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Research Article

# Structural Features of Copper Doped Heavy Metal Oxide Based Glasses

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### *Abstract*

*Lead antimony borate glasses containing different concentrations of CuO ranging from 0 to 2.0 mol% have been prepared by conventional melt quenching technique. Later, glasses were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Optical absorption and FTIR spectra of these samples also have been carried out. XRD and SEM studies confirmed the amorphous nature of samples. From the optical absorption spectra it is observed that copper ion exist in $Cu^+$ and $Cu^{2+}$. IR spectra indicated that the concentration of more orderly structural units viz., $BO_4$, and $Sb^VO_4$ is low in the network of the glass $C_{20}$.*


***Keywords:*** *Antimony glasses, optical absorption, copper ion, IR spectra.*

## 1. Introduction

Transition metal ions doped glass materials are expected to be promising candidates as gain media for ultra-broadband optical fiber amplifiers, tunable lasers and ultra-short pulse lasers in telecommunication. This is because of the dominance of non-radiative losses over the relaxations of excited states of transition metal ions/lasing spices in these materials. Heavy metal oxide based glasses like $PbO$-$Sb_2O_3$ have attracted an enhanced interest in recent years due to the reason that they exhibit large nonlinear optical susceptibility ($\chi^3$) coefficient, that makes them suitable for potential applications in non-linear optical devices (such as optical switchers, limiters etc.), broad band optical amplifiers operating around 1.5 μm. $Sb_2O_3$ based glass ceramics exhibit significant transparency in the far infrared region and possess high refractive index.

CuO containing glasses are also draw special attention because of the p-type semiconducting property due to the thermally excited hopping of the small polaron from the $Cu^+(3d^{10})$ to $Cu^{+2}(3d^9)$ state . In glasses, copper ions exist in two stable ionic states viz., monovalent $Cu^+$ ions (cuprous) which does not produce coloring for the glass samples, divalent $Cu^{2+}$ ions create color centers that produces blue and green glasses. The color of the glass depends on the $Cu^{2+}$ content, its specific coordination, composition and basicity of the glass. From the literature survey, it was found that most of the studies on environment of copper ions in various inorganic glasses have been limited to phosphate, silicate and borate glasses. Thus the present work is focused at structural details of copper ions in $PbO$–$Sb_2O_3$-$B_2O_3$ glass system.

## 2. Experimental Methods

For the present study, a particular composition (40−*x*) PbO–30 $Sb_2O_3$– 30 $B_2O_3$: *x* CuO (0<x<2.0) is chosen. The details of compositions and corresponding labels are as follows:

$C_0$: 40 PbO- 30 $Sb_2O_3$- 30 $B_2O_3$
$C_5$: 39.5 PbO- 30 $Sb_2O_3$-30 $B_2O_3$: 0.5 CuO
$C_{10}$: 39.0 PbO- 30 $Sb_2O_3$-30 $B_2O_3$: 1.0 CuO
$C_{15}$: 38.5 PbO- 30 $Sb_2O_3$-30 $B_2O_3$: 1.5 CuO
$C_{20}$: 38.0 PbO- 30 $Sb_2O_3$-30 $B_2O_3$: 2.0 CuO

Analytical grade reagents of $Sb_2O_3$, $H_3BO_3$, PbO and CuO chemical powders in appropriate amounts (all chemicals were used without further purification, all in mol%) were thoroughly mixed in an agate mortar and melted using a thick-walled platinum crucible in temperature range of 950 -1000 °C in a PID temperature-controlled furnace for about 25 minutes. The resultant bubble-free melt was then poured in a brass mould and subsequently annealed at 350 °C. The amorphous nature of samples was identified by XRD using an Xpert PRO'analytical X-ray diffractometer with Cu K$\alpha$ radiation. The microstructures were observed with scanning electron microscopy (SEM; Hitachi model S-3400N) using polished surfaces. Optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 300-1000 nm up to a resolution of

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0.1nm using a Cary 5E UV–visible–NIR spectrophotometer. The dimensions of the samples used for these measurements were ~1.0 cm × 1.0 cm × 0.2 cm. Infrared transmission spectra are recorded on a JASCO-FT/IR –5300 spectrophotometer with a resolution of 0.1 $cm^{-1}$ in the range 400-2000 $cm^{-1}$ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa.

## 3. Results and Discussion

### *3.1 XRD Patterns*

X-ray diffraction spectra of PbO-$Sb_2O_3$-$B_2O_3$: CuO glasses are shown in Fig. 1. Amorphous nature of glass samples was confirmed from the spectra that shows absence of sharp peaks. It is also another indication for the absence of sign of crystallinity that might be possible during the quenching process of glass sample.

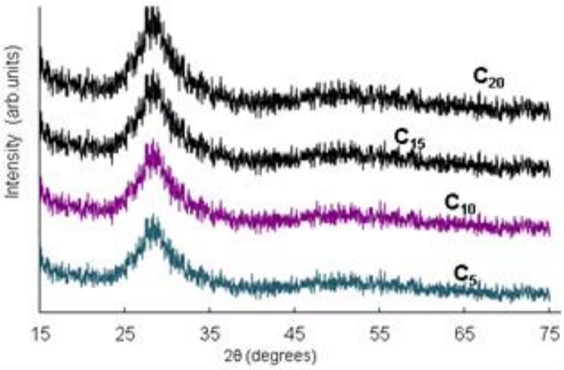


**Fig. 1** X-ray diffraction patterns of PbO-Sb2O3-B2O3:CuO glasses.

### *3.2 SEM Pictures*

Scanning electron microscopy (SEM) pictures for some of the PbO-Sb2O3-B2O3: CuO glasses are presented in Fig. 2. SEM pictures are useful to explore the entire morphology of the glass samples. These pictures taken clearly indicate that prepared glass samples do not contain any sort of crystal grains confirming amorphous nature.

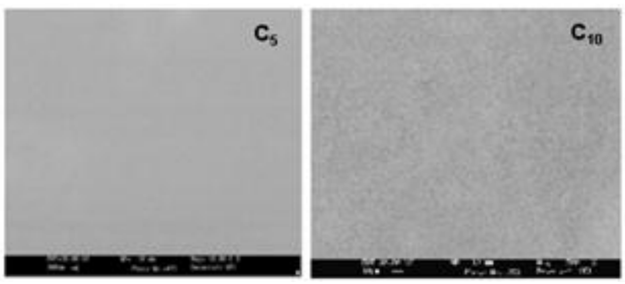


**Fig. 2** SEM pictures of some of PbO-$Sb_2O_3$-$B_2O_3$: CuO glasses

### *3.3 Optical Absorption Spectra*

Using optical absorption spectra, electronic structures of amorphous semiconducting materials can be explored. Specifically, uv-visible spectroscopy is frequently used technique for structural characterization of glass materials when they doped with transition metal oxides. Optical absorption spectra of PbO-$Sb_2O_3$-$B_2O_3$: CuO glasses recorded at room temperature is shown in Fig. 3. From the spectra, it is very clear that the absorption edges are found to be shifted gradually towards higher wavelength with CuO addition. The spectrum of glass sample $AC_{15}$ exhibits two bands; a small kink at 400 nm may be ascribed to $3d^{10} \rightarrow 3d^9\ 4s^1$ transition; and another broad band peaking at about 750 nm was assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of $Cu^{2+}$ ions. Intensity and half width of second band found to be increased with the content of CuO. It is also evident from the spectra that initially there would be larger presence of $Cu^+$ ions which will be converted further into $Cu^{2+}$ ions with rise of CuO. From this spectra, it can be concluded that sample with low content of CuO exhibits more intensity of kink and sample with high content of CuO exhibiting high intensity and broadening of second band. The broadening of this band may be attributed to the superposition of three electron transition in 'd' orbitals corresponding to $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions .

The octahedrally co-ordinated $Cu^{2+}$ ions act as modifiers induce non-bridging oxygens (NBOs) in the glass network. The higher the concentration of these modifier ions, the higher is the concentration of NBOs in the glass matrix. This leads to an increase in the degree of localization of electrons, thereby increasing the donor centers in the glass matrix. The presence of larger concentrations of these donor centers decreases the optical bandgap and shifts the absorption edge towards the higher wavelength side. More specifically, the red shift of $E_g$ with the increase in the content of CuO is associated with a decrease in the exchange interactions between the p electrons in the conduction band in $Sb_2O_3$ and the localized d electrons of the tetrahedrally distorted copper ions.

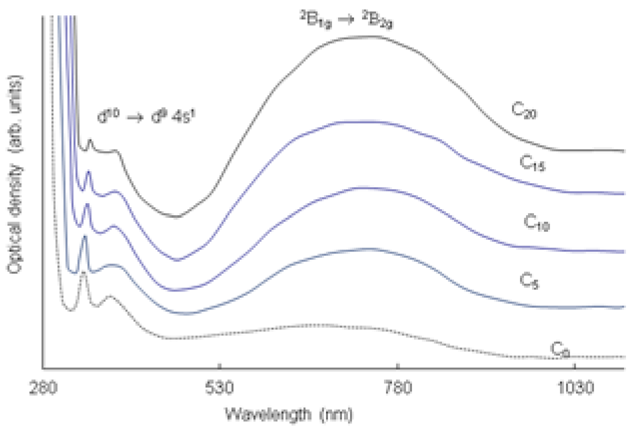


**Fig. 3** Optical absorption spectra of PbO-$Sb_2O_3$-$B_2O_3$: CuO glasses

### *3.4 Infrared Spectra*

Fig. 4 shows the infrared spectrum of glass sample $C_5$. It revealed three conventional bands originated from borate groups at 1414 $cm^{-1}$ (due to $BO_3$ units), 1112 $cm^{-1}$ (due to $BO_4$ units) and another band at 714 $cm^{-1}$ due to bending vibrations of B-O-B linkages . In this spectrum, the $\nu_1$ vibrational band of $SbO_3$ units is appeared at 931$cm^{-1}$ whereas the □$_2$ and □$_4$ bands seem to be missing. The $\nu_3$ vibrational bands merged with the band due to bending vibrations of B-O-B linkages and may have formed a common vibrational band due to B-O-Sb linkages.

With the gradual increase in the concentration of CuO, the intensity of $BO_3$ and $SbO_3$ structural units is observed to increase where as that of the band due to $BO_4$ structural unit is observed to decrease. In addition, a band due to $PbO_4$ structural groups at about 470 $cm^{-1}$ is also observed in the spectra of all the samples. Thus the PbO-$Sb_2O_3$-$B_2O_3$: CuO glass network is expected to have $BO_3$, $BO_4$, $SbO_3$, $Sb^VO_4$, and $PbO_4$ structural units. This observation clearly suggests that there is a larger degree of disorder in the networks of the glass samples with increase in the content of CuO.

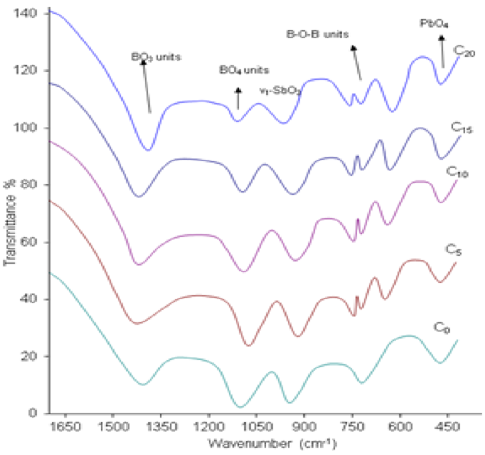


**Fig. 4** IR spectra of PbO-$Sb_2O_3$-$B_2O_3$: CuO glasses

## Conclusions

PbO-$Sb_2O_3$-$B_2O_3$: CuO glasses have been synthesized by melt quenching with different concentrations of CuO and further samples were characterized by XRD, SEM, and spectral studies viz., optical absorption and IR. XRD studies indicated that prepared glasses have pure amorphous structure. From the IR spectra, it is observed that that there is a larger degree of disorder in the networks of the glass samples with increase in the content of CuO. The optical absorption studies have indicated that copper exist in both the valence states viz., $Cu^+$ and $Cu^{2+}$. Finally the analyses of all results indicated that there will be growing degree of structural disorder with increase in the content of CuO.

## References


K. Terashima, T. Hashimoto, T. Uchino and T. Yoko, Optical properties of $Sb_2O_3$-$B_2O_3$ binary glasses, (1996), *J. Ceram. Soc. Japan*, 104, 1008-1014.

T. Satyanarayana, I.V. Kityk, M. Piasecki, P. Bragiel, M.G. Brik, Y. Gandhi, N. Veeraiah, Structural investigations on PbO-$Sb_2O_3$-$B_2O_3$: CoO glass ceramics by means of spectroscopic and dielectric studies, (2009), *J. Phys:. Cond. Mater.*, 21, 245104 (16 pp).

J.C. Sabadel, P. Armand, D. Cachau-Herreillat, P. Baldeck, O. Doclot, A. Ibanez and E. Philippot, Structural and Non-linear optical characterizations of tellurium oxide based glasses: $TeO_2$-BaO-$TiO_2$, (1997), *Solid State Chem*., 132, 411-419.

S.V.G.V.A. Prasad, G. Sahaya Baskaran, N. Veeraiah, Spectroscopic, magnetic and dielectric investigations of BaO–$Ga_2O_3$–$P_2O_5$glasses doped by Cu ions, (2005), *Phys. Status Solidi A*, 202, 2812-2828.

J.V. Bellini, M.R. Morelli, R.H.G.A. Kiminami, Ceramic system based on ZnO-CuO glass, (2008), *Mater. Lett*., 62, 335-337.

B.S. Bae, M.C. Weinberg, Optical absorption of copper phosphate glasses in the visible spectrum, (1994), *J. Non-Crst. Solids*, 168, 223-231.

Baldassare Di Bartolo, (Ed.), Spectroscopy of Solid-State Laser–Type Materials, (1987), Plenum Publishing Corporation, New York, p. 238-589.

L. Srinivasa Rao, M. Srinivasa Reddy, D. Krishna Rao and N. Veeraiah, Influence of redox behavior of copper ions on dielectric and spectroscopic properties of Li $_2$O–$MoO_3$–$B_2O_3$: CuO glass system, (2009), *Solid State Sci.*, 11, 578-587.

G. Naga Raju, M. Srinivasa Reddy, K.S.V. Sudhakar, N. Veeraiah, Spectroscopic properties of copper ions in ZnO-$ZnF_2$ -$B_2O_3$ glasses, (2007), *Opt. Mater.*, 29, 1467-1474.

T. Satyanarayana, K. Srinivasa Rao, N.T.V. Naga Lakshmi and G. Nagarjuna, Dielectric studies on alkali borate glasses mixed with iron oxide, (2014), *Solid State Phenomena*, 207, 69-96.

K.J. Rao, Structural Chemistry of Glasses, (2002), Amsterdam. Elsevier.

T. Satyanarayana, I.V. Kityk, K. Ozga, M. Piasecki, P. Bragiel, M.G. Brik, V. Ravi Kumar, A.H. Reshak, N. Veeraiah, Role of titanium valence states in optical and electronic features of PbO–$Sb_2O_3$–$B_2O_3$:$TiO_2$ glass alloys, (2009), *J. Alloys Compds.*, 482, 283-297.


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