Properties of copper phosphate glasses

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Introduction

Oxidation-reduction equilibria in glasses have been extensively studied[1,2,3] in various oxide glasses containing transition-metal ions, such as copper. These glasses are interesting because of their semiconducting properties[4,5,6,7,8]. Indeed copper exists in glass forming oxide melts as metallic copper (Cu^0), cuprous (Cu^+) and cupric (Cu^{2+}) ions. So the conduction can take place by the transfer of electrons from the low to high valence states.

In the present study, we have prepared $50CuO_x$-$50P_2O_5$ (molar %) glasses with different copper valences using glucose in order to increase and to control the Cu^+ content. These glasses were studied by infrared and electrical conductivity. We have studied the mechanism of conduction versus the Cu^+ content and the temperature of these glasses.

Experimental procedure

Preparation of $50CuO_x$-$50P_2O_5$ glasses

Mixtures of CuO and $NH_4H_2PO_4$ are heated from 20°C to 1000°C in an alumina crucible in an electric furnace with a melting time of 15 hours, the melts are poured onto an iron plate. The copper in these glasses exists only as cupric ions (Cu^{2+}). In order to increase and control the [Cu^+] ratio with $[Cu^+]=[Cu^+]/([Cu^+]+[Cu^{2+}])=[Cu^+]/[Cu_{Total}]$, the glasses were ground and glucose (0, 1, 2, 3, 4 and 8 wt%) was added. Then the mixtures were remelted at 1000°C for 10 minutes. The melts were casted on an iron plate at room temperature. The glasses were kept in an desiccator to prevent reactions with moisture.

Chemical analysis

Phosphorus content was determined by a colorimetric method with the yellow vanado-molybdate complex. Total copper (as Cu^{2+}) was determined by iodometric using HNO_3 as oxidising agent. The Cu^+ content was evaluated by cerate titration method under nitrogen atmosphere. The alumina content was obtained by ICP, the % wt is inferior at 0.1. The compositions of glasses are reported in Table 1.

A.c. conductivity

The samples used for electrical conductivity measurements were ground and polished with SiC discs. Electrical connexions were obtained by gold sputtering on both sides. The conductivity was measured by using the complex impedance method (Solarton 1170) and the measurements were taken in the frequency range (1 to 10^6) Hz and temperature range (300 to 573K) with two heating and cooling processes.

FTIR analyses

FTIR spectra were recorded with a Perkin Elmer spectrometer in the wave number range 400 to 2000 cm^{-1} at room temperature. Samples were prepared by mixing and grinding glass powder with spectroscopic grade dry KBr powder, and then compressed to form thin pellets for measurements.

Results and discussion

Synthesis

The variation in $[Cu^+]$ ratio with glucose is shown in Fig. 1. The concentration of Cu^+ increases with glucose addition. When the $[Cu^+]$ ratio increases, the colour of glasses changes from green to tan. We have obtained the same evolution in colour that Bae et al[9]. The oxidized glasses are blue-green whereas the reduced glasses are tan.

Chemical analysis

The actual compositions of glasses differ very slightly from the nominal composition due to vaporization of phosphorus. The contamination from alumina crucible was observed, but the % wt Al being inferior at 0.1, we can suggest that the effect of Al on properties of glasses is negligible.

FTIR analyses

FTIR spectra of $50CuO_x$-$50P_2O_5$ glasses in the frequency range between 400 and 2000 cm^{-1} were obtained. The spectra contain a set of bands in the 1280-724 cm^{-1} region that are due to the stretching vibrations of metaphosphate glasses viz. : 1262-1279 cm^{-1} (ν_{as} PO2), 1153-1164 cm^{-1} ($\nu_s PO_2$, shoulder), 904-913 cm^{-1} (ν_{as}P-O-P), two modes 780 and 724 cm^{-1} (ν_s P-O-P), where ν_{as} and ν_s are the asymmetric and symmetric stretching frequencies respectively . The absorption band near 1056-1067 cm^{-1} is assigned to $P\text{-}O^-$ groups (chain end). The band around 457-480 cm^{-1} is attributed to deformation modes of PO_4^{3-} groups. All the spectra are quite similar, which suggests that glass structure does not change significantly in the examined range of chemical compositions.

A.c. conductivity

The temperature dependence of the conductivity obtained (from the complex impedance plots) of glass A is shown in Fig. 2. We can observe that the conductivity during the first descent is not superposed at these first rise, and then the conductivity stabilizes. After the measurements of conductivity, we have analyzed the glass surface and we have detected the presence of copper oxide by X-ray Diffraction. So, we can suppose either the existence a superficial conductivity because CuO is a electronic conductor good, or a reorganization of glass during the first rise. This behaviour has already been observed by Duran et al[5].

Glass	Glucose	CuO	Cu_2O	P_2O_5 (mol %)	$[Cu^+]=(Cu^+/Cu^++Cu^{2+})$	Colour
A	0	49.8	0.5	49.7	0.02	Blue-green
B	1	46.5	3.2	50.3	0.12	Dark-green
C	2	40.5	7.5	52	0.27	Dark-green
D	3	36.4	10	53.5	0.36	Dark-brown
E	4	29.1	13.9	56.9	0.46	Tan
F	8	23	16	61	0.74	Tan

Table 1 : compositions of $50CuO_x$-$50P_2O_5$ glasses

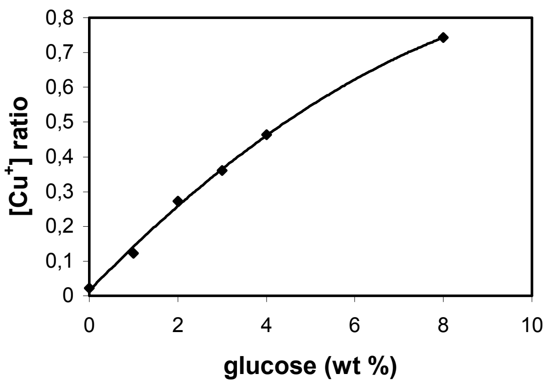

Figure 1 : evolution of Cu^+ ratio in $50CuO_x$-$50P_2O_5$ glasses with glucose addition

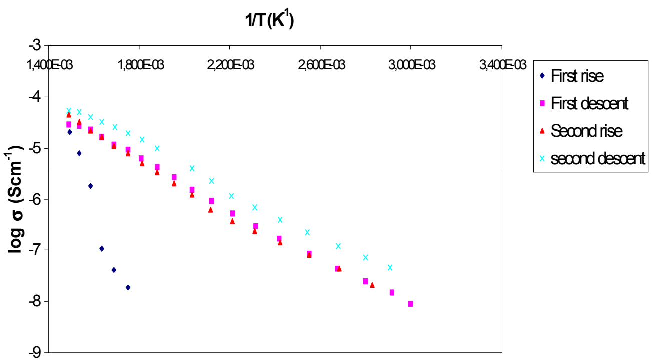

Figure 2 : evolution of glass A electrical conductivity with inverse temperature

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