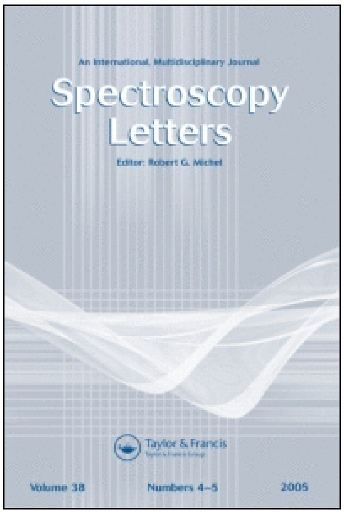

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Dielectric Measurements as a Function of Temperature of Sodium-Lithium Phosphate Glasses Evaluated at 10 MHz and 9 GHz

P. Bergo[a]; J. M. Prison[b]
[a] Food Engineering Department, Universidade de São Paulo, Pirassununga, SP, Brazil [b] Energy and Nuclear Research Institute, Brazilian Nuclear Energy Commission, SP, Brazil

To cite this Article Bergo, P. and Prison, J. M.(2007) 'Dielectric Measurements as a Function of Temperature of Sodium-Lithium Phosphate Glasses Evaluated at 10 MHz and 9 GHz', Spectroscopy Letters, 40: 4, 659 — 665
To link to this Article: DOI: 10.1080/00387010701301246
URL: http://dx.doi.org/10.1080/00387010701301246

Spectroscopy Letters, 40: 659–665, 2007

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010701301246

Dielectric Measurements as a Function of Temperature of Sodium-Lithium Phosphate Glasses Evaluated at 10 MHz and 9 GHz

P. Bergo
Food Engineering Department, Universidade de São Paulo,
Pirassununga, SP, Brazil

J. M. Prison
Energy and Nuclear Research Institute, Brazilian Nuclear Energy
Commission, SP, Brazil

Abstract: Dielectric constant measurements can be performed at temperatures greater than room temperature; some techniques are shown in this work. The dielectric constant of phosphate glasses, measured in the X-band microwave range, was determined using a microwave setup assembled to measure the shift in the standing wave pattern produced by the insertion of the sample inside the waveguide. The glass system $50P_2O_5 \cdot 25Li_2O \cdot 25Na_2O$ was chosen in this work due to its lower melting point and lower transition temperature (T_g) values. The dielectric constant of the glass studied in this work increases in the temperature range 25–330°C, as shown by the results at radio and microwave frequencies. The method of standing wave shift was applied, and it is shown to be a useful tool to estimate the T_g of glasses. This assumption was confirmed by differential thermal analysis technique. Measurements were compared to that at 10 MHz by impedancimetric methods.

Keywords: Capacitance, dielectric, glass, shorted-line

Received 30 October 2006, Accepted 8 February 2007
Address correspondence to P. Bergo, Depto. de Engenharia de Alimentos, FZEA-USP, Rua Duque de Caxias norte, 225, 13630-000 Pirassununga, SP, Brazil. E-mail: pvabergo@yahoo.com.br

INTRODUCTION

It is well-known that at frequencies reaching the optical region, the permanent dipoles cannot follow the fast electric field variations, and the contributions to the dielectric constant become vanishing. On the other hand, the thermal vibrations of molecules contribute with an additional polarization, due to an increased average value of the permanent dipole moment, and therefore, it is an additional contribution to the increase of the dielectric constant value ε'.[1–4] In such cases, the polarizability decreases with frequency and increases with temperature. Measurements of dielectric properties are, therefore, important to study the above properties that occur in all dielectrics.

Several techniques are available to measure dielectric constants of bulk, liquid, and gaseous materials, covering frequencies from some hertz to optical frequencies. At radio frequency, impedancimetric method is used,[5] whereas at microwave region, the technique of perturbed resonant cavity is mostly used to perform measurements of dielectric properties.[6] Some techniques to achieve temperatures greater than 25°C can be adapted in a specific system and are described in this work.

The study of dielectric properties of glasses is very important in recent technology, where the glass can be used as insulator material for high-voltage applications (e.g., capacitors for high-voltage, high-frequency circuits, dielectrics for transmission lines, and specific elements for use in high-frequency resonators).[7]

The aim of this work is to describe some techniques at higher temperatures necessary to evaluate the dielectric constant ε' of phosphate glasses containing some flux oxides (Li_2O and Na_2O), at temperatures ranging from 25°C to 330°C, and in the range of microwave electromagnetic radiation. This glass system was chosen due to its lower T_g value,[8] in relation to borosilicate glasses. Different microwave methods[9–11] can be used to determine the dielectric behavior of the glasses; the shorted-line method was chosen for this work. A technique for dielectric measurements performed at 10 MHz is described, at temperatures ranging from 25°C to 330°C, to compare with the results obtained at microwave frequency. Differential thermal analysis (DTA) was also applied[8] in order to estimate the value of T_g of the glasses.

MATERIALS AND METHODS

The glass system investigated in this work has the composition $50P_2O_5 \cdot 25Li_2O \cdot 25Na_2O$, the quantity expressed in mol%. The glass was prepared using weighed amounts of reagent-grade raw materials $NH_4H_2PO_4$, NaOH, and LiOH. The batch was homogenized for about 30 min and melted in alumina crucible in air using an electric furnace, at 1000°C for 2 hr. The melt was quenched in a mold, annealed at 270°C for 2 hr, and the six faces of a single bulk sample were polished to fit exactly inside the sample-holder with dimensions 1.0 × 2.3 × 1.5 cm^3. The glass presented electrical resistance greater than some megaohms, measured with a digital multimeter (Minipa, Brazil), being thus a good insulator. Melting temperature is above 800°C.

The dielectric constant ε' of the glass sample 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 (sample-holder), and the dielectric constant was obtained from the measurement of the shift in the standing wave pattern. Details, equations, and procedures are well described in Ref. 9. 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).

The dielectric constant ε' measurements were carried out in the temperature range 25–330°C. The uncertainty in the temperature measurement was approximately ±5°C. The temperature control was achieved by means of an electric tape surrounding tightly 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 effects of dilation of waveguide were negligible. (*Note*: The slotted waveguide was protected by a heat sink placed in the waveguide, in order to dissipate the heat.)

The measurements of dielectric constant ε' at 10 MHz and temperatures ranging from 25°C to 330°C were performed using an impedance analyzer mode. HP-4192A (Hewlett Packard, USA) as a capacimeter mode. The sample (the same glass used at microwave measurements) was placed

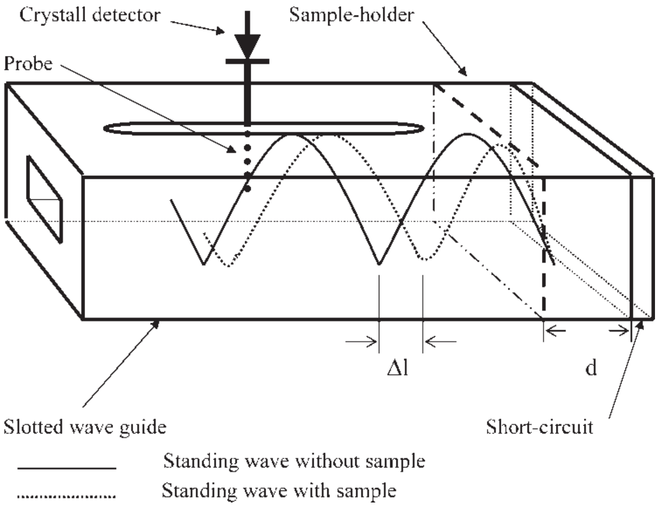

Figure 1. Microwave setup showing the standing wave shift due to the sample placed in the sample-holder.

between two parallel metallic plates (brass), forming a capacitor. The plates were mounted in a refractory insulator material to support high temperatures. The sample-holder was placed inside an electric furnace, to control the temperature, and ordinary copper wires were used to connect the sample-holder to the impedancimeter. The values of ε' were achieved from the ratio of the capacitance of sample-holder containing the glass (C) and capacitance of the empty sample-holder (C_o). (*Note*: The capacitance of empty sample-holder presents no variations with increasing temperature and its value was fixed.)

Differential thermal analysis (DTA; Netzch 404B, Germany) was also used to determine the transition temperature (T_g) of the glass. The glass was reduced to powder in order to fit inside an appropriate crucible. The heating rate was approximately 30°C/min.

RESULTS

The dielectric constant ε' of the glass investigated in this work, measured at 9.00 GHz, was evaluated from the measurement of the phase shift Δl of the standing wave pattern. Figure 2 shows the variation of the dielectric constant ε' as a function of temperature of the glass containing the flux oxides at microwave frequency.

The dielectric constant values seem to increase more rapidly for temperatures beyond 275°C. This temperature, in principle, could be related to the T_g of this glass compared with that obtained by DTA. Figure 3 shows the measurements of dielectric constant ε' of the glass, evaluated at 10 MHz from measurements of the ratio of capacitance of the sample-holder with and without the sample.

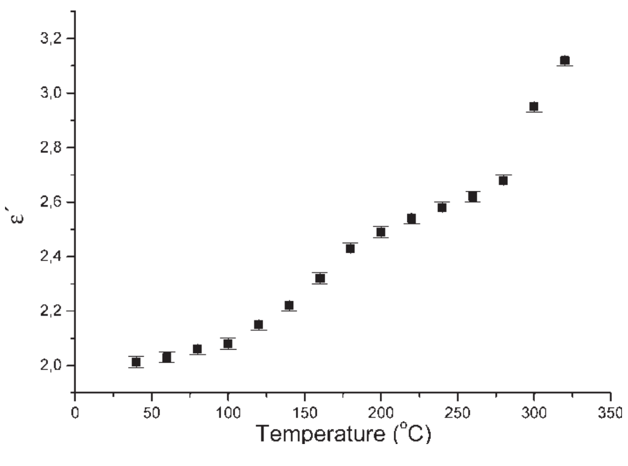

Figure 2. Dielectric constant ε' of the glass $25Na_2O \cdot 25Li_2O \cdot 50P_2O_5$ measured at 9 GHz and temperatures from 25°C to 330°C.

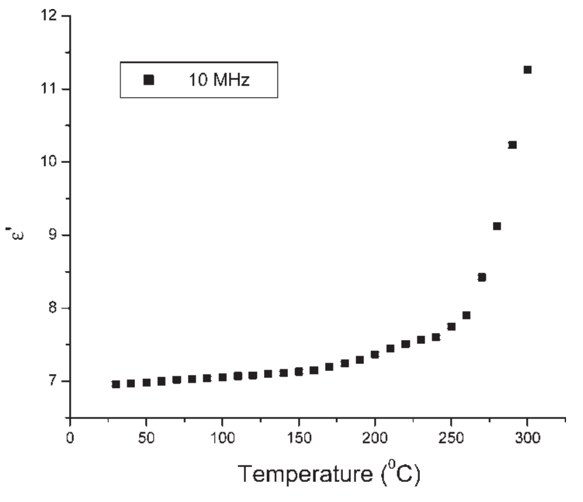

Figure 3. Dielectric constant ε′ of the glass $25Na_2O \cdot 25Li_2O \cdot 50P_2O_5$ measured at 10 MHz and temperatures from 25°C to 330°C.

At both frequencies, it was observed that the dielectric constant increases as a function of temperature. The temperature affects the polarization state of the permanent dipoles by increasing the amplitude of the thermal vibrations of the charges and contributing therefore to the dielectric constant ε′.

A small shoulder near 200°C was observed in both curves depicted in Figs. 2 and 3. This effect can probably be caused by the increased mobility of the light ions Li and Na in the glass structure with increasing temperature. Figure 4 shows the DTA curve, as well as the value of T_g of this glass.[8]

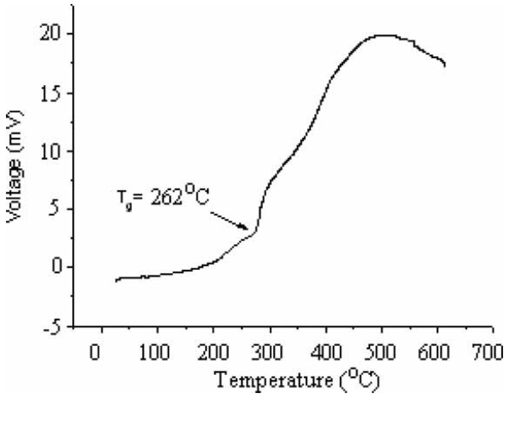

Figure 4. DTA curve for the glass $25Na_2O \cdot 25Li_2O \cdot 50P_2O_5$ showing the approximate value of T_g.

Table 1. T_g of the glass $25Na_2O \cdot 25Li_2O \cdot 50P_2O_5$ obtained by DTA, shorted-line (9.00 GHz), and impedancimetric (10 MHz) method

Method	T_g
DTA	$262 \pm 10°C$
Impedancimetric	$265 \pm 10°C$
Shorted-line	$275 \pm 10°C$

Table 1 shows a comparison between the values of T_g obtained by the three methods described in this work.

CONCLUSIONS

The measurements of the dielectric constant at microwave region, in phosphate glasses containing some flux oxides (Na_2O, Li_2O) for several values of temperatures, were performed, and the behavior was compared with that observed at 10 MHz. The effect of temperature can be related to the anharmonic distortion that possibly occurs in the structural units, increasing the amplitude of thermal vibrations of the dipoles, which contributes to the polarizability in the structure, leading to an increase in the dielectric constant. The glass transition temperature could be estimated, because the value of the inflexion observed in the curve of dielectric constant against temperature coincided with the T_g of this glass, as checked by DTA. Finally, the shoulder observed near 200°C can be related to the mobility of the ions Na and Li in the glass structure. In conclusion, the microwave techniques were found to be sensitive in the study of several physical properties of materials, such as composition, temperature, and so forth, serving as a complement to other studies.

ACKNOWLEDGMENT

We would like to thank the financial support from FAPESP-Fundação de Amparo à Pesquisa do Estado de São Paulo (process no. 00/12813-6).

REFERENCES

1. Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill Book Company: New York, 1955.
2. Subbalakshmi, P.; Veeraiah, N. Dielectric dispersion and certain other physical properties of PbO-Ga_2O_3-P_2O_5 glass system. *Mater. Lett.* **2002**, *56*, 880–888.
3. Novikov, V. N. Anharmonicity of vibrations and quasielastic scattering in glasses. *Phys. B Phys. Condens. Matter* **1999**, *263–264*, 343.

4. Fuoss, R. M. A dielectric study of plasticized polyvinylidene chloride. *J. Am. Chem. Soc.* **1941**, *63*, 385–392.
5. Rocha, M. S. F.; Pontuschka, W. M.; Blak, A. R. Radiation induced capacitance in barium aluminoborate glasses. *J. Non-Cryst. Solids* **2003**, *321*, 29–36.
6. Wu, J. M.; Huang, H. L. Microwave properties of zinc, barium and lead borosilicate glasses. *J. Non-Cryst. Solids* **1999**, *260*, 116–124.
7. Gough, C. E.; Ormeno, R. J.; Sibley, A.; Hein, M.; Nishizaki, S.; Maeno, Y. Microwave spectroscopy of novel superconductors. *J. Phys. Chem. Solids* **2002**, *63*, 2187–2193.
8. Kaoua, S.; Krimi, S.; El Jazouli, A.; Hlil, E. K.; de Waal, D. Preparation and characterization of phosphate glasses containing titanium and vanadium. *J. Alloys Compds* **2007**, *429*, 276–279.
9. Roberts, S.; Hippel, A. A new method for measuring dielectric constant and loss in the range of centimeter waves. *J. Appl. Phy.* **1946**, *17*, 610–614.
10. Lance, A. L. *Introduction to Microwave Theory and Measurements*; McGraw-Hill Book Company: New York, 1964.
11. Bergo, P.; Pontuschka, W. M.; Prison, J. M.; Motta, C. C. Microwave insertion loss measurements in phosphate glasses containing transition metal oxides. *Measure. Sci. Technol.* **2006**, *17*, 855–858.