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SYNTHESIS AND DIELECTRIC MEASUREMENTS OF LEAD AND LEAD CHLORIDE PHOSPHATE GLASSES

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ABSTRACT

A series of binary lead phosphate glasses $(PbO)_x(P_2O_5)1\text{-}x$ and lead chloride phosphate glasses, $(PbCl_2)_x(P_2O_5)_{1-x}$ have been successfully synthesized with x ranging from 0.1 to 0.5. The objective of the research is to determine the effect of mole fraction and temperature on dielectric properties of phosphate glasses. Frequency ranging from 10^{-2} to 10^6 Hz was chosen. The results obtained for the binary lead phosphate glasses showed that the addition of PbO or $PbCl_2$ into the system will decrease the number of cross-links, hence increases the number of the non-bridging oxygen that will eventually weaken the structure bonds of the glasses. We can also say that the stiffness of the lead phosphate glass was decreasing as the mole fraction of PbO or $PbCl_2$ increases. At room temperature, the value of the imaginary component of complex dielectric, ε'' was seen to decrease with a slope of –1 as the frequency was increase whilst the real part, ε' also decreased in parallel with ε'' as the frequency was decreased but later flatten out towards high frequency. The trend was present in both the lead and lead chloride phosphate glasses. This low frequency dispersion could be due to the hopping of electrons or an ion in a potential double well arising at some localized defect. However as the temperature was increased, we found that the behavior of ε'' was inversely proportional to frequency while ε' remained relatively constant at all frequency measured. This response is usually associated with direct current conduction in the material in the relevant frequency range.

INTRODUCTION

Glasses are among the most ancient materials used by human civilization and knowledge of them has been acquired over many centuries. PbO is a modifier lead glasses. It is a good flux which, for an equal softening effect, does not reduce electrical resistivity as much as the alkali oxides. It yields glasses with high refractive index and density, a low softening temperature (temperature at which the glass flow readily under load). Commercial importance is found in the production of radiation shield windows, fluorescent lamp envelopes, electrical glasses, optical glasses, lead crystal for art ware and low melting solder-sealing glasses (Rothenbery, 1976). Glass and glass ceramic material containing phosphates are of particular interest for the purpose of bio-ceramics, glass to metal seals and semiconductor materials (Shar, 1992). In addition, phosphate glasses doped with silver find applications in batteries (Kawamura and Shimoji, 1986). Phosphorous pentoxide, P_2O_5 is the main material for the formation of the phosphate glasses. Phosphate glasses are known to form tetrahedral structure unit with each phosphorous atom share with four oxygen atoms. One of the oxygen atom forms a double bonding with phosphorous atom. The other oxygen atoms form a single bonding with PO_4 tetrahedral unit.

METHODOLOGY

Analytical grade of phosphorous pentoxide, P_2O_5, lead oxide, PbO and lead chloride, PbCl, were used in the preparation of the binary lead phosphate glass. For synthesizing the glass, 20 g batches of calculated amount of P_2O_5 and PbO were well mixed with a glass rod in an alumina crucible of 50 cm^3 capacity. The crucible was covered and then put into the electric furnace. Two furnaces were used in the experiment. The first one was which was set at 500^oC was used to dry the chemical and also to start the chemical reaction. This temperature was set because the melting point of P_2O_5 is 580^oC and therefore no chemical reaction will take place in the first furnace. After the chemical was kept in the first furnace for 30 minutes, it was moved to the second furnace where the temperature was set at 1000^oC. At that temperature, the chemical substance will melt and chemicals will react with one another. The purpose of the second furnace is to ensure that the reaction of the chemical substances is carried out rapidly and also to minimize the loss of P_2O_5. However, some P_2O_5 gas will be released and this gas is taken out from the second furnace through a pipe. After 60 minutes, the crucible was taken out from the second furnace and the melt was then poured into a mould.

The mould is made of stainless steel and is 5 mm in height and 15 mm in diameter. The mould was preheated to 400^0C in the first furnace to reduce thermal shock when the melt is poured into it. After the melt has solidified, the glass is removed from the mould. The glass sample is then transferred to the first furnace and annealed at 400^0C, which is a temperature approximately 10^0C above the glass transition temperature, for 60 minutes after casting the melt. This is done to relieve the stress thus preventing the sample from cracking. The furnace is then switched off and the glass is left inside for another 60 minutes before it is taken out and kept in a dissicator. The glass samples prepared are transparent, free from bubbles and colorless. Both faces of the glass sample are then polished and coated with silver conductive paint and are left to dry at room temperature overnight. The conductive paint is used as an electrode for our measurement.
The complex capacitance of lead oxide and lead chloride phosphate glasses investigated using a dielectric spectrometer over a frequency range of 10^{-2} Hz to 10^6 Hz. The dielectric spectrometer consists of a H.F Frequency Response Analyzer (Schlumberger Technologies) coupled to a Chelsea Dielectric Interface. A signal of 1 V(rms) was generated using a frequency analyzer and passed to the sample. The returning signal was analyzed in terms of the complex capacitance at each frequency. Each point represents an average of at least four measurements. The study focussed on the variation of the capacitance C' and the relative loss factor C'' at different temperatures and different mole fraction x.

RESULTS AND DISCUSSION.

The series binary lead phosphates glasses, (PbO)x(P2O5)1-x and lead-chloride phosphate, (PbCl)y(P2O5)1-y were successfully prepared with the mole fraction ranging from 0.1 to 0.5. All the glasses prepared were transparent, colorless and free from bubble The frequency dependence of the real (ε') and imaginary (ε'') parts of the dielectric constant of lead phosphates and lead-chloride phosphate glasses on a log-log scale is shown in Fig. 1 and 2. The dielectric spectrum of both type of glasses show no loss peak and both ε' and ε'' show strong dispersion in the low frequency region.

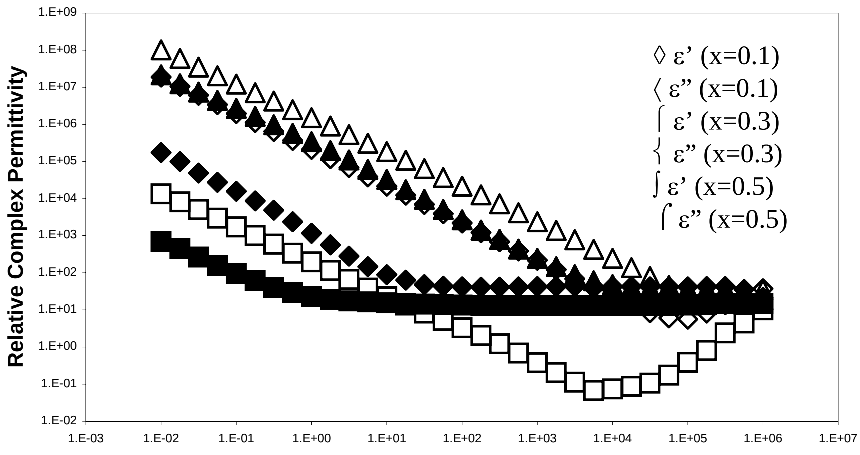

Fig. 1. The frequency dependence of the complex permittivity of $(PbCl_2)_x(P_20_5)_{1-x}$ glasses at room temperature for different mole fraction

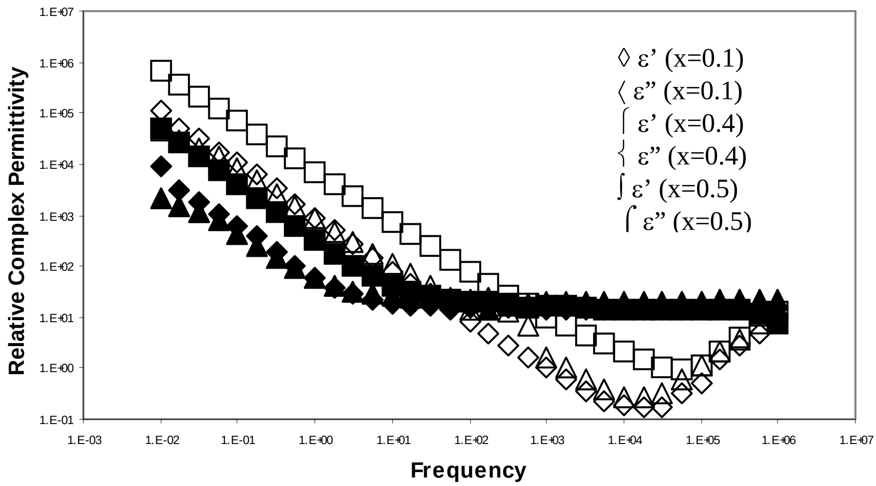

Fig. 2. The frequency dependence of the complex permittivity of $(PbO)_x(P_20_5)_{1-x}$ glasses at room temperature for different mole fraction

The variation of the complex permittivity with temperature at different frequencies for different mole fraction is depicted in Fig. 3 and 4 for the $(PbCl_2)_x(P_20_5)_{1-x}$ glasses and Fig 5 and 6 for the $PbO)_x(P_20_5)_{1-x}$ glasses. For the $(PbCl_2)_x(P_20_5)_{1-x}$ glasses, at mole fraction, x=0.25, the dispersion of ε’ at low frequencies was much weaker than ε” at all temperatures studied. Nevertheless, the variation of the ε’ rises as strongly as the ε” towards low frequency when the mole fraction was increased to x=0.5. For the $(PbO)_x(P_20_5)_{1-x}$ glasses, we see the opposite pattern occurs whereby there was strong dispersion of both ε’ and ε” at low frequencies for the lower mole fraction (x=0.1) while dc-like conduction, i.e. ε’ remains constant while ε” rises as 1/ω as frequency is increased, for the higher mole fraction (x=0.4).

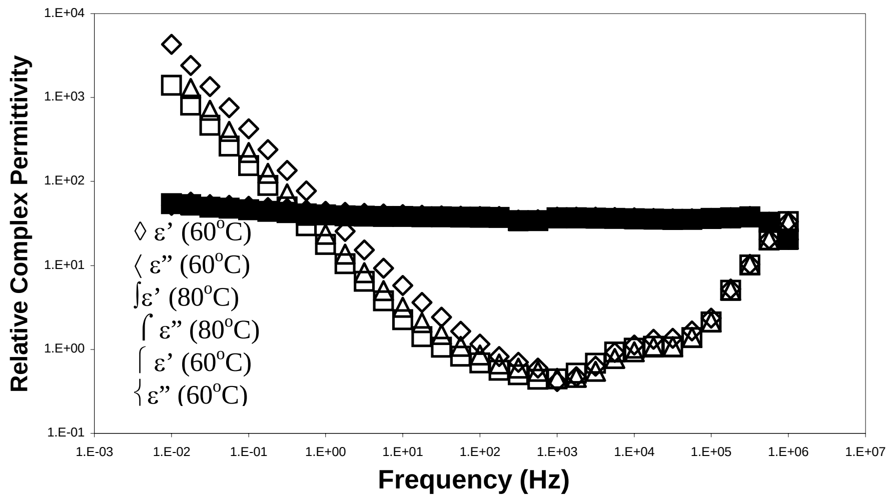

Fig. 3. The frequency dependence of the complex permittivity of $(PbCl_2)_x(P_20_5)_{1-x}$ glass at various temperatures for mole fraction x=0.25

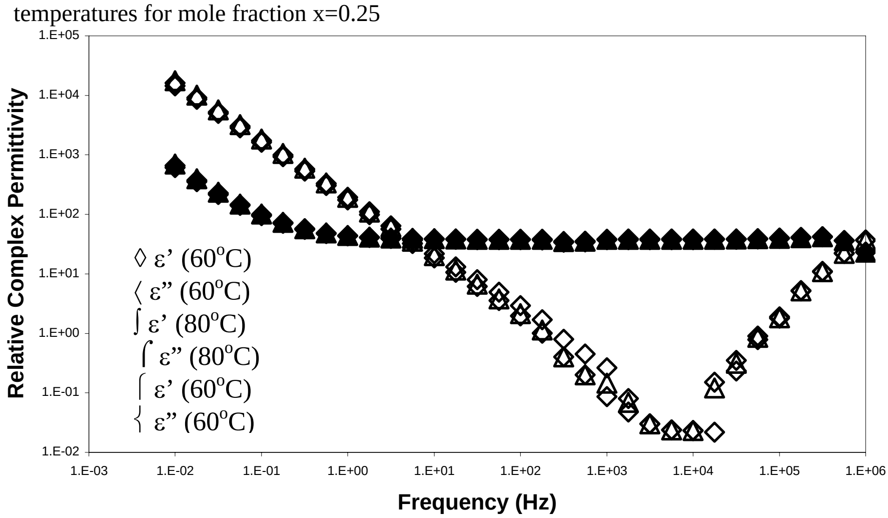

Fig. 4. The frequency dependence of the complex permittivity of $(PbCl_2)_x(P_20_5)_{1-x}$ glass at various temperatures for mole fraction x=0.50

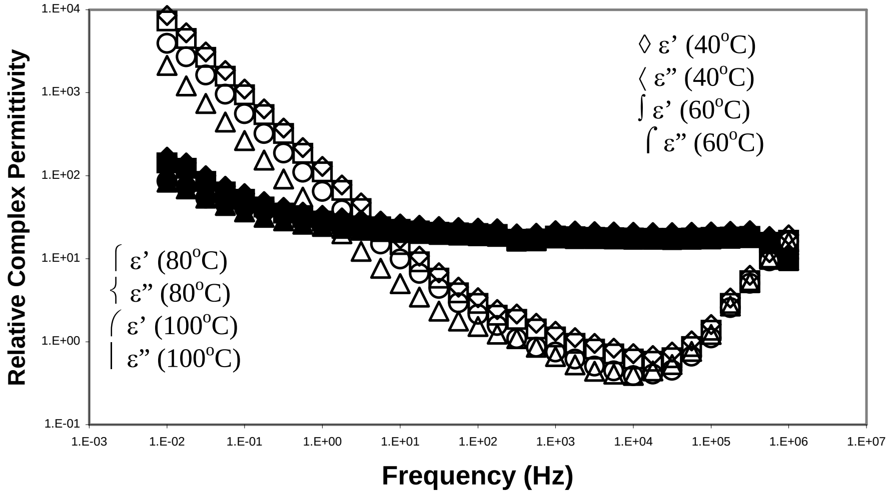

Fig. 5. The frequency dependence of the complex permittivity of $(PbO)_x(P_20_5)_{1-x}$ glass at various temperatures for mole fraction x=0.1

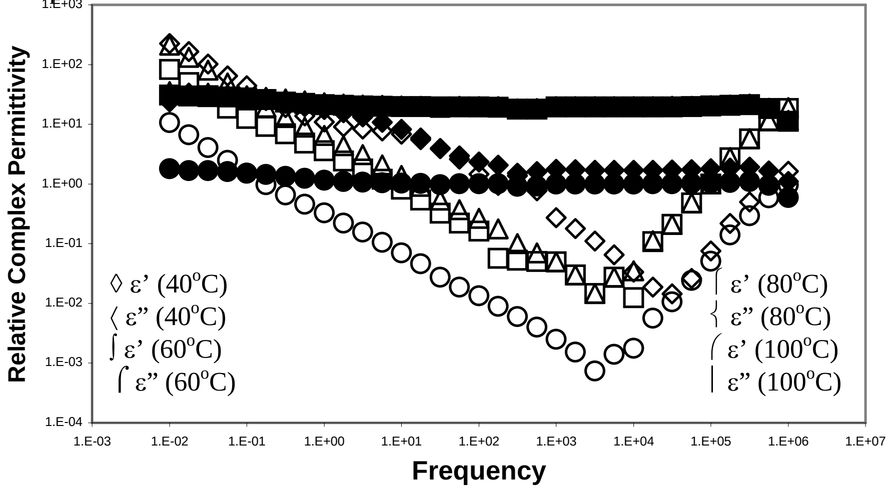

Fig. 6. The frequency dependence of the complex permittivity of $(PbO)_x(P_20_5)_{1-x}$ glass at various temperatures for mole fraction x=0.4

As can be seen from Fig. 1 and 2, the values of ε' at the high frequency spectrum or ε_∞' increases as the composition of the glass modifier PbO or $PbCl_2$ increases. This is probably due to the increase in the proportion of the large easily polarizable Pb^{2+} ions. The strong dispersion in both the components of the complex dielectric constant as was found in Figures 1, 2, 4 and 5 is usually referred to as low frequency dispersion (LFD). The responses as shown in Figures 3 and 6 where the real part remains constant while the imaginary part varies according to the reciprocal of the angular frequency ω is associate to the effect due to d.c. conductivity.

The LFD response can be explained through the following relationship [Jonscher, 1983],

$$\varepsilon^* = \varepsilon_r^{'} - i\varepsilon_r^{"} = \varepsilon_\infty + \frac{\sigma}{i\varepsilon_o\omega} + \frac{a(T)}{\varepsilon_o}\left(i\omega^{n(T)-1}\right) \qquad [1]$$

where σ is the dc conductivity, a(T) represents the strength of the polarizibility and n(T) is the temperature dependent exponent.
Expanding the last term of Eqn. [1] and equating the real and imaginary term, we get

$$\varepsilon^{'} = \varepsilon_\infty + \sin(n(T)\frac{\pi}{2})\omega^{n(T)-1}\frac{a(T)}{\varepsilon_o} \qquad [2]$$

$$\varepsilon^{"} = \frac{\sigma}{\varepsilon_o\omega} + \cos(n(T)\frac{\pi}{2})\omega^{n(T)-1}\frac{a(T)}{\varepsilon_o} \qquad [3]$$

At low frequencies, the second term of Eqn. [2] which represent the charge carrier becomes dominant and therefore for a constant n gives a straight line with a slope equal to n-1 in the log-log plot of ε' and frequency. As we increase the frequency, the charge carrier term becomes increasingly less dominant and thus the existance of a linear decrease in the low frequency region and when it the contribution becomes neglible at high frequncies, the response flatten out.

CONCLUSIONS

A series of binary lead phosphate glasses $(PbO)_x(P_2O_5)$1-x and lead chloride phosphate glasses, $(PbCl_2)_x(P_2O_5)_{1-x}$ have been successfully synthesized with x ranging from 0.1 to 0.5. and their dielectric behaviour studied. We found that as the dielctric constant increases as the content of Pb^{2+} ions increases. The dielectric response of these glasses can be explained through the Low Frequency Dispersion phenomena.

REFERENCES

[1] Jonscher, A.K. 1983. Dielectric Relaxation in Solids. Chelsea Dielectric Press: London.
[2] Kawamura, J. and Shimoji, M. 1986 The AC conductivity of superionic glasses, J.of Non-Crystalline Solid 79, pp 367-381.
[3] Rothenbery, G.B. 1976. Glass Technology. London: NOYES Data Corporation.
[4] Sahar, M.R. 1992. Preparation and Properties of Chloride Phosphate Glass. 21 Century Vision 2020, Department of Physics, Universiti Putra Malaysia.