JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 24, No. 9-10, September – October 2022, p. 494 - 498

Spectroscopic characterization of P_2O_5-CaO-B_2O_3: CuO glasses

KAVITI VENKATA RAO[1], GUNNAM NAGARJUNA[1], R. RAMBABU[3]
[1]*Department of Chemistry, Jawaharlal Nehru Technological University Kakinada -533003, Andhra Pradesh, India*
[2]*Department of Chemistry, S.R.R. & C.V.R. Government Degree College, Vijayawada – 520004, Krishna District, Andhra Pradesh, India*
[3]*Department of Chemistry, G.V.P. College of Engineering, Madhurawada – 530048, Visakhapatnam, Andhra Pradesh, India*

Synthesis of P_2O_5-CaO-B_2O_3 glasses doped with CuO in the range 0.5 to 2.0 mol% using melt quenching technique is done. Initial characterization of samples by XRD and SEM techniques was carried out. XRD patterns confirm the amorphous nature to all samples which was further supported by SEM pictures. Later, optical absorption and photoluminescence spectra for all the samples in the visible and infrared region were recorded. Two significant optical absorption bands in the regions 325 – 340 nm and 550 – 800 nm were noticed. Optical band gap is decreased with the CuO addition. Emission spectra have exhibited one broad band at about 350 – 500 nm and sharp kink at 600-760 nm assigned to transition of single Cu+ centers and Cu+-Cu+ pairs. Increasing structural degree of disorder has been observed with rise of CuO that could be due to octahedrally coordinated divalent copper ions.

(Received November 17, 2020; accepted October 5, 2022)

Keywords: Copper ions, Color centres, XRD, SEM, Optical absorption

1. Introduction

Lot of research being carried out on glass materials as they are comparatively cheap, relatively easier to produce and mainly, samples with broad range of composition may be prepared based on required optical/electrical/biological/thermal properties. Phosphate based glasses are considered as potential candidates for optical filter applications including solid state electrolytes, sealing materials and medical use due to their superior physical properties viz., low softening temperature, low melting & glass transition temperatures, high thermal expansion coefficient and high ultraviolet transmission compared with conventional silicate glasses [1-4]. Special attention has been given to borophosphate based glasses due to their prominent applications as suitable media for different optical fibers & solid state lasers considering their importance in telecommunication sector [5-7]. B_2O_3 is one of the five fundamental glass network formers. It has BO_3 and BO_4 structural units. Addition of modifying oxides to B_2O_3 will cause non-bridging oxygens through modification of structural clusters from sp^2 planar BO_3 to stable sp^3 tetrahedral BO_4. P_2O_5 is another glass network former with PO_4 tetrahedron network structural units through covalent bonding. Calcium oxide breaks the borate and phosphate glass network that causing bonding defects leading to network disorder. Thus, CaO will be an added advantage in achieving required properties.

Copper oxide has lot of influence on optical, mechanical and electrical properties of borophosphate glasses even though small amount is added to the parent glass system. In particular, p-type semiconducting property of copper ions has drawn particular consideration that makes them suitable for electronic device applications. Generally, monovalent Cu^+ and divalent Cu^{2+} stable ionic states are possible for copper ions. Monovalent copper ions do not produce color whereas divalent ions cause blue and green glasses. Studies on structural features of copper ions are limited to borate, silicate, borosilicate and phosphate glasses. Hence, the present work is focused to evaluate structural modifications of copper ions through spectroscopic properties of P_2O_5-CaO-B_2O_3 glasses and also physical parameters including impact of glass composition.

2. Experimental section

(58-x) P_2O_5-17 CaO-25 B_2O_3: x CuO ($0.5 \leq x \leq 2.0$ mol %) glass composition is selected for the study after many attempts. Samples' labeling with necessary composition details are presented below.

$PCBC_0$: 58 P_2O_5 -17 CaO-25 B_2O_3
$PCBC_5$: 57.5 P_2O_5 -17 CaO-25 B_2O_3: 0.5 CuO
$PCBC_{10}$: 57.0 P_2O_5 -17 CaO-25 B_2O_3: 1.0 CuO
$PCBC_{15}$: 56.5 P_2O_5 -17 CaO-25 B_2O_3: 1.5 CuO
$PCBC_{20}$: 56.0 P_2O_5 -17 CaO-25 B_2O_3: 2.0 CuO

Analytical grade reagents of ammonium dihydrogen phosphate $NH_4H_2PO_4$, calcium carbonate $CaCO_3$, boric acid H_3BO_3, and copper oxide CuO were taken as starting materials. Calculated quantities of reagents in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar and melted in a ceramic pan in the temperature range of 900 to 1050 °C for two hours using PID controlled high temperature furnace. After confirming bubble free molten liquid, melts were poured on to desired molds with subsequent annealing at 350°C for one and half hour followed by gradual cooling to room temperature. Resultant glass samples were ground well and polished to the required dimensions. X-ray diffractometer (XRD, Rigaku D/Max ULTIMA III) operating at 50kVand 30mA with a CuKα radiation source was used to determine the nature and phase compositions of glass powders. With the help of scanning electron microscope, morphological details of glass samples were recorded. In order to evaluate physical parameters, the density "d" of the bulk samples was determined to an accuracy of (± 0.0001) by Archimedes' principle. Optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 250-1000 nm with a resolution of 0.1nm using UV-3092 spectrophotometer. The photoluminescence spectra of glass samples were carried out using F-2500 FL Spectrophotometer, Hitachi with a resolution of 2.5 nm.

3. Results and discussion

At first, calculation of physical parameters was done as they provide very important information about structural changes in the glasses with rise in CuO content. The density values of all samples were measured by Archimedes principleusing *o*-xylene (99.99% pure) as immersion liquid. The density of the glass samples increase with increasing CuO content was observed. Structural modifications, glass former positions and change in coordination of glassy ions were assumed as few reasons for density increase. It is also observed that the values of average molecular weight, M found to decrease with the content of copper oxide while ion concentration found to increase. It might be due to difference in atomic weight of P_2O_5 and copper [6]. Copper ion concentration N_i, mean copper ion separation r_i and polaron radius r_p were calculated with the experimental values of density and average molecular weight M. All these parameters are shown in Table 1. The rise in CuO causes decreasing trend of r_i&r_p which resulted increasing disorder in the glass structure.

X-ray diffraction patterns of P_2O_5-CaO-B_2O_3 pure and CuO doped glasses carried out are presented in Fig. 1. Patterns of none of the samples shown significant peaks, but all samples exhibited broad peak in the range of angle of diffraction 25° – 28° which supports the amorphous nature to all samples. Further, it also confirms no crystallization signs which might be possible during preparation of samples. CuO addition to parent glass system did not cause any changes in XRD patterns.

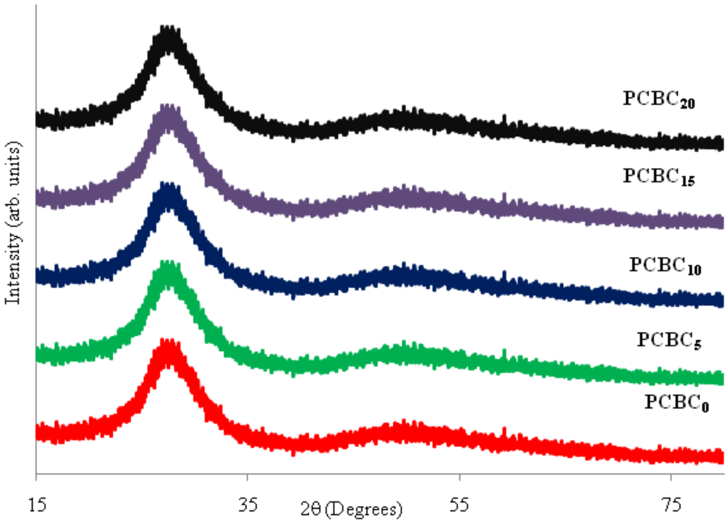

Fig.1. XRD patterns of P_2O_5-CaO- B_2O_3: CuO glasses (color online)

In order to confirm the amorphous nature exhibited by XRD patterns, scanning electron microscopic (SEM) pictures of few samples have been carried out and also to provide morphological information of glass samples. SEM pictures with magnification of 10 μm for PCBC$_5$, and PCBC$_{20}$ samples were presented in Fig. 2. All the images have clearly indicated no signs of presence of micro crystals that validate amorphous nature to all the samples including pure glass. Thus, it can be concluded that result of SEM pictures is in good agreement with XRD scans.

Table 1. Physical parameters of P_2O_5-CaO-B_2O_3: CuO glasses

Sample	**Avg. Mol. Wt. (g/mol)**	**Density (g/cm^3)**	**Conc. of 'Cu' ions N_i (10^{21}/cm^3)**	**Interionic distance of 'Cu' ions r_i(A°)**	**Polaron radius r_p(A°)**
$PCBC_0$	191.593	2.569	---	---	---
$PCBC_5$	190.571	2.589	4.09	6.252	2.519
$PCBC_{10}$	189.550	2.609	8.29	4.941	1.991
$PCBC_{15}$	188.528	2.629	12.59	4.298	1.732
$PCBC_{20}$	187.506	2.649	17.02	3.888	1.567

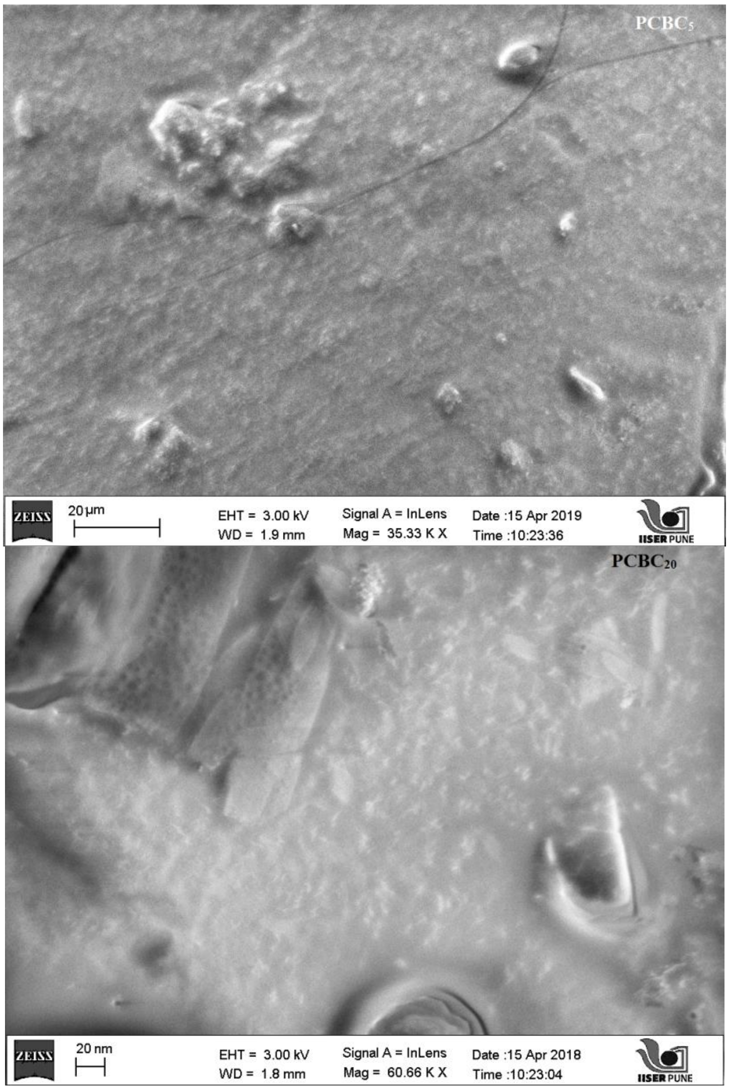

Fig.2. Scanning electron microscopic pictures of P_2O_5-CaO-B_2O_3: CuO glasses

Room temperature optical absorption spectra of CuO doped P_2O_5-CaO-B_2O_3 glasses in the spectral region 200 nm to 1000 nm is shown as Fig.3. Two small bands are observed in the range about 340 to 380 nm that could be due to $3d^{10} \rightarrow 3d^9\, 4s^1$forbidden transitions of Cu^+ ions. After the addition of CuO, the intensity and half-widths of small and large kinks found to increase slightly which might happen due to large density of Cu^+ ions. Another prominent broad band has noticed in the wavelength region 580 nm to 940 nm in the glass samples corresponding to energy transfer $^2B_{1g} \rightarrow {}^2B_{2g}$ of divalent copper ions occupied octahedral symmetry [2, 9, 10]. A slight increase of width of wide band with CuO rise has been observed. Interesting observation is that intensity and half-width of broad absorption band found to increase at the expense of small two bands. Thus it allows us to conclude that large existence of divalent ions converted from monovalent copper ions with CuO rise might be possible. Significant result is that pure glass sample $PCBC_0$ has absorption edge at lower wavelength side, but CuO addition has made red shift in the absorption edge. The octahedrally coordinated Cu^{2+} ions produce non-bridging oxygens moved the absorption edge to the region of longer wavelengths that is presented in Table 2. Further, it is also observed that optical band gap found to be diminished with CuO that might be due divalent Cu ions occupied in octahedral position causing large number of donor centres through non-bridging oxygens. The details of cut-off wavelength, band position and optical band gap of all the samples are given in Table 2.

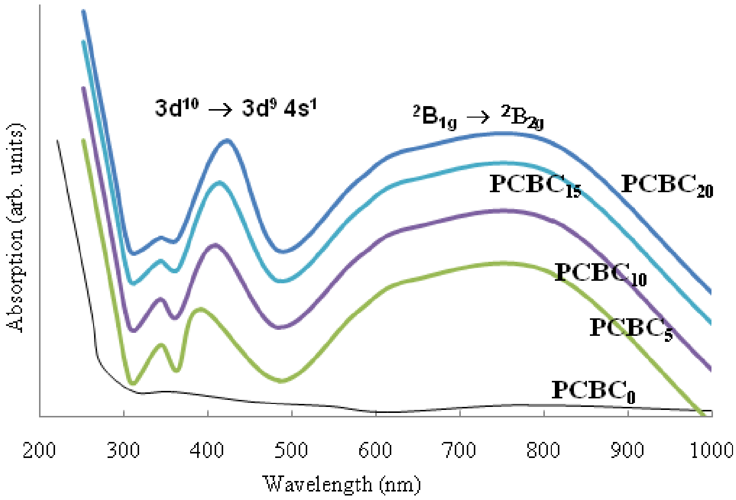

Fig. 3. Optical absorption spectra of CuO doped P_2O_5-CaO-B_2O_3glasses (color online)

Emission spectra of P_2O_5-CaO-B_2O_3 doped with CuO glasses is presented in Fig. 4. All the glasses excited at their absorption cut-off wavelengths. One wide band in the wavelength region at about 340 – 500 nm and another prominent band at about 600 – 760 nm have been observed in the spectra of all the samples. Observed emission bands are attributed to $^3D_1 \rightarrow {}^1S_0$ single Cu^+ centers and Cu^+- Cu^+ pair transitions respectively [2, 6, 9, 10]. With increase in the content of CuO, decrement of the intensity and half-width corresponding to both the emission bands is noticed.

Table 2. Summary of data on optical absorption spectra of P_2O_5-CaO-B_2O_3: CuO glasses

Sample	Cut-off wavelength (nm)	$^2B_{1g} \rightarrow {}^2B_{2g}$ (nm)	Optical band gap E_o(eV)
$PCBC_0$	251	---	---
$PCBC_5$	288	798	2.95
$PCBC_{10}$	295	802	2.92
$PCBC_{15}$	302	809	2.87
$PCBC_{20}$	307	811	2.84

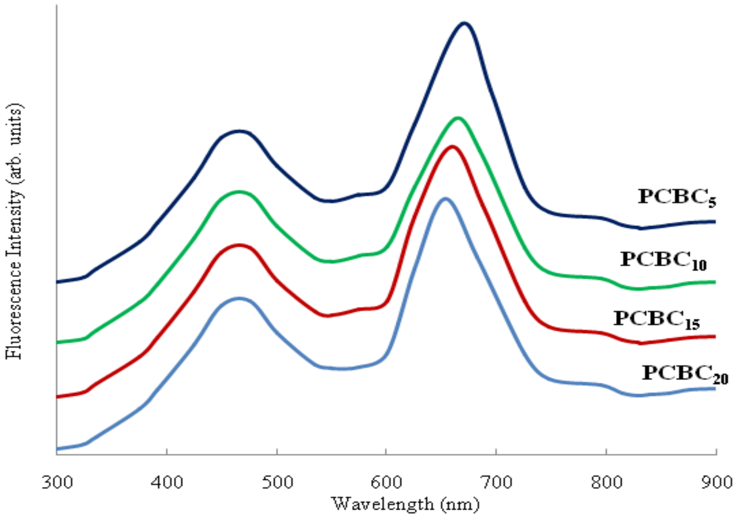

Fig.4. Fluorescence spectra of P_2O_5-CaO-B_2O_3: CuO glasses recorded at room temperature (color online)

Slight half-width changes (ranging from 90 nm to 130 nm) are associated with the concentration of Cu^+ ions. The sample $PCBC_5$ found to exhibit highest intensity among all glass samples that could be due to large concentration of Cu^+ ions in that sample. The conversion of copper ions from monovalent to divalent has already been confirmed from optical absorption spectra. Further, it also supports the existence of large concentration of divalent ions occupying octahedral coordination in $PCBC_{20}$ sample. Thus, the sample $PCBC_{20}$ found to exhibit both the emission bands with less intensity. It is worth mentioning here that Cu^+ ions act as modifier ions similar to PO_4& BO_4 structural units. An emission band of copper ions in the visible region makes this glass system apt for optical filter applications.

4. Conclusion

P_2O_5-CaO-B_2O_3: CuO glasses were synthesized using melt-quenching technique. The X-ray diffraction studies indicated the non-crystalline nature to glasses. SEM pictures also confirmed amorphous nature and in good agreement with XRD scans. Variation of physical parameters with the content of CuO suggests rising structural irregularity. Optical absorption spectra indicated three bands; two bands in the region about 325 – 340 nm and third band about 550 – 800 nm; further decrease in band gap is observed due to increasing donor centres. Emission spectra have exhibited one wide band in the range about 340 – 500 nm and another prominent band at about 600 – 760 nm corresponding to monovalent copper ions. Maximum intensity and half-width for the glass sample $PCBC_5$ are seen for both the emission peaks out of all samples. The emission bands in the visible region of copper ions excited with their absorption edges (lower energy) make them suitable materials opto-electronic device applications.

References

[1] Ch.Vijay Kumar, M. Sreenivasulu, B. Rupa Venkateswara Rao, Optik **221**, 165291 (2020).

[2] T. Satyanarayana, B. Rambabu, G. Nagarjuna, P. Syam Prasad, P. Venkateswara Rao, J. Optoelectron. Adv. M. **21**(7-8), 530 (2019).

[3] D. Bellucci, A. Sola, I. Cacciotti, C. Bartoli, M. Gazzarri, A. Bianco, F. Chiellini, V. Cannillo, Mater. Sci. Eng. C **42**, 324 (2014).

[4] T. Satyanarayana, T. Kalpana, N. Veeraiah, J. Lumin. **130**, 506 (2010).

[5] D. E. Day, Z. Wu, C. S. Ray, P. Hrma, J. Non-Cryst. Solids **241**, 12 (1998).

[6] S. Shailajha, K. Geetha, P Vasantharani, Bull. Mater. Sci. **39**(4), 1009 (2016).

[7] D. Ehrt, W. Seeber, J. Non-Cryst. Solids **129**, 19 (1991).

[8] S. Selomuly, S. Ski, K. Pita, C. H. Kam, Q. Zhang, S. Buddhudu, Mater. Sci. Eng. B **100**, 136 (2003).

[9] R. P. S. Chakradhar, K. P. Ramesh, J. L. Rao, J. Ramakrishna,J. Phys. Chem. Solids **64**, 641 (2003).

[10] T. Satyanarayana, G. Nagarjuna, K. Ravikiran, Solid State Phenomena **207**, 55 (2014).

---

[*] Corresponding author: gnrgjcn@gmail.com