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Spectral studies on CuO in sodium–calcium borophosphate glasses

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Abstract. Transparent borophosphate glasses doped with CuO were prepared by melt quenching technique. X-ray diffraction (XRD), optical and luminescence properties of sodium–calcium borophosphate glasses doped with CuO have been studied. The XRD results showed the amorphous nature of the sample. The introduction of CuO was favourable for the colour changes from light blue to dark bluish green colour. Direct optical energy bandgaps before and after doping with different percents of copper oxide obtained in the range 4.81–2.99 eV indicated the role of copper in the glassy matrix by ultraviolet (UV) spectra. The glasses have more than 80% transparency for emission wavelength range, and strong absorption bands due to the charge transition of the Cu^+ and Cu^{2+} ions were observed. The emission bands observed in the UV and blue regions are attributed to $3d^9 4s$–$3d^{10}$ triplet transition in Cu^+ ion.

Keywords. XRD; optical bandgap; luminescence; copper phosphoborate glass.

1. Introduction

In recent years, glasses doped with transition metal ions have attracted a great deal of attention, because of their memory and photoconducting properties. They also find wide applications in solid-state lasers, luminescent solar energy concentrators and fibre optic communication devices [1].

Borophosphate glasses are promising host materials for optical applications because of their good optical properties, low-refractive indices, low dispersion and good transparency from the ultraviolet (UV) to the near-infrared regions [2,3]. These glasses have higher chemical durability than phosphate glasses due to the composition of boron oxide in the structural network, mostly in the form of BO_4 tetrahedral, which transforms metaphosphate chain into three-dimensional network [4].

In view of these qualities, these glasses are considered as materials for optical components such as IR domes, optical filters, modulators, memories and laser windows. They also have widespread applications in many different areas, e.g., as anode material for Li ion batteries (based on tin borophosphate glasses) [5,6], electrolytes in electrochemical devices [7,8], bonding agents [9] of fuel cell refractory ceramics sealing glasses [4], non-linear optical devices [10] and as low-melting glass solders or glass seals [11] derived from the phosphate sealing materials [12]. The Cu^{2+} ions provide useful information regarding the structure of their network environment in a glass, as their electronic and electron spin resonance spectra are simple [13].

Na_2O causes a reduction in the melting point and facilitates the homogenization of the glass system, thereby decreasing the possible structural defects [14]. The role of Na_2O in the B_2O_3 network is to modify the host structure through the transformation of the structural units of the borate network from $[BO_3]$ to $[BO_4]$.

Copper phosphate glasses have interesting electrical conduction and optical absorption in the visible light, resulting in colouration of the glass. In addition, copper in sodium borophosphate glasses has improved chemical durability; therefore, copper contributes to the stabilization of the glass structure. From the technological importance of these glasses as well as their interesting properties and potential applications, it would be interesting to study the role of CuO in the formation of a glass.

Glasses have important advantages over crystals because of their potentially higher doping levels of rare-earth ions, flexible geometry and ease of fabrication. The broad spectral features in glasses also favour energy transfer process. Our paper is a continuation of research concerning the behaviour of transition metal ions in glasses of various chemical compositions based on their optical spectra. Several techniques can be used to prepare glass, but the inexpensive, simple and time-saving way is known as the melt quenching technique. Because of its attractive properties such as high transparency, radiation and thermal stability, photon energy, non-radiative relaxation rates and low melting point, the borate glass becomes one of the most promising materials for advanced technology applications, such as thermoluminescence dosimeters, lasers and optoelectronic applications and second-harmonic generation media [15].

In this study, we present spectral properties of Na_2O–CaO–B_2O_3–P_2O_5:CuO glasses. In addition, an attempt has

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been made to estimate the structural changes in the CuO-doped borate glassy network using X-ray diffraction (XRD), transmittance and luminescence properties.

2. Experimental

All the reagents were of analytical grade and employed as received without further purification. The composition of the glass was Na_2O, CaO, P_2O_5, B_2O_3 and CuO, for which the oxide composition and sample code are listed in table 1. The starting materials were reagent grade of Na_2CO_3, CaO, P_2O_5 and B_2O_3. Stoichiometries mixture of Na_2CO_3, CaO, P_2O_5 and B_2O_3 were weighed and mixed thoroughly in an agate mortar and pestle for about 2 h to get good homogeneity. The batch mixture was transferred into an alumina crucible. The crucible was covered and heated in an elastic furnace for about 6 h at the temperature of 930 K to allow the phosphate to decompose and react with other batch constituent before melting occurs, ordinarily. The glass samples were then annealed in an oven at 130 K for 2 h to reduce thermal stresses. The glass samples were polished using diamond disc and diamond powder to produce parallel opposite surfaces for ultrasonic velocity measurements. The photograph of the glass samples is shown in figure 1.

Table 1. Composition of glass system.

Sample code	Composition (mol%)				Dopant (CuO)
	Na_2O	CaO	P_2O_5	B_2O_3	
S_0	26.9	24.4	2.6	46.1	0.00
S_1	26.9	24.4	2.6	46.1	0.05
S_2	26.9	24.4	2.6	46.1	0.10
S_3	26.9	24.4	2.6	46.1	0.15
S_4	26.9	24.4	2.6	46.1	0.20
S_5	26.9	24.4	2.6	46.1	0.25
S_6	26.9	24.4	2.6	46.1	0.30
S_7	26.9	24.4	2.6	46.1	0.35
S_8	26.9	24.4	2.6	46.1	0.40
S_9	26.9	24.4	2.6	46.1	0.45
S_{10}	26.9	24.4	2.6	46.1	0.50
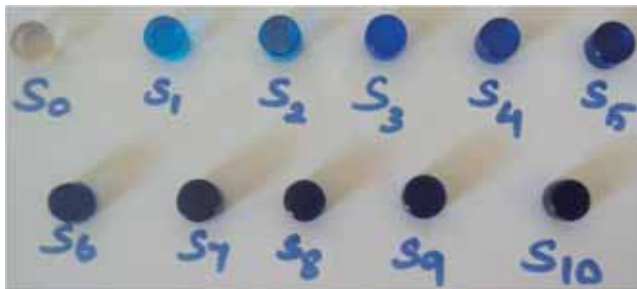
Figure 1. Photograph of NCPBC glass samples.

3. Results and discussion

3.1 *XRD*

XRD spectrum was recorded for undoped and doped glasses using XPERT-PRO diffractometer operated at 40 kV voltage and 30 mA current from $10°$ to $80°$, utilizing $CuK\alpha$ radiation source (λ-1.54060 Å). The scans were controlled by the Diffrac AC software program. The XRD patterns of all samples are shown in figure 2a and b.

Figure 2a shows the XRD spectrum of the prepared undoped and doped glass samples S_0 to S_4. For sample S_0, there was no characteristic peak, which corresponds to any crystalline phase. For S_1 to S_4 samples, the vitreous phase coexists with a crystalline phase and the pattern shows large maxima overlapped with the peaks characteristics of the crystalline phase. The reference data for the interpretation of the XRD patterns were obtained from JCPDS X-ray diffraction card files. The crystalline peak, $CaNaB_5O_9$, in sample S_1 was matched with JCPDS file no. 370827. The crystalline peaks, $CaCuP_2O_7$ and $Ca_9CuNa(PO_4)_7$, in sample S_2 were matched with JCPDS file nos 430012 and 460401, respectively. The crystalline peaks, $CaNaB_5O_9$ and $NaCuPO_4$, in sample S_3 were matched with JCPDS file nos 780294 and 370827, respectively. The crystalline peaks, $CaNa_3B_5O_{10}$ and $CaNaB_5O_9$, in sample S_4 were matched with JCPDS file nos 780295 and 370827, respectively. The results indicated that the CuO glass structure is monoclinic for the samples S_1, S_3, S_4, and rhombohedral for S_2 sample.

The structure of the samples S_1 to S_4 changed due to the increase in intensity from 375.43 a.u. (S_1) to 383.84 a.u. (S_2). The crystalline peaks (S_1 to S_4) became narrow with the increase in doping content CuO. The grain size too increased from 207.74 nm (S_1) to 496.67 nm (S_4) (table 2).

Figure 2b shows the XRD patterns of the prepared doped glasses S_5 to S_{10}, indicating no diffraction peaks. The spectrum gives a broad halo at low angles $\sim30°$ for the glass samples. This confirms the complete amorphous nature as well as a long-range structural disorder of glasses [16–18].

3.2 *Optical properties*

Analysis of optical spectra is one of the most beneficial tools to figure out the electronic structures of amorphous semiconductors. The reflectance spectra of the CuO doped and undoped borate glasses are shown in figure 3a–c. The principle of the technique is that a photon with energy greater than the bandgap energy will be absorbed. There are two kinds of optical transitions at the fundamental absorption edge: direct and indirect transitions. In both cases, electromagnetic waves interact with the electrons in the valence band, which are raised across the fundamental gap to the conduction band. For glasses, the expression of the absorption co-efficient $\alpha(v)$ as a function of photon energy hv for direct and indirect transitions was given by Davis and Mott:

$$\alpha(v) = \alpha_0(hv - E_g^{opt})^p / hv, \tag{1}$$
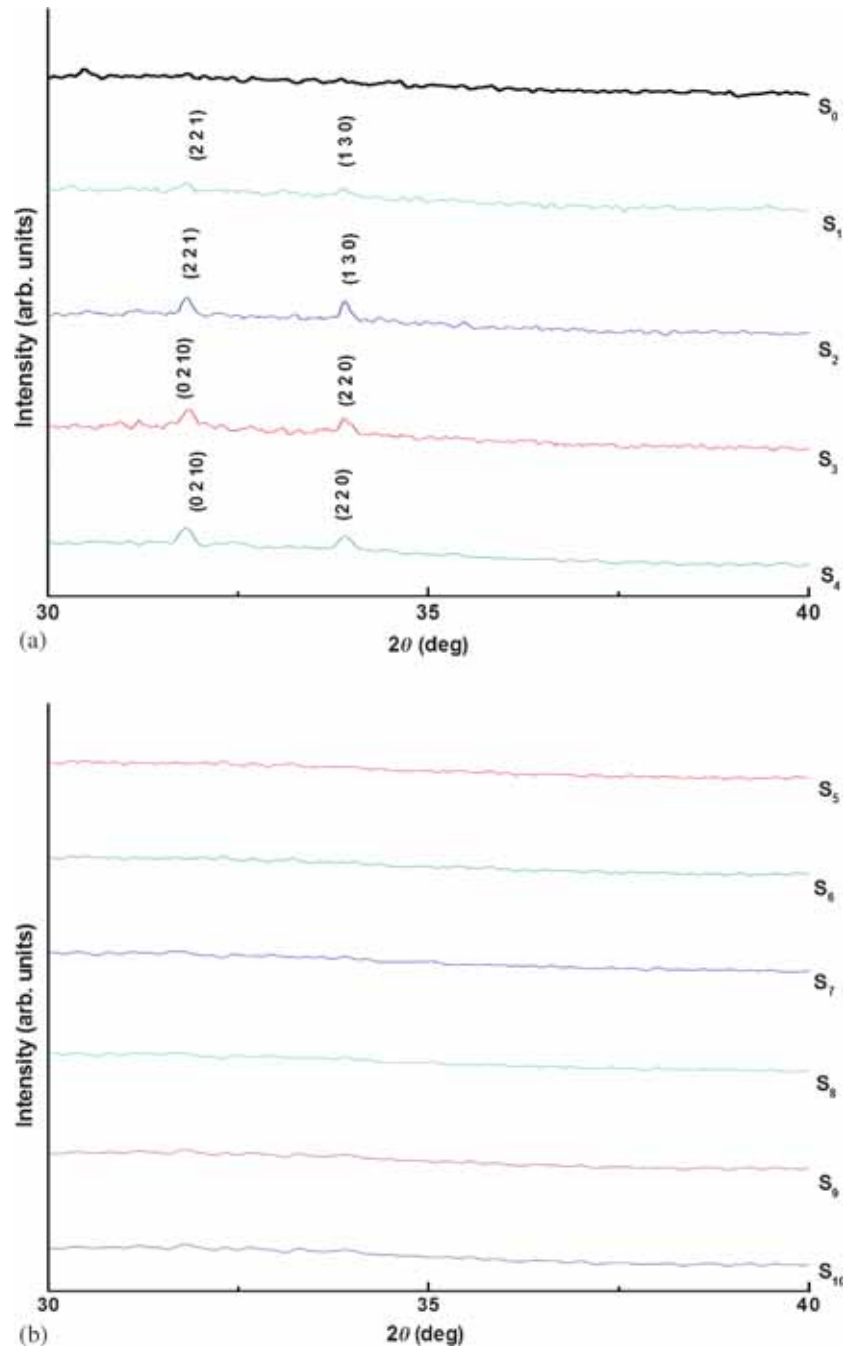
Figure 2. XRD patterns for samples (**a**) S_0 to S_4 and (**b**) S_5 to S_{10}.

where E_g^{opt} is the optical bandgap energy in eV (optical bandgaps in glasses are closely related to the energy gap between the valence band and conduction band), α_0 the energy independent constant and p an index, which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for absorption; $p = 1/2$ for allowed direct transitions, 3/2 for direct forbidden transitions, 2 for allowed indirect transitions and 3 for indirect forbidden transitions [19]. For vitreous materials, indirect transitions ($p = 2$) are valid according to the Tauc's relations [20].

The variation of $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$ is shown in figure 4a–k for the studied glasses. The values of E_g^{opt} were obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for indirect transitions and $(\alpha h\nu)^2 = 0$ for direct transitions [21].

Figure 3a–c shows a diffuse reflectance spectra of the as-synthesized pure and CuO-doped glasses in the spectral region of a pure sample, there is a broad band at 348.10 nm. When the doping component was added, the bands get shifted to 357 nm (S_1), 360.75 nm (S_2), 372.04 nm (S_3), 383.33 nm (S_4), 402.15 nm (S_5), 404.71 nm (S_6),
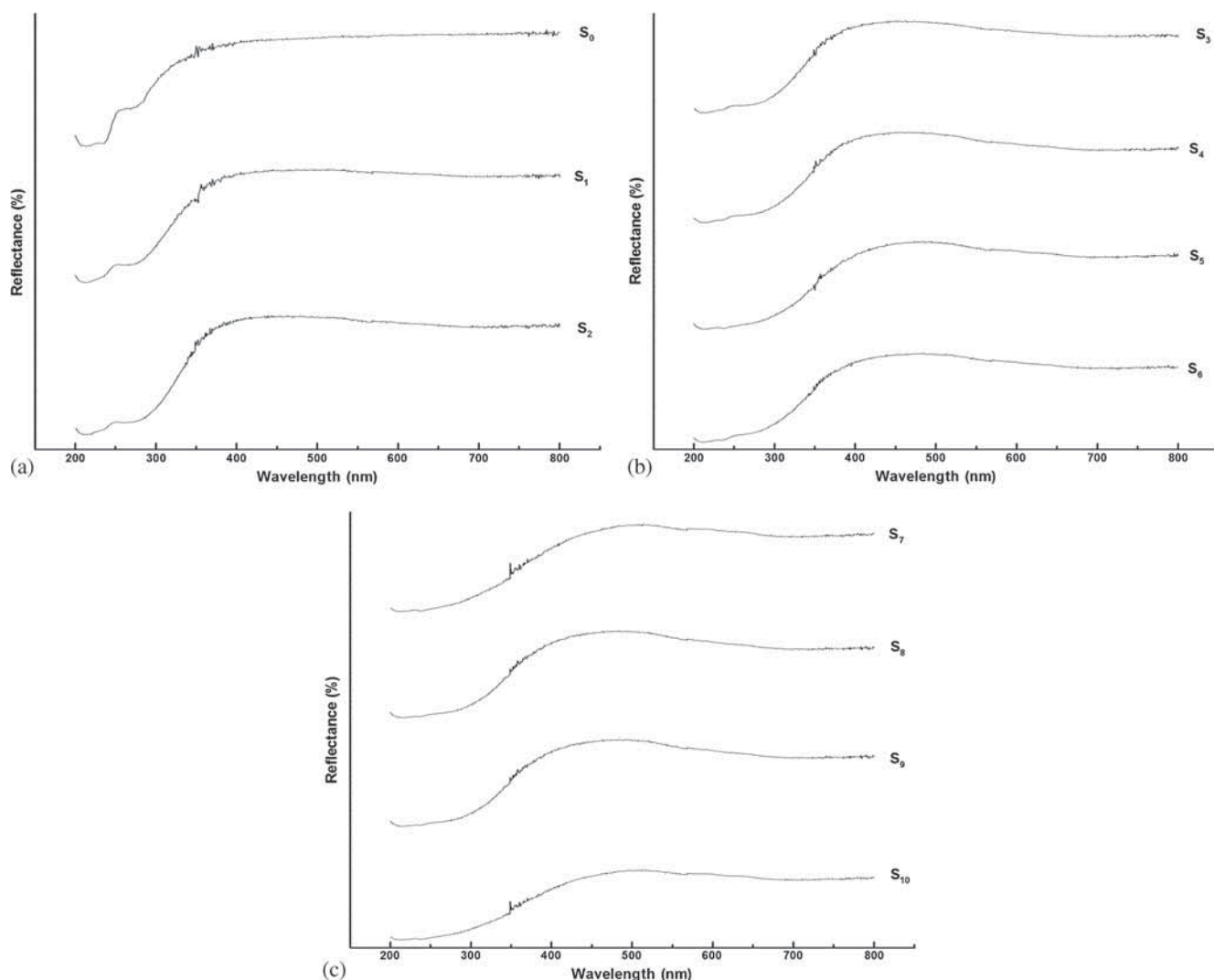
Figure 3. Reflectance spectra for samples (**a**) S_0 to S_2, (**b**) S_3 to S_6 and (**c**) S_7 to S_{10}.

407.27 nm (S_7), 439.94 nm (S_8) and 444.90 nm (S_9). This change may be due to the presence of CuO. By increasing the molarity of the dopant component to 0.5 mol%, the band gets shifted towards 466.28 nm (S_{10}).

Thus, the increasing distortion with change in chemical composition can be related to the change in polarizability of the oxygen ions surrounding the Cu^{2+} ions, and to its dependence on the field strength of the network former and modifier ions.

The density and bandgap energy were calculated and are shown in the table 3. Density responds to variations in glass composition sensitively in technological practice. Density of glass, in general, is explained in terms of a competition between the masses and the size of the various structural groups present in the glass. Accordingly, the density is related to how tightly the ions and ionic groups are packed together in the structure. The increase in copper oxide content leads to decrease in density. This result may due to the fact that CuO plays the role of network modifier and introduces excess structural free volumes.

Figure 4a–k shows the bandgap energy for the samples S_0 to S_{10}. Optical absorption study in glasses has proved to be very useful for elucidation of optical transition and electronic band structure of these materials. In CuO-doped glasses, copper ions exist in two stable ionic states as Cu^+ and Cu^{2+}. When the content of CuO increases from 0.05 to 0.5 mol%, the values of optical bandgap energy decreases from 4.81 to 3.73 eV for samples S_0 to S_4, but for the sample S_5 a slight change in bandgap value (3.03 eV) was noted, as crystalline nature changes to amorphous, and further the bandgap value decreases from 3.31 to 2.99 eV for the samples S_6 to S_{10}. Srikumar *et al* [22] showed that with the increase in the CuO content in the borate glasses, a large number of donor centres are created, the excited states of localized electrons originally trapped on Cu^+ sites begin to overlap with the empty 3d states on the neighbouring Cu^{2+} sites, and as a result, the polaron band becomes more extended into the main bandgap. This new polaronic development can lead to a significant shrinkage in the bandgap, as the concentration of
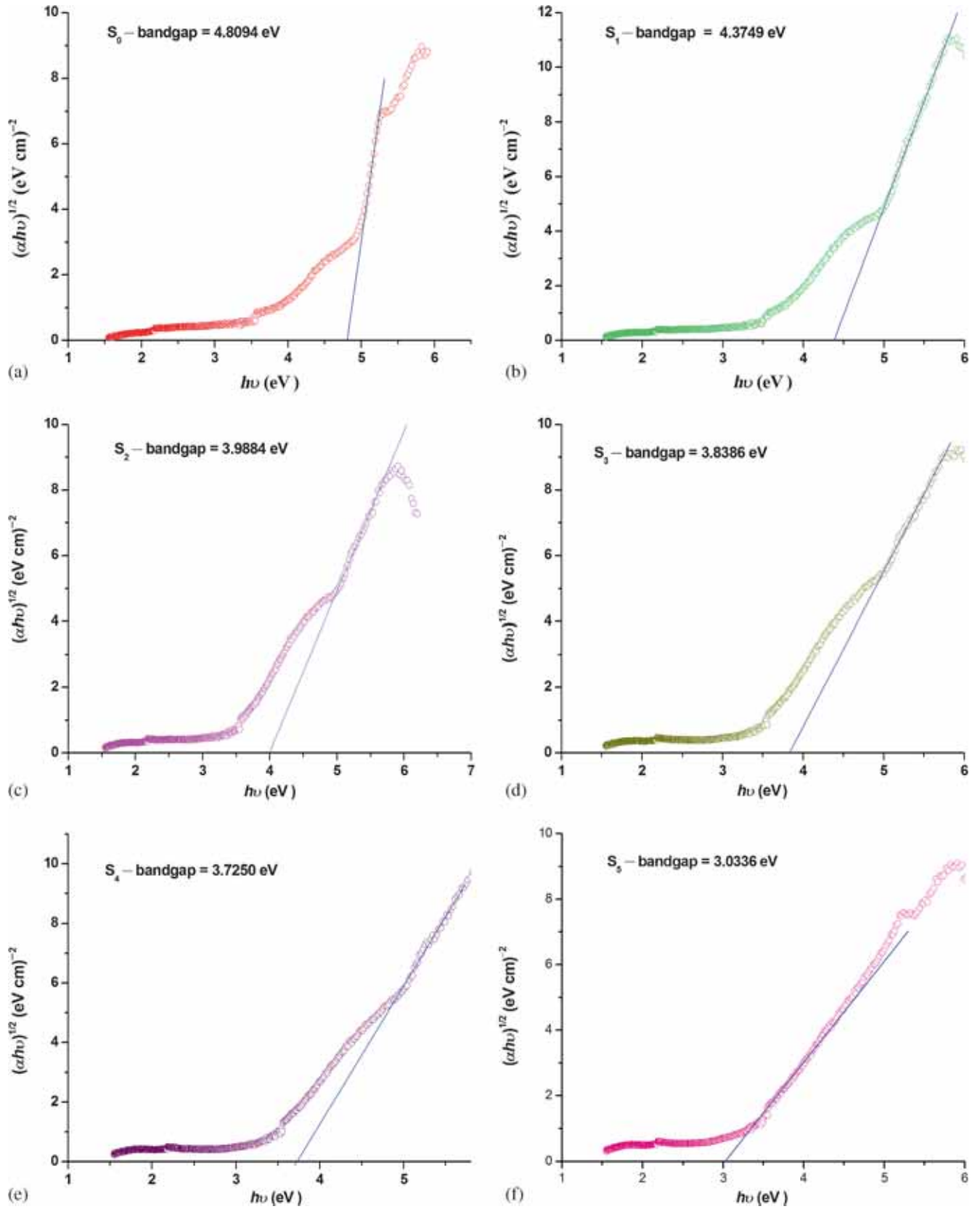
Figure 4. UV spectra for glass samples (**a**) S_0, (**b**) S_1, (**c**) S_2, (**d**) S_3, (**e**) S_4, (**f**) S_5, (**g**) S_6, (**h**) S_7, (**i**) S_8, (**j**) S_9 and (**k**) S_{10}.
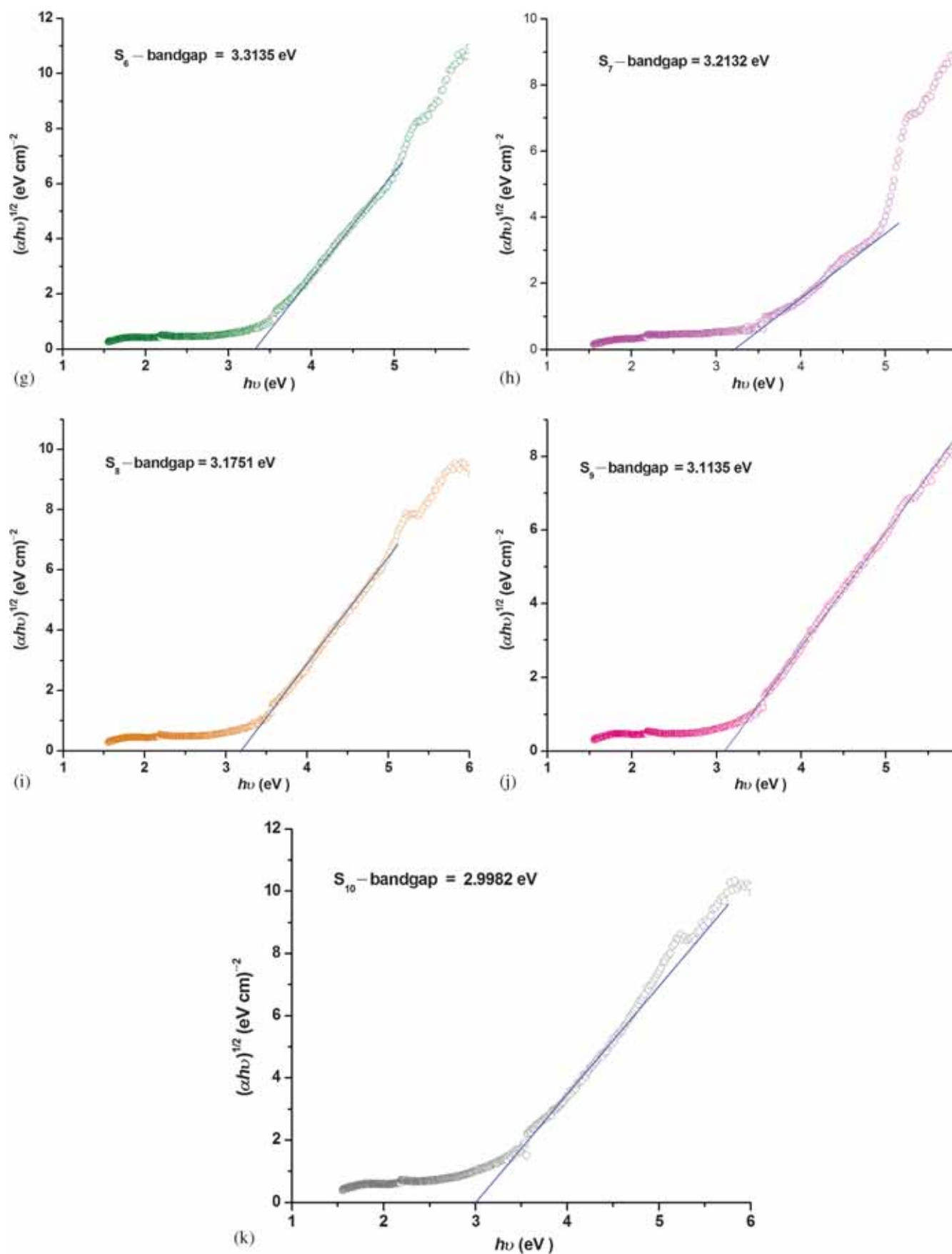
Figure 4. (Continued.)

Table 2. XRD parameters of samples S_1 to S_4.

Samples	Observed 2θ (degrees)	*hkl*	*d*-spacing	Grain strain (nm)	Intensity of crystalline peaks
S_1	10.1179	1 0 1	8.7427	398.9	374
	33.9194	2 2 2	2.6429	207.7	
S_2	31.8278	2 2 1	2.8117	826.5	386
	33.9004	1 1 12	2.6444	639.2	
S_3	31.8582	2 1 2	2.8091	823.3	405
	33.9002	2 2 2	2.6442	496.7	
	47.2326	3 0 3	1.9244	216.1	
S_4	31.8067	1 1 2	2.8135	494.0	384
	33.8982	2 2 2	2.6445	496.7	

Table 3. Direct energy bandgap of pure and CuO-doped borate glasses.

Samples	Density, ρ (g m^{-3})	E_g (eV) for direct
S_0	1.2821	4.81
S_1	1.3040	4.38
S_2	1.3152	3.98
S_3	1.3245	3.84
S_4	1.3284	3.73
S_5	1.3321	3.03
S_6	1.3399	3.31
S_7	1.3410	3.21
S_8	1.3464	3.18
S_9	1.3548	3.11
S_{10}	1.3621	2.99

CuO is increased up to 0.5 mol%. Thus, we can conclude that the decreases of the optical bandgap energy with increase in CuO content may be due to the fact that the optical absorption in the studied glasses is dominated by the polaronic transfer between the Cu^+ and Cu^{2+} ions [23].

The lowering of bandgap energy suggests that non-bridging oxygen (NBO) ion concentration increases in the glass network. The non-bridging orbits have higher energies than the bonding orbitals, contribute to the valence band maximum shifting to higher energies and reduce the bandgap.

In the present investigation, optical absorption edge is observed to be shifted towards a red colour with increasing the content of copper ion in the glass network. The concentration of NBOs effectively influences the optical edge (optical bandgap) of Na_2O-CaO-P_2O_5-B_2O_3:CuO glasses. The addition of copper ion increases localized electrons because of an increase in donor centre in the glass network; the presence of higher concentration of these donor centres decreases the optical bandgap and it is responsible for the red shift of the optical absorption edge.

3.3 Photoluminescence

Emission and excitation spectra of the polished glasses were evaluated using the LS 45 Luminescence Spectrometer at wavelength range from 200 to 800 nm. The results are shown in figures 5 and 6.

Figure 5 shows the emission spectra of CuO-doped sodium–calcium phosphoborate glasses. According to several reports available [24–27], oxide-based glasses demonstrate charge transfer (CT) bands in the UV region due to the absorption of UV radiation by oxygen ligands around the cation, which normally fall in the wavelength range 200–800 nm [28]. The emission spectra show three peaks around 460, 500 and 523 nm, with excitation peak wavelength of 388 nm. The strong emission peak wavelength of 460 nm band is slightly shifted towards longer wavelength with the increase in CuO content in the host glass and also the line width. The emission peak at 460 nm is due to Cu^{2+} ions in the glass. Ignatouych *et al* [29] reported luminescence studies on copper ions doped with lithium tetraborate glasses. They observed broad emission band around 460 nm. In the present work, we observed a broad emission band around 460 nm. This band is assigned to $3d^9 4s$–$3d^{10}$ triplet transition in Cu^+ ions [13,30,31]. Similar results were also reported by Padlyak *et al* [32]. In the excitation spectrum, the two bands observed at 388 and 522 nm are related to the CT bands.

Figure 6 shows two peaks around 388 and 522 nm, with emission peak wavelength of 460 nm. Luminescence excitation spectrum of the sample has the strongest peak at 388 nm, it exhibits blue luminescence around 400 nm. The transmittance and luminescence spectra are wider, which are the characteristic of amorphous materials [33]. On the other hand, Puppalwar *et al* [34] showed that further increase of Cu concentration adversely affects the PL intensity. This effect is attributed to the quenching concentration phenomena; the quenching is mainly due to the element's substitution that occurred between the copper and the oxygen atom inside the glass host [15].
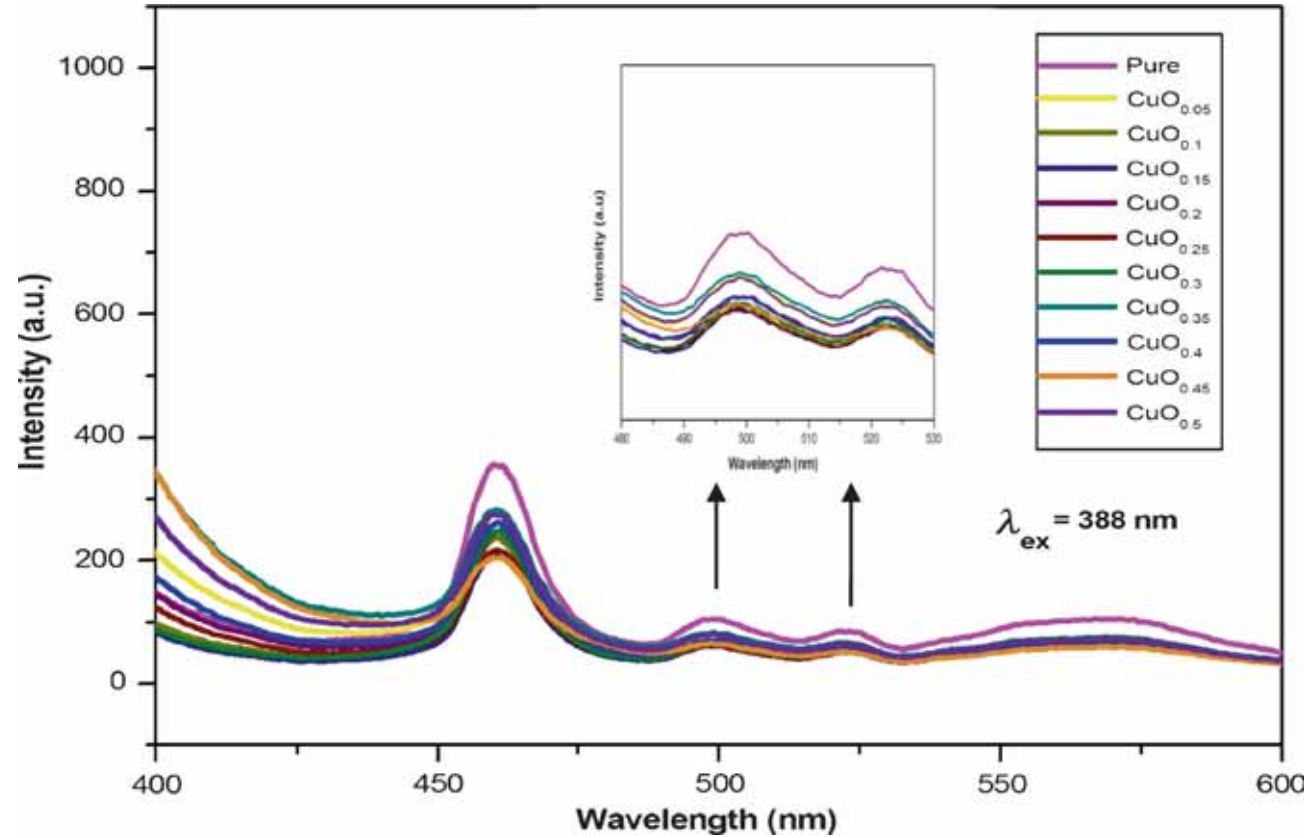
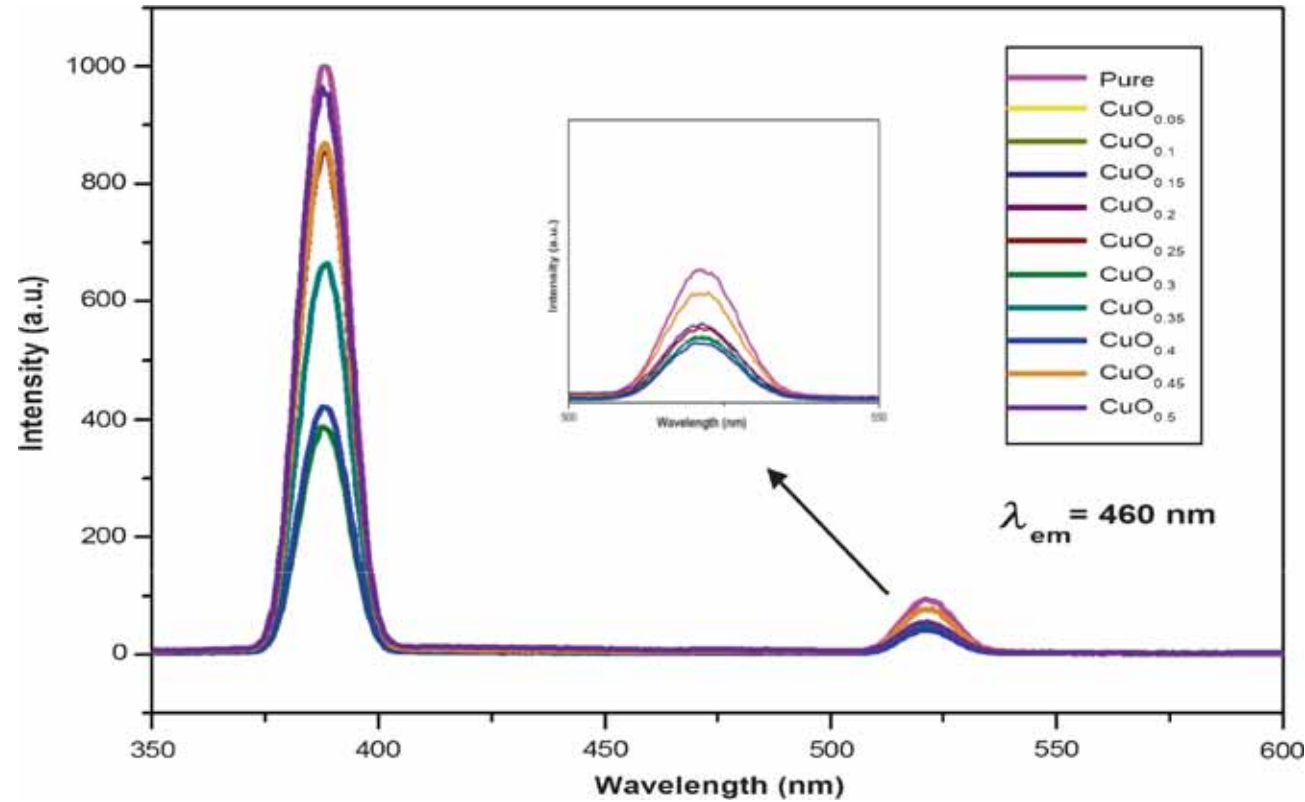**Figure 5.** Emission spectra of CuO-doped borate glasses.

Figure 6. Excitation spectra of CuO-doped borate glasses.

4. Conclusion

Powder XRD pattern confirms the amorphous and crystalline nature of the glass samples. From the optical absorption spectral, the values of direct energy bandgap E_{opt} of the glass system were found to be strongly and systematically compositional dependent and sensitive to the addition of CuO. The values of the E_{opt} range from 4.81 to 2.99 eV, showing change in the structural order of glass as a result of incorporation of CuO as a part of the network structure. The change in grain size and the intensity of peaks in XRD peaks and the reduction in the energy bandgap from 4.81 to 2.99 eV reveal the substitution of Cu^{2+} ions into the borate glasses, formation of NBOs and red shift of optical absorption edge. The analysis of these results has indicated that there is a gradual formation of copper ions Cu^+ and Cu^{2+} sites in the borate network to increase in the content of CuO. Due to the bandgap energy decreases, the NCPBC glasses become semiconducting material after addition of transition metal (copper) ions. From the luminescence results, the UV and blue region are attributed to $3d^94s$–$3d^{10}$ triplet transition in Cu^+ ion.

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