Dielectric properties of barium phosphate glasses doped with transition metal oxides

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Abstract

The effect of addition of small amounts of the transition metal (TM) ions of Co, Fe and Mn to the composition of barium phosphate glasses on the dielectric properties is studied by measurements of the dielectric constant ε', insertion loss L and microwave absorption spectra of the glass system $x\mathrm{TM} \cdot (1-x)(0.6\mathrm{P_2O_5} \cdot 0.4\mathrm{BaO})$, where $0 \leqslant x \leqslant 0.12$ is the atom-gram fraction of the transition metal. The dielectric constant at 9.00 GHz, determined by the shorted-line method (SLM), has the minimum value of $\varepsilon' = 1.77 \pm 0.02$, at room temperature for $x = 0$, and increases with x following a different law for each of the TM. There is no similar behavior reported up to date and a further investigation is necessary in order to explain the nature of these transitions considered. A minimum of $\varepsilon' = 5.50 \pm 0.05$ at the frequency of 100 kHz was obtained using impedance analysis at the same conditions. For cobalt, it was observed a linear increase of ε' in the temperature range of $25 \leqslant x \leqslant 250\,°\mathrm{C}$, at the frequency of 9.00 GHz, with the slope $\mathrm{d}\varepsilon'/\mathrm{d}T = (12.2 \pm 0.8) \times 10^{-4}\,\mathrm{K^{-1}}$ for $x = 0$ that decreases to $(9.0 \pm 0.8) \times 10^{-4}\,\mathrm{K^{-1}}$ for $x = 0.12$. The absorption coefficient α, measured at 9.00 GHz by insertion loss, increased from 0.15 to 1.03 cm^{-1} for Co content varying from 0.00 to 0.12 atom-gram, indicating the contribution of dispersive microwave scattering. Two peaks appeared at the approximate frequencies of 8.7 and 10.9 GHz, respectively, in the microwave absorption spectra, with maximum intensity at $x = 0.04$ followed by a further decrease with increasing Co content. Their nature is still a matter of further investigation.
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1. Introduction

Phosphate glasses have several advantages over borate and silicate glasses because their thermal expansion coefficients, ultraviolet transmission, and melting temperatures [1–3]. However, because of chemical durability and hydration of such glasses, several works and techniques to improve the chemical durability and to reduce hydration of these glasses have been reported [4,5], as well as describing the physical properties of phosphate glasses doped with iron and other metal oxides [6].

Some polarization mechanisms in barium aluminoborate glasses exposed to X-ray irradiation reported in [7] were attributed to the interaction of a radio frequency AC potential and intrinsic or radiation-induced electrical dipoles. Rocha et al. argued that such contributions to the dielectric constant are provided by intrinsic dipoles induced by ionizing irradiation formed by pairs of glass modifier ions balancing the charge of a given structural unit, or by electron–hole pairs of radiation-induced electrical charges from either a boron–oxygen hole center (BOHC$^+$) [8] and a boron electron center (BEC$^-$) [9], or a BOHC$^+$ and a Fe^{2+} impurity

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ion (a Fe^{3+} ion that has trapped an electron) [7]. It is reasonable to suppose that similar effects will be observed also in barium phosphate glasses, where the possible intrinsic dipoles are the Ba^{2+} ions compensating a pair of non-bridging oxygens (NBOs) and electron–hole pairs of phosphorus oxygen hole center ($POHC^+$), or oxygen hole center (OHC^+) of a NBO and a phosphorus electron center (PEC^-) [10]. In addition, we expected that in the non-irradiated phosphate glasses doped with TM: Co, Fe, Mn there will be found 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. The polarization contributions to the dielectric constant were attributed to the existence of degrees of freedom [11] associated with the allowed orientations of the permanent dipoles from charge pairs as described above.

At higher frequencies, permanent dipoles cannot respond to the electric field variation and the contributions to the dielectric constant decrease to almost zero [12]. The thermal vibrations of molecules 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 increase of the dielectric constant, ε' [13–15].

Among the several techniques available to measure the dielectric constant, ε', of materials in the range of microwave frequencies (10^8–10^{11} Hz) [16,17], it is usual to employ a resonant cavity containing the sample [17]. A change in the resonant frequency, taking the empty cavity as reference, gives a measure of the ε', whereas a change in the quality factor gives the dielectric loss, ε'', of the sample.

The aim of this work is to study the effect of additional dipoles, introduced by doping with TM ions the base glass $0.6P_2O_5 \cdot 0.4BaO$, selected by its good stability and chemical durability. The choice of the addition of TM oxides is another way to introduce new dipoles in the system, as compared with the means of ionizing irradiation used by Rocha et al. [7]. The polarization state of the samples was evaluated by means of measurements of dielectric constant, ε', insertion loss [17] and microwave spectroscopy of the glasses. The shorted-line method (SLM) [16,17], i.e., a waveguide with short-circuit, was used to determine the dielectric constant ε' of the glasses, at 9.00 GHz due to its simplicity and ease to get the results. In addition, measurements at 100 kHz were performed by means of impedance analysis [7] at room temperature in order to make an estimative of the response of the permanent dipoles in both frequencies [12]. Also, measurements of microwave transmitted signal amplitude through the glasses as a function of frequency (8–12 GHz) were performed for different concentrations of transition metal oxides.

2. Experimental

The glasses studied in this work have the composition $xTM \cdot (1 - x)(0.6P_2O_5 \cdot 0.4BaO)$, where TM = Co, Fe, Mn, and x represents the atom-gram fraction of the transition metal, as shown in Table 1.

The glasses were prepared by weighing reagent grade amounts of raw materials $NH_4H_2PO_4$, $BaCO_3$, MnO_2, Fe_2O_3 and CoO (Merck). The batch was homogenized for about 30 min and melted in alumina crucible in air using an electric furnace, at 1000 °C for 2 h. The liquid was quenched in a mould, annealed at 470 °C for 2 h (near the T_g of these glasses), and the six faces of a single bulk sample were polished to fit inside the sample-holder with dimensions $1.0 \times 2.3 \times 1.5$ cm^3. The wave-guide is the standard WR-90 ($a = 22.86$ mm; $b = 10.16$ mm). In this way, there is no ambiguity in the measurements.

The glasses containing iron have brown color; those containing manganese are transparent whereas those containing cobalt have a dark blue color.

The SLM 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 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 [16]. The shift in the standing waves 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, the shift Δl of the reference minimum was measured. After standard microwave measurement technique it is suitable that the sample length d should be located somewhere between $\lambda_g/4$ and $\lambda_g/2$, where λ_g is the guided wavelength and this way there is no ambiguity in the measurement analysis. The dielectric constant ε' was evaluated from the following expression

Table 1
Transition metal content in the glass $xTM \cdot (1 - x)(0.6P_2O_5 \cdot 0.4BaO)$

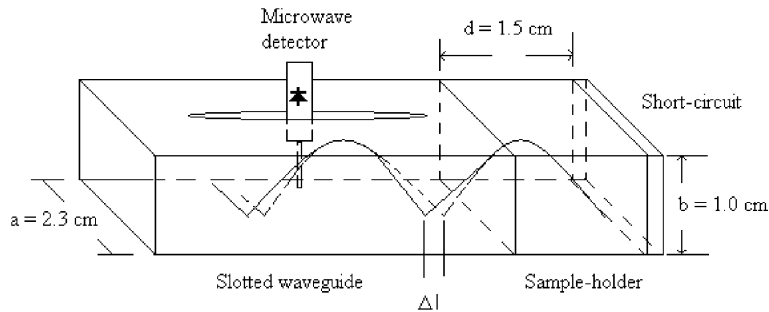| xCo (a.g.)	xFe (a.g.)	xMn (a.g.)
0	0	0
0.04	0.06	0.03
0.08	0.12	0.06
0.12	0.18	0.09

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.

[17], which relates the dielectric constant with an intermediate parameter, y

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

and the parameter y can be evaluated by means of the equation

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

In the above equations, the meaning of the parameter y that appears in the Eqs. (1) and (2) is a multivalued dimensionless unknown parameter [17]. It is adjusted using an estimated dielectric constant using Eq. (2). Then the closest y that satisfies (1) is substituted in Eq. (2) giving the measured, ε'. The 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 the standing wave mode, and a is the width of the wave guide (TE_{10} mode).

The dielectric constant ε' measurements were carried out in the temperature range 25–220 °C (samples containing Co). The uncertainty in the temperature measurement was approximately ±5 °C. The heat was applied by means of an electric tape surrounding the sample-holder. An electronic device controlled the current and a K-type thermocouple and a digital thermometer (Minipa Mod. MT-520) monitored the sample temperature.

The dielectric constant, ε', has also been measured at 100 kHz for comparison and was performed by using an impedance analyzer (HP-4192A). This technique is described elsewhere [7].

Measurements of insertion losses were performed at constant frequency of 9.00 GHz using a piece of waveguide without and with an inserted glass sample of dimensions $1.0 \times 2.3 \times 1.5\,cm^3$ 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). The insertion loss measured in decibels per centimeter L

(dB/cm) of the glasses as a function of Co 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 measured in mW. The L (dB/cm) is related to the absorption coefficient (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.

The spectra of the microwave attenuation of glasses containing different amounts of Co in the frequency range of 8–12 GHz were performed using a sweep microwave generator (HP-3050B) connected at the input of a piece of waveguide and the response was measured by a scalar network analyzer (HP-8756A) connected to the waveguide output. The geometry of the sample inserted in the waveguide is the same as described above.

3. Results and discussions

The SLM dielectric constant of the samples was evaluated at 9.00 GHz by measuring the Δl, by means of the expressions (1) and (2), whereas at 100 kHz, the dielectric constant of the same glasses was evaluated using impedance analysis method [7]. The results of the dielectric constant for increasing Co content are shown in Fig. 2, together with the measurements performed at 100 kHz, at room temperature. The dielectric constant, ε', measured at 100 kHz is greater than that obtained at 9.00 GHz, as shown in Fig. 2.

The measured dielectric constant can be attributed to the presence of permanent electrical dipoles in the glass [7] that arise from charged pairs formed by the positively charged defects on metal ions and negatively charged groups, such as the Q_n (n-coordinated tetrahedral glass forming structural units). For non-irradiated phosphate glasses containing a glass structure modifier oxide, such as BaO, the charge compensation pairs of Ba^{++} ions and PO_4 tetrahedrons of $n \leqslant 2$ (i.e., containing one or more NBOs making a single bond with phosphorus) are the dipolar units to contribute for the measured ε'. Now, if we add oxides of TM impurities to the glass composition, the fraction of cations occupying glass-modifying
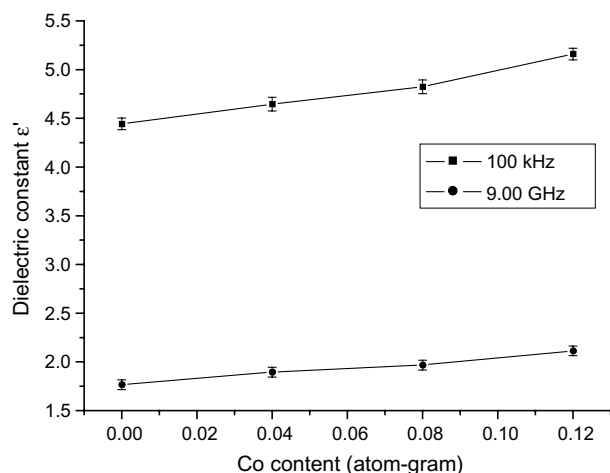
Fig. 2. Dielectric constant ε' of the glass $xCo \cdot (1-x)(0.6P_2O_5 \cdot 0.4BaO)$, as a function of x, measured at 9.00 GHz and 100 kHz, at room temperature. The lines are drawn between data symbols as guides for the eyes.

Fig. 3. Dielectric constant ε' of the glass $xCo \cdot (1-x)(0.6P_2O_5 \cdot 0.4BaO)$ as a function of x, measured at 9.00 GHz and temperatures ranging from 25 °C to 220 °C. The errors shown for the temperature in the data are the same for all the data. It is shown that the ε' increases approximately linearly with temperature in this interval, as indicated by the straight lines drawn for each set of data symbols.

sites, an additional number of similar dipoles is expected to be found. The addition of modifier oxides implies in the introduction of an excess of oxygen to the glass structure, giving rise of more NBOs and consequently, more electrical dipoles in the glass. The dielectric constants at 9.00 GHz of the samples of barium phosphate glasses of $x = 0.04$, 0.08 and 0.12, respectively, in the range of 25–220 °C are shown in Fig. 3. It is shown that for all the samples the ε' increases linearly with temperature in this range, with the slope $d\varepsilon'/dT = (12.2 \pm 0.8) \times 10^{-4} K^{-1}$ for $x = 0$ decreasing to $(9.0 \pm 0.8) \times 10^{-4} K^{-1}$ for $x = 0.12$.

The temperature effect on the polarization state of the permanent dipoles, contributing to the dielectric constant, [18] is well known [19,20], as it is shown by the results of the dielectric constant, that increases monotonically in the range temperature (25–220 °C) for the samples doped with Co (see Fig. 3).

Fig. 4 shows the insertion loss, measured in terms of the reciprocal of transmittance $T^{-1} = P_0/P$ at 9.00 GHz of the samples as a function of Co content. The absorption coefficient increased from 0.15 to 1.03 cm^{-1} for Co content varying from 0.00 to 0.12 atom-gram, indicating the contribution of dispersive microwave scattering.

Fig. 5 shows the attenuation in the transmitted microwave signal through the glasses as a function of the frequency and cobalt content. The measurements were performed in the frequency range 8–12 GHz, using the same experimental setup as in the case of the insertion loss measurements. For the base glass ($x = 0.00$) we note the presence of absorption maximum at about 9.8 GHz and a broad profile extending below 8.8 GHz. For the cobalt doped glasses the main absorption band at 9.8 GHz has shifted to lower frequencies showing a decrease in its amplitude for samples doped with
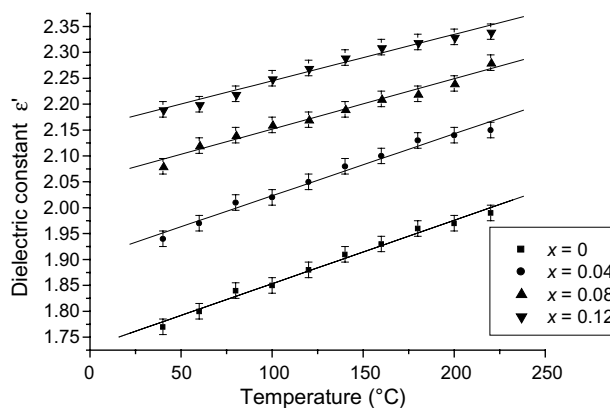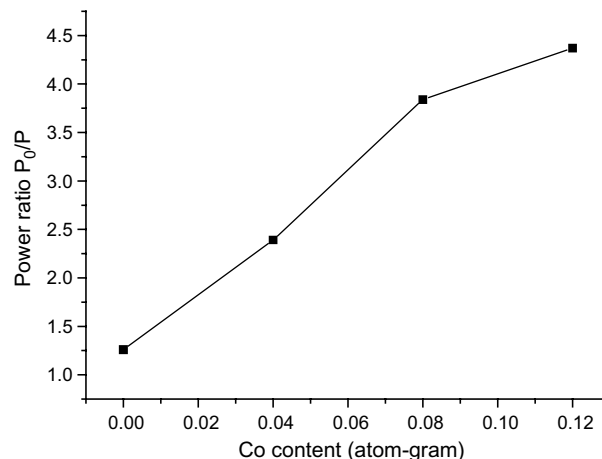

Fig. 4. Relative insertion loss, P_0/P, measured at 9.00 GHz for the glass $xCo \cdot (1-x)(0.6P_2O_5 \cdot 0.4BaO)$, at room temperature. The error bars for the experimental data are smaller than the size of the symbols. Lines are drawn between data symbols as guides for the eyes.

increasing amount of Co ($x = 0.08$–0.12). The broad profile has also shown a similar decrease with increasing x. In addition, two peaks appeared at the approximate frequencies of 8.7 and 10.9 GHz, respectively with maximum intensity at $x = 0.04$ followed by a further decrease with increasing Co content. All these observed absorption peaks have vanished at about $x = 0.12$. To our knowledge, there is no similar behavior reported up to date and a further investigation is necessary in order to explain the nature of these transitions. As the sample thickness of all the samples were equal to $d = 1.5$ cm, the spectra normalization condition was fulfilled.

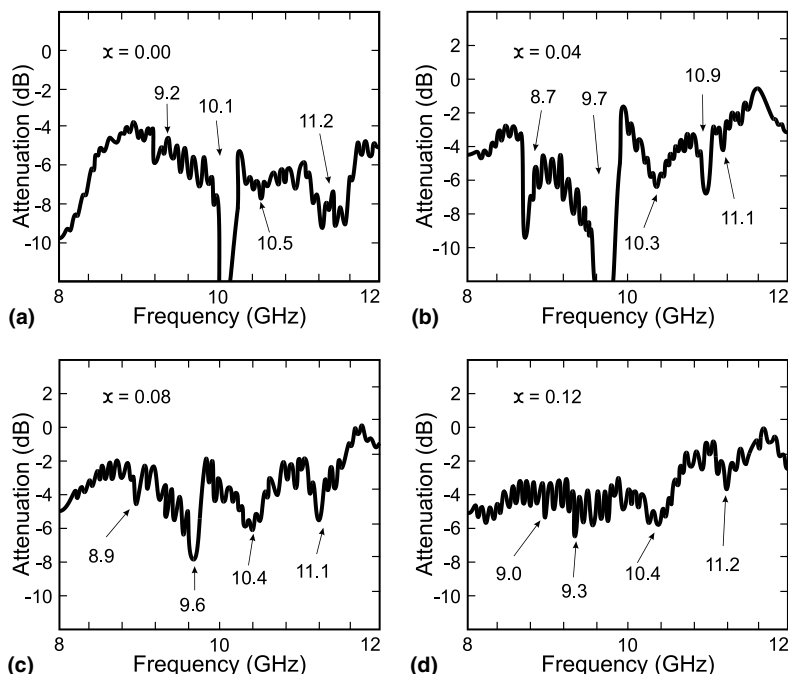Fig. 6 shows the dielectric constant, ε', of the samples containing different Fe concentrations, performed at

Fig. 5. Microwave signal transmitted through the glass $x\,Co \cdot (1-x)(0.6P_2O_5 \cdot 0.4BaO)$, ($x = 0.00$ (a), 0.04 (b), 0.08 (c), 0.12 (d)). Sample thickness = 1.5 cm. Measurements performed at room temperature.

room temperature and frequencies of 100 kHz and 9.00 GHz.

As in the case of the glasses containing different Co concentrations (Fig. 2), the dielectric constant, of the glass containing iron is smaller at 9.00 GHz than at 100 kHz.

Finally, Fig. 7 shows the dielectric constant of a sample doped with different amounts of Co, Fe and Mn, measured at 9.00 GHz and room temperature, as a function of the specific TM ion concentration. The different
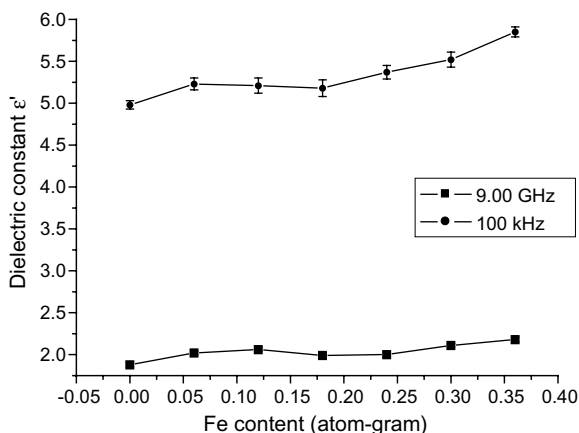

Fig. 7. Comparison of dielectric constant ε' measured at 9.00 GHz and room temperature for the glasses doped with Co, Fe and Mn. Lines are drawn to link the data symbol of each set of symbols.

behavior observed for the addition of Fe is probably due to the appearance of Fe clusters for concentrations higher than about 5 atom-gram %, as reported for different iron-doped oxide glasses [21].

4. Conclusions

For both frequencies (9.00 GHz and 100 kHz), the dielectric constant increases with TM content, indicating that the TM ions contribute to the electrical polarization of the glasses.

Fig. 6. Dielectric constant ε' of the glass $x Fe \cdot (1-x)(0.6P_2O_5 \cdot 0.4BaO)$ obtained at room temperature and at 9.00 GHz and 100 kHz. The error bars for the experimental data are smaller than the size of the symbols. Lines are drawn between data symbols as a guide for the eyes.
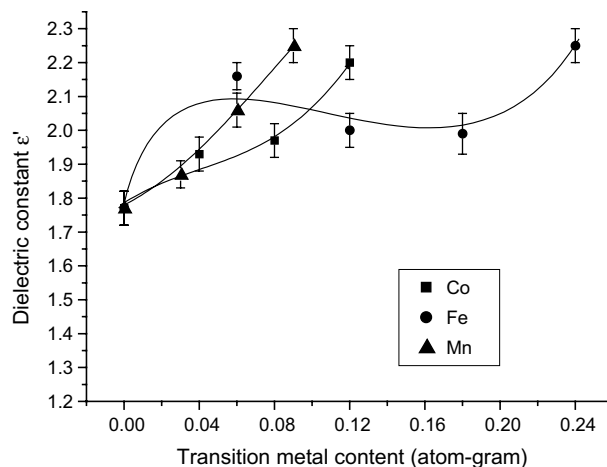
The base glass $0.6P_2O_5 \cdot 0.4BaO$ has the minimum value of $\varepsilon' = 1.77 \pm 0.02$ at the frequency $9.00\,GHz$ and $\varepsilon' = 5.50 \pm 0.05$ at $100\,kHz$. A linear increase was observed in the temperature range of $25 \leqslant x \leqslant 250\,°C$ for cobalt addition, with the slope $d\varepsilon'/dT = (12.2 \pm 0.8) \times 10^{-4}\,K^{-1}$ for $x = 0$ that decreases to $(9.0 \pm 0.8) \times 10^{-4}\,K^{-1}$ for $x = 0.12$.

The increase of the insertion loss for phosphate glasses doped with $0 \leqslant x \leqslant 0.12$ Co 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, of decreasing intensity that vanishes at 0.12 atom-gram of Co 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.

The measurements of the transmitted microwave signal through the glasses as a function of the frequency and cobalt content, performed in the frequency range 8–$12\,GHz$, the presence of absorption maximum at about $9.8\,GHz$ and a broad profile extending below $8.8\,GHz$ for the base glass ($x = 0.00$). For the cobalt doped glasses the main absorption band at $9.8\,GHz$ has shifted to lower frequencies showing a decrease in its amplitude for samples doped with increasing amount of Co ($x = 0.08$–0.12) and the broad profile has also shown a similar decrease with increasing x. Two peaks appeared at the approximate frequencies of 8.7 and $10.9\,GHz$, respectively with maximum intensity at $x = 0.04$ followed by a further decrease with increasing Co content. All the observed absorption peaks have vanished at about $x = 0.12$. There is no similar behavior reported up to date and a further investigation is necessary in order to explain the nature of these transitions.

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