



Investigation of some dielectric properties of phosphate glasses doped with iron oxides, by a microwave technique

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ABSTRACT

The effects of iron ions on dielectric properties of lithium sodium phosphate glasses were studied by non-usual, fast and non-destructive microwave techniques. The dielectric constant (ϵ'), insertion loss (L) and microwave absorption spectra (microwave response) of the selected glass system $x\text{Fe}_2\text{O}_3 \cdot (1-x)(50\text{P}_2\text{O}_5 \cdot 25\text{Li}_2\text{O} \cdot 25\text{Na}_2\text{O})$, being $x = 0, 3, 6, \dots, 15$ expressed in mol.%, were investigated. The dielectric constant of the samples was investigated at 9.00 GHz using the shorted-line method (SLM) giving the minimum value of $\epsilon' = 2.10 \pm 0.02$ at room temperature, and increasing further with x , following a given law. It was observed a gradual increasing slope of ϵ in the temperature range of $25 \leq t \leq 330$ °C, at the frequency of 9.00 GHz. Insertion loss (measured at 9.00 GHz) and measurements of microwave energy attenuation, at frequencies ranging from 8.00 to 12.00 GHz were also studied as a function of iron content in the glass samples.

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1. Introduction

Phosphate glasses have several advantages over borate and silicate glasses due to their thermal expansion coefficient, ultraviolet transmission, and melting temperature [1–3]. In order to improve the chemical durability and physical properties of phosphate glasses, different metal oxides and other elements have been incorporated to the glass network [4–6].

Recently, the study of dielectric properties of glasses have gained important attention, mainly in the study of insulators, conductors, semiconductors, and other materials used in the industry, communications, high power devices and others. The dielectric behavior of glasses can be explained by some polarization mechanisms, which always involves the presence of intrinsic dipoles formed by charged pairs, as described in some classical works [7–9]. It is reasonable to suppose that similar effects will be observed also in barium phosphate glasses, where the possi-

ble intrinsic dipoles are the Ba^{2+} ions compensating a pair of non-bridging oxygens (NBOs) and electron-hole pairs of phosphor oxygen hole center (POHC^+), or oxygen hole center (OHC^+) of a NBO and a phosphor electron center (PEC^-) [10]. In addition, in the non-irradiated phosphate glasses doped with transition metal (TM) oxides such as Co, Fe and Mn, it can be expected some extrinsic dipoles of electrically charged TM ions, found at the glass-modifier sites, compensating the extra charges of the NBOs for each structural units of PO_4 : Q_0 , Q_1 , Q_2 and Q_3 having 0, 1, 2 and 3 bridging oxygens (BOs), respectively. Additional dipoles such as a POHC^+ and a TM ion that has trapped the complementary electron of an $e^- - h^+$ are expected only after ionizing irradiation and therefore will not be considered in the present work.

On the other hand, the polarization contributions to the dielectric constant can be attributed to the existence of degrees of freedom associated with the allowed orientations of the permanent dipoles formed by the charge pairs [11]. In the optical region, the permanent dipoles cannot respond to the electric field variations and the contributions to the dielectric constant decrease to almost zero.

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At frequencies in the infrared, microwave and radio frequency, the contributions of the permanent dipoles begin to increase, attaining the maximum polarizability (response) in the static electric field [12]. The thermal vibrations of molecules also contribute with an additional polarization due to an increased average magnitude of the permanent dipole moment and therefore, it is an additional contribution to the increasing of the dielectric constant, ϵ' [13–15].

Among several techniques available to study the dielectric properties of materials in the range of microwave frequencies (10^8 – 10^{11} Hz), it is usual to employ a resonant cavity containing the sample. The values of ϵ' are obtained from the changes in the resonant frequency (taking the empty cavity as reference) whereas the changes in the quality factor, the dielectric loss ϵ'' of the sample. Another alternative technique useful to study the dielectric properties of insulators is the shorted-line termination [16,17].

Therefore, the aim of this work was to investigate the effects of the addition of iron ions, temperature and frequency on the polarization state of the glass samples by means of systematic determination of dielectric constant ϵ , insertion loss and microwave spectroscopy (microwave response spectra) of the glass $x\text{Fe}_2\text{O}_3 \cdot (1-x)(50\text{P}_2\text{O}_5 \cdot 25\text{Li}_2\text{O} \cdot 25\text{Na}_2\text{O})$. The method of shorted-line, i.e., a waveguide with short-circuit, was used to determine the dielectric constant ϵ' of the glasses at 9.00 GHz. Also, measurements of microwave transmitted signal through the glasses as a function of frequency (8.00–12.00 GHz) were performed for different concentrations of transition metal oxides.

2. Materials and methods

2.1. Glass preparation

The glasses studied in this work have the following composition: $x\text{Fe}_2\text{O}_3 \cdot (1-x)(50\text{P}_2\text{O}_5 \cdot 25\text{Li}_2\text{O} \cdot 25\text{Na}_2\text{O})$, where x represents the amount of iron oxide ($x = 0\%$, 3%, 6%, ..., 15%). The glasses were prepared by weighing reagent grade amounts of raw materials $\text{NH}_4\text{H}_2\text{PO}_4$, Na_2CO_3 , Li_2CO_3 and Fe_2O_3 (Merck). The batch was melted and homogenized for

about 30 min. in an alumina crucible, inside an electric furnace, at 100 °C for 2 h under ordinary atmosphere. The liquid was quenched in a mould in form of block, annealed at 270 °C for 2 h, and after the quenching process, the six faces of a single bulk sample were polished in order to fit inside the sample-holder with dimensions $1.0 \times 2.3 \times 1.5 \text{ cm}^3$. The glasses containing iron have a brown color.

2.2. Dielectric measurements

The dielectric constant ϵ' of the samples was measured using the microwave setup shown in Fig. 1, supplied by a reflex klystron operating at 9.00 GHz. The sample was fitted against the short-circuit termination of a slotted waveguide of the microwave setup for the measurements. The dielectric constant was obtained from the measurement of the shift Δl in the standing wave pattern [16]. The shift in the standing waves, caused by the presence of a dielectric material placed inside the waveguide, was measured using a crystal detector and a probe, free to move along a longitudinal slot of a piece of waveguide assembled at the end of the device (see Fig. 1).

Starting with an empty sample-holder, one of the minima of the standing wave pattern was chosen as the reference point. Placing the sample against the short-circuit end, a shift Δl of the reference minimum was measured, as depicted in Fig. 1. The dielectric constant ϵ was evaluated from the expression (1) below, which relates the dielectric constant with an intermediate parameter y [17].

$$\epsilon' = \left(y \frac{\lambda_0}{2\pi d} \right)^2 + \left(\frac{\lambda_0}{2a} \right)^2 \quad (1)$$

The parameter y can be evaluated by means of the Eq. (2)

$$\frac{\tan(y)}{y} = \frac{\lambda_g}{2\pi d} \tan \left[2\pi \frac{\Delta l + d}{\lambda_g} \right]. \quad (2)$$

In the above equations, λ_0 and λ_g are the wavelengths in free space and inside the waveguide, respectively, d is the thickness of the sample, Δl is the measured shift in

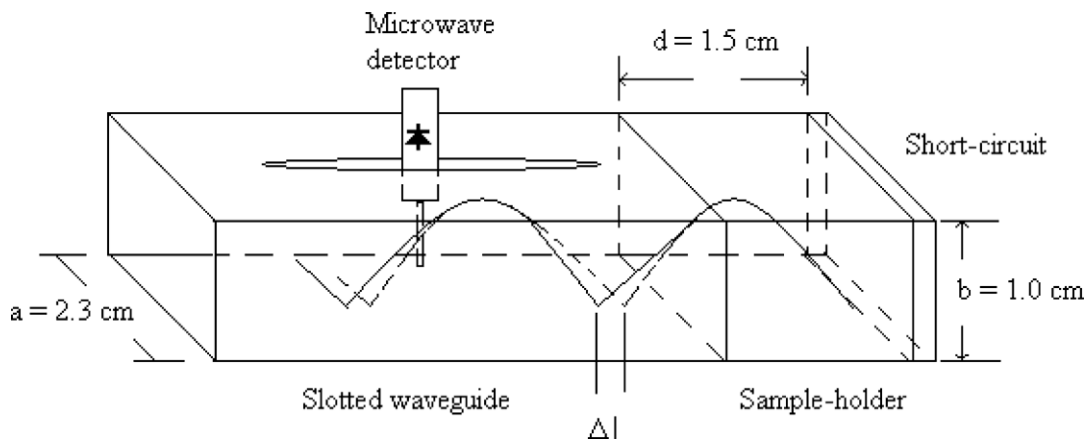


Fig. 1. Microwave setup showing the shift Δl in the standing wave pattern caused by the insertion of a sample inside the sample-holder. Full and dashed standing wave lines denote conditions in absence and presence of the sample, respectively.

the standing wave mode, and a is the width of the wave guide (TE_{10} mode).

These measurements were also carried out in the temperature range 25–330 °C. The heat was applied by means of an electric tape surrounding the sample-holder. An electronic device was used to control the current, and a K -type thermocouple was also used, attached to a digital thermometer (Minipa Mod. MT-520, Brazil), in order to collect the glass temperature. The uncertainty in the temperature measurement was approximately ± 5 °C.

For each glass sample and temperature, the shift Δl of the standing wave pattern was collected three times, giving thus, an average on the dielectric constant value.

2.3. Insertion loss measurement

Measurements of insertion loss were performed at constant frequency of 9.00 GHz using a piece of waveguide containing the glass sample of dimensions $1.0 \times 2.3 \times 1.5$ cm³ occupying the inner volume of length $d = 1.5$ cm. The input power was supplied by a reflex klystron, and the output power was collected by a microwave detector at the end of the waveguide, connected to the power meter (Mod. HP-432B, USA). The insertion loss measured in decibels per centimeter L (dB/cm) of the glasses as a function of iron content was obtained from the power ratio of the empty (P_0), and in the presence of the glass sample (P). P_0 and P are given in mW. The L (dB/cm) is related to the absorption coefficient α (cm⁻¹), by the expression L (dB/cm) = 4.343α (cm⁻¹), where α (cm⁻¹) = $(1/d) \ln(P_0/P)$, and d is the sample thickness in cm. All output powers measurements were performed in triplicate.

2.4. Microwave response spectra

The microwave response spectra as a function of the glass samples was obtained in the frequency range of

8.00–12.00 GHz, by means of a sweep microwave generator (HP-3050B, USA), with the output attached to a small waveguide patch. The response was measured by a scalar network analyzer (HP-8756A, USA), connected to the other port of this waveguide. The sample was placed inside this waveguide piece, in order to study the attenuation of the microwave signal. The microwave attenuation energy as a function of frequency was obtained for glasses containing different amounts of iron. The geometry of the sample inserted in the waveguide is the same as described above. Each measurement was performed in duplicate; the spectra were very similar, confirming the repeatability of the experiments.

3. Results and discussions

The dielectric constant values (ϵ') of the glass samples, as a function of iron content, were obtained from the measurements of the Δl , and determined by means of the expressions (1) and (2). The values are shown in Fig. 2. Measurements were performed at 9.00 GHz, and room temperature.

The dielectric constant ϵ of the glass samples was found to increase with the introduction of iron oxide. This can be attributed to the presence of permanent electrical dipoles in the glass that arise from charged pairs formed by the iron cations and negatively charged groups, such as the Q_n ($n = 0, 1, 2, 3$ for phosphate glasses) [12]. The Fe_2O_3 ions create bound defects, produced in the glass network, giving rise to the permanent dipoles, contributing to the polarization of the material [13]. However, it can be observed a minimum in the values of dielectric constant for a certain iron concentration, and above this value, the dielectric constant increases further. This effect is related to the fact that iron ions can exist in more than one valence state, and depending on the valence state and location in the glass structure, the contributions to the polarization become

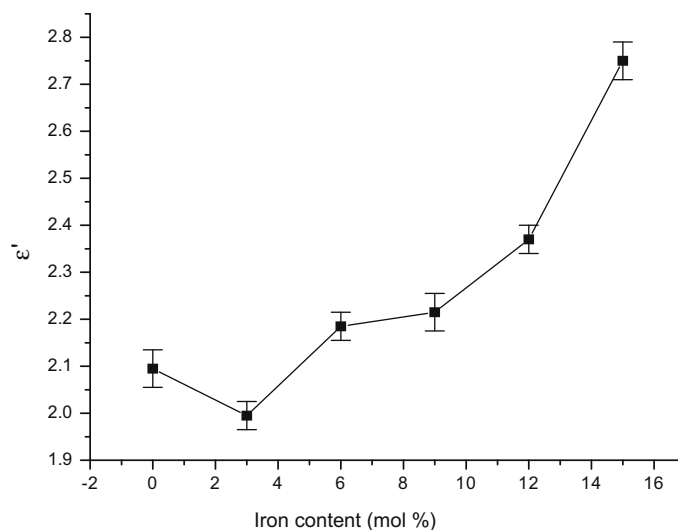


Fig. 2. Dielectric constant ϵ' of the glass $xFe_2O_3 \cdot (1-x)(50P_2O_5 \cdot 25Li_2O \cdot 25Na_2O)$, as a function of x , measured at 9.00 GHz, at room temperature. The lines are drawn between data symbols as guides for the eyes.

more or less pronounced. This effect has been described by several authors [18–24]. The dielectric constants of these samples were also measured in the range of room temperature to approximately 330 °C. The results are shown in Fig. 3.

The temperature also affects markedly the polarization state of the permanent dipoles, by increasing the amplitude of the thermal vibrations of the charges and therefore, contributing to the dielectric constant, ϵ' [25,26]. The results show that the slope $d\epsilon'/dT$ is not constant, and the dielectric constant ϵ' increases in the range temperature (25–330 °C). This measurement could not be performed for that glass without iron, due to particular reasons.

Fig. 4 shows the insertion loss, evaluated at 9.00 GHz, measured in terms of the reciprocal of transmittance $T^{-1} = P_0/P$ of the samples as a function of iron content.

The absorption coefficient increased from 0.15 to 1.03 cm^{-1} for iron content varying from 0% to 15%, indicating the contribution of dispersive microwave scattering.

Fig. 5 shows examples of the microwave response spectra of the glasses as a function of the frequency and iron oxide content ($x = 3\%$, 6%, 9%, 12% in Fig. 5a–d, respectively). The measurements were performed in the frequency range 8.00–12.00 GHz, and at room temperature.

It can be noticed an intense absorption peak at about 9.8 GHz in the spectrum of the glass with $x = 3\%$, as well as other peaks with less amplitude. The spectra normalization condition was fulfilled in principle, once the sample thickness of all the samples was kept equal to $d = 1.5$ cm. Also, it can be found that the main absorption band shifted to lower frequencies, showing a decrease in its amplitude for samples doped with increasing amount of iron ($x = 9\%$

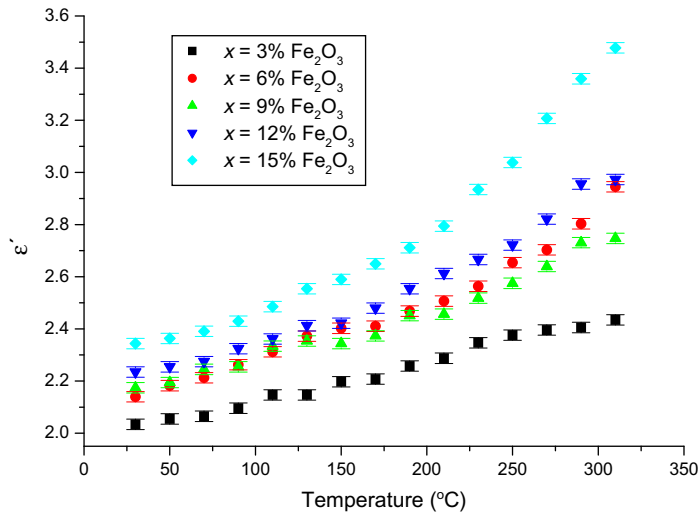


Fig. 3. Dielectric constant ϵ' of the glass $x\text{Fe}_2\text{O}_3 \cdot (1-x)(50\text{P}_2\text{O}_5 \cdot 25\text{Li}_2\text{O} \cdot 25\text{Na}_2\text{O})$ as a function of x , measured at 9.00 GHz and temperatures ranging from 25 °C to 330 °C.

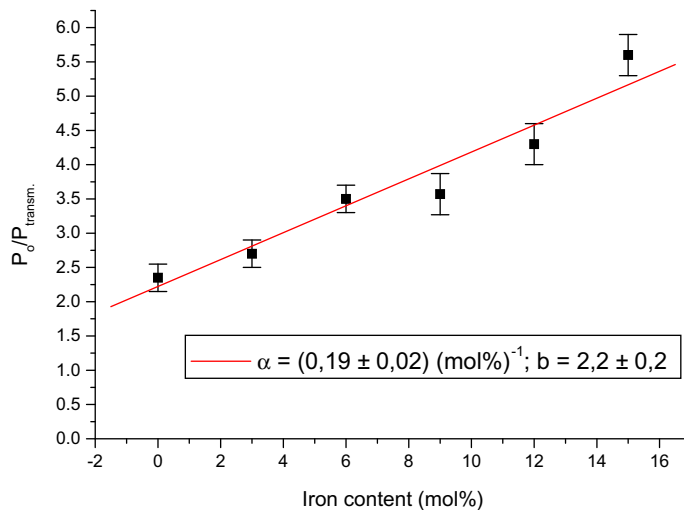


Fig. 4. Relative insertion loss, P_0/P , measured at 9.00 GHz for the glass $x\text{Fe}_2\text{O}_3 \cdot (1-x)(50\text{P}_2\text{O}_5 \cdot 25\text{Li}_2\text{O} \cdot 25\text{Na}_2\text{O})$, at room temperature.

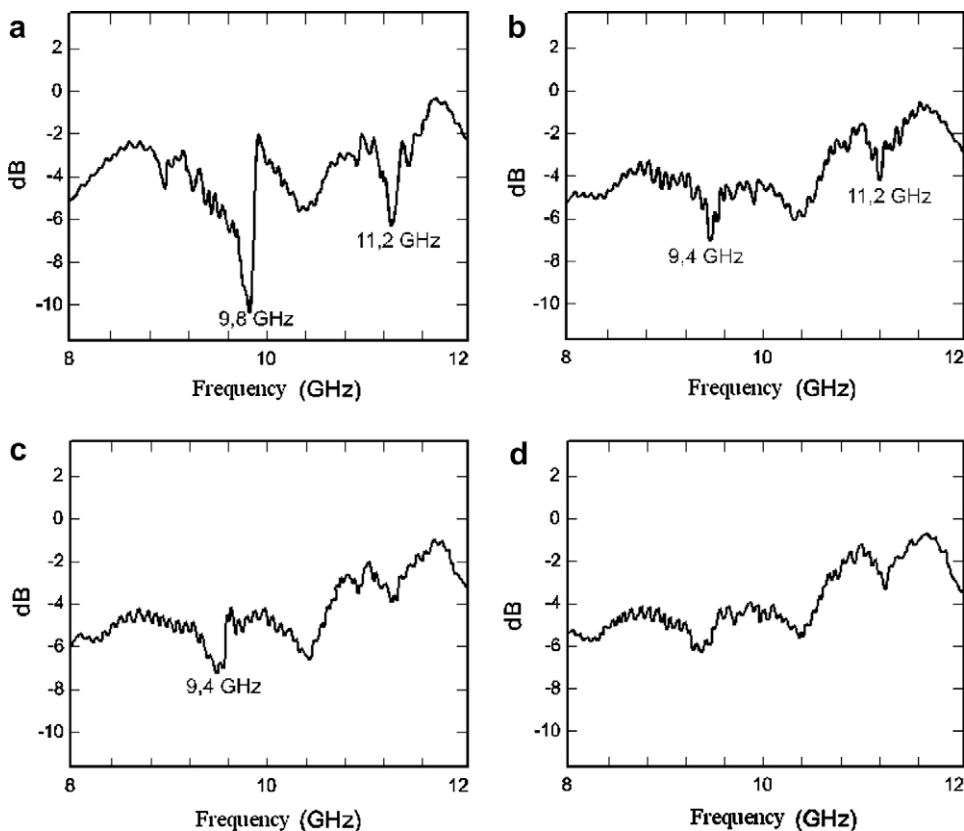


Fig. 5. Examples of microwave response spectra of the glass $x\text{Fe}_2\text{O}_3 \cdot (1-x)(50\text{P}_2\text{O}_5 \cdot 25\text{Li}_2\text{O} \cdot 25\text{Na}_2\text{O})$, where (a) $x = 3\%$; (b) $x = 6\%$; (c) $x = 9\%$; (d) $x = 12\%$ iron oxide. Spectra for that sample with $x = 0\%$ displayed spectra very close to the spectra for $x = 12\%$. Sample thickness = 1.5 cm. Measurements were performed at room temperature.

and 12%). Spectrum of that glass containing 0% iron was very similar to that obtained for glass containing 12% iron (not shown here due to particular reasons). This behavior can be related to the changes in the iron ion valence, when incorporated in the glass structure, as observed in the dielectric measurements.

4. Conclusions

At microwave frequency (9.00 GHz), the dielectric constant ϵ was found to increase with iron content, due to the introduction of bound defects created by the iron ions in the glass network, leading to the formation of permanent dipoles, contributing therefore to the electrical polarization of the glasses. An average increasing in the thermal vibrations with temperature and an increased average magnitude of the dipoles are indicated by the increase in the dielectric constant with increasing the iron content. These effects occur in most glasses containing TM oxides, as can be seen in the literature. The increasing of the insertion loss for phosphate glasses has increased the absorption coefficient α from 0.15 to 1.03 cm^{-1} (at a fixed frequency of 9.00 GHz) indicating the contribution of dispersive microwave scattering.

It was observed a shift at the main absorption band (peak) at about 10 GHz to lower frequencies, and a

decreasing intensity that vanishes for concentration of iron beyond 9% content. Possibly, these absorptions come from TM ions located at local sites of tetrahedral or octahedral symmetry, having oxygen atoms as their nearest neighbors. The explanation is under investigation, requiring probably the help of some concepts at Quantum Mechanic level.

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