Solid State Science and Technology, Vol. 17, No 1 (2009) 166-172
ISSN 0128-7389

EFFECT OF ZnO ON DIELECTRIC PROPERTIES AND ELECTRICAL CONDUCTIVITY OF TERNARY ZINC MAGNESIUM PHOSPHATE GLASSES

S. F. Khor , Z. A. Talib, , W. M. Daud, and B. H. Ng

Department of Physics, Faculty of Science, University Putra Malaysia, 43400, UPM, Serdang, Selangor

ABSTRACT

Five different compositions of the ternary system $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ containing 8, 10, 13, 15 and 18 mol % of ZnO have been prepared by melt quenching technique. The complex permittivity studies were presented in the frequency range of 0.01 Hz to 1 MHz and over the temperature range from 303 to 573 K. The empirical data has been analyzed by mean of curve-fitting technique based on Havriliak-Negami model. Small broad dipolar relaxation peak is well described at frequencies between 10^3 - 10^6 Hz within the range of temperatures studied while at low frequency the spectrum is dominated by dc conduction which was evidence by $1/\omega$ slope in the loss factor versus frequency plot. With increasing ZnO concentration, the dielectric (ε') and dielectric strength ($\Delta\varepsilon$) both show an increasing trend while the dc conduction behaved in the opposite direction. The excessive zinc ions occupying interstitial position rather than substitutional position among the glassy network have been suggested to be the reason behind the declining values of the dc conduction. These results are discussed in light of the structural change on account of modification effect and Zn^{2+} ions tending located in the interstitial position within the glassy matrix rather than participate in the network.

INTRODUCTION

Phosphate glasses are both scientifically and technologically important materials because of their structural versatility to accept several cation and/or anion exchanging. These features allow reengineering of glass formulation, which leads to advances in their physical properties as well as for commercial exploitation purpose by mean of investigating on the relationship between the composition, structure and properties of those materials The study on dielectric properties such as dielectric constant, dielectric loss and ac conductivity of phosphate glasses over a wide range of frequency and temperature is expected not only to reveal comprehensive idea about the nature and origin of the loss occurring in these materials as well as conduction mechanism but may also provide information on structural aspect of the glasses [1, 2]. The present study reports the dielectric properties and conductivity performed on $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ glasses over a wide range of compositions, temperatures and frequencies.

Corresponding Author: zainalat@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 1 (2009) 166-172
ISSN 0128-7389

THEORY

Data from dielectric spectroscopy can be analyzed using four different complex formalisms; impedance, Z*, admittance, Y*, permittivity, ε^*, and electric modulus, M*. These formalisms are interrelated, i.e.,

$$Z^* = \frac{1}{Y^*} = \frac{1}{j\omega\varepsilon^* C_\circ} = \frac{M^*}{j\omega C_\circ}$$

where ω is angular frequency, and $C_\circ$ is the empty cell capacitance.

The dielectric properties of usual interest are the real (ε') and imaginary (ε'') components of the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$. The permittivity of a material reflects the molecular relaxation and transport processes of the material which depend on many parameters such as temperature, time, and pressure [3].

The empirical data of this study was sufficiently fitted by using Havriliak-Negami (HN) dielectric relaxation function, superimposed by a conductivity term as shown below:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \sum_{k=1}^{m} \left\{ \frac{\Delta\varepsilon_k}{\left[1 + (i\omega\tau_k)^{\alpha_k}\right]^{\beta_k}} + \varepsilon_{\infty_k} \right\} - i\left(\frac{\sigma_\circ}{\varepsilon_\circ \omega} \right)^n \quad (1)$$

where $\sigma_\circ$ is the dc conductivity, $\Delta\varepsilon_k$ is the dielectric strength of the *k*th relaxation, τ_k is the relaxation time of the *k*th component, α is the width parameter, β is the asymmetry parameter, ε_{∞_k} is the infinite permittivity of the *k*th relaxation, n is an exponential factor. The complex permittivity of the studied glasses has been modeled by assuming the circuit in Figure 1. The equivalent circuit consists of two HN terms, a capacitance and resistance which is in parallel combination. The capacitance, C and resistance, R described the high frequency permittivity and dc conduction respectively. The first HN-function represents the small broad loss peak in the high frequency range of dielectric loss factor plot while the second HN-function represents electrode polarization.

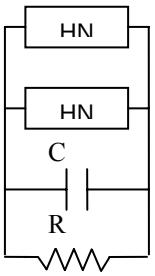

Figure1: Equivalent circuit used to model the $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ response.

Corresponding Author: zainalat@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 1 (2009) 166-172
ISSN 0128-7389

EXPERIMENTAL METHOD

The starting chemical powders, phosphorus (V) oxide (99.99%), magnesium oxide (98%) and zinc oxide (99.7%) were weighed and mixed together in an alumina crucible in appropriate quantities to constitute a 15-20 g batch. The crucible was covered and heated in an electric furnace for about 1 hour at a temperature of 400^{o}C. The crucible was then transferred to another electric furnace and kept at 1200^{o}C for 2 hours. The melt was stirred occasionally every 20 minutes to ensure homogeneity and proper mixing. Each melt was cast by pouring it into a preheated stainless steel cylindrical two-split mould to form glass rods of about 20 mm long and 10 mm in diameter. After casting each glass was immediately transferred to an annealing furnace, and held at temperature of 400^{o}C for 1 hour and slowly cooled to room temperature. The samples were prepared by cutting the glasses into disc-form and both faces of the samples were polished using silica carbide in order to get a glass with smooth and parallel faces. Pure aluminum (99.999% Al) was evaporated onto both sides of the samples as electrode by using Vacuum Coating (Edwards Auto 306). The samples were stored in a desiccator until dielectric relaxation measurements were performed by using Alpha High-Resolution Dielectric Analyzer (Novocontrol).

RESULTS AND DISCUSSION

Dielectric materials have four distinguishable polarization mechanisms, namely electronic, atomic, orientation and interfacial or space charge polarization [4]. Figure 2 shows the dielectric response of $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ for x = 15 which is a representative of the dielectric characteristic behaviour for all glasses studied. As clearly observed in Figure 2(a) that step-like decreases of the dielectric constant occurs at below 10^2 Hz and is found to increase with increasing temperature which is corresponding to electrode polarization effect. However, its corresponding loss peak cannot be seen in the ε′ spectra on account of the dominant influence of conduction losses. For the present series of glasses no obvious dispersion was detected at higher frequency range from the spectra. However, from curve-fitting analysis a dispersion is revealed which is corresponding to the first HN-function. At low frequency the ε" spectrum is dominated by dc conduction which was indicated by the 1/ω slope of the loss factor plot shown in Figure 2(b). ε″ is found to increase with increasing temperature and small broad dielectric loss peak at higher frequency range has been observed. The position of these loss peaks is gradually shifted toward higher frequencies with increasing temperature.

Corresponding Author: zainalat@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 1 (2009) 166-172
ISSN 0128-7389

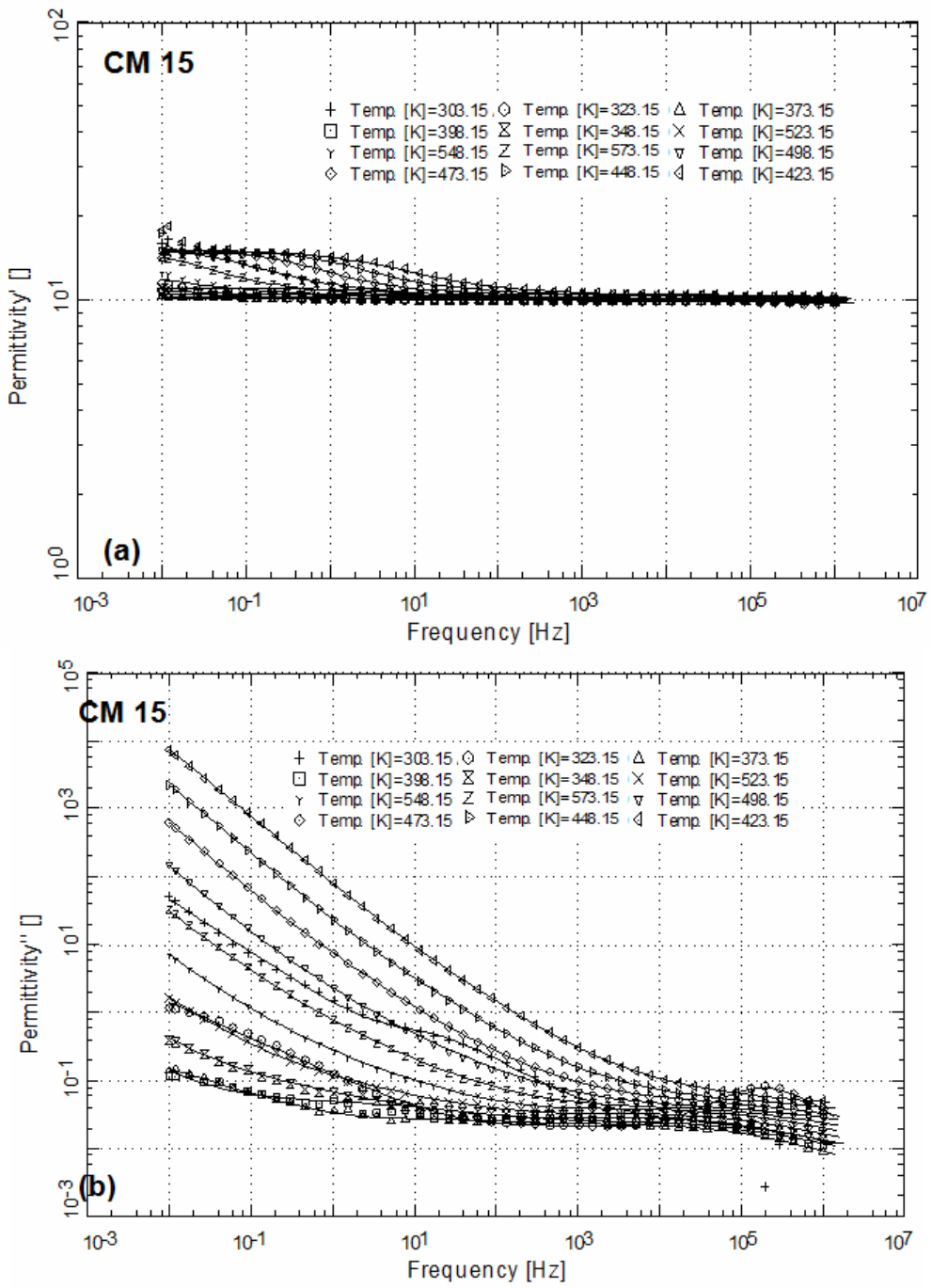

Figure 2: Dielectric permittivity (a) and dielectric loss factor (b) in the frequency domain for $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ glasses at x = 15. Solid line indicates fitting by the Havriliak-Negami equation superimposed with a conductivity term by using Winfit.

Corresponding Author: zainalat@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 1 (2009) 166-172
ISSN 0128-7389

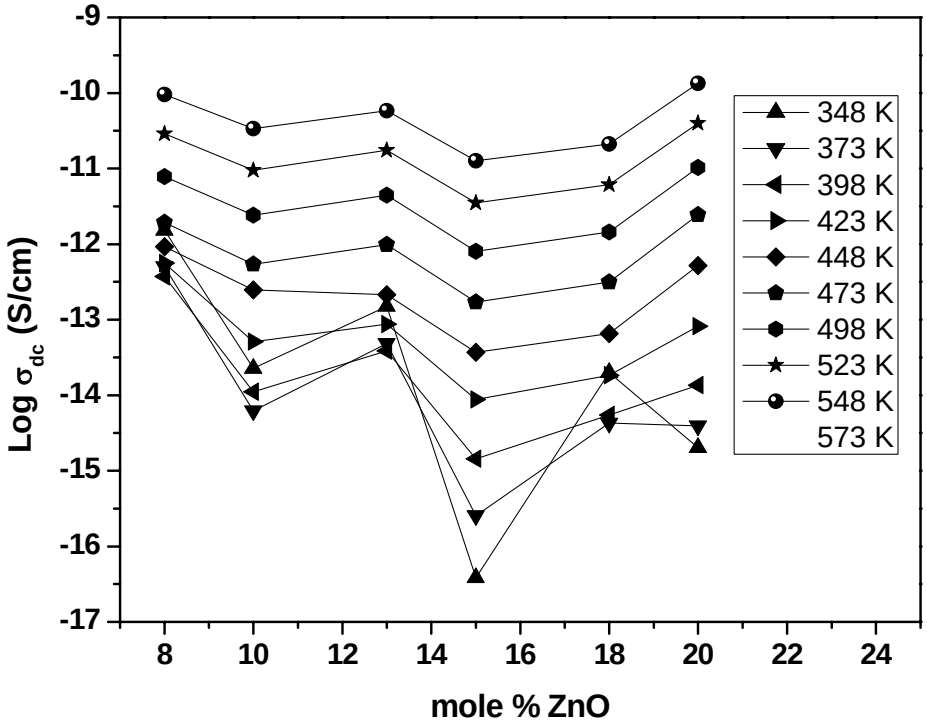

Figure 3: The variation of dc conduction for $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ glasses at different temperatures.

Figure 3 shows that the dc conduction (σ_{dc}) slightlydecreases as ZnO content is raised up to x = 18 and increases for x = 20. This increase may be attributed to the conversion of the glass ultraphosphate to metaphosphate composition. $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ glasses have a complex composition and are an admixture of network formers, intermediates and modifiers. In the present system with the amount of MgO fixed, the higher the ZnO concentration, the lower is the P_2O_5 concentration. Thus, rasionally the almost same amount of non-bridging oxygen (NBO) sites was created initially by MgO which act as modifier [5]. Moreover, gradually increases of the ZnO concentration at relatively small content suggested further induced NBO sites. Such Zn^{2+} ions more likely located in the interstitial position within the glassy matrix rather than participate in the network on purpose to balance the net of columbic charges of the structure. Consequently, the structure of glass became more open and dipolar density increases. It is evident from Table 1 that the results of the density and molar volume increases and decreases respectively with the ZnO content. Therefore, the relatively free mobile ions (Mg^{2+}) experience impeding effect along the conduction path and σ_{dc} decrease. Temperature is another contributing factor to σ_{dc} by mean of thermally activated hopping movements. As thermal energy in the material is gradually enhanced, more and more charge carriers succeed in overcoming the binding energy i.e., attraction force among glassy network and able to diffuse in longer distances [6].

Corresponding Author: zainalat@science.upm.edu.my

Solid State Science and Technology, Vol. 17, No 1 (2009) 166-172
ISSN 0128-7389

Table 1: Variation of density (ρ) and molar volume (V_m) of CM series sample.

SAMPLE CODE	DENSITY, ρ (g cm^{-3}) mol^{-1}) [± 0.001 g cm^{-3}]	MOLAR VOLUME, V_m (cm^3 [± 0.001 cm^3 mol^{-1}]
CM 08	2.552	41.773
CM 10	2.584	40.787
CM 13	2.586	40.053
CM 15	2.627	38.907
CM 18	2.674	37.602
CM 20	2.695	38.860

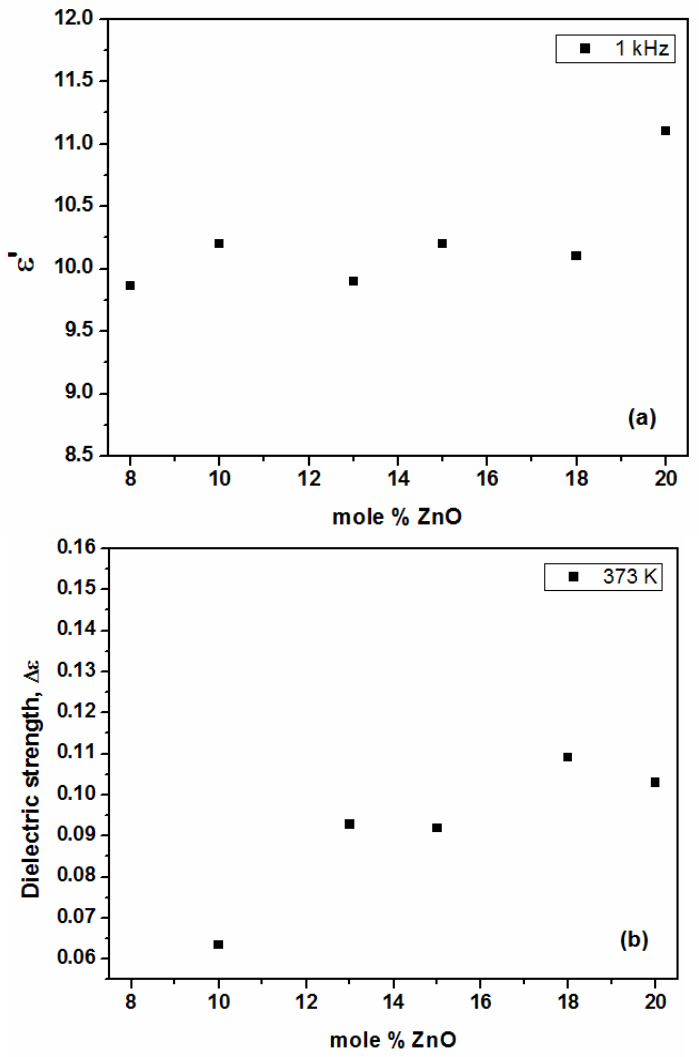

Figure 4: (a) Composition dependence of the dielectric constant measured at 1 kHz at temperature 473 K. (b) The dielectric strength, $\Delta\varepsilon$, as a function of ZnO concentration for $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ glasses at 373 K.

Corresponding Author: zainalat@science.upm.edu.my

Variation of ε′ values with ZnO concentration is shown in Figure 4(a). The increasing trend is ascribed to the rise of dipolar density and this increase in polarization. The variation in the dielectric strength, $\Delta\varepsilon$ as a function of ZnO concentration is presented in Figure 4(b). The dielectric strength values defined by $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ can be extracted from the fitting of the Havriliak-Negami equation. Dielectric strength represents the maximum polarizability that it can withstand in the applied electrical field without breaking down. Polarizability is greatest at those frequencies at which all dipoles can oscillate in response to the field. This figure illustrates that $\Delta\varepsilon$ increases with increasing ZnO concentration up to 18 mol % indicates the amount of dipolar density contribute to the polarization is raised. This results are expected and in line with the discussion above.

CONCLUSION

The dielectric permittivity of $(ZnO)_x(MgO)_{30}(P_2O_5)_{70-x}$ with different ZnO concentrations is frequency and temperature dependent. The variation of frequency and temperature are attributed to polarization and ion diffusion. From the thorough analysis of the experimental data, dc conduction loss dominates at low frequencies and small broad dipolar type relaxation occurs as observed in dielectric loss factor plot. The dielectric data are analyzed in permittivity formalism by Havriliak-Negami model. On composition dependence, dielectric strength and dielectric permittivity results reveal that dipolar density is raised on account of Zn^{2+} ions tend to localized at interstitial instead of substitution position within the glassy matrix as the ZnO concentration is low.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support by the Malaysian government through the Ministry of Science, Technology and Innovation and Malaysian Academy of Sciences grant No. 5486512

REFERENCES

[1]. G. Murali Krishna, N. Veeraiah, N. Venkatramaiah, R. Venkatesan (2008). *J. Alloys Compd.* **450**.
[2]. G. Sahaya Baskaran, M. V. Ramana Reddy, D. Krishna Rao, N. Veeraiah (2008). *Solid State Commun.***145**.
[3]. N. Bano and R. A. Hashmi (1996). *IEEE trans. Dielectr. Electr. Insul.*, Vol. **3** No. 2
[4]. T. Sankarappa, M. Prashant Kumar, G. B. Devidas, N. Nagaraja, R. Ramakrishnareddy (2008). J. Molecular Structure,.
[5]. Munia Ganguli, K. J. Rao (1999). *J. Non-Cryst. Solids* **243**, 251-267
[6]. H. Rawson (1980). *Properties and Applications of Glass: Glass Science and Technology 3*. Elsevier Science Publishers B. V., 237.

Corresponding Author: zainalat@science.upm.edu.my