Preparation and characterization of copper (Cu$^{2+}$) ions doped Zincaluminoborophosphate (ZnAlBP) glasses

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Abstract. The Glass configuration of 40 ZnO + 25 H$_3$BO$_3$ + (x-30) P$_2$O$_5$ + (5) Al$_2$O$_3$: x CuO (0<x<0.8) have been prepared and investigated by XRD, EPR, Optical absorption and FTIR techniques. Zincaluminoborophosphate (ZnAlBP) glasses doped with Cu$^{2+}$ ions are prepared using melt quenching technique at 1250 °C for 2h. The obtained glasses are blue in colour with good transparent nature. The XRD result shows that the prepared glasses are amorphous in nature. The UV-Vis spectra of Cu$^{2+}$ doped titled glasses show a strong broad band at 800 nm which is due to $^{2}$B$_{1g}$→$^{2}$B$_{2g}$ transition. The room temperature EPR spectra exhibit four weak parallel and one perpendicular component of Cu$^{2+}$ ions. The g and A values are calculated for all the concentrations of Cu$^{2+}$ ions and are reported. The number of spins shows the non-monotonic behaviour. The FTIR spectra shows different modes of P-OH, P=O, Zn-O and BO vibrations.

1. Introduction
Glasses have many technological packages because of their versatile electrical and optical characteristics. The oxide glasses played an essential role in numerous fields like science, medicinal drug and other industry [1]. Borate was proven as a super glass former including fast ionic conductors with low expansion and have high thermal stability and good solubility [2, 3]. One of the important properties of the Boro phosphate glasses is that it can acts as a band pass filter in the ultraviolet-visible region. Reported EPR spectra of ZnO-B$_2$O$_3$–Al$_2$O$_3$ and P$_2$O$_5$–B$_2$O$_3$–Al$_2$O$_3$ glasses containing, Cu$^{2+}$ and Mn$^{2+}$ions at room temperature and discussed the results in terms of the glassy regions of the phase diagram.[4]. Replacements of phosphorous without changing the Boro phosphate glass systems are also called “blended-glass former effect” in modifier concentrations within the glass community [5]. Transition metal (TM) ions in the glasses have strong optical, magnetic and electrical impacts. Several studies have been available on the transition metal ions doped inorganic glass systems. The glasses containing TM ions exhibit memory and photo conducting properties [6, 7]. Zinc is a beneficial transition metal ion for optoelectronic studies with outstanding electro-optic properties and it turned into attracted in a super quantity of interest for packages. ZnO acts as an excellent glass modifier because of
its ionic cross linkages between distinct phosphate anions [8, 9]. However, incorporation of few boron atoms into the phosphate glass can increase the stability and durability [10]. A few oxide glasses doped with the transition metal ions along with copper showed semi conducting nature [11]. Copper doped Boro phosphate glasses exhibit exciting electric and optical properties and make the host as a suitable for fast-ionic conductors, intense lasers [12].

2. Experimental

The borate glasses having the formula 40 ZnO + 25 H$_3$BO$_3$ + (30 – x) P$_2$O$_5$ + 5Al$_2$O$_3$+ x CuO (x = 0.2, 0.4, 0.6, and 0.8 wt. %) were prepared. The conventional melt quenching process was adopted for the preparation and the samples were air quenched. The chemical compositions used in the present glass system given in table 1. The used chemicals of ZnO, B$_2$O$_3$, P$_2$O$_5$, Al$_2$O$_3$ and CuO are of AR grade. Approximately, each 15g powders were manually mixed and then melted in a furnace in the silica crucible at 1250 °C nearly 2 hours. The samples are further annealed at 400°C for 5 hours to become free from the structural stress. The EPR spectra were scanned in the magnetic field from 250mT to 360mT. The X-Ray diffraction pattern were recorded with XRD (SHIMADZU-6100) using copper k$_a$ radiation in the range 2θ= 10-80°. UV-V is absorption spectrum has been measured from 200-1000 nm wavelength range. Glass samples of thickness 1mm were used for optical measurements. Fourier Transform infrared spectra (FTIR) of glasses were measured using a JASCO-FTIR-6200 spectrometer in the range 400-4000cm$^{-1}$by using Kbr pellet.

Table 1. Compositions of the glasses (all in wt. %) studied in the present work

| Glass code       | ZnO | H$_3$BO$_3$ | P$_2$O$_5$ | Al$_2$O$_3$ | CuO | Color      |
|------------------|-----|-------------|------------|-------------|-----|------------|
| ZnAlBP           | 40  | 25          | 30         | 5           | -   | Color less |
| ZnAlBP: Cu 0.2   | 40  | 25          | 29.8       | 5           | 0.2 | Light blue |
| ZnAlBP: Cu 0.4   | 40  | 25          | 29.6       | 5           | 0.4 | Blue       |
| ZnAlBP: Cu 0.6   | 40  | 25          | 29.4       | 5           | 0.6 | Blue       |
| ZnAlBP: Cu 0.8   | 40  | 25          | 29.2       | 5           | 0.8 | Blue       |

3. Results and discussion

3.1 XRD Analysis

The powder XRD studies were carried out for all concentrations of the prepared samples. The measurements were carried out in the range of 10° < 2θ < 80° angles. A single broad hump was observed and no other sharp peaks were identified in the entire spectra. The low intense broad peak nearly centred at 2θ = 28° indicates the amorphous nature of the glasses [13]. The XRD pattern of pure ZnAlBP and ZnAlBP (x) Cu (x= 0.2, 0.4, 0.6, 0.8) doped glass network is shown in figure (1).
3.2 Electron Paramagnetic resonance (EPR) of the glass system

No EPR signal is observed in the pure ZnAlBP glass confirming that the starting materials used in the present work were free from transition metal impurities. The EPR spectra exhibit four parallel components and one perpendicular component shown in figure (2) [14-16]. The dipole-dipole interaction of nuclear spin leads to exhibit resonance signals characteristic of copper ions in the ZnAlBP glasses. The perpendicular components are not well resolved, though some hyperfine structure is observed.

![EPR pattern of the ZnAlBP glasses](image)

**Figure 2.** EPR pattern of the ZnAlBP glasses

3.3 Calculation of no. of spin concentration (N) and Susceptibility

The spin concentration (N) participating in resonance in this glass system was calculated for different concentrations of copper 0 ≤ x ≤ 0.8 wt%. We have evaluated the no. of spins (N) participating in the resonance at $g = 2.379$ by comparing the area under the absorption curve with that of have standard known concentration (CuSO$_4$.5H$_2$O). It is observed that the number of spins essentially increases up to 0.4 wt.% from 0.2 wt.% and decreased to 0.6 wt.% and again increased 0.8 wt.% which exhibit the Non-monotonic nature. The variation of N w.r.t dopant ion concentration may be due to the structural changes occur during the sample preparation. Figure (3) shows a plot drawn between spin concentration and copper concentrations for this glass system and it is clear that as the concentration of Cu$^{2+}$ ions is increased [17].

The magnetic susceptibility ($\chi$) of the paramagnetic ion Cu$^{2+}$ has been calculated at room temperature using the expression [18].

$$\chi = \frac{N g^2 \beta^2 (I+\frac{1}{2})}{3K_B T}$$

(1)

Where the terms have their usual meanings [16].

The paramagnetic susceptibility was calculated for ZnAlBP: Cu$^{2+}$ (0.2-0.8 wt. %) glass samples and a plot drawn for the reciprocal of susceptibility ($1/\chi$) as a function of concentrations is shown in figure (4). From the graph, the susceptibility of the samples decreases with the concentrations of copper in the host matrix.
Figure 3. A plot of no. of spins (N) Concentration of Cu$^{2+}$ in ZnAlBP glasses.

Figure 4. A plot of susceptibility ($1/\chi$) Against of Cu$^{2+}$ions doped ZnAlBP glasses.

3.4 Optical absorption spectra

UV-VIS spectra for glass compositions exhibit single broad peak as shown in figure (5). In optical absorption, (0.2) Cu ions forms a peak at 747 nm (13,386) cm$^{-1}$ and (0.8) Cu ions forms a peak at 784 nm (12,755) cm$^{-1}$ respectively. This can be attributed to the presence of Copper ion in the glass of Zinaluminoborophosphate. The Optical study of the wavelength region 200-1000 nm. The Optical absorption spectra are attributed to $^2B_{1g} \rightarrow ^2B_{2g}$ transition in the distorted octahedral sites of copper ions.

Figure 5. UV- VIS Spectra of ZnAlBP: Cu (0.2 - 0.8 wt %) glass samples.

3.5 Urbach energy ($\Delta E$) and optical band gap ($E_{opt}$)

The absorption coefficients in Urbach’s tail region have been given as a function of photon energy by the equation [19].

$$\alpha = \alpha_0 \exp \left( \frac{hv}{\Delta E} \right)$$

(2)

Where $\alpha_0$ is a constant, $\Delta E$ is the Urbach's energy defined as the energy gap between localized tail states in the forbidden band gap. The values of Urbach energy ($\Delta E$) were calculated from the reciprocal of the slope of the straight line from the plots of ln ($\alpha$) vs hv and the data are listed in Table 2. The $\Delta E$ values decreases from 1.770 to 0.379 eV due to increase of Cu$^{2+}$ content figure (7). This can be explained by the addition of copper ions in the glasses decreases the degree of disordering the fragments of the glass network. This indicate that these glasses possess minimum number of defects.

The optical band gap energies ($E_g$) of the glasses were obtained from their ultraviolet absorption edge by plotting $(\alpha h\nu)^{1/2}$ as function of photon energy hv as shown in Figure (6) and included in Table 2. The
cations play an indirect but significant role; the conduction band is influenced by the glass forming anions [20]. The values of optical band gap ($E_g$) slightly decrease with increase of CuO concentration and results in the increase of bonding defects and non-bridging oxygens [21].

Figure 6. A Plot of $(\alpha h\nu)^{1/2}$&h$\nu$ for ZnAlBP: Cu (0.2 - 0.8 wt %) glasses

Figure 7. In $\alpha$&h$\nu$ for ZnAlBP: Cu (0.2 - 0.8 wt %) glasses

3.6 Optical basicity of the glass ($A_{tb}$)

The calculated and theoretical optical basicity ($A_{tb}$) are listed in table 2. The basicity values are decreasing from 1.129 to 0.757 Zincaluminoborophosphate glasses [22].

The theoretical values of optical basicity ($A_{tb}$) of the glass can be estimated using the formula

$$A_{tb} = \sum_{i=1}^{n} \frac{Z_i r_i}{\gamma_i}$$  \hfill (3)

Where $n$ is the total number of cations present, $Z_i$ is the oxidation number of the $i^{th}$ cation, $r_i$ is the Ratio of number of $i^{th}$ cations to the number of oxides present and $\gamma_i$ is the basicity moderating parameter of the $i^{th}$ cation.

$\gamma_i$ can be calculated from the following equation:

$$\gamma_i = 1.36(x_i-0.26)$$  \hfill (4)

Where $x_i$ is the Pauling electronegativity of the cation.

It is observed that the value of the optical basicity decreases and it starts to increase with the increase of ionic radius of Zincaluminoborophosphatedoped Cu$^{2+}$ ions.

| Glass code | Optical basicity ($A_{tb}$) | Optical band gap ($E_g$) (eV) | Urbach energy ($\Delta E$) (eV) |
|------------|-----------------------------|-------------------------------|-------------------------------|
| ZnAlBP     | 1.1297                      | 4.49                          | 1.170                         |
| ZnAlBP: Cu 0.2 | 0.7608                    | 3.92                          | 0.657                         |
| ZnAlBP: Cu 0.4 | 0.7598                    | 3.74                          | 0.476                         |
| ZnAlBP: Cu 0.6 | 0.7588                    | 3.67                          | 0.422                         |
| ZnAlBP: Cu 0.8 | 0.7577                    | 3.50                          | 0.379                         |
3.7 Fourier Transform Infrared Spectroscopy (FTIR) Studies

Figure (8) Represents FTIR spectra of ZnAlBP glasses doped with copper ions (x = 0.2, 0.4, 0.6, 0.8). The peaks present for undoped sample are at 539, 532, 538, 538, 543 cm\(^{-1}\), 1128 and 1630 cm\(^{-1}\), while the Cu\(^{2+}\)-doped samples slight shifted. For 0.6Cu\(^{2+}\)-doped samples an additional peak is observed at 2352 cm\(^{-1}\).
The presence of copper ions mostly in tetragonally distorted octahedral prepared glasses was confirmed by XRD spectra.

The determination of the vibrational modes of borate glasses are (1) from 1200 to 1600 cm\(^{-1}\) vibrations of BO\(_3\) units [26]. Symmetrical vibration of PO\(_4\) units (14). The spectra additionally reveal a group of distinguished absorption bands within the infrared variety 2352 cm\(^{-1}\) due to hydroxyl or water companies and these are chronic in the compositions [27]. The observed and 1114 cm\(^{-1}\) to 1128 cm\(^{-1}\) is due to the PO\(_4\) units [6]. 1458 cm\(^{-1}\) is vibration BO\(_2\) different units [27]. 775 cm\(^{-1}\) the transmittance peak intensity is decreasing Al\(_2\)O\(_3\) mol percentage due to the BO\(_3\)-O-BO\(_4\) bending vibrations. 1421 cm\(^{-1}\) is attributed to the stretching vibrations of B-O in BO\(_2\)O\(_3\) units from different groups [28]. Some peaks 3423 cm\(^{-1}\) to 3434 cm\(^{-1}\) can be assigned to OH group of element or H\(_2\)O [31].

The bands observed from the IR spectra and their composition shown it table 4. The determined to be vibrational modes of borate glasses are (1) from 1200 to 1600 cm\(^{-1}\) vibrations of BO\(_3\) units [26]. Symmetrical vibration of PO\(_4\) units (14). The spectra additionally reveal a group of distinguished absorption bands within the infrared variety 2352 cm\(^{-1}\) due to hydroxyl or water companies and these are chronic in the compositions [27]. The observed and 1114 cm\(^{-1}\) to 1128 cm\(^{-1}\) is due to the PO\(_4\) units [6]. 1458 cm\(^{-1}\) is vibration BO\(_2\) different units [27]. 775 cm\(^{-1}\) the transmittance peak intensity is decreasing Al\(_2\)O\(_3\) mol percentage due to the BO\(_3\)-O-BO\(_4\) bending vibrations. 1421 cm\(^{-1}\) is attributed to the stretching vibrations of B-O in BO\(_2\)O\(_3\) units from different groups [28]. Some peaks 3423 cm\(^{-1}\) to 3434 cm\(^{-1}\) can be assigned to OH group of element or H\(_2\)O [31].

### Table 3. The spin-Hamiltonian parameters and molecular orbital bonding Coefficients of Cu\(^{2+}\) doped glasses

| Glass       | g\(_\parallel\) | g\(_\perp\) | \(\Delta\) \((10^4)\) | \(g/\Delta\) \(cm^{-1}\) | (N) per \(kg(10^{20})\) \((^{2}B_{1g} \rightarrow ^{2}B_{2g})\) \(cm^{-1}\) | Transition | \(\alpha^2\) | \(\beta^2\) | \(\Gamma_{\pi}\) | \(\Gamma_{\sigma}\) |
|-------------|-----------------|-------------|------------------------|--------------------------|-------------------------------|-------------|-------------|-------------|-------------|-------------|
| ZnAlBP      | 2.379           | 2.070       | 126                    | 188                      | 1.2939                        | 13386       | 0.7948      | 0.9005      | 19.9        | 44.71       |
| Cu 0.2      | 2.381           | 2.067       | 116                    | 204                      | 5.3107                        | 12594       | 0.7663      | 0.9397      | 12.0        | 50.92       |
| Cu 0.4      | 2.374           | 2.070       | 120                    | 197                      | 1.0187                        | 12468       | 0.7707      | 0.9089      | 18.4        | 49.97       |
| Cu 0.6      | 2.384           | 2.070       | 112                    | 212                      | 8.0811                        | 12755       | 0.7558      | 0.9565      | 8.8         | 53.21       |

### Table 4 The FTIR band positions and their band assignments of ZnAlBP glass samples.

| Sample/ Band assignment | Host | Cu 0.2 | Cu 0.4 | Cu 0.6 | Cu 0.8 | References |
|------------------------|------|--------|--------|--------|--------|------------|
| Zn – O Stretching vibration | 548  | 532    | 538    | 538    | 543    | [14]       |
| B-O symmetric stretching BO\(_4\) units | 1024 | 1024   | 1024   | 1024   | 1024   | [28]       |
| O-P –O                  | 1114 | 1120   | 1121   | 1121   | 1122   | [29]       |
| B – O of BO\(_3\) groups | 1457 | 1442   | 1407   | 1421   | 1458   | [26]       |
| Bending of P-OH         | 1608 | 1608   | 1608   | 1608   | 1630   | [27]       |
| OH Group                | ......| ......  | ......  | 2352   | ......  | [27]       |
| BO\(_3\)-O-BO\(_4\)     | 755  | 755    | 755    | 755    | 755    | [28]       |
| OH Group element or H\(_2\)O | 3423 | 3434   | 3434   | 3434   | 3434   | [31]       |

### 4. Conclusion

Zincaluminoboro phosphate ZnAlBP(x) Cu, 0 ≤ x ≤ 0.8 wt% glasses were successfully prepared by adopting melt quenching technique. The spin-Hamiltonian parameters in ZnAlBP glasses indicate that the Cu\(^{2+}\) ions are in octahedral coordination with a tetragonal distortion. The amorphous nature of the prepared glasses was confirmed by XRD spectra. The Optical absorption studies of these glasses indicate the presence of copper ions mostly in tetragonally distorted octahedral positions. It is observed that the...
from the nature and position of the absorption band observed, it can be inferred that the band corresponds to $^{2}B_{1g} \rightarrow ^{2}B_{2g}$ transition. By correlating the EPR and optical data, the molecular orbital bonding coefficient is evaluated. This value suggests that the in-planes $\sigma$ bonding in the glasses is moderately covalent in nature. Spin-Hamiltonian parameters do not vary with the change in copper ion concentration. The paramagnetic susceptibility ($\chi$) is found to obey Scurie’s law. FTIR spectra in which symmetrical, asymmetrical stretching and bending vibrations along with OH groups have been observed.

5. References

[1] Ashok B, Vijaya Kumar R and Kistaiah P 2015 J. Non-Cryst. Solids 47 426
[2] Sreekanth Chakradhar R P, Murali A and Lakshmana Rao J 1999 J. Alloys Compd. 29 265
[3] Devde G N, Upender G, Chandru Mouli V and Ravange L S 2015 Adv. Phys.
[4] Ramesh Kumar V, Rao J L and Gopal N O 2005 Mater. Res. Bull. 40 1256
[5] Hima Bindu S, Siva Raju D, Vinay Krishna V, Rajavardhana Rao T, Veera Brahmam K and Linga Raju Ch 2016 Opt. Mater. 62 655
[6] Upender G, Kamalaker V, Vardhani C P and Chandra Mouli V 2009 Indian J. Pure App. Phys. 47 55
[7] Ramadevudu G, Shareefuddin Md, Sunitha Bai N, Lakshimpathi Rao M and Narasimha Chary M 2000 J. Non-Cryst. Solids 278 205
[8] Yang S W, Chiang H Y, Lai Y S, Wu F B, Chuni Fu and Yi-Mu Lee 2015 Ceram. Int. 41 877
[9] Rada M, Chelcea R, Rada S, Rus L, Dura R, Nistor T, Rusa T, Culea E 2013 Spectrochim. Acta A Mol. Biomol. Spectrosc. 102 414
[10] Kashif I and Ratep A Applied Physics A 10.1007/S00339-015-9329-3.
[11] Jose A and Jimenez 2016 Physica B Condens. Matter 92 498
[12] Wongsing T, Kaewkha J, Limsuwan P, Kedkaew C and Enggi P 2012 Procedia engineering 32 807.
[13] Ismail S F, Sahar M R and Ghoshal S K 2016 Mater. Charact. 111 177
[14] Srinivas Rao N, Shashidhar Bale, Purnima M, Srinivasu Ch, Samee M A, Siva Kumar K and Syed Rahman 2009 Physika B Condens. Matter 404 1875
[15] Upender G, Chinna Babu J and Chandra Mouli V 2012 Spectrochimica Acta Part A 89 39
[16] Sumalatha B, Omkaram I, Rajavardhana Rao T and Ling Raju Ch 2011 J. Non-Cryst. Solids 357 3143
[17] Srinivasulu K, Omkaram I, Obeid H, Suresh Kumar A and Rao J J L 2012 Physica B Condens. Matter 407 4741
[18] Linga Raju C, Gopal N O, Reddy B C V and Rao J L 2007 Mater. Charact. 61 423.
[19] Zamytatin O A, Plotnichenko V G, Churbanov M F, Zamytatina E V, Sumalatha and Karzanov V V 2017 J. Non-Cryst. Solids
[20] Shiv Prakash Singh, Chakradhar R P S, Rao J L and BasudebKarmakar 2013 J. Magn. Magn. MMater 346 21
[21] Altaf M, Chaudhry M A and Siddiqi S A 2005 Glass Phys.Chem 31 597
[22] Prakash P G and Rao J L 2004 J. Mater. Sci 39 193
[23] Sivaramaiah G, Lakshmana Rao J 2013 J. Alloys Compd 551 399
[24] Murali Krishna R, Andre J J, Pant R F and Seth V P 1998 J. Non-Cryst. Solids 232 50
[25] Ardelean I, Peteanu M, Burzo E and Ciocricas F 1995 Solid state communications 1038 1098
[26] Sreedhar B, Lakshmana Rao J and Lakshman S V J 1990 J. Non-Cryst. Solids 124 216
[27] Roshan Lal and Sharma N D 2005 Indian J. Pure Appl. Phys. 43 833
[28] Razvan Stefan, Eugen Culea and PetruPascuta 2012 J. Non-Cryst. Solids 358 839
[29] Vedeaneu N, Magdas D A and Stefan R 2012 J. Non-Cryst. Solids 358 3170
[30] Chinna Babu J, Suresh S and Chandra Mouli V 2005 Indian J. Pure Appl. Phys. 43 833
[31] Zakiyyulrahman Takai, Rajinder Singh Kundal, MohdKamarulzaki Mustafa, SalizaAsman, Aisha Idris, Yusuf Shehu, Jibrin Mohammad, Miftahu Gambo Idris and Mansur Said 2019 Materials Research 22 (1) : e2010404
[32] Raheem Ahmed Mohamad and Shareefuddin Md 2019 Spr. Nature Sciences 5 019

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