from recent studies it was concluded that these ions can primarily display high valence or tetrahedral coordination states in these host glass and some of them display shielding behavior against increasing gamma irradiation. A similar result has been drawn about this sort of host glass having heavy metal oxide (PbO) rather than Na_2O or Li_2O in another recent work that involves spectrum analyses on 3d-transition metal ions in high lead borate glass [7].

Copper, a 3d transition metal, is used to make a variety of glasses for a variety of purposes, including colored glasses of red glass hematite, azurite, and gems, as well as appearing as a microelement in soil active glasses, antibacterial fertilizer, and semi-conducting materials when present in high concentrations. Copper is known to occur in glasses such as cupric (Cu^{2+}), cupric (Cu^{+}), and metallic (Cu), while it is considered that when melted in the atmosphere, most oxide glasses do not produce metallic copper.

Copper's electrical structure and optical

absorbance differ in each of its two valence states. The proportion of each species is determined by the glass form, composition, copper ion concentration, and melting conditions [8-10]. The glass shape, content, and melting environment all have an impact on the stability of common Cu^{+} and Cu^{2+} ions [4,11].

The presented work aims to synthesize and investigate the glassy matrix of nominal composition xCuO-(20-x)BaO-30Bi_2O_3-50B_2O_3 through combined optical and FTIR spectral data. Optical parameters were calculated for further prediction of the refractive index of the studied glasses.

2. Experimental Work

2.1. Materials

Samples of the studied glass system were prepared from reagent grade materials Bi_2O_3 supplied by Panreac, CuO supplied by M & Baker LTD laboratory chemicals used as received, Barium carbonate as a source of barium oxide while boric acid H_3BO_3 was used as a source of borate matrix both supplied by ADWIC company.

2.2. Sample preparation and composition

Borate glasses containing bismuth, barium, and copper ions were prepared by conventional melt annealing technique. Glass samples were melted in an electrically heated furnace in porcelain crucibles for 2 h in the temperature range 1100–1250 °C depending on the glass composition. Samples were rotated and shacked thoroughly at fixed time intervals (every 30 min) to ensure homogeneity and to remove air bubbles. The molten glasses were poured on preheated stainless steel mold of the required dimensions and transferred immediately to an annealing muffle at 350 °C for 1 h which was turned off and kept to cool gradually to room temperature at a rate of 30 °C/h. Detailed sample compositions were listed in Table 1. While Figure (1) shows the color change of BaBiBCu glass samples with a change in the glass composition. It was observed that the color gradually changed from yellow to dark green color

2.3. Sample characterization

The FTIR absorption spectral data of different samples were carried out utilizing the KBr pellets technique. The spectra are measured in the region of 4000-400 cm^{-1} with a spectral resolution of 2 cm using a Nicolet is10 FTIR spectrometer. The obtained spectrum was normalized to the spectrum of a blank KBr pellet and was corrected to eliminate the background and dark currents using two-point baseline correction. The normalization is necessary to eliminate the concentration effect of the powder sample in the KBr disc. UV-Vis. absorption spectra of the polished prepared glass samples with a constant thickness (2 mm ± 0.1) were immediately measured in the wavelength range of 200-2500 nm using a double beam spectrophotometer (JASCO 670, Japan) to investigate variations in some of the optical physical parameters of studied glasses due to structural changes results from a change in the glass composition.

Table 1: Composition of the prepared glasses

Sample	Composition (mol%)			
	Bi_2O_3	BaO	B_2O_3	CuO
BaBiBCu 0	20	30.000	50	0.000
BaBiBCu 1	20	29.875	50	0.125
BaBiBCu 2	20	29.750	50	0.250
BaBiBCu 3	20	29.625	50	0.375
BaBiBCu 4	20	29.500	50	0.500
BaBiBCu 5	20	29.000	50	1.000
BaBiBCu 6	20	28.000	50	2.000

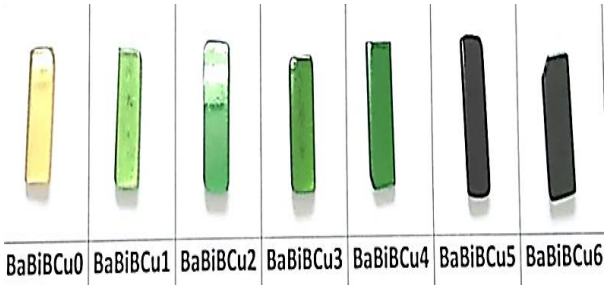


Figure (1) Prepared BaBiBCu glassy samples containing different Cu concentrations.

3. Results and Discussion

3.1. Fourier transform infrared (FTIR)

Figure 2 demonstrates the FTIR spectral data within the region 4000 – 400 cm^{-1} of the prepared barium bismuth borate glass containing variable amounts of copper oxide. The characteristic broadband related to the water molecules was observed at 3424 cm^{-1} and assigned to the O-H stretching vibrational modes. While the peak observed at 930-1197 cm^{-1} is due to the tensile vibration of the trigonal BO^{-3} units of the tetrahedral (BO^{-4}) units and the band at 1200-1600 cm^{-1} BO stretching vibrations, respectively. The B-O-B

bond bending of the borate network was correlated with 700-720 cm^{-1}. The band at 1228 cm^{-1} refers to the Bi-O-B function group [12-15]. The band at 400-600 cm^{-1} refers to the cation modifier. Band position and their assignment can be summarized as shown in Table (2).

BO_3 and BO_4 peak's relative areas were integrated to calculate the N4 using the next formula [16, 17]:

$$N_4 = \frac{BO_4}{BO_4 + BO_3}$$

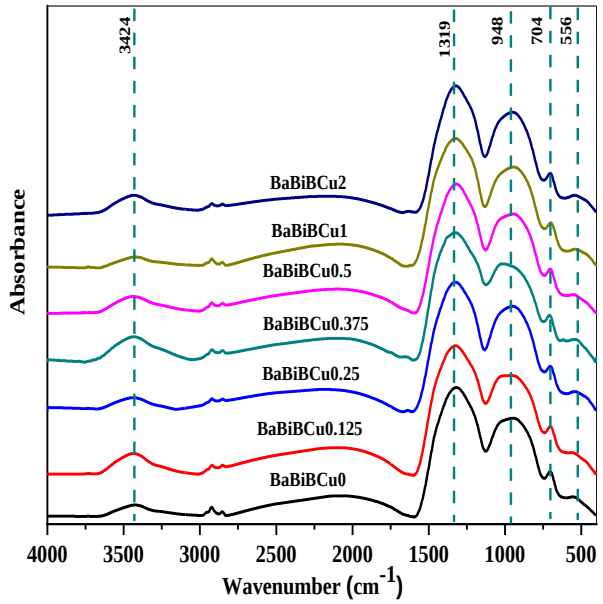


Figure (2) FTIR Spectral data of the studied glasses.

Table (2) FTIR peak assignment.

Wavenumber (cm^{-1})	Assignment
3424	Molecular water
1323	B–O stretching vibrations of BO_3 units in metaborate, perborate, and orthoborate groups
951	B-O bond stretching of tetrahedral [BO_4] units connected by bismuth cations, presence of B-O-Bi bond
704	Bending vibrations of B-O-B linkages of $[BO_3]^{3-}$ group
543	Bi–O bending vibration in the BiO_6 units

Figures 3 and 4 reveal the deconvoluted spectral data of the base glass and one of the glasses that contain an appropriate amount of copper oxide combined with the variation of residuals within the studied spectral range as an example. It was noticed that only reliable bands were considered and the (r^2-value) of the regression was nearly 0.99. In addition, the maximum value of the difference between experimental and theoretical data not exceeds ± 0.015 from the normalized spectral data.

Figure 5 displays the N_4 as a function of BO_4 content to estimate the BO_4 effect on the change of the relative population of tetrahedral units BO_4 and triangle units BO_3. It is observed that N_4 values varied according to the BO_4 concentration. It would appear that the addition of BO_3 tends to decrease BO_4 units.

The presence of BO_3 and BO_4 structural groups was combined with the appearance of specific peaks within the FTIR spectra of the studied glasses related to such vibrational groups that are usually overlapped leading to the smearing of the less intense peaks.

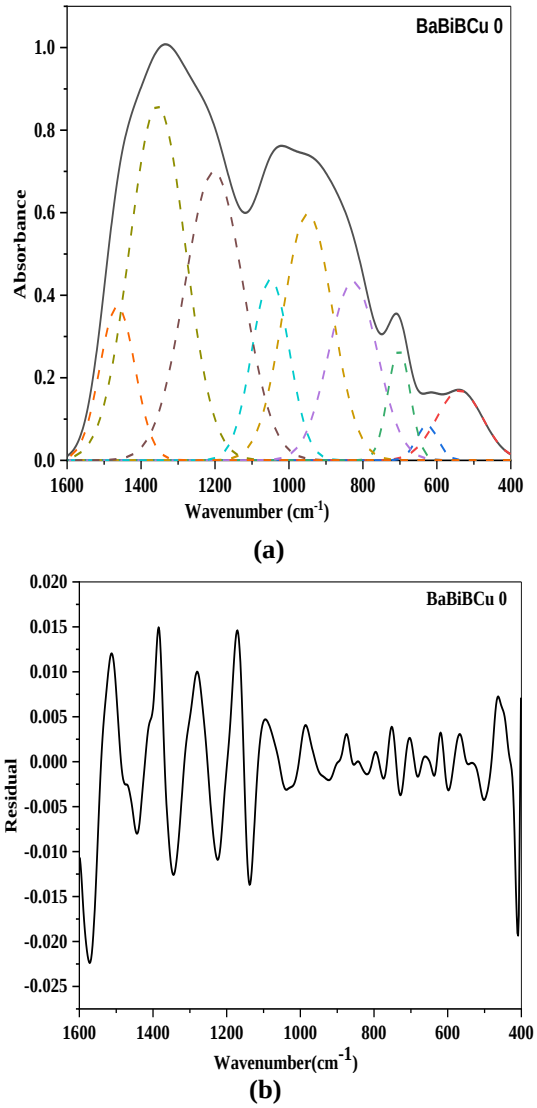


Figure (3) FTIR deconvolution of base glass.

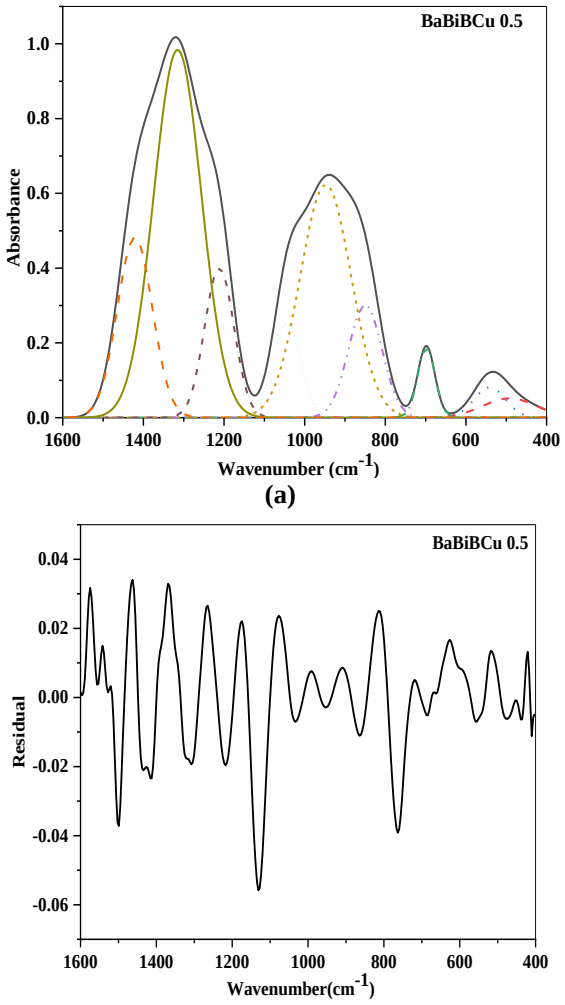


Figure (4) FTIR deconvolution of glass containing 0.5 mol% copper oxide.

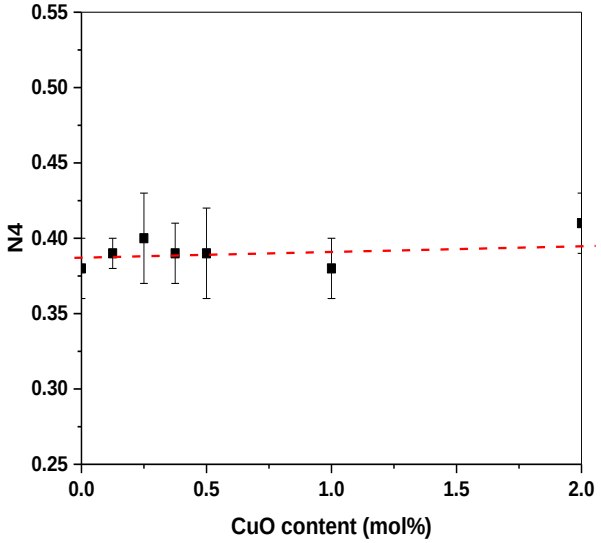


Figure (5) The ratio of four coordinated boron N4 versus copper oxide concentration (mol%).

Gaussian convolutions can be observed in the studied FTIR spectral data in the form of broadening or shoulders in descending lopes. The inverse problem, deconvolution of such data can help in understanding the structural variation resulting from the change in the composition of the studied glassy sample for specific applications. Spectral bands are usually considered as multiple overlapping Gaussian peaks where their sum can correlate with the experimental measured one. The suggestion of the number and position of the convoluted peaks based both on previously analyzed spectral data of similar glasses containing nearly similar forming oxides presented in literature and/or the second derivative of the experimental Normalized FTIR data after corrections for background and dark current noises [14,17]. Some authors [18-20] suggest too many peaks to calculate the relative area of each broadband based on statistical measures representing the proportion of the variance of dependent variables correlated with inde-pendent on in the regression model (R-squared or r^2) which are considered inaccurate.

It was observed that the fraction of the four coordinated boron was slightly changed and can be considered constant due to the addition of the copper oxide in the doping level. The change in the N4 values can be attributed to the structural changes combined with the conversion of BO_4 to BO_3 units. Such changes are usually combined with destroying BO_4 units that may be converted to either BO_3 or/and BO_2O^- units with the generation of non-bridging oxygens. Therefore, the addition of copper ions in the such glass appears to influence the glass network neighboring BO_3.

3.2. UV/Visible optical absorption spectral data

UV/Visible optical absorption spectral data or electronic transitions can be considered a quantitative technique that is used to measure how much a chemical substance absorbs light. To do this, the amount of light passing through a sample is compared to the amount of light passing through a reference sample or a blank.

Spectra associated with molecules that absorb energy in the ultraviolet and/or visible regions to excite n-electrons from bonding or non-bonding states to higher anti-bonding orbitals can be used to estimate information about the electronic transitions of the examined material in various states. The difference between higher and lower occupied molecular states (HUMO-LOMO) and the optical energy gap can likewise be derived from such spectral

data.

In the Brillouin zone, the conduction band's minimum energy state and the valence band's maximum energy state are both defined by a crystal momentum (k-vector). The material has an "indirect gap" if the k-vectors are different. When the crystal momentum of electrons and holes in both the conduction and valence bands is the same, the band gap is called "direct," and an electron can emit a photon directly.

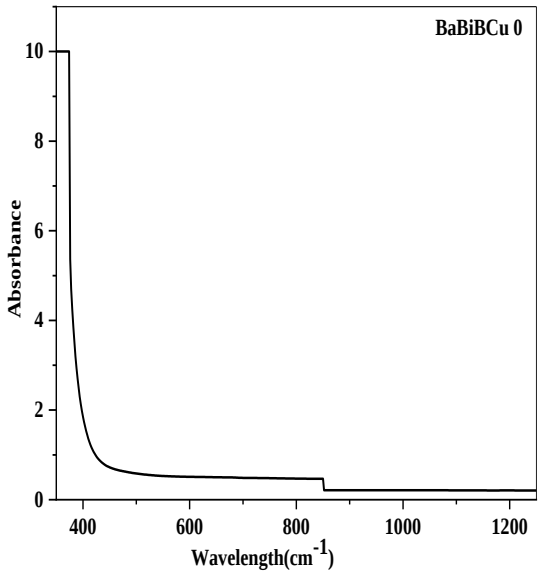
A photon cannot be released in an "indirect" gap because the electron must transit through an intermediary state to transmit momentum to the crystal lattice.

The absorption coefficient (α) is generally connected to photon energy (hν) by the well-known equation:

$$(\alpha h\upsilon) = \beta(h\upsilon - Eg)^n$$

where β is a constant called the band tailing parameter, Eg is the energy of the optical band gap, and n is the power factor of the transition mode, which depends on whether the material is crystalline or amorphous. Tauc's relation states that graphing $(\alpha h\upsilon)^{1/2}$ vs photon energy (hυ) may results in a straight line intercepted by the extrapolation of this straight line, yielding the value of the indirect optical energy gap (Eg) while graphing $(\alpha h\upsilon)^2$ vs photon energy (hυ) may yield an indirect optical energy gap (Eg).

Electronic spectral data in combination with Tauc plots of base glass and exemplified sample that contains a fixed amount of copper oxide (BaBiBCu0.5) were shown in figures (6 and 7).



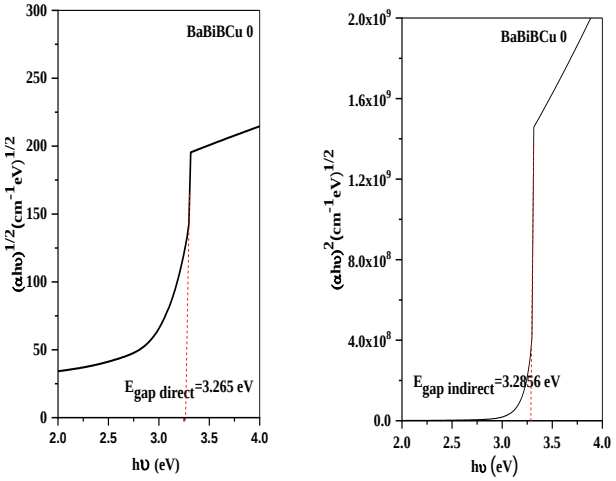


Figure (6) Electronic spectral data in combination with Tauc's plots of base glass

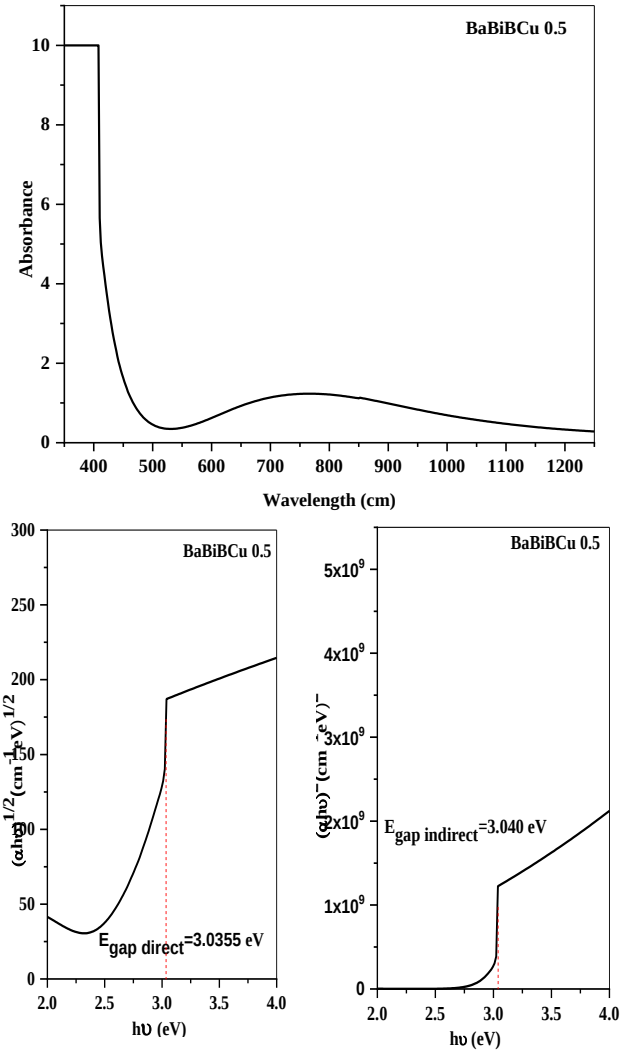


Figure (7) Electronic spectral data in combination with Tauc's plots of glass (BaBiBCu0.5).

Figures 6 and 7 show the UV/Vis. electronic transition of the studied samples along with Tauc's plot adopted to calculate the direct and

indirect transitions. Obtained spectra show a strong charge transfer band located within the range from 230-250 nm based on the glass composition and concentration of dopant copper ions and attributed to $n \rightarrow \pi^*$ transition. In addition, the optical energy gap can be calculated using the wavelength λ_{edge} in the intersection of the fundamental absorption edge with the x-axis using the formula; $E_g = h\,c/\lambda_{edge}$ and by using Tauc's plot represented as plots of $[(\alpha h\nu)^{\frac{1}{2}}$ and $(\alpha h\nu)^2]$ versus photon energy hν. In both direct and indirect transitions, the energy gap E_g can be estimated from the X-axis intercept. Obtained values of the energy gap can be listed in the table (3).

Table (3) absorption edge and calculated energy gaps of the studied glasses.

Cu %	λ_{edg} nm	E_{opt} eV	E_{direct} eV	$E_{indirect}$ eV
0.000	379.33	3.269	3.266	3.285
0.125	435.58	2.841	2.055	3.018
0.250	399.72	3.101	3.060	3.112
0.375	407.47	2.040	3.050	3.054
0.500	409.90	3.034	3.030	3.040
1.000	459.25	2.705	2.710	2.710
2.000	442.16	2.801	2.810	2.810

4. Conclusions

Glasses belonging to the system *x*CuO-(20-*x*)BaO-30Bi_2O_3-50B_2O_3 mol% were successfully synthesized via the traditional melt quenching route. The change in transition metal (copper oxide) concentration at expense of the barium oxide was retraced via Fourier transform infrared (FTIR) and UV/Vis. spectroscopic techniques. FTIR spectral data point to the presence of both BO3 triangular and BO_4 tetrahedral structural groups in addition to the linkage with both heavy metal oxide BaO and transition metal oxide (copper oxide). A minor change in the structural groups was observed through the minor changes in the values of four coordinated boron and attributed to the dopant level of added transition metal. A change in the optical energy gap was observed with the addition of copper oxide combined with the appearance of a broad band at about 785 nm attributed to the presence of copper ions within the matrix.

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