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Mixed electronic–ionic conductivity in semiconducting $CaO–PbO–Fe_2O_3–P_2O_5$ glasses

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Abstract

Several properties of semiconducting $CaO–PbO–Fe_2O_3–P_2O_5$ glasses have been measured. These properties include density, IR, DSC, and DC conductivity. The change in the structure for the present glasses shows that with increasing CaO content there is a corresponding decrease in the number of Q^1 phosphate units and an increase in the non-bridging oxygens (NBOs) as more Q^0 phosphate units are formed in the glass. The decrease in the density, d, and glass transition temperature, T_g, is due to the lower degree of cross-bonding between the calcium and NBOs in Q^0 phosphate units resulting in a weakening of glass network. The nearly constant DC conductivity and activation energy for glasses containing $\leqslant 12$ mol% CaO is attributed to an ion–polaron interaction which is responsible for the low mobility of the calcium ions that shows no detectable contribution to the DC conductivity. With increasing CaO content, up to 24 mol%, the DC conductivity increases which is directly related to an increase in the mobility of the calcium ions. An increase in the number of non-bridging oxygens that appear in the neighborhood of the calcium ions is responsible for an increase in the ionic conductivity.

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Keywords: Phosphate glasses; Electronic conductivity; Ionic conductivity; SPH

1. Introduction

Conventional phosphate glasses typically have a relatively poor chemical durability [1], which often limits their practical applications. However, several studies have shown that chemical durability of phosphate glasses can be improved by the addition of various oxides such as Al_2O_3 and Fe_2O_3 [2]. As a result, iron phosphate glasses are now of interest for several technological and biological applications [3].

Recent investigations of iron phosphate glasses have shown that the addition of lead–iron to phosphate glasses had a significant effect on the glass transition temperature, thermal expansion coefficient and chemical durability [4,5]. It have been suggested that the chemical durability of lead–iron phosphate glasses is attributed to the replacement of P–O–P bonds by the more resistant P–O–Fe or P–O–Pb bonds [6,7].

In alkali or alkaline-earth iron phosphate glasses, the electrical conductivity generally consists of both ionic and electronic conduction. The ionic conduction is proportional to the alkali concentration, while the electronic conduction follows the hopping theory [8,9]. However, the motion of the alkali ions and electrons is independent of each other. This is consistent with the previous results [10], which assume that mobile electrons or polarons are attracted to the oppositely positive charged alkali or alkaline-earth ions and move together as neutral entities. Such a migration does not involve any net displacement of electric charge, so, this process does not contribute to total conductivity [7].

In the present work, several physical properties of glasses were studied according to the general formula of $(x+6)$ $CaO–(y-28)$ $PbO–(y-26)$ $Fe_2O_3–(y-40)$ P_2O_5, where $x = 0$, 6, 12 and 18 mol%, and $y = 0$, 2, 4 and 6 mol%, respectively. The physical properties measured for the

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present work include density, IR, DSC, and DC conductivity. Special attention was paid to the relation between structure and electrical conductivity of the present glasses that exhibit a mixed electronic–ionic conduction with predominance of either electronic or ionic depending on their composition.

2. Experimental

The glasses were prepared from reagent grade $CaCO_3$ PbO, Fe_2O_3 and P_2O_5. The mixture was melted in platinum crucibles in an electric furnace for 1 h at temperatures ranging between 1200 and 1250 °C as required for each composition. The melting temperature of a mixture increased with the increase of CaO content. Melts were rapidly quenched between two brass plates to form glass samples of ~1.5 mm thickness. The IR spectra of glass samples were recorded over the range 400–1500 cm^{-1} by a conventional KBr pellet method on a Fourier transform infrared (FT-IR) spectrophotometer (Perkin-Elmer 1760 X). The density, d, of glass for each composition was evaluated by the Archimedes method using toluene as an immersion liquid. Differential scanning calorimeter (DSC) of the samples was investigated using a Shimadzu DSC-50 with heating rate 20 °C/min. For conductivity measurements, disk-shaped samples of 6 mm diameter were prepared and polished using very fine lapping paper. Silver paste electrodes were then painted on both faces of each sample. The DC conductivity, σ, of the as-quenched glasses was measured at temperature between 313 and 503 K. Before measurement, the ohmic behavior (I–V) was ascertained from the linearity of the voltage current characteristics.

3. Results and discussion

3.1. Density and DSC

Fig. 1 shows the effect of CaO on density, d, of the present glass system. As shown, density decreases with increasing CaO content. This could be explained by considering the formation of Ca–O–P linkages [11,12] with strong Ca–O ionic bond. Thus, the substitution of a shorter ionic Ca–O bond by a longer covalent Pb–O bond leads to the open structure of the glasses. On the other hand, the density of glasses decreases from 4.37 to 4.22 g/cm^{-3} with increasing CaO content as a result of a weakening of cross-linking within glass network [13].

Fig. 2 shows the dependence of T_g upon the addition of CaO. From the figure it is clear that T_g decreases as CaO content increases in glass. A systematic decrease of 49 K in T_g is registered between extreme compositions. We suspect that the nature of bonding is responsible for the variation of T_g. In CaO-rich glass, the nature of bonding is predominantly ionic and becomes largely covalent in glass with the highest PbO content. We assume that in this case lead can be incorporated into the network resulting in the formation of P–O–Pb linkages. The former P–O–Pb linkages with a covalent character thus appears to link the phosphate chains which yields a mixed network forming character, in accordance with the increase of T_g [13]. On the other hand, it is known that T_g and d decrease with decreasing bond strength and cross-linking in the phosphate glasses [13]. The decrease in T_g and d for the present glasses is due to the lower degree of cross-bonding between the calcium ions and non-bridging oxygens (NBO)

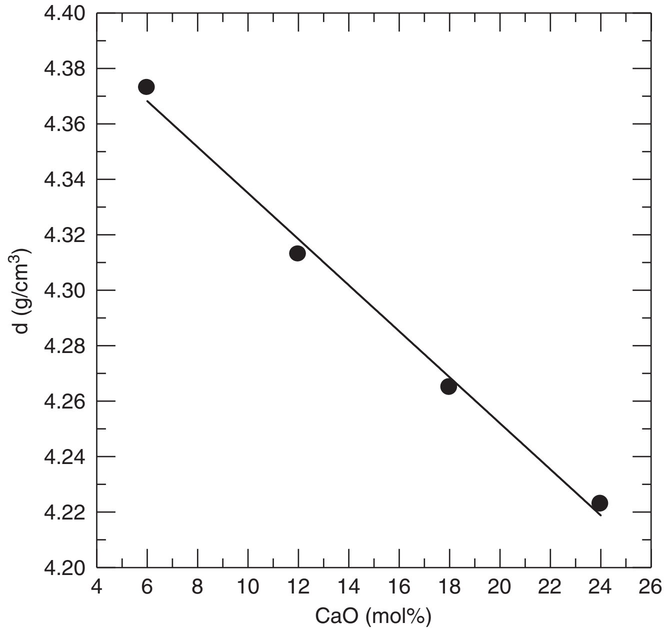

Fig. 1. Composition dependence of density, d, for CaO–PbO–Fe_2O_3–P_2O_5 glasses.

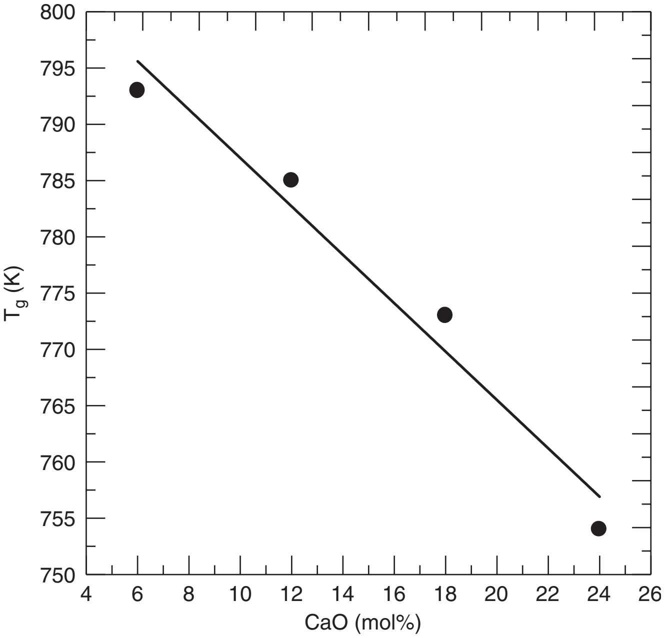

Fig. 2. Composition dependence of glass transition temperature, T_g, for CaO–PbO–Fe_2O_3–P_2O_5 glasses.