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Preparation and studies of TMI ion doped Na-Borophosphate Glasses

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Abstract

Sodium borophosphate glasses doped with transition metal Cu ion glasses having compositions of $20Na_2O - 20ZnO - 25B_2O_3 - (35\text{-}X) P_2O_5 - X CuO$ (X= 1-6) were prepared using conventional melt quench method. Density, Transmission spectra, FT-IR spectra, conductivity and chemical durability characteristics were measured as a function of copper content for different glass samples. The initial decrease in the density is due to addition of CuO. Further addition of CuO i.e. 6% leads to the increase in density. Optical band gap for different glass samples as measured from transmission characteristics were found to be in the range 2.5-3.5 eV. IR spectroscopy have been employed to investigate the $20Na_2O - 20ZnO - 25B_2O_3 - (35\text{-}X) P_2O_5 - X CuO$ glasses in order to obtain information about the role of Cu ion and ZnO in the formation of glass network. Electrical studies have been carried out to understand the effect of transition metal ion. The conductivity measured in the range of 238K to 423K obeys Arrhenius law. The observed conductance (σ) increases with increase in TMI content. The dissolution rate for Cu ion doped NZBP glasses was seen. It results that introduction of Cu and Zn ions increase the chemical durability.

Keywords: Phosphate glasses, transition metal ion (TMI), electrical conductance, optical properties.

Introduction

The oxide glasses containing transition metal ions (TMI) are of great interest because of their semiconducting properties, which arise from the presence of TMI in multivalent states. Among different types of glasses, the phosphate based glasses have been interested due to their applications[1-3]. Due to their poor chemical durability only the limited studies have been reported on them[4]. However, incorporation of few boron atoms into the phosphate glass network has been shown to increase chemical durability of the phosphate glasses[5]. Borophosphate glasses are one of the important classes of glassy materials as they possess a variety of other useful properties. To our knowledge, there are no many reports in the literature on the studies of borophosphate glasses containing TMI.

In the present study, we report the optical, electrical, structural and chemical durability studies of Cu^{+2} ions in Sodium Zinc Borophosphate glasses. Chemical durability of phosphate glasses greatly improved by addition of ZnO because Zn ion acts as an ionic cross linker between different phosphate anions, inhibiting hydration reaction. Therefore chemically durable glass composition in the sodium zinc borophosphate (NZBP) glass system was chosen as starting composition of our studies. In corporation of CuO is also expected to improve the chemical durability of the phosphate glasses. Therefore, it is interesting to study the effect of CuO in ZnO containing borophosphate glass.

Material and Methods

Glass preparation: Sodium borophosphate glass doped with TMI Cu ion was prepared by conventional melt-quench technique. Glasses with compositions, $20Na_2O - 20ZnO - 25B_2O_3 - (35\text{-}X) P_2O_5 - X CuO$ (X= 1-8), were prepared using analytical grade compounds of $NaNO_3$, ZnO, H_3BO_3, $NH_4H_2PO_4$ and $CuSO_4$ as starting materials. The content of CuO was varied from 1-8 mol%. These chemicals were thoroughly mixed and ground for 30-40 min in a mortar pastel and then the charge (25g) was melted in alumina crucible using muffle furnace for 4-5 hrs at temperature ranging from 800-1100^{0}C depending on composition. When the melt was thoroughly homogenized and attained desirable viscosity it was poured either onto metal plate or into graphite moulds. The prepared glass was the annealed at appropriate temperatures (between 300 and 400^{0}C) for 2 hrs and stored in desiccator prior to evaluation.

Glass characterization: Density was measured for all glass samples at room temperature using xylene as the immersion liquid. Molar volume was calculated from the knowledge of obtained density.

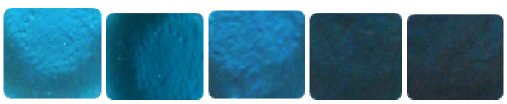
XRD patterns for the glass powders were recorded in the 2θ range of 10-80^0 on a computer controlled X-ray diffractometer with Cu K_α source.

The UV and visible optical transmission for glass samples were measured by using double beam spectrophotometer covering the range 200-1100 nm.

The IR infrared absorption spectra of the glasses were measured at room temperature in the wave number range 400–4000 cm^{-1} by computerized FTIR spectrometer. Glass powder mixed with anhydrous KBr in ratio 2:200 mg i.e. glass powder: KBr respectively. The weighed and thoroughly mixed mixture was then subjected to a pressure of 5 tones / cm^3 to produce clear homogeneous discs. The infrared absorption was measured immediately after preparing the required disc.

Electrical conductivity measurements were carried out on these samples using precision impedance analyzer (Agilent 4294 A) in the frequency rang 40 Hz to 20 MHz at different temperature. The impedance analyzer was interfaced to a personal computer using GPIB add on card and the recorded data was stored on the computer. The relative chemical durability was estimated by measuring the weight loss of a polished glass after immersion in 10% HCl and 10% NaOH for 72 hrs at room temperature.

Cu doped Na- Borophosphate Glasses: The structures and properties of glasses in the Cu ion doped glass system have been investigated.



Cu-1% Cu-2% Cu-3% Cu-4% Cu-6%
Photographs of Cu ion doped investigated glass samples

Results and Discussion

We have obtained in all the bubble free glass samples. XRD patterns confirm the glassy nature of the samples with the broad halo peak obtained at 2θ range of 20–30^0.

The variation of density (ρ) and molar volume (Vm) with variation CuO mole% for all glass samples is shown in figure 1. In the present investigations the observed anomalous behavior is i.e. minimum density at 4% of CuO. The initial decrease in the density is due to addition of CuO. As a result, a decrease in density with addition of CuO is observed as in figure 1. Further addition of CuO i.e. 6% leads to the increase in density. An initial decrease in density with addition of 1% CuO is observed, further addition of CuO (<3%) in the glass network results in the erection of ionic cross-linking between non bridging oxygens (NBOs) of two different chains, thereby reinforcing glass structure[6-8].

The glasses with and without CuO doping have been characterized with UV – visible spectrophotometer and it has shown interesting results. Figure 2 represents the transmittance spectra of the (a) 0% (b) 1% (c) 2% (d) 3% (e) 4% (f) 6% (g) 8% CuO doped polished glass samples. The adsorption edge cut off shifts towards the longer wavelength with increase in the concentrations of CuO. The 3% CuO doped glass shows 82 nm shift and 6% CuO doped glass shows 125 nm shift. This interesting behavior implies the CuO nano crystals formation in the phosphate glass.

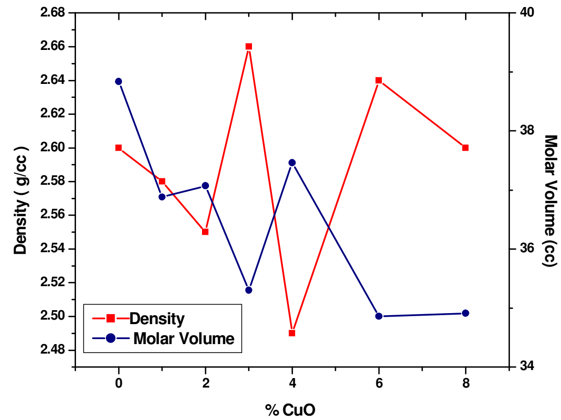


Fig 1: Variation of Density & Molar volume with mol% of CuO

Figure-1
Variation of Density and Molar volume with mol% of CuO

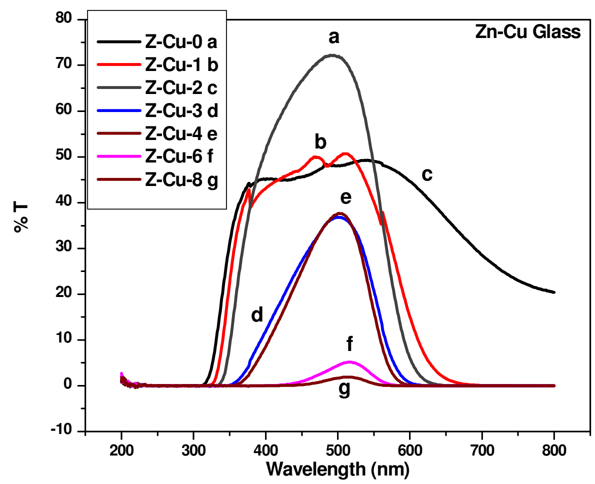


Figure-2
UV transmission spectra of Sodium Zinc Borophosphate glasses doped with Cu ions.

Table 1 summarizes the band gap values at the respective UV cut offs for the various CuO doped glasses. Figure 3 reveals the dependence of band gap on the percentage of CuO doped in the glass. The graph shows that band gap increases as per the increase in the % of CuO doping. This clearly reveals the possibility of the CuO nano crystals formation in the glass matrix. Interestingly, higher doping from (1-4%) gives the characteristic absorption peaks at around 502-516 nm (strong peak around at 350 nm – 600 nm). This peak is owing to the existence of Cu^+ ions. The Cu^+ imparts the greenish-blue color to the glass and gives characteristics absorption or transmission. The peaks observed around 502-516 nm are in blue–green region of the absorption spectra has been assigned to $3d^{10} \rightarrow 3d^9 45^1$ transition of Cu^+ ion[9-10]. The P_2O_5 acts as reducing agent in the melts and accelerating the reduction of Cu^{2+} to Cu^+ ions.

IR transmission spectra are shown in figure 4, which represent the characteristics of the various phosphate glass samples i.e. (a) Cu=1%, (b) Cu=2% (c) Cu=3%. The vibrational modes observed are mainly due to the phosphate network which appears in the range 700 – 1500 cm[1 11]. The peak obtained at 830 cm^{-1} for Z-1, 816.14 cm^{-1} for Z-2, 815.33 cm^{-1} for Z-3 and 825.33 cm^{-1} for Z-4 glass samples shows the characteristic of the vibrations of bridging P-O-P groups. There is no appreciable change in the characteristic of stretching vibrations in low and higher concentration of CuO content glasses. The peaks obtained at 1649.14, 2360.80, 2339.04, 2339.92, 2360.11, 3199.41 and 3732.86 cm^{-1} are assigned to water, OH. POH vibrations originating mostly for moisture attack on phospate glass[12]. With the introduction of increasing

Table-1
UV cut off and band gap of different CuO doped glasses

Sr. No.	% CuO Doped	UV cut off λ_C nm	Band E_o Gap (eV)
1	0	352	3.511
2	1	361	3.423
3	2	372	3.322
4	3	434	2.848
5	4	441	2.802
6	6	477	2.591
7	8	489	2.527

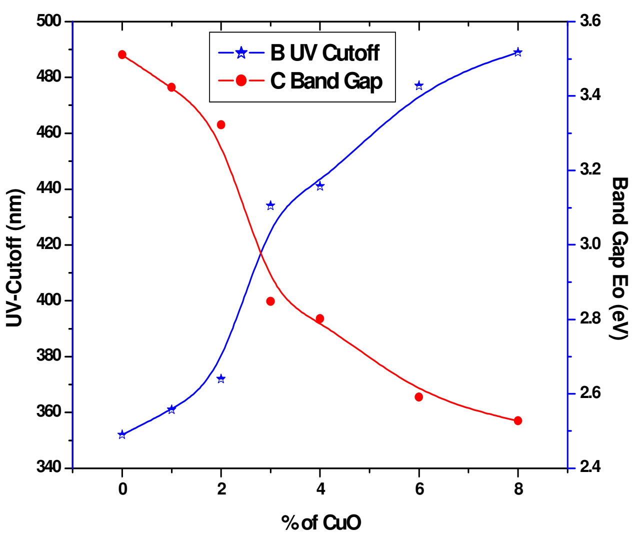


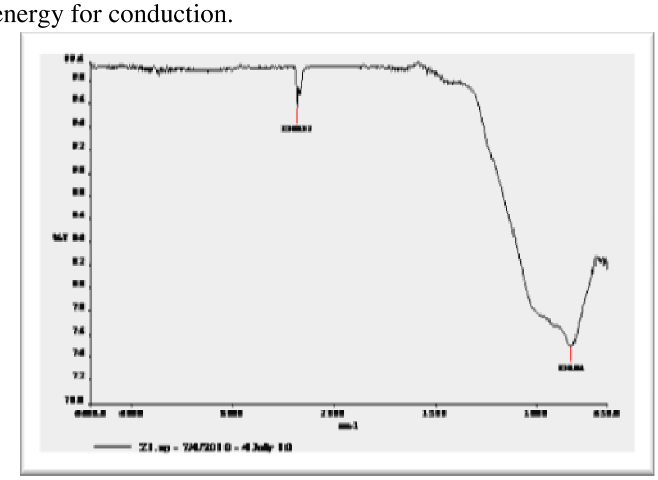
Figure-3
Plot of dependence of band gap on the %CuO doping

CuO concentrations (1 to 4%) the IR spectra [figure 4 (a), (b), (c) and (d)] reveal some small changes but the main characteristic bands due to phosphate network remain unchanged. Figure 4 shows the IR spectra of the glasses containing contents of P_2O_5 which replaced by the introduction of CuO content and keeping the Na_2O, ZnO and B_2O_3 constant. The obtained IR spectra reveal, nearly the same spectral characteristic features even though by the addition of CuO by replacing P_2O_5 content. It results there is no much more effect of doping CuO content. The pyrophosphate groups are predominant structure units in all these glasses. The identical IR spectra for all these glasses clearly indicate that the structure of PO_4 chains doesn't get affected by Cu^{+1} and Cu^{+2} ions in the glass. This indicates that the function of bridging oxygen's (P-O-P) is unaffected by glass compositions[13-14]. However the absorption peak CuO, which should appears at 620 cm^{-1} has not appeared in these glasses. This band seems to be completely broken down as a consequence of the P-O-Cu stretching vibrations being modified into the P-O-Cu-O-Zn bands.

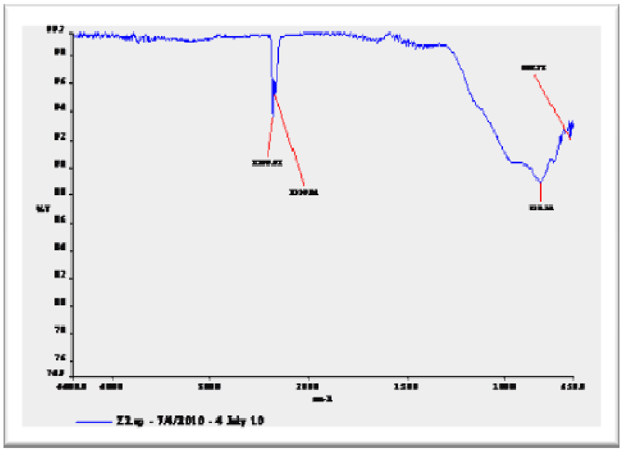
A series of transition metal ion i.e. Cu^{+2} ions doped Na-Zinc borophosphate glasses have been investigated for conductivity in the temperature range 238 K to 423 K. The electrical conductivity measurements were performed using impedance analyzer (Agilent 4294 A) over a wide frequency range 40Hz to 20 MHz. In the studied temperature range the measured conductivity (σ) varied from 1.78×10^{-5} to 23.76×10^{-5} ohm^{-1} m^{-1}. The temperature dependence of conductivity (σ) was observed to be semiconducting. The observed trend in increase in range the measured conductivity (σ) varied from 1.78×10^{-5} to 23.76×10^{-5} ohm^{-1} m^{-1}. The temperature dependence of conductivity (σ) was observed to be semiconducting. The observed trend in increase in conductance (σ) with increase in TMI content is in agreement with literature[15-16]. Figure 5 (a) and (b) represents the variation of electrical conductivity with frequency and fig.6shows the temperature dependence of conductivity (σ) for Cu ion doped sodium zinc borophosphate glasses. The linear relationship between logarithm of conductivity and inverse of temperature for all the samples indicates that following Arrhenius law is satisfied.

$$\sigma = \sigma_0 \exp^{(-Ea/KT)}$$

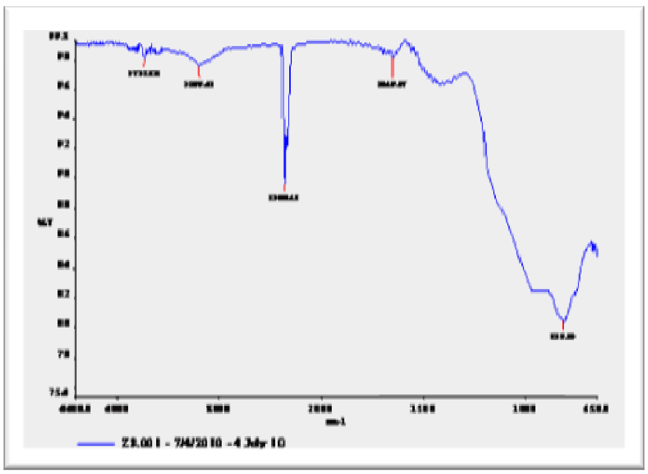
Where σ_0 = constant for given glass i.e. 8.854×10^{-12} F/m; K is Boltzmann's constant i.e. 8.6×10^{5} eV and E_a is the activation energy for conduction.



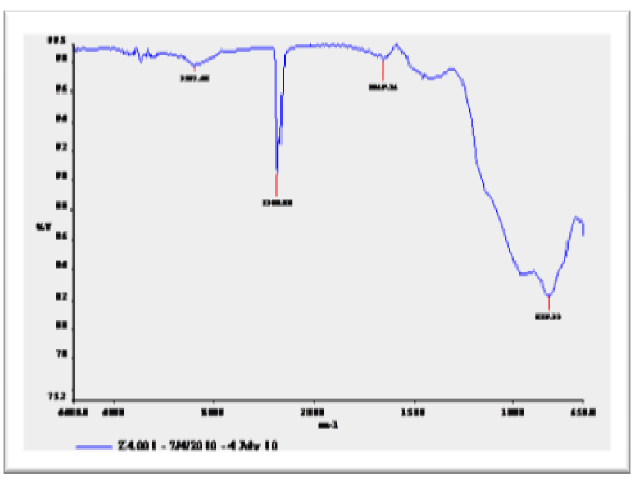
(a) Cu=1%



(b) Cu= 2%



(c) Cu= 3%



(d) Cu= 4%

Figure-4

FTIR spectra of 20Na$_2$O – 20ZnO – 25B$_2$O$_3$ – (35-x) P$_2$O$_5$ – XCuO glass samples

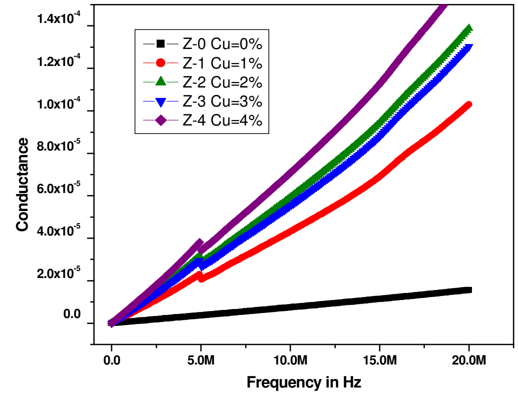


Figure-5(a)

Conductance of 20Na$_2$O20ZnO-25B$_2$O$_3$-(35-x)P$_2$O$_3$ glass at 25^{oc}

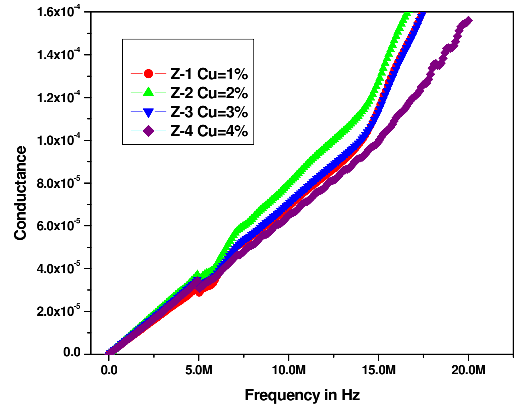


Figure-5(b)

Conductance of 20Na$_2$O20ZnO-25B$_2$O$_3$-(35-x)P$_2$O$_3$ glass at 100^{oc}

The values of E_a were calculated from the linear portion of curves in figure 6. The calculated values of E_a and conductivity values are listed in table 2, it results that the conductivity increases with increase in temperature and at higher frequency. All the investigated glasses exhibit the similar behavior. The flat portion of the conductivity curve increases at higher temperature and at high frequency. At low frequency the curve is non linear and as the frequency increases the curve is more linear.

Table-2

Conductivity and Ea for Cu doped glasses at 423K and at 20MHz.

Glass Code	Mole% CuO	Conductance σ	Activation Energy Ea (eV)
Z-1	1	2.20×10^{-5}	2.8217
Z-2	2	2.39×10^{-5}	2.2628
Z-3	3	2.30×10^{-5}	1.5355
Z-4	4	1.66×10^{-5}	2.3436

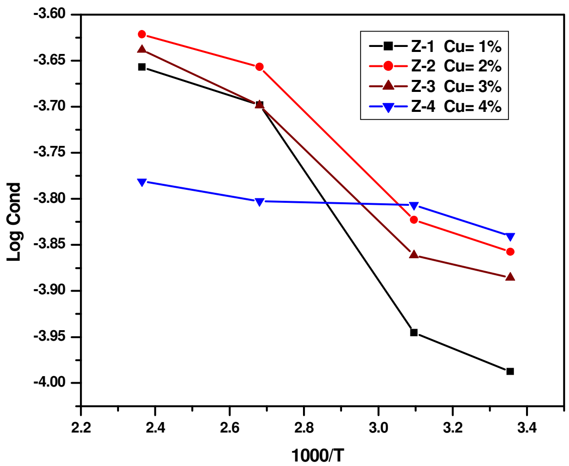
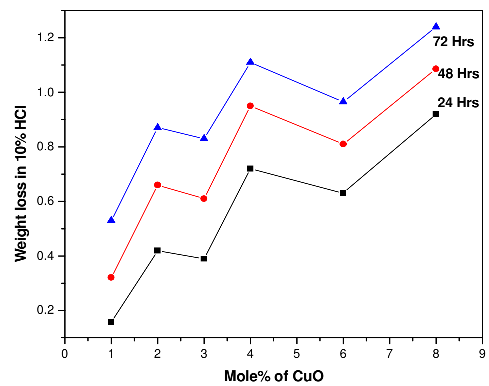
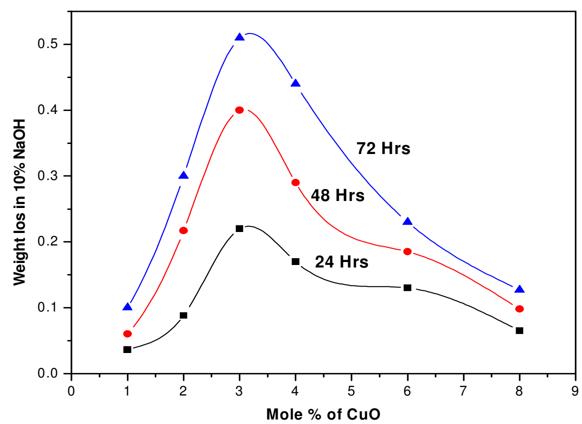


Figure-6
Arrhenius plot for $20Na_2O$-$20ZnO$-$25B_2O_3$-$(35-x)P_2O_6$ glasses

In the determination of degradation mechanisms, it is important to outline the types of reaction that may take place between acid/alkali and phosphate glasses. Polished samples of Cu ion doped sodium zinc borophosphate glasses were exposed for 72 hrs of exposure. In these investigated glass samples the release of ZnO, P_2O_5 and other constituents from phosphate glasses in aqueous acid / alkali solution is due to the hydrolysis reaction[17]. The plot of weight loss observed and a content of CuO shown in figure 7 (a) and (b). The dissolution rate for Cu ion doped NZBP glasses was seen to be low. It results that introduction of Cu and Zn ions increase the chemical durability. From the observed result, it is noticed that weight loss in HCl is more than NaOH. The weight loss of investigated glass samples in NaOH is increases with increase in CuO content up to 3% and decreases from 4% CuO; but in HCl initially the weight loss is rapidly up to 3% and from 4% CuO the weight loss takes slowly.





Conclusion

Cu-doped sodium zinc borophosphate glasses have been investigated. The density values for the investigated glasses are nonlinear it is due to TMI.. The peaks in UV spectra occur due to the existence of Cu^+ ion, which imparts greenish blue color to the glass. The investigated glasses showed the vibrational modes only due to the P-O-P groups in phosphate network. There is no appreciable change in the characteristic of stretching vibration in low and higher concentrations of CuO content glasses. The observed trend in increase in conductance (σ) with increase in transition metal ion content and the temperature dependence of conductivity (σ) was observed to be semiconducting. The chemical durability of these glasses has found to be improved due the introduction of modifier cum network former Zn and dopant Cu.

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