EFFECT OF PHOSPHATE GLASS COMPOSITION ON Cu\textsuperscript{2+}/Cu\textsubscript{Total} RATIO

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Abstract
50CuO\textsubscript{x}–50P\textsubscript{2}O\textsubscript{5} and 40CuO\textsubscript{x}–60P\textsubscript{2}O\textsubscript{5} (molar %) glasses with different copper valence states (0<(Cu\textsuperscript{+})/(Cu\textsuperscript{+}+Cu\textsuperscript{2+})<0.91 were synthesized by adding glucose during glass melting. The Cu\textsuperscript{+} and Cu\textsubscript{Total} contents were determined by chemical analysis. The [Cu\textsuperscript{+}]/(Cu\textsuperscript{+}+Cu\textsuperscript{2+}) ratios of 40CuO\textsubscript{x}–60P\textsubscript{2}O\textsubscript{5} glasses are higher than those 50CuO\textsubscript{x}–50P\textsubscript{2}O\textsubscript{5} glasses because the ultraphosphate being more acidic than metaphosphate, the formation of reduced specie is favoured. The glasses are homogeneous until 8 wt % of glucose, above of this value, the glasses crystallize.

Introduction
Oxidation-reduction equilibria in glasses have been extensively\textsuperscript{1,2,3} studied in various oxide glasses containing transition-metal ions, such as copper. These glasses are interesting because of their semiconducting properties. Indeed copper exists in glass forming oxide melts as cuprous (Cu\textsuperscript{+}) and cupric (Cu\textsuperscript{2+}) ions. So the conduction can take place by the transfer of electrons from the low to high valence states.
In the present work, we prepared 50CuO\textsubscript{x}–50P\textsubscript{2}O\textsubscript{5} and 40CuO\textsubscript{x}–60P\textsubscript{2}O\textsubscript{5} (molar %) glasses with different copper valences using glucose in order to increase and to control the Cu\textsuperscript{+} content. The Cu\textsuperscript{+} and Cu\textsubscript{Total} content were determined by chemical analysis.
Experimental procedure

*Preparation of glasses*

The nominal compositions examined in the present study are \(50\text{CuO}-50\text{P}_2\text{O}_5\) and \(40\text{CuO}-60\text{P}_2\text{O}_5\). Mixtures of \(\text{CuO}\) and \(\text{NH}_4\text{H}_2\text{PO}_4\) 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 heated 250°C. The copper in these glasses exists essentially as cupric ions (\(\text{Cu}^{2+}\)). In order to increase the \([\text{Cu}^+]\) ratio (with \([\text{Cu}^+]\)\_ratio\(=\frac{[\text{Cu}^+]}{([\text{Cu}^+]+[\text{Cu}^{2+}]})\)), 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. We realized three times the experimental procedure for each glass.

*Chemical analysis*

Phosphorus content was determined by a colorimetric method with the yellow vanadomolybdate complex. Total copper (as \(\text{Cu}^{2+}\)) was determined by iodometric using \(\text{HNO}_3\) as oxidising agent. The \(\text{Cu}^+\) content was evaluated by cerate titration method under nitrogen atmosphere. The alumina content was obtained by ICP, the % wt is inferior at 0.1.

*Results and discussion*

The actual composition of \(40\text{CuO}-60\text{P}_2\text{O}_5\) glasses differs from the nominal composition (Table 1). Indeed the ultraphosphate glasses (>50 mol% \(\text{P}_2\text{O}_5\)) are difficult to synthesize because of \(\text{P}_2\text{O}_5\) vaporization. The contamination from alumina crucible was studied in binary phosphate glasses. It is reported that alumina incorporation affects the oxidation–reduction equilibrium of copper when the glasses are melted between 1100°C and 1200°C but not at 1000°C. The % wt Al being inferior at 0.1, we can suggest that the effect of Al on \([\text{Cu}^+]\) ratio is negligible.

**TABLE 1**: compositions of \(50\text{CuO}-50\text{P}_2\text{O}_5\) and \(40\text{CuO}-60\text{P}_2\text{O}_5\) glasses.

<table>
<thead>
<tr>
<th>Batch composition (%molar)</th>
<th>Analysed composition (%molar)</th>
<th>[Cu⁺] ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CuO</td>
<td>% P₂O₅</td>
<td>% CuO</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>52.8</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>43.2</td>
</tr>
</tbody>
</table>
The variation of $[\text{Cu}^+]$ ratio in 50CuO$_x$–50P$_2$O$_5$ and 40CuO$_x$–60P$_2$O$_5$ with glucose is shown in Fig. 1. The concentration of Cu$^+$ increases with glucose addition. The $[\text{Cu}^+]$ ratios of 40CuO$_x$–60P$_2$O$_5$ glasses are higher than those of 50CuO$_x$–50P$_2$O$_5$. These results are consistent with the works of Morsi et al.$^2$. Indeed the total copper concentration in phosphate glasses affects the redox equilibrium. The increasing of $[\text{Cu}^+]$ ratio with increasing of CuO content from 43.2 to 52.8 is attributed to the increase of the glass basicity. So the equilibrium is displaced towards the oxidized state. When the $[\text{Cu}^+]$ ratio increases the colour of glasses varies from green to tan. We have obtained the same evolution in colour that Bae et al.$^4$. The oxidized glasses are blue–green and the reduced glasses are tan.

**Conclusion**

The oxidation–reduction equilibrium of copper in 50CuO$_x$–50P$_2$O$_5$ and in 40CuO$_x$–60P$_2$O$_5$ glasses has been controlled by adding glucose during glass melting. The $[\text{Cu}^+]$ ratio increases with glucose addition. In 50CuO$_x$–50P$_2$O$_5$ and in 40CuO$_x$–60P$_2$O$_5$ glasses, we can reduce the copper at 74% and 91% respectively. When the CuO concentration increases the $[\text{Cu}^+]$ ratio decreases because of the increasing of the glass
basicity. For glucose adding superior at 8%wt, the glasses are not homogenous the Cu⁺ ions are reduced into Cu⁰ (metallic copper).

References