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Dielectric properties of P_2O_5–Na_2O–Li_2O glasses containing WO_3, CoO or Fe_2O_3

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Abstract

The aim of this work was to study some polarization mechanisms in phosphate glasses containing different transition metal oxides, performed at radio frequency (100 kHz) and in the microwave region (9 GHz). Cobalt, iron and tungsten oxides were chosen for the present investigation. The results show that the dielectric constant increases linearly with increasing Co concentration, whereas for iron and tungsten ions, the dielectric constant values were found to decrease up to a given concentration and further, increase for higher concentration of W and Fe. This anomaly was observed both at 100 kHz and 9.00 GHz and was attributed to the valence state of the transition metal ions in the glass structure. The dielectric constant is lower in the microwave region, due to structural relaxation mechanisms.

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1. Introduction

Transition Metal (TM) ions can exist in different valence states when integrated in the glass structure. The cobalt ions are commonly found in the valence state Co^{2+} [1], whereas iron, tungsten, molybdenium, and others, can be present in more than one valence state, depending on the properties of the modifiers and glass formers, size of the ions in the glass structure, their field strength, etc. [2–11]. Depending on the valence state, the ions of TM can occupy substitutional or interstitial positions in the glass network. When the ions enter the glass structure at substitutional positions, there exists a possibility of a cross linkage between the glass former and modifier occurring, reducing the space charge polarization, whereas when the ions enter the interstitial positions, there will occur a weakening of the glass network and the creation of permanent dipoles formed by the cations and non-bridging oxygens (NBO's), depending on the concentration of the TM ions in the glass structure. The response of these permanent dipoles decreases with increasing frequency due to its relaxation time. These statements can be accessed by measurements of dielectric properties, performed at different frequencies, temperature and material composition.

Measurements of dielectric properties of glasses are usually performed at frequencies below some MHz, in which impedancimetric methods are used. On the other hand, at higher regions, these measurements become less frequent, being limited to studies of ferroelectric materials used in radar and telecommunications applications. The aim of this work was, thus, to perform measurements of dielectric constant of glasses containing different transition metal oxides, at radio and microwave frequencies, in order to investigate the response of the permanent dipoles as a function of frequency and glass composition. The dielectric constant of the phosphate glasses containing cobalt, iron or tungsten was measured at 9.00 GHz by a suitable method, originally described in Ref. [12,13]. The results were compared to that obtained at 100 kHz. The glasses have the following composition $(1-x)(25Li_2O{\cdot}25Na_2O{\cdot}50P_2O_5){\cdot}x(\mathrm{TMO})$ where TM = Fe_2O_3, CoO or WO_3. These glasses possess several advantages, such as

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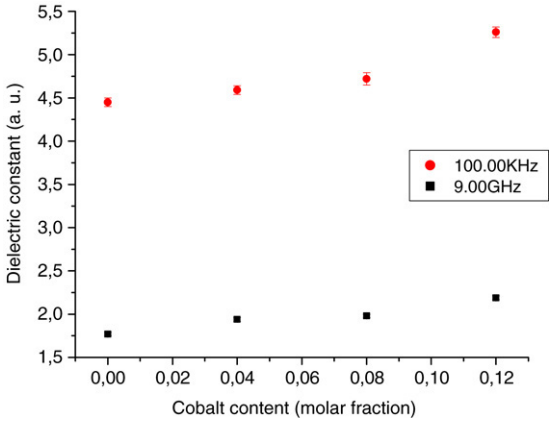

Fig. 1. Dielectric constant ε' of the glass $(1-x)(25Li_2O{\cdot}25Na_2O{\cdot}50P_2O_5){\cdot}x$ (CoO), measured at 9.0 GHz, together with that measured at 100 kHz and room temperature.

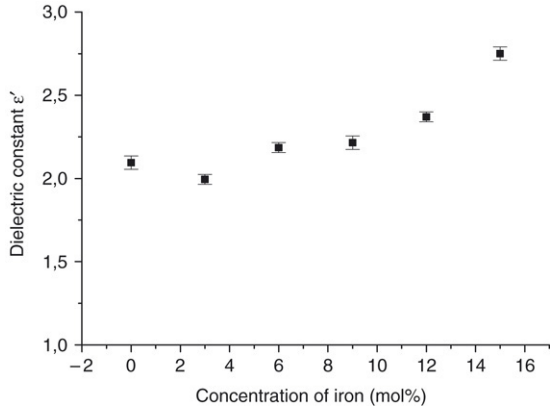

Fig. 2. Dielectric constant ε' of the glass $(1-x)(25Li_2O{\cdot}25Na_2O{\cdot}50P_2O_5){\cdot}x$ (Fe_2O_3), measured at 9.00 GHz and room temperature. (*Note*: measurements at 100 KHz were not performed for this glass set.)

low glass transition temperature (Tg), and can easily be ground and polished.

The glasses were prepared by weighing reagent grade amounts of raw materials $NH_4H_2PO_4$, NaOH, LiOH, CoO, Fe_2O_3 and WO_3 (Merck). The batch was homogenized for about 30 min and melted in an alumina crucible in air using an electric furnace, at 900 °C for two hours. The liquid was quenched in a mould, annealed at 270 °C for two hours, and further the six faces of a single bulk sample were polished in order to fit inside the sample-holder with dimensions 1.0 × 2.3 × 1.5 cm^3. The dielectric constant ε' of the samples was measured using a microwave setup supplied by a reflex klystron operating at 9.00 GHz. The sample was positioned against the short-circuit termination of the slotted waveguide of the microwave setup and the dielectric constant was obtained from the measurement of the shift Δl in the standing wave pattern. Details of the setup and the measurements can be found in Refs. [12,13]. Finally, measurements at 100 kHz were performed by an impedance analyzer HP-4192A. The samples were placed between two metallic parallel plates, forming a capacitor (cell). The ratio of the capacitance of the cell containing the sample and the capacitance of the empty cell gave the values of dielectric constant ε'. Measurements were also performed at room temperature.

The values of dielectric constant ε' of the glass $(1-x)(25Li_2O{\cdot}25Na_2O{\cdot}50P_2O_5){\cdot}x(CoO)$, for $x = 0, 4, 8, 12$ expressed in mol%, obtained from the measurements of Δl and room temperature, together with that measured at 100 kHz, are plotted in Fig. 1.

The results show that the dielectric constant increases linearly with the cobalt concentration increasing, at both frequencies. The cobalt ions, occupying predominantly interstitial positions in the glass structure, form permanent dipoles, contributing to the dielectric constant. The values of ε' of the glass $(1-x)(25Li_2O{\cdot}25Na_2O{\cdot}50P_2O_5){\cdot}x(Fe_2O_3)$, for $x = 0, 3, 6, \ldots 15$ expressed in mol%, performed at microwave frequency, are plotted in Fig. 2. The dielectric constant ε' of the glass $(1-x)(25Li_2O{\cdot}25Na_2O{\cdot}50P_2O_5){\cdot}x(WO_3)$ where $x = 0, 2.5, 5, 7.5, 10$ and 15 (mol%), measured at 9.00 GHz, together with that measured at 100 kHz, at room temperature, are shown in Fig. 3.

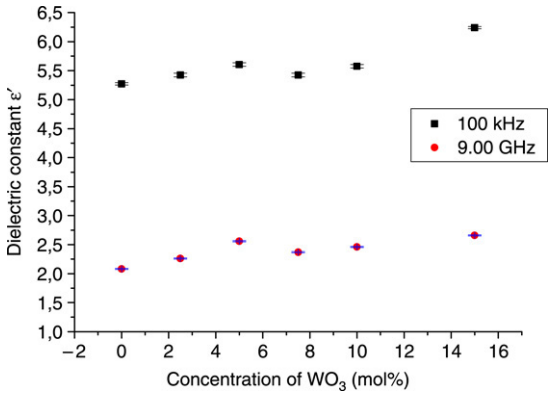

Fig. 3. Dielectric Constant ε' of the glass $(1-x)(25Li_2O{\cdot}25Na_2O{\cdot}50P_2O_5){\cdot}x$ (WO_3), measured at 9.00 GHz and for comparison, at 100 kHz. Measurements were performed at room temperature.

The results of Figs. 2 and 3 show that for low concentrations of both iron and tungsten, the values of dielectric constant seem to decrease up to the concentrations around 6%–8%. Beyond these concentrations, the dielectric constant increases. For low concentrations of TM, the ions occupy preferentially substitutional positions in the glass network, reinforcing the covalent bonds between the TM and glass former. This reduces the polarization, reducing therefore the dielectric constant [3–9,14,15]. Iron ions, in these glasses, are expected to exist in the Fe^{3+} state; however, as the concentration of Fe_2O_3 increases, there is a possibility for a gradual conversion of these ions into Fe^{2+} states that occupy interstitial positions. These statements can be extended to tungsten oxide. For higher concentrations of TM, the ions seem to occupy the interstitial positions of the glass, contributing to the polarization. Also, the dielectric constant is higher for lower frequencies, as shown by the comparison of the results in Figs. 1 and 3. The response of the permanent dipoles decreases as the frequency increases. At microwave frequencies, some permanent dipoles could still be capable of polarization, following the fast electric

field variations, as shown by the increasing dielectric constant values evaluated in this region. Therefore, the valence state of the transition metal oxide plays an important role on the polarization mechanisms in the glass structure.

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