



Characterization of borate glasses doped with copper oxide for optical application

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Abstract

Borate glasses having the formula $x \text{CuO} - (50 - x) \text{B}_2\text{O}_3 - 30 \text{Na}_2\text{O} - 20 \text{ZnO}$ where $x = 0, 0.2, 0.5, 1, 4$ and $7 \text{ mol}\%$ were investigated. The samples were prepared using the conventional melt-quenching technique. Physical properties were studied such as; X-ray diffraction, FTIR spectra, and UV–visible transmission. The optical basicity, average electro negativity have been estimated. The estimated optical basicity, unlike electron negativity, exhibits an increase with increasing the CuO content. FTIR spectra show that BO_4 ratio decreases with increasing CuO content leading to the formation of non-bridging oxygen's. Some optical parameters such as the optical band gap, band tail width, crystal field strength and the UV and NIR cut off were determined. The transmission spectrum revealed that the glassy samples containing high content of copper oxide behave as bandpass filters at higher content. The characterized parameters of these filters were found to be highly affected by the addition of CuO. In these glasses the broad absorption band observed at the wavelength 550 nm is characterized by the existence of Cu^{2+} ions. The optical absorption and ESR studies suggest that, the Cu-ions exist in the Cu^{2+} state and act as modifiers by increasing the degree of disorder in the glass network. Hence, the present system behaves as a bandpass filter in the ultraviolet–visible region.

Keywords Alkali borate glasses · Optical properties · Bandpass filter · FTIR and ESR

1 Introduction

Spectroscopic properties of transition metal (TM) in borate glasses have been subjected to extensive studies. This is due to their technological, unique properties and commercial important applications (da Silva et al. 2013; Kesavulu et al. 2010; Kuang et al. 2017; Pisarski et al. 2009; Asghar et al. 2009; Giridhar et al. 2011; Terczynska-Madej et al. 2011).

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Due to d–d transitions of copper, one of the 3d TMs, imparts greenish and bluish colors depending on the valence state and the ligand field. Copper can exhibit Cu^{2+} , Cu^+ and Cu^0 valence states which can coexist together. The glass forming ability depends on the copper valency state (Abdelghany et al. 2015). Glasses doped with copper oxide acts as a bandpass filter that allow certain wavelengths and prevent other wavelengths of light from passing through it. The width of the bandpass filter exists in wavelengths range is from 0.1 to 100 nm. Bandpass filter is combination of long pass and short pass filter. Some filters acts by selective transmittance and absorption, which known as colored glass bandpass filters (Asghar et al. 2009). Boron oxide is one of the most important glasses forming material (Wen et al. 2016; Shashidhar Bal et al. 2008; Lakshminarayana and Buddhudu 2006; Narayana-Reddy et al. 2008; Chinna Babu et al. 2005). It is a particularly suitable optical material because of its low cost, high transparency, high sensitivity, low melting point, high thermal stability, different coordination numbers, easy fabrication, shaping and mass production (Srinivasa Rao et al. 2008; Ardelean et al. 2005; Mohammed et al. 2017). The electronic structure of the copper atom is $3d^{10} 4s^1$, and the usual oxidation states are Cu^+ and Cu^{2+} . The cuprous ion Cu^+ does not produce coloring, due to that the 3d is complete and no d–d transition can take place. While the cupric ion Cu^{2+} absorbs light in visible region and creates color, due to that the d–d transition taking place in the incomplete d shell. Thus, most glasses which contain Cu^{2+} have a sky blue to green color depending on the base glass compositions. Colors produced in glasses by Cu^{2+} ions have been interpreted from the view point of ligand field theory (Abdelghany et al. 2015; ElBatal et al. 2011; Wongsing et al. 2012; ElBatal et al. 2010). ZnO is considered as a promising candidate as a modifier with a wide band gap which allows its usage as a potential optical material (Thulasiramudu and Buddhudu 2006). It is well established that the addition of CuO cause serious changes in glass properties for example, the increment of copper with specific concentration enhances the luminescence properties, above this concentration showed an adverse effect on the luminescence intensity (Alajerami et al. 2012).

The aim of this work is to study some of the physical properties to examine the effect of increasing CuO at the expense of B_2O_3 in the glass system under investigation in order to obtain a bandpass filter in the ultraviolet–visible region.

2 Experimental technique

For the fabrication of the glass system the melt-quenching technique was used, this technique is based on heating the oxides up to the melting temperature then quickly cooling it to below its transition temperature (T_g). This technique is inexpensive, simple and time-saving way (Alajerami et al. 2012). The starting compounds used were: CuO (98%, Aldrich), H_3BO_3 (99% from Nasr Lab., Egypt), Na_2CO_3 (99.5% from Nasr Lab., Egypt) and ZnO (99.9% Aldrich). Appropriate quantities of ingredients were weighed using an electric single pan balance of 10^{-4} g sensitivity, and thoroughly mixed by mortar and pestle. Each composition was taken in an open porcelain crucible and melted in an electric furnace at a temperature rang of 900–950 °C for 1 h. The crucible was shaken to ensure homogeneity. The molten glass was then poured between two brass plates. A part of the prepared samples were polished carefully with fine emery paper in order to study their optical measurements using JENWAY (6405 UV/visible) spectrophotometer covering the wavelength range from 200 to 1100 nm. As well as parts were crushed to fine powder by an agate mortar. X-ray data was checked by using a Philips Analytical X-ray diffractometer (PW3710) with a

copper tube anode of wavelength $K\alpha_1 = 1.5460 \text{ \AA}$ and $K\alpha_2 = 1.54439 \text{ \AA}$. Infrared measurements were recorded using FTIR Nicolet 6700 in the range ($4000\text{--}400 \text{ cm}^{-1}$). Electron spin resonance, ESR, spectra was measured using an ESR Bruker spectrometer “EMX, ER 4119HS”, operating in X-band frequency.

3 Results and discussion

3.1 X-ray diffraction

Figure 1 shows X-ray patterns of $x=0.0$ and 7.0 mol% samples which is taken as a representative examples. The spectrum does not reveal any crystalline phase i.e. it shows no continuous or discrete sharp peaks but exhibits a broad hump ($2\theta \sim 30^\circ$), which reflects the characteristics of amorphous and is a typical feature of borate glasses. The absence of well-defined diffraction peaks rules out the occurrence of long range atomic arrangement, and clearly confirms the glassy nature of the samples (Mohammed et al. 2017; Ahmad 2014).

3.2 Density

The density was measured at room temperature using the conventional Archimedes method (Farouk et al. 2013) with carbon tetrachloride (density = 1.592 g/cm^3) as an immersion liquid. Values of the estimated density and the calculated molar volume (V_M) variation of the glass samples are presented in Fig. 2. The density exhibit increases with increasing the CuO content, this is most probably related to two reasons: the replacement of lower atomic mass ($B_2O_3 = 69.62$) by higher atomic mass ($CuO = 79.547$) and the transformation of BO_4 structural units with smaller volume into BO_3 structural units with larger volume.

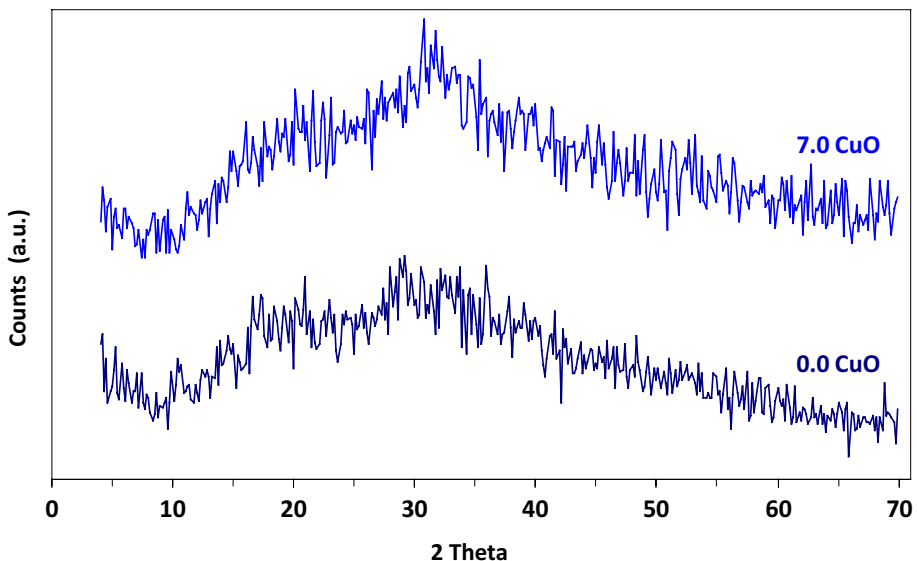


Fig. 1 The XRD patterns of the selected samples $x=0$ and 7 mol%

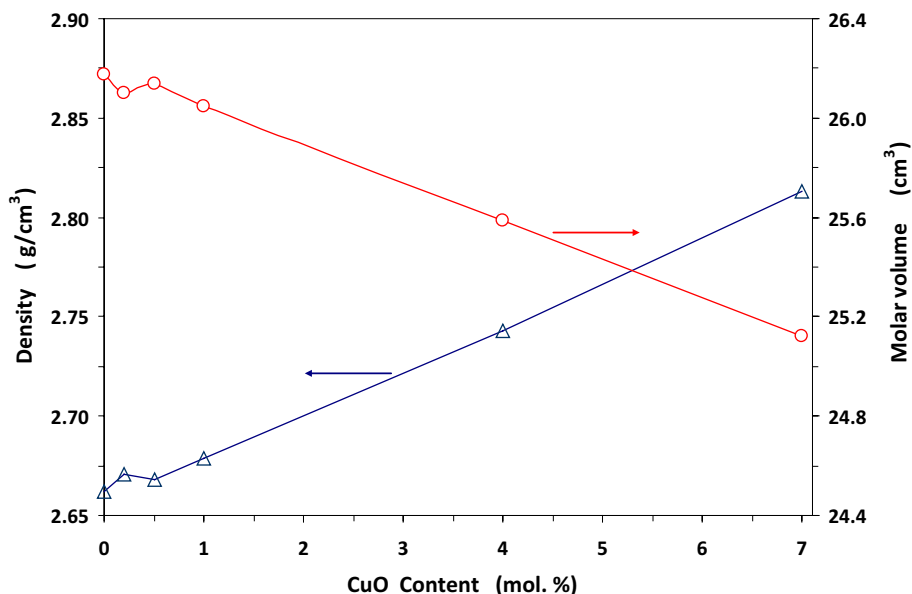


Fig. 2 Density and molar volume composition dependence for all glasses

The obtained density and its V_M follow opposite trend, which is the normal behavior (Wen et al. 2016; Shashidhar Bal et al. 2008; Ardelean et al. 2005; Moustafa et al. 2008).

3.3 FTIR spectra

Infrared spectroscopy is usually used to get information regarding the structural units of the glass network. It is well established that the vibrations of structural units are independent of the vibrations of the other neighboring units (Pascuta et al. 2009). The obtained FTIR spectra are presented in Fig. 3. The vibrational modes of the borate glass are usually observed in three spectral regions as tabulated in Table 1. The first broad band, which extends over the range $1200\text{--}1600\text{ cm}^{-1}$, is due to that the B–O asymmetric stretching vibration band of trigonal BO_3 units (Karthikeyan et al. 2005; Karthikeyan and Mohan 2003; Sindhu et al. 2006; Hassan 2013). The second lies between 800 and 1200 cm^{-1} and is usually ascribed to B–O bond bending and stretching of the tetrahedral, BO_4 units (Karthikeyan et al. 2005; Karthikeyan and Mohan 2003; Sindhu et al. 2006; Hassan 2013). The third band located at 700 cm^{-1} is due to the bending of B–O–B in trigonal BO_3 units (Karthikeyan et al. 2005; Karthikeyan and Mohan 2003; Sindhu et al. 2006; Hassan 2013). Finally, the observed broad band at $\sim 3450\text{ cm}^{-1}$ is due to O–H vibration mode of water (Terczynska-Madej et al. 2011; Hassan 2013; Varsamis et al. 1999; Bhattacharya and Ghosh 2006; Hudgens and Martin 1996; Hverhoef and Den-Hartog 1995). The shoulder is observed between 400 and 550 cm^{-1} according to the presence of Zn–O tetrahedral bending vibrations of ZnO_4 units (Ahmad et al. 2014; Tarte 1963). In addition, the overlapped band with BO_3 units around 1600 cm^{-1} is resulting from the vibration mode of O–H groups (Ahmad et al. 2014; Naresh et al. 2012; KrishanMurthy et al. 2000; Boonin et al. 2011). In order to obtain information of the units in the borate glasses, the bands have been deconvoluted (Pascuta et al. 2009).

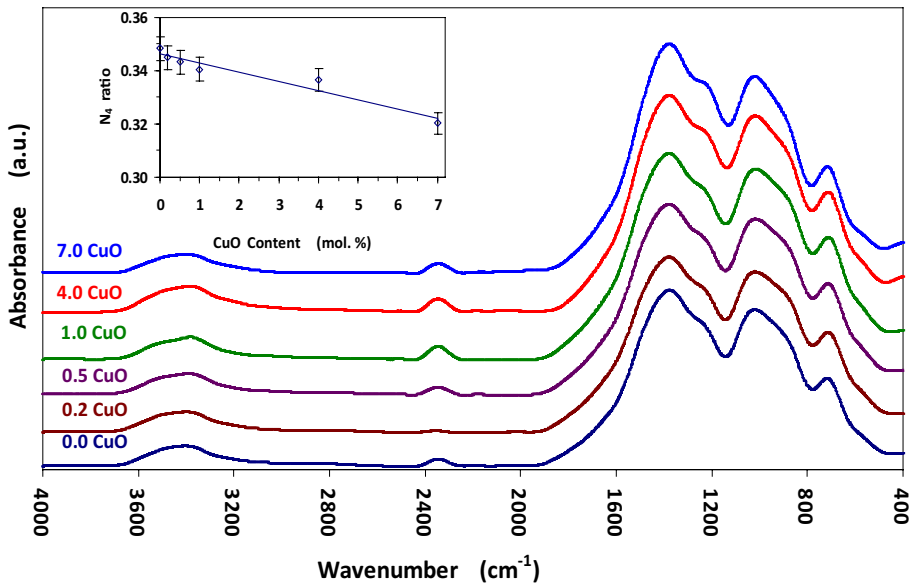


Fig. 3 FTIR spectra of all glassy samples (inset figure represents the N₄ ratio composition dependence)

The broad bands are most likely due to the overlapping of individual bands. These characteristic parameters can be used to estimate the fraction of N₄ of BO₄ units in the borate network. Then, N₄ can be defined as the ratio of the BO₄ units to the total (BO₃ + BO₄) units (Pascuta et al. 2009; Saddeek et al. 2008; Pascuta et al. 2008). The calculated N₄ ratio decreases with increasing the dopant ratio as represented in the insert Fig. 3, leading to the formation of NBO's. The negative charge on NBO's facilitates the excitation of electrons with higher wavelengths (Chanshetti et al. 2011). The above arguments suggest that N₄ ratio is the most prominent factor in increasing density and decreasing molar volume.

3.4 Optical basicity

Acid–base properties of oxide glasses can be explained by the optical basicity in terms of the electron density. It reflects the ability of the glass to donate a negative charge to the probe ion (Santhan Kumar et al. 2013; Zhao et al. 2008). The empirical formula of the optical basicity (Λ) can be calculated by using the average electronegativity (χ_{av}) as (Duffy and Ingram 1992; Duffy 2002):

$$\chi_{av} = \sum_i x_i \chi_i \tag{1}$$

$$\Lambda = \frac{0.75}{\chi_{av} - 1.35} \tag{2}$$

where x_i is the concentration percentage and χ_i is the electronegativity of any oxide compounds. In this study, we can use the Allen scale table of the electronegativity values (Allen 1989). As shown in Fig. 4, the calculated optical basicity magnitudes follow an

Table 1 Assignment of the FTIR bands as showed in all prepared samples

Band position (cm ⁻¹)	Assignment	References
1200–1600	Asymmetric stretching vibrations of trigonal units	Moustafa et al. (2008), Pascuta et al. (2009), Karthikeyan et al. (2005) and Karthikeyan and Mohan (2003)
800–1200	Rocking stretching of B–O bond on the tetrahedral units	
~700	Bending of B–O–B in trigonal units	
400–550	Presence of Zn–O tetrahedral bending vibrations of ZnO ₄ units	Hudgens and Martin (1996) and Hverthoef and Den-Hartog (1995)
1600	Vibration mode of O–H groups overlapped with BO ₃ units	Hudgens and Martin (1996), Ahmad et al. (2014), Tarte (1963) and Naresh et al. (2012)
3450	O–H vibration mode of water	Terczynska-Madej et al. (2011), Karthikeyan and Mohan (2003), Sindhu et al. (2006), Hassan (2013), Varsamis et al. (1999) and Bhattacharya and Ghosh (2006)

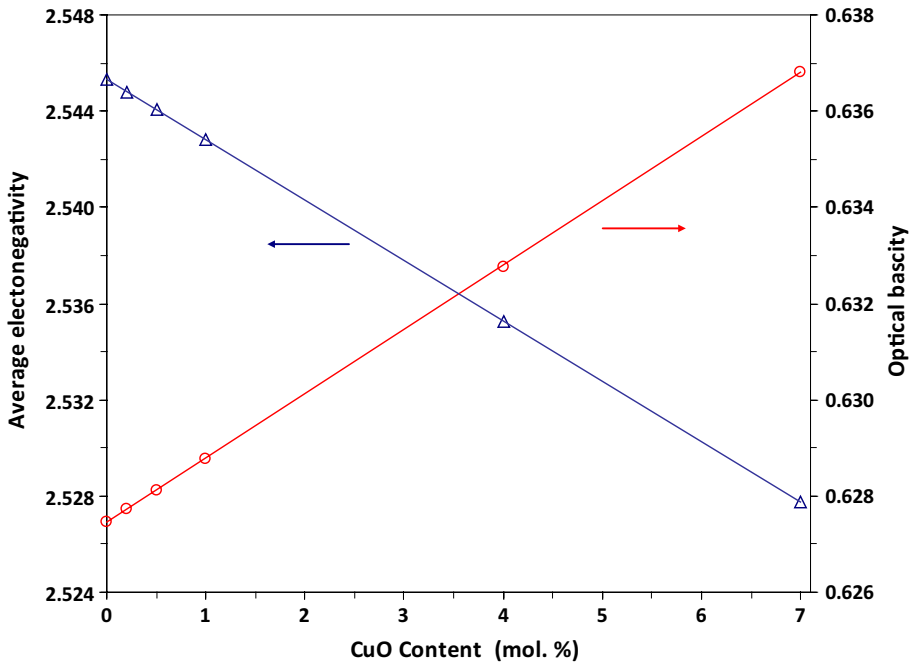


Fig. 4 The average electronegativity and theoretical optical basicity of the investigated glasses

opposite behavior to the average electronegativity values. The optical basicity is increased linearly by increasing CuO content. This is mainly caused by the fact that CuO has a higher polarizability and higher optical basicity (due to its larger ionic radii) than Na₂O, ZnO and B₂O₃. The optical basicity increases with the increasing of polarizability. It is well known that Cu²⁺ ions are highly polarizable; this facilitates the liberation of electrons, which explain the reduction of band gap.

3.5 Optical measurements

Ultraviolet and visible transmission spectra were obtained for finely polished glass samples. The glass samples appeared to the naked eyes is bubble-free and transparent. The copper-free sample is colorless whereas the samples containing copper have a blue-green/green color that becomes deeper in color with increasing copper content. The transmission results of the investigated glasses are presented in Fig. 5a. The spectra revealed a transmitted band in the visible region, i.e. it exhibits bandpass filter behavior. At low CuO content, a broad non-symmetrical band is observed. The bands become narrower with red-shift and become more symmetrical by increasing CuO content. The observed shift in the onset of the absorption can be accounted for by the conversion of bridging oxygen to non-bridging oxygen's (NBO's); as shown in the FTIR results. The obtained filters exhibit single band-pass with double band stop in UV and NIR as shown in Fig. 5b. It should be mentioned that all samples show high absorption in both UV and NIR regions. The dependence of cut off on UV and NIR sides of CuO content are listed in Table 2. Generally, filters are characterized by three parameters: central wavelength λ_{\max} , full width at half maximum

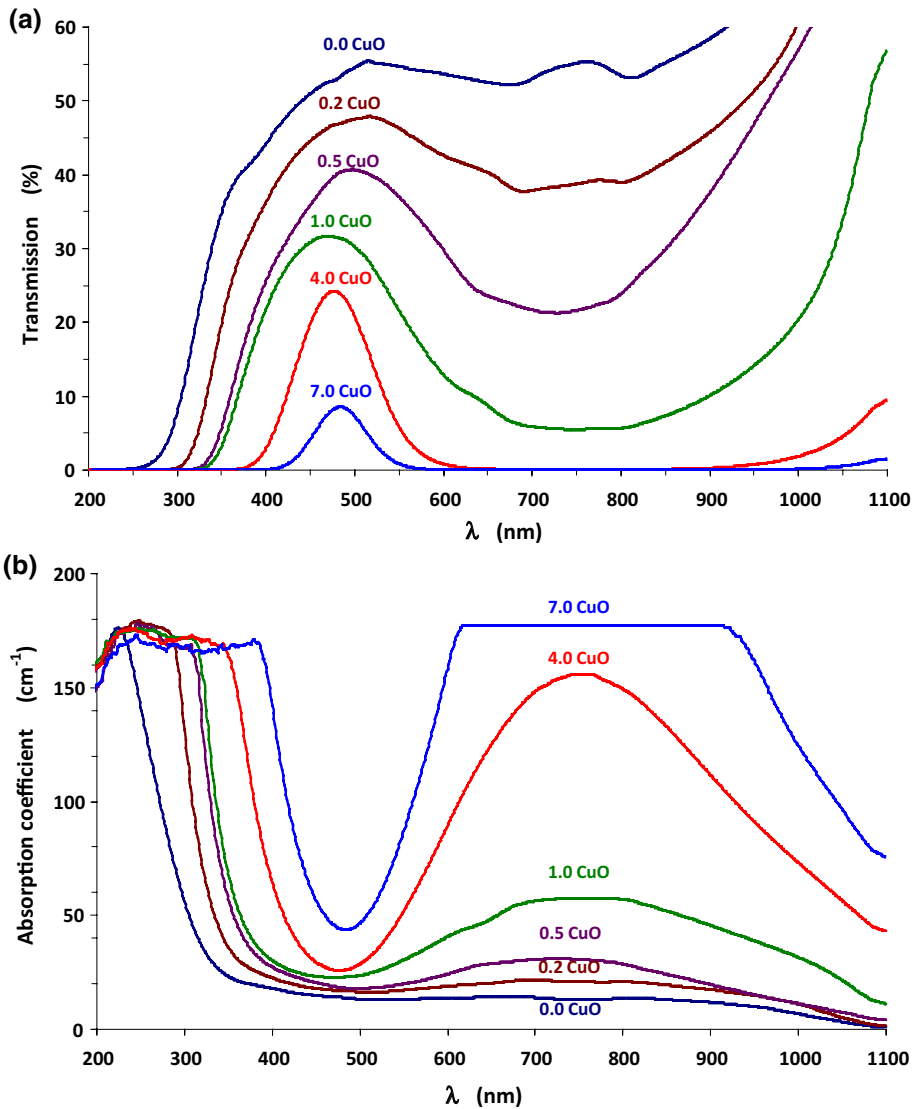


Fig. 5 **a** Optical transmission **b**, absorption coefficient as a function of wavelength of the x CuO-(50- x) B₂O₃-30Na₂O-20ZnO glasses

(FWHM) and the area—related to the transmitted energy. The dependence of such parameters is recorded in Table 2. The center of the peaks is located at about 500 nm i.e. it is between green and blue regions. The copper band cutting in UV and NIR is a result of the fact that copper has two absorption bands, one in UV and the other in near infrared. Moreover, when increases the dopant ratio, the band shifts and the absorption of the UV band increases until the threshold in the contents of copper oxide begins to have a cut off in the near infrared region. Figure 4a and Table 2 shows the peak height of the transmitted band decreases with increasing the dopant content, because the filters are generally used

Table 2 The cut UV, Vis and NIR the band stop, band gap E_g /tails E_t energy and the crystal field strength (10Dq) for the investigated samples

x CuO (mol%)	Band stop wave-length (nm)		Visible band characterization				Band gap energy		10Dq (cm ⁻¹)
	UV	NIR	Center (nm)	FWHM (nm)	Area	Height	E_g (eV)	E_t (eV)	
0	200–245	–	–	–	–	–	3.04	0.612	–
0.2	200–294	–	–	–	–	–	3.25	0.435	–
0.5	200–309	–	–	–	–	–	3.11	0.405	1385
1	200–321	–	–	–	–	–	3.03	0.417	1299
4	200–348	740–766	478	81.9	2494	24.3	2.52	0.421	1289
7	200–394	612–927	485	56.4	595	8.4	2.33	0.425	1254

to either lower the overall intensity of the light or to restrict the wavelength (Asghar et al. 2009). For sake the determination of the absorption mechanism, one should apply the well-known relation (Khor et al. 2013):

$$\alpha h\nu = B(h\nu - E_g)^n \tag{3}$$

where B is constant called band tailing parameter, E_g is the optical band gap energy and n factor depends on the transition type and material structures. In the amorphous case, indirect transitions are more frequent absorption mechanism. This is due to the fact that in the amorphous systems, the transitions are not symmetrical so the linear momentum is not conserved i.e. it is not a good quantum number. Plotting $(\alpha h\nu)^{0.5}$ as a function of photon energy $h\nu$, the E_g can be determined by extrapolating the linear segment of the curve to the $h\nu$ axis where $(\alpha h\nu)^{0.5} = 0$. To estimate the Urbach energy or band tail width (E_t) one should apply Urbach relation:

$$\alpha = \alpha_0 \exp(h\nu/E_t) \tag{4}$$

where α_0 is constant and E_t is usually interpreted as the band tail width of the localized states in the band gap. Urbach plots are dependent on the natural logarithm of the absorption coefficients, $\ln \alpha$, and the photon energy, $h\nu$. The obtained values of E_t were estimated by determining the slopes of the linear window of the curves. The obtained values of E_g and E_t are tabulated in Table 2 and shows opposite trend to each other. Firstly the E_g increases by the addition of CuO ($x = 0.2$ mol%), which can be attributed to the blocking effect phenomena of the Cu ion on the overall mobility of Na ions, according to the larger ionic radii of Cu ions compared with Na ions. Further addition of CuO (for $x > 0.2$ mol%), the E_g decreases with increasing copper oxide. This can be attributed to the electronic conduction mechanism, to the exhibition of the mixed conduction and to the ionic–electronic mechanism (Santhan Kumar et al. 2013). A similar behavior was observed in the electrical study by Khawaja et al. (1986). The implantation of copper oxide to the glass matrix causes an increase of the disorder degree, confirming the density results. This is most likely because copper addition reduces the average binding energy (cohesive energy).

On the other hand, the copper doped samples have a blue-green color. Moreover, with increasing CuO content, the color becomes dark green; the green color is an indication that the Cu has a divalent oxidation state. Hence, the spectrum shows a single very broad band around ~775 nm as shown in Fig. 5b; this can be identified as a d–d transition due to the Cu²⁺(d⁹) ions in the octahedral field corresponding to the electronic transition

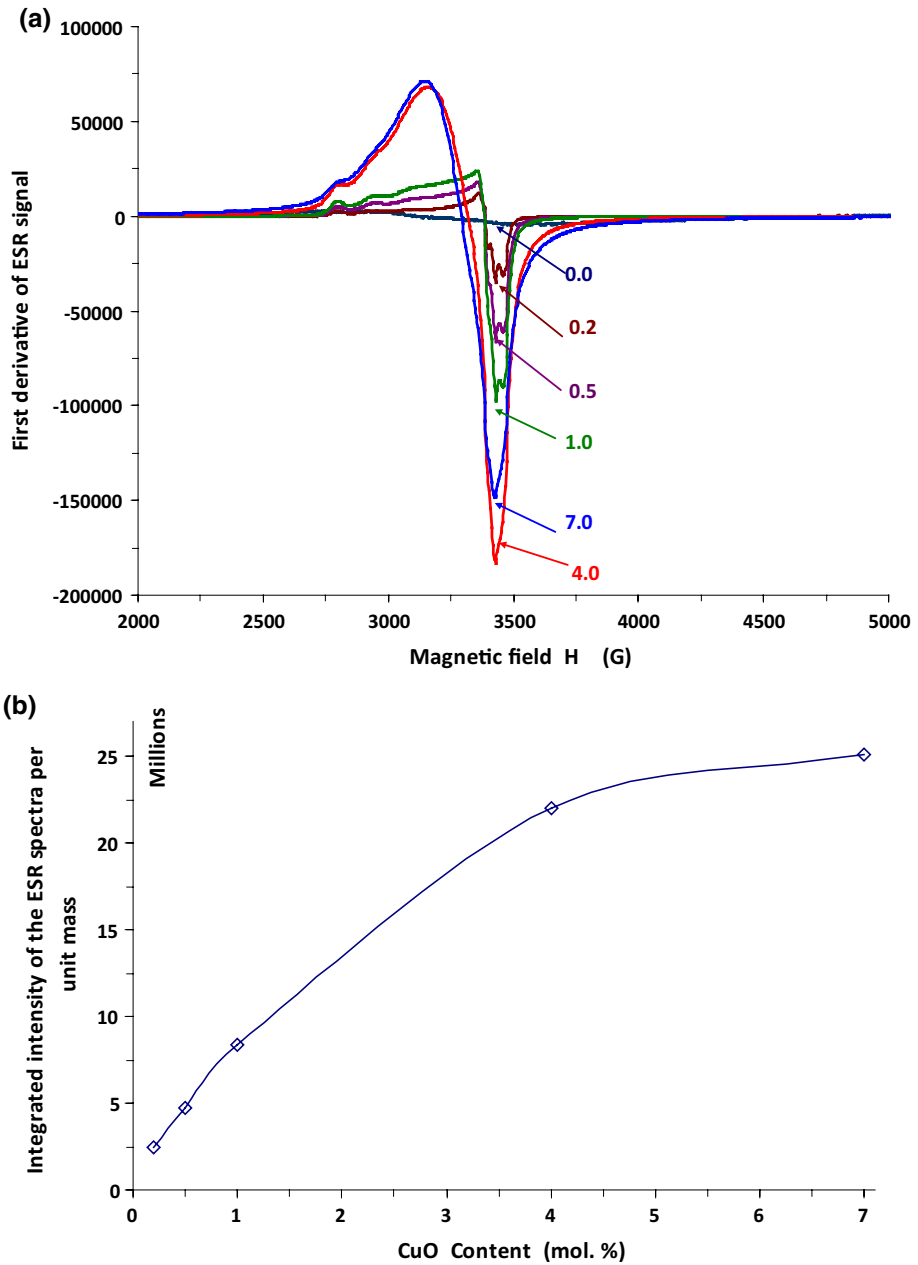


Fig. 6 **a** ESR spectra of all the investigated glasses at room temperature, **b** the variation of ESR intensity with CuO content

${}^2E_g \rightarrow {}^2T_{2g}$. The lack of the symmetrical absorption can be interpreted by the Jahn–Teller distortion (Lever 1984; Ballhausen 1962; Bae and Weinberg 1994; Cotton and Wilkinson 1988). Additionally, from the complementary of colors, the absorbed color is red which

confirms that copper is in the divalent state. The crystal field splitting of d orbits of copper in the divalent state can be evaluated by using the ligand field theory; the transition energy between the e.g. orbitals remains constant and is equal to the crystal field strength parameter (10Dq) without distortion, which can be estimated using the following equation (Lever 1984; Ballhausen 1962):

$$10Dq = \nu \quad (5)$$

where ν is the absorption band position in energy units. The 10Dq composition dependence is presented in Table 2, and it shows that the splitting of d levels decreases with the introducing of the dopant content, corresponding to the decreasing of the average electronegativity, confirming the optical basicity calculation.

3.6 ESR spectra

Electron spin resonance (ESR) measurement of all the glassy samples have been performed at room temperature, as presented in Fig. 6a. The obtained spectra show the main signal around the magnetic field of the order of 3350 Gauss ($g=2.09$) corresponding to the presence of the copper on the Cu^{2+} forms (Yao et al. 2016; Andronenko et al. 2004) confirming the optical data. There were no magnetic features in the copper free sample, indicating that the host glass was free from any paramagnetic centers. This was in agreements with the optical data, which exhibited a colorless sample for $x=0$ and colored for doped samples with copper. The bivalent copper ion is located at the center of the octahedron or the tetrahedron, as well as at high concentrations of alkali content and/or low concentration of copper ions. The octahedral units which are elongated along the tetragonal axis were formed in the structure of glasses (Andronenko et al. 2004). As shown in Fig. 6b, the integrated intensity was calculated per unit mass; the signal's intensity is found to be increased with increasing CuO content, due to the increasing of paramagnetic centers in the glass host. An increase in the bivalent copper ion concentration causes an increase in the number of individual octahedral units (Andronenko et al. 2004).

4 Conclusion

The various structural investigations carried on the investigated samples have been found to be in good agreement with each other. Study of XRD patterns confirms the glassy nature of the prepared samples. The introduction of CuO into the glass matrix leads to an increase in glass density. From the Spectroscopic studies such as FTIR carried out on the samples it has been found that there is a gradual conversion of BO_4 tetrahedral units into BO_3 trigonal units in the glass network. Based on the UV-visible optical absorption and ESR studies in the present study, it is concluded that the CuO acts as a network modifier in the divalent state. It is also found that the addition of the CuO content causes a decreasing of the optical band gap energy. The optical absorption spectrum reveals that the prepared samples behave as a bandpass filter at higher content in the visible region. The data obtained suggests the possibility of controlling the filtering effect.

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