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ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT OF MAGNESIUM PHOSPHATE GLASSES

A.A. HIGAZY

Physics Department, Faculty of Science,
Menoufia University.

ABSTRACT

AC complex-impedance measurements were carried out on the prepared $MgO\text{-}P_2O_5$ *glasses in the frequency range 0.1-100 kHz, and temperature range 293-573 K. The low frequency Cole-Cole dependence of the Z" (Z') impedance and the linear dependence of* ε" (ε') *dielectric constant, revealed that the conduction mechanism in the present glass system is mainly ionic. The DC-electrical conductivity, the activation energy and the relaxation energy are found to be rather sensitive to the glass composition. It is found from the obtained data, that the* $MgO\text{-}P_2O_5$ *glass system can be divided into two compositional regions.*

INTRODUCTION

Phosphate glasses have considerable potential for applications in optical data transition, detection, sensing and laser technologies (e.g. neodymium phosphate glasses have been widely used in lasers). However, the interest in the electrical properties of phosphate glasses has been sustained since vanadium phosphate glasses behaved as n-type semiconductors[1].

Phosphate glasses containing transition metal oxides such as V_2O_5-P_2O_5[2,3], CuO-P_2O_5[4], Fe_2O_3-P_2O_5[5], WO_3-P_2O_5[6] and CoO-P_2O_5[7] have received a great deal of attention due to the existence of the transition metal ion in more than one valence state. Electrical conduction in these glasses takes place as a result of electrons jumping from metal ions with a low valency state to others with a higher valency, i.e. these transition metal oxide glasses exhibit electronic conduction mechanism. Relatively, little work has been reported[8,9] on electrical conductivity of glasses which exhibit ionic conduction such as alkali oxide glasses.

To establish a picture of the conduction mechanism the electrical properties of some phosphate glasses have been studied[10,14] using the complex impedance analysis. The dependence of impedance and capacitance on both frequency and temperature has been investigated. The complex impedance ($Z^*=Z'+jZ''$) is considered as a contribution of both real Z' and imaginary Z'' parts. The frequency dependence of both the real Z' and imaginary Z'' parts of the impedance permits the separation of the sample resistance for the grain bulk, R_b, from the surface, R_s. Z' and Z'' are given by the established relationships:

$$Z' = R_b + R_s / [1 + (\omega C R_s)^2], \qquad (1)$$

$$Z'' = j\omega C_s R_s^2 / [1 + (\omega C R_s)^2], \qquad (2)$$

where ω is the angular frequency, C is the capacitance and $j = (-1)^{1/2}$. It is clear that $Z' = R_b + R_s$ at zero frequency (d.c.), whereas it equals R_b at high frequencies. Therefore, the complex semicircle Z'' (Z') impedance diagram reflects bulk resistance at high frequencies, however, contribution of the surface resistance increases upon shifting towards the d.c. frequency.

The present work was undertaken to report on some important electrical features of the prepared magnesium phosphate glasses. Also, one objective has been to find out whether the glass compositions have any recognizable influence on the electrical properties of these glasses.

EXPERIMENTAL TECHNIQUE

Glass Preparation

Magnesium-phosphate glasses were prepared from laboratory (P_2O_5 mol. wt. 141.95) and Analar magnesium oxide (MgO, mol. wt. 40.31), using alumina crucibles. The reagents were mixed in approximately 50 g quantities, initially heated in an electric furnace at 773 K for 1 h. This allows the P_2O_5 to decompose and react with MgO before melting would ordinarily occur. After this treatment, the mixture was placed for 2 h in a second furnace held at 1773 K. The molten glass was stirred occasionally with an alumina rod to ensure homogenous melts. The melt was cast into two mild-steel split moulds heated to 473 K to form glass rods 2 cm long and 1.6 cm in diameter. Then each glass was immediately transferred to an annealing furnace held at 773 K for 1 h. After this time, the furnace was switched off and glasses were allowed to cool to room temperature at an initial cooling rate of 3 K/min. This procedure was employed to prepare glasses with a glass formation range from 10 to 60 mole % MgO (starting compositions).

The Electrical Conductivity Measurements

For the measurements of DC-electrical conductivity, electrodes were formed by brush painting silver paste. The DC-conductivity was measured as function of temperature, using a spring-loaded sample holder in a wirewound cylindrical furnace. DC-electrical conductivity measurements were made using a Keithley electrometer model 616, with a smoothing adjustable power supply (0 to 1 kV). A fixed voltage of 300 V was applied. The temperature of the specimen was measured by means of a chrome-alumel thermocouple.

The DC-electrical conductivity (σ) of each specimen was then calculated using the formula:

$$\sigma = L / RA \qquad (3)$$

where L is the thickness of the sample (cm), A is the cross-sectional area of the electrode (cm^2) and R is the resistance (Ω).

Measurements of the electric impedance and capacitance, diskshaped samples of diameter 16 mm and thickness 4 mm are cut and polised. The samples were coated on two opposite sides with silver paint and placed between the two electrodes of a sample holder. The measurements were performed in the frequency range 0.1-100 kHz, operated at 0.8 V, using a Hioki 3520 LCR tester and over a temperature range 293-573 K.

The impedance $|Z|$ and the phase angle (ϕ) data were read directly from the impedance meter. Then the values of the real, Z', and imaginary, Z'', parts of impedance can be determined. The capacitance, C, and the loss factors, tan δ, were also measured to estimate the permittivity of different frequencies and temperatures.

RESULTS AND DISCUSSION

The complex Z" (Z') impedance diagrams for MgO-P_2O_5 glasses are shown in Figs. 1-a, 1-b and 1-c as examples for glass compositions 10, 35 and 55 mole % MgO content. The complex Z" (Z') impedance diagrams for all the studied glasses showed semi-circles at low frequencies and straight lines at high frequencies. This behaviour of Z" (Z') dependence of the present glass samples may be attributed to ionic conduction (15-25) in the bulk material which is confirmed by the linear dependence of the dielectric constants ε" (ε'), as shown in Fig. 2. This revealed that the charge carriers are mobile ions.

In glasses, cations forming strongly covalent and therefore directional bonds with oxygen are described[26] as part of the glass network, whilst cations which are linked to oxygen atoms in glass via predominantly ionic (and therefore non-directional bonds) are described as residing interstitially. Based on the above statement and according to the calculated fractional ionic character values (FIC) [27], it may conclude that cations like Mo, P, Si and Co always reside in network forming position and cations like Zn and Be are able to occupy network forming sites as well as interstitial positions in glasses. However, both Na and Mg appear to belong to the category of ions which can occupy interstitial positions in glasses. So it may consider that, for the studied glass system the Mg ions enter the glass network interstitially (see Fig. 3). Hence, some network bonds (P-O-P) are broken and replaced by ionic force between Mg ion and singly bonded oxygen atoms. This is consistent with their results i.e. the ionic conduction may predominated in MgO-P_2O_5 glasses. due to Mg^{+2} mobile ions.

The DC-conductivity for the studied glasses is first calculated from the DC-resistance R_0, which is obtained from the intersection of the low frequency semi-circle with the axis of the real part of the impedance (Z'), using equation (3) (see Figs. 1-a, 1-b and 1-c as an examples). The variation of DC-conductivity, σ_{DC1}, (obtained from the Z" (Z') semi-circle dependence) with temperature and MgO content is shown in Fig. 4-a. On the other hand, the DC-conductivity, σ_{DC2}, calculated from the measured voltage (300V) and current values at different temperatures for samples is represented in Fig. 4-b. From inspection of this figure, it is observed that there is a pronounced discontinuity in the compositional dependence of both σ_{DC1} and σ_{DC2} at 35 mol % MgO, at fixed temperature, which indicates a structural change in the glass network.

According to Tarasov [28], in Na-P_2O_5 glasses, Na ions enter the glass network interstitially, hence, some network bonds (P-O-P) are broken and replaced by ionic force pairs between the Na ions and singly bonded atoms. In his investigation he found that the breaking down of the network tends to decrease the elastic moduli, but the simultaneous filling up of the vacancies amidst the network by the interstitial Na ions (i.e. the increased packing density) will tend to increase the moduli, because of the reduced averaged interatomic spacing. Since, Na and Mg appeared to belong to the category of ions which can occupy interstitial positions in glasses and according to Tarasov argument, the addition of MgO to the vitreous structure of P_2O_5 may increase the number of non-bridging oxygen atoms i.e. the Mg ions enter the glass network interstitially (see Fig. 4). So if one assumed that the only effect of adding Mg cations was to break down the network bond (P-O-P) and produce extra ionic bonds and mobile ions (Mg^{+2}), then an increase in electrical conductivity with MgO content would be expected for the entire vitreous range of the present glass system. Experimentally, this effect increases the electrical conductivity (σ_{DC1} and σ_{DC2}) up to 35 mol % MgO content. However, beyond 35 mole % MgO, the addition of MgO decreased the values of σ_{DC1} and σ_{DC2}. This decrease may be due to simultaneous filling up of the vacancies amidst the network by the interstitial Mg metal ions (i.e. the increased packing density). This will reduce the average interatomic spacing, which decreases the mobility of charge carriers.

The DC-electrical conductivity (σ_{DC1} and σ_{DC2}) is well represented at temperatures by the expression:

$$\sigma = \sigma_0 e^{-E/kT} \qquad (4)$$

where k is the Boltzmann constant, T is the absolute temperature σ_0 is a constant and E is the activation energy. The plot of log σ against reciprocal temperature T^{-1} is shown in Fig. 5 (a and b) for σ_{DC1} and σ_{DC2}, respectively. From inspection of this figure it is observed that the log σ versus T^{-1} shows straight lines at high temperature values ($T>373K$) for all glass samples. This may prove that the activation energy for the studied glasses in the temperature range 373-573 K is independent of temperature. Fig. 6 (a and b) shows the variation of the activation energy with MgO content. This result confirm the behaviour of D.C. conductivity.

The permittivity dependence on frequency and temperature is analysed according to the well established relations of dielectric relaxations[29-34]. The real dielectric constant ε' depends on angular frequency ω, following the fractional power law,

$$\varepsilon' \propto (\omega)^{n-1} \qquad (5)$$

where n is varying with the conduction mechanism. Low-loss systems show high n, whereas it drops to zero for high-loss systems. The above relation can be written as:

$$\log \varepsilon' = \log A - (1-n) \log \omega \qquad (6)$$

Fig. 7 (a and b) and (c and d) showed the plot of log ε' versus log ω for glass compositions 10 and 55 mole % MgO, respectively, at different temperatures (as an example). From inspection of this figure, it is observed that ε' shows a strong frequency dependence at frequencies lower than 1.0 kHz. The high frequency plateau response of ε' is a typical Debye response for the proposed conduction system. The values of (1-n) in Equation 6 are obtained from the slopes of the straight lines of Log ε' against log ω, at low frequencies < 1.0 kHz, for all glass samples. These obtained (1-n) values are plotted against the temperature in Fig. 8 (a and b). The variation of (1-n) with temperature shows a linear increase up to 375 K and then decreases linearly up to 573 K. Based on the latter response to temperature, the relaxation energy E_R is calculated, using the expression[32]:

$$1-n = (6k/E_R)\, T \qquad (7)$$

Fig. 9 shows the variation of the calculated relaxation energies, E_{RL} (low temperature range 293-375 K) and E_{RH} (high temperature range 375-573 K), with MgO content. The behaviour of the relaxation energy represented in Fig. 9 shows the two compositional regions which had been found in the plots of the compositional dependence of the electrical conductivity and the activation energy for $MgO-P_2O_5$ glasses.

The AC-conductivity can be estimated based on the dielectric data[35], using the following expression:

$$\sigma_{AC} = (\varepsilon\,\omega/4)\tan\delta = 0.5\,f\,\varepsilon'' \qquad (8)$$

where tan δ is the dielectric loss and f is the frequency. Consistent with the variation of the dielectric constant (Fig. 7). The AC-conductivity increases with frequency (Fig. 10). Also it shows a temperature dependence, where value of σ_{AC} decreases for temperatures 293 K and 373 K and then shows an increase for the temperature 523 K, which correlates with that of the σ_{DC1}-conductivity. The AC-conductivity, σ_{AC}, of the charge carriers increases often rapidly with frequencies greater than 10 kHz and more significantly at higher temperatures (T > 373 K), probably because of thermally enhanced ion mobility and increased lattice defects.

CONCLUSION

From the foregoing analysis of the behaviour of Z'' (Z') impedance and ε'' (ε') dielectric constant diagrams, it is found that the conduction mechanism in the studied glasses is mainly ionic. For all glasses the Mg ions enter the glass network interstitially, which is in consistent with the results, i.e. the ionic conduction due to Mg^{+2} mobile ions. The variation of DC-conductivity with temperature gives straight lines at high temperature values (373-573 K), which shows that the activation energy in this temperature range is independent on temperature. It is also, observed that the AC-conductivity increases rapidly with frequencies greater than 10 kHz and more significantly at higher temperatures.

The compositional dependence of the DC-conductivity, the activation energy and the relaxation energy showed a pronounced discontinuity at 35 mole % MgO.

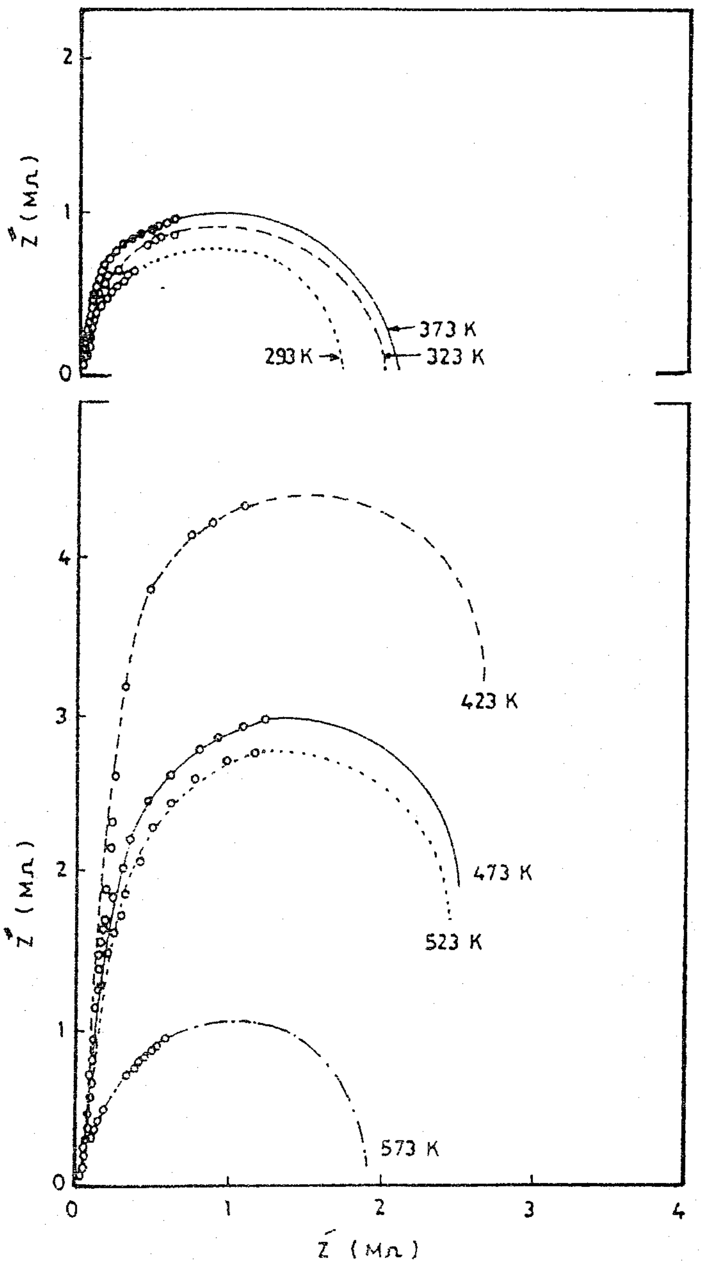

Fig. (1-a): The complex-plane impedance at different temperatures, for a 10 mole % MgO glass sample.

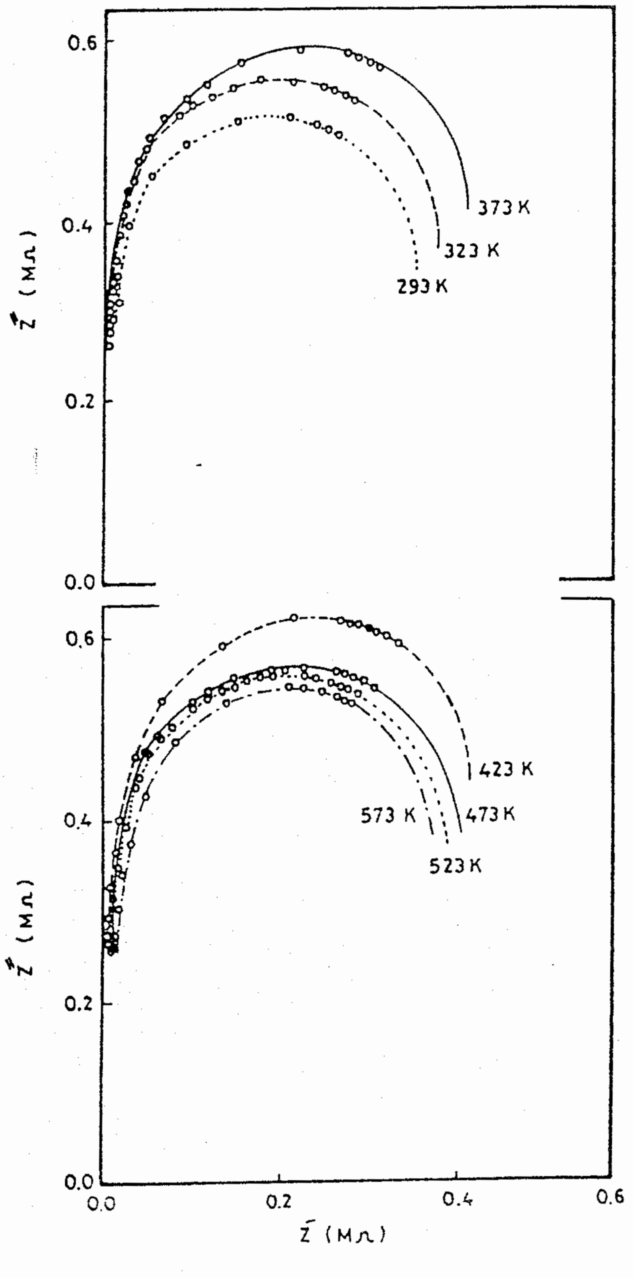

Fig. (1-b): The complex-plane impedance at different temperatures, for a 35 mole % MgO glass sample.

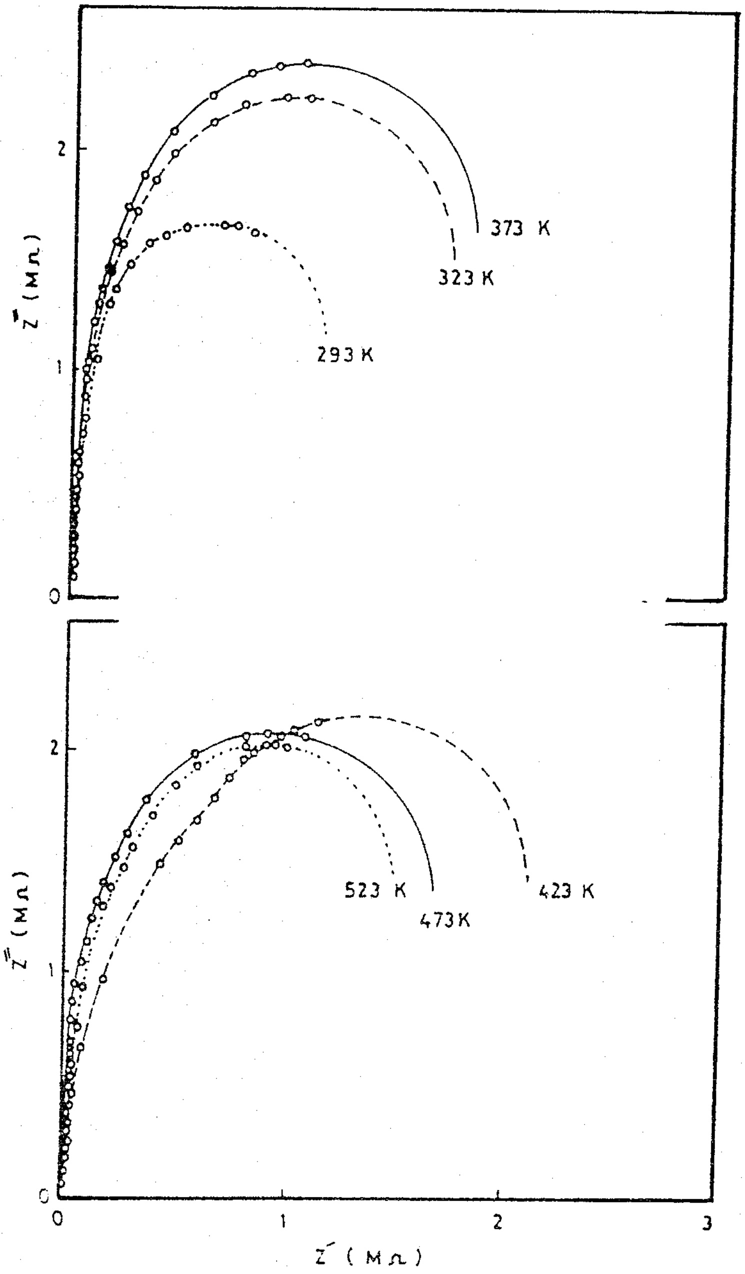

Fig. (1-c): The complex-plane impedance at different temperatures, for a 55 mole % MgO glass sample.

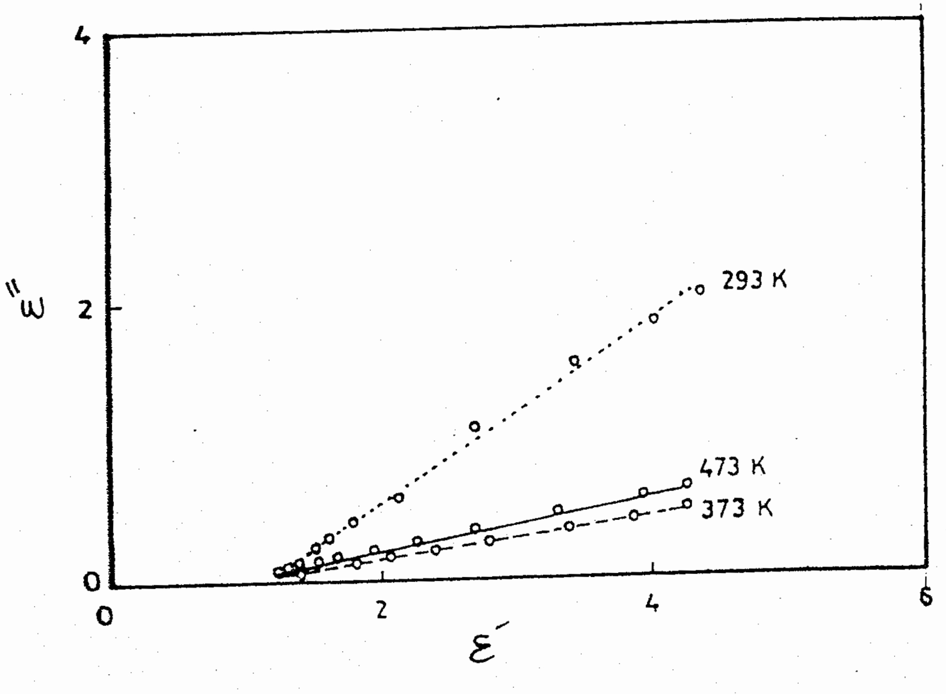

Fig. (2): Variations of ε'' with ε' at different temperatures for a 55 mole % MgO glass sample.

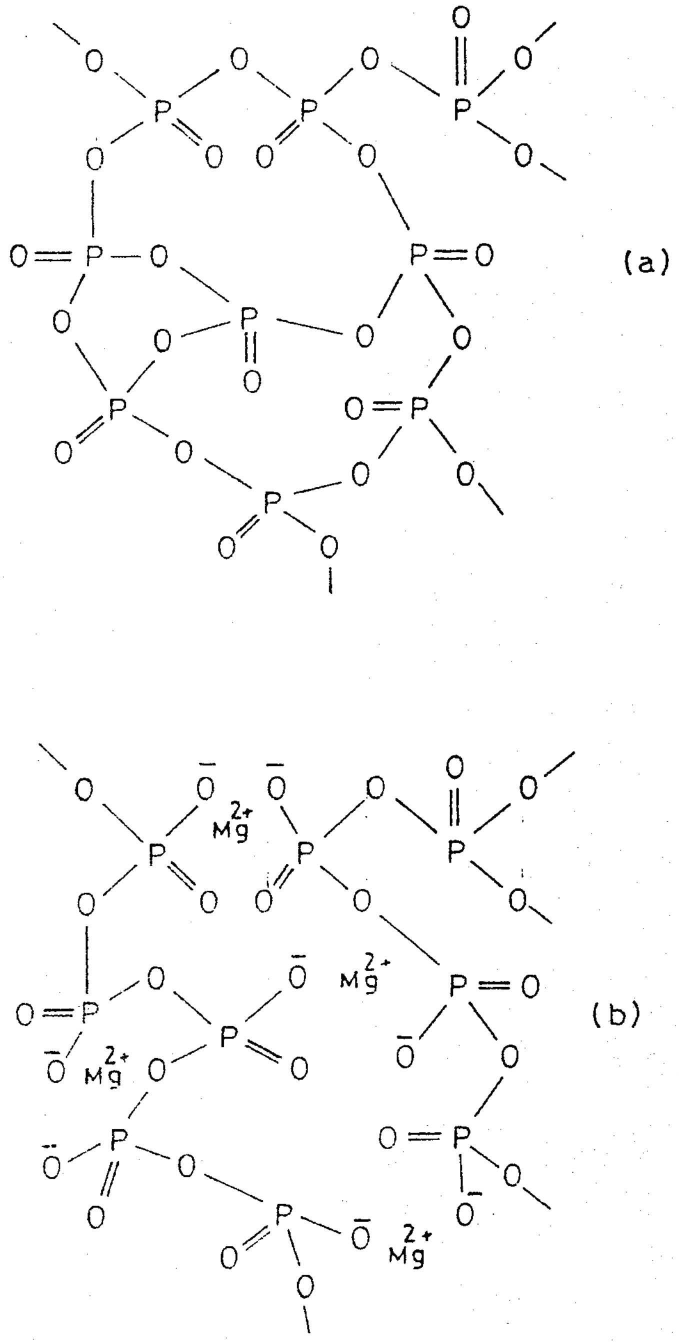

Fig. (3): Schematic two-dimensional representation of the structure of $MgO\text{-}P_2O_5$ binary phosphate glasses; (a) composed of the basic glass former, P_2O_5 and (b) showing the effects of Mg cation content on the glass former.

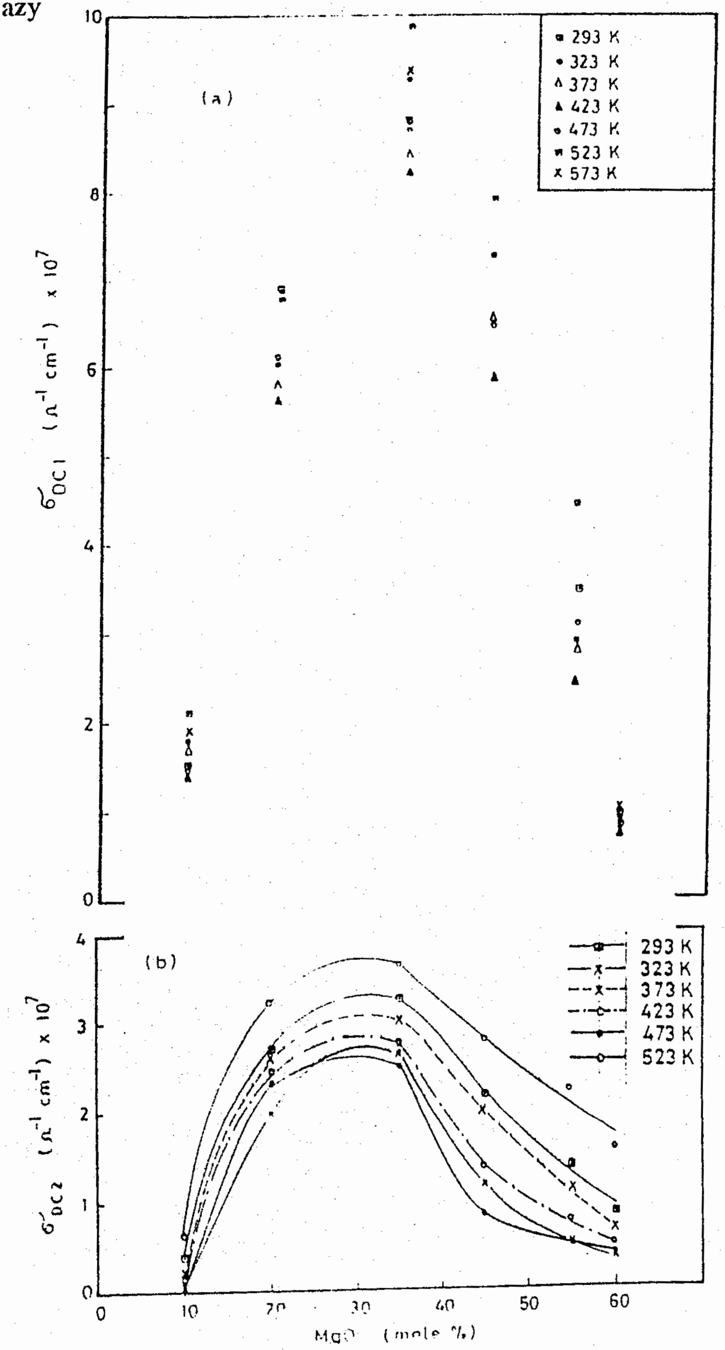

Fig. (4): Variations of (a) DC-conductivity, σ_{DC1}, calculated from complex-plane impedance diagram and (b) DC-conductivity, σ_{DC2}, calculated from, the voltage and current measurements, with MgO content.

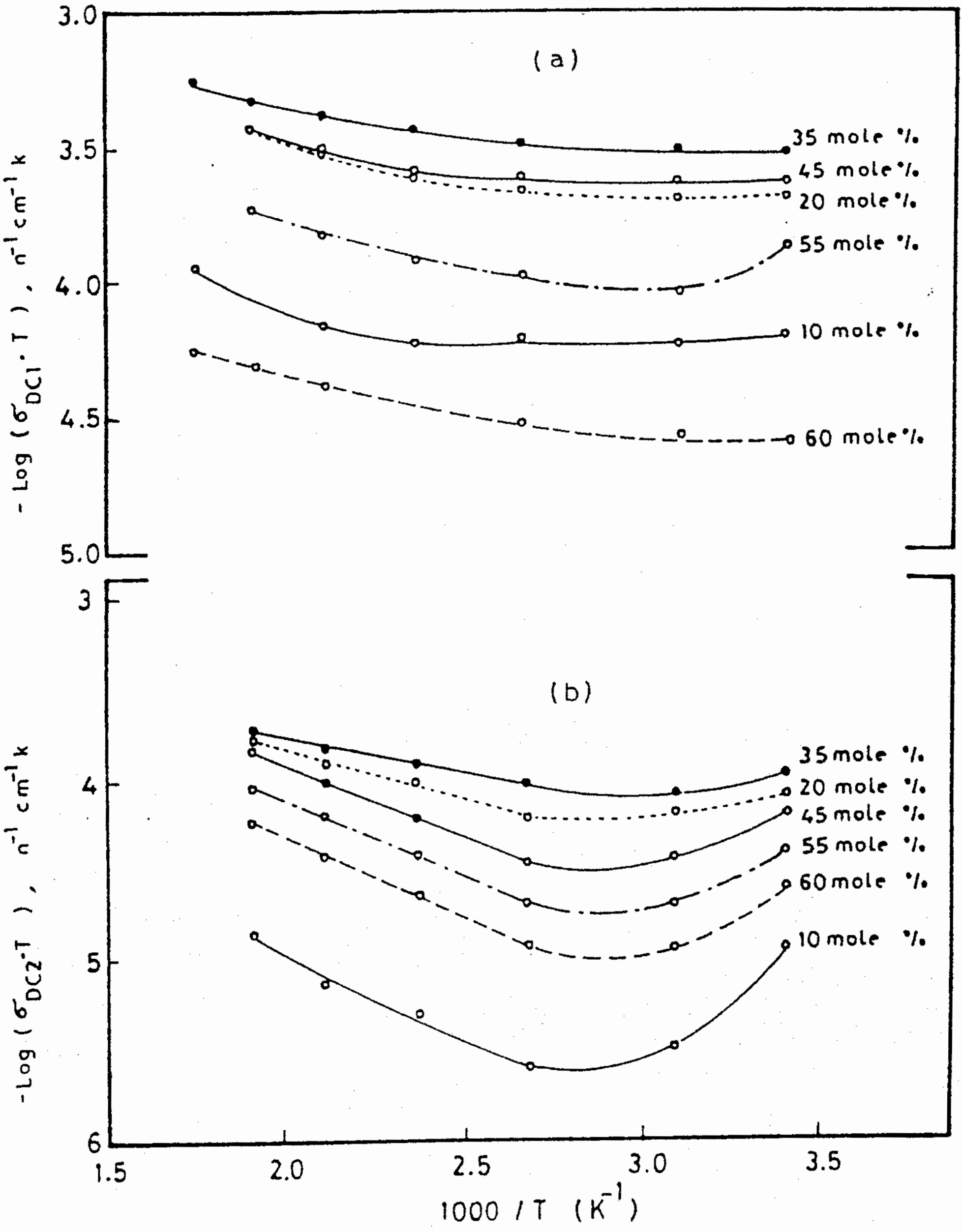

Fig. (5): Variations of (a) Log (σ_{DC1}.T) and (b) Log (σ_{DC2}.T) with (1000/T).

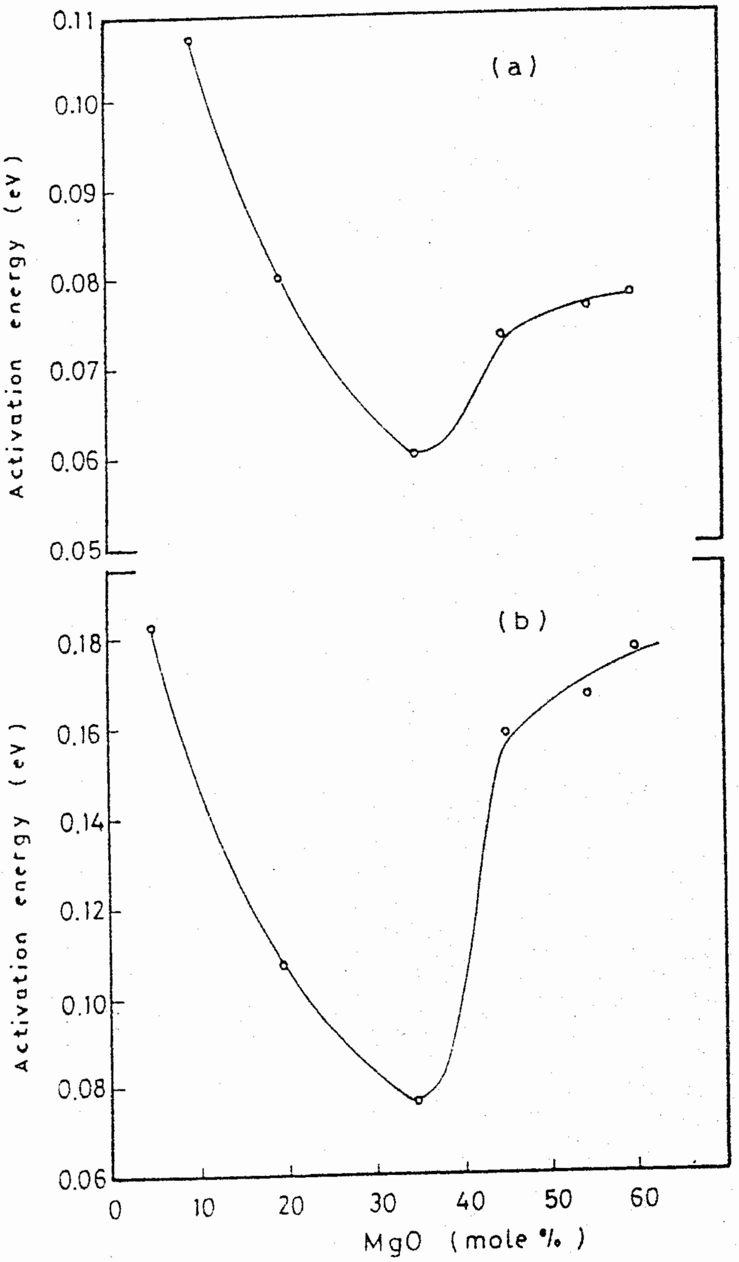

Fig. (6): Dependence of (a) the calculated activation energy using σ_{DC1} and (b) the calculated activation energy using σ_{DC2}, on the glass compositions.

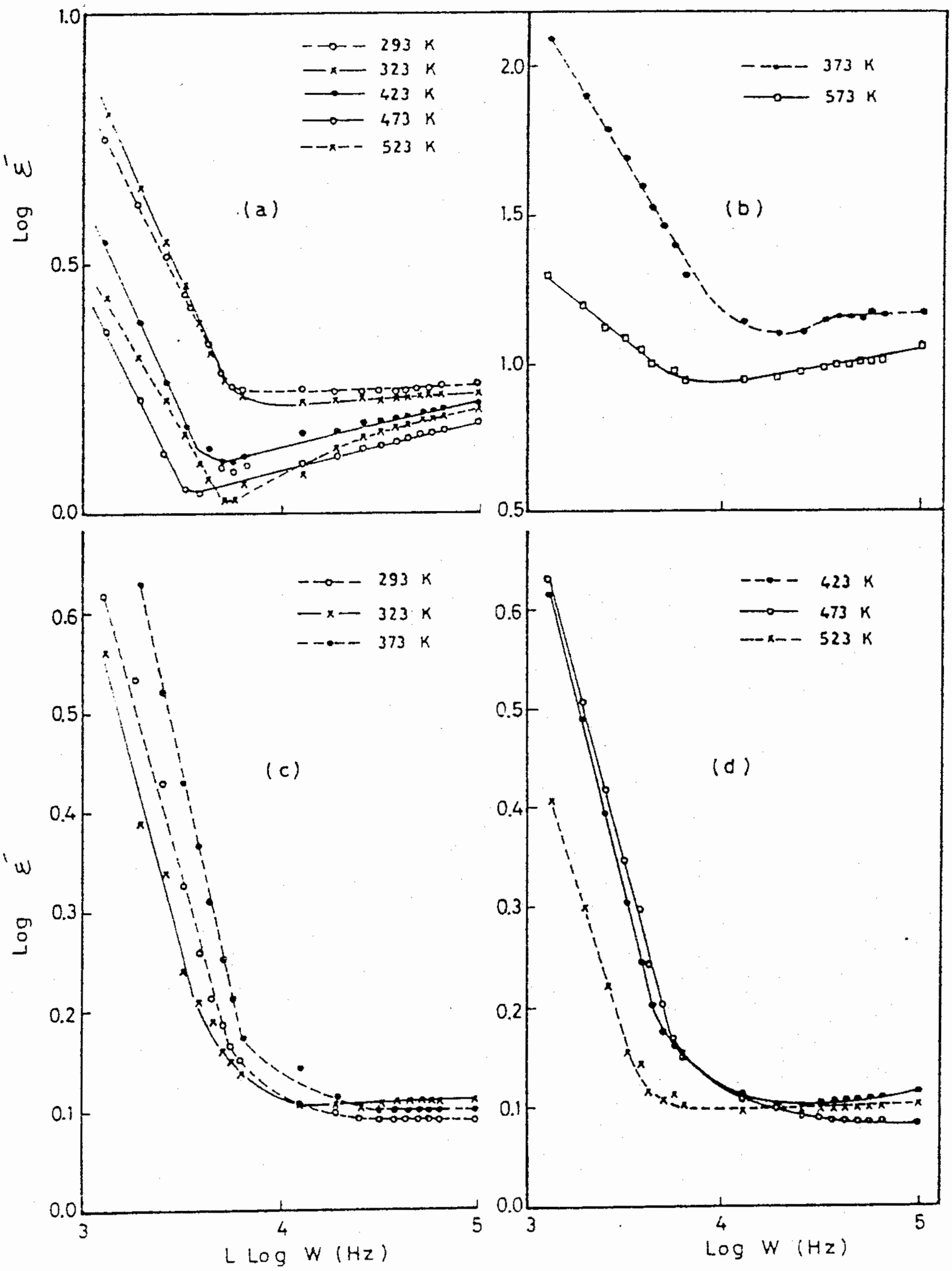

Fig. (7): Variations of the logarithmic dependence of dielectric constant ε' on frequency (a and b) for 10 mole % MgO and (c and d) for 55 mole % MgO glass samples.

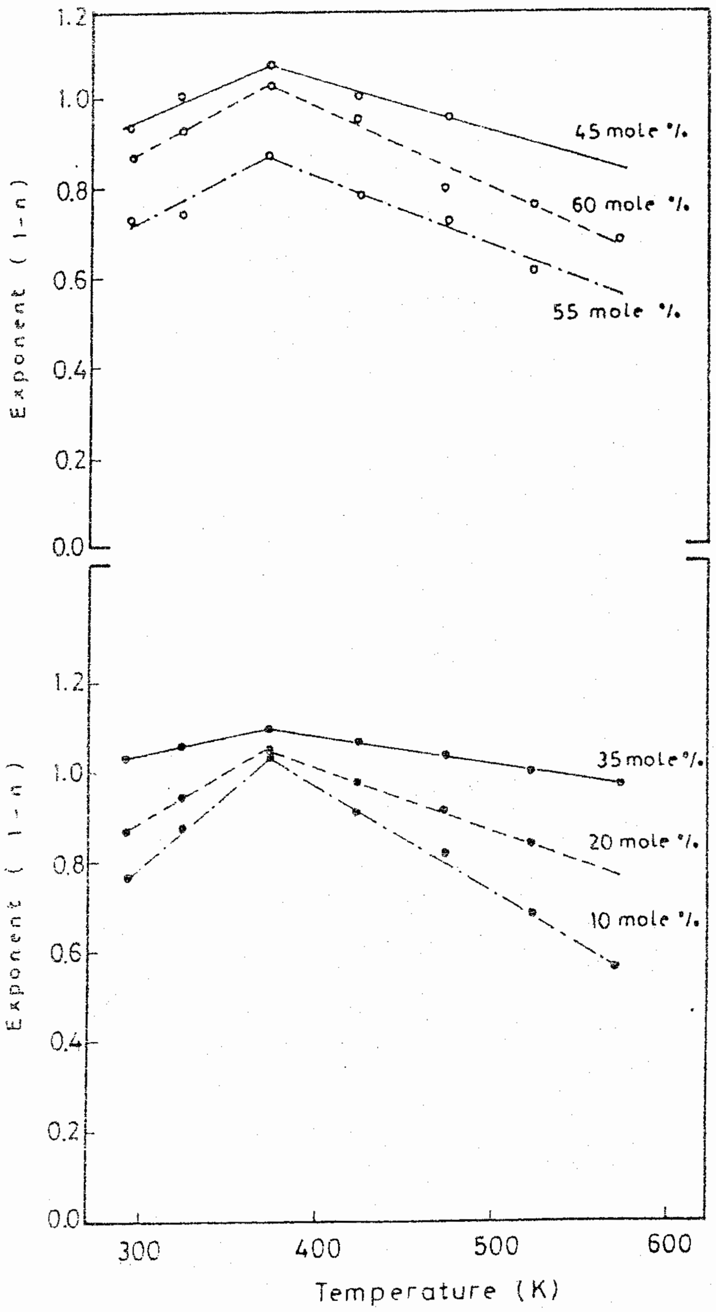

Fig. (6): Dependence of the exponent (1-n) on temperature.

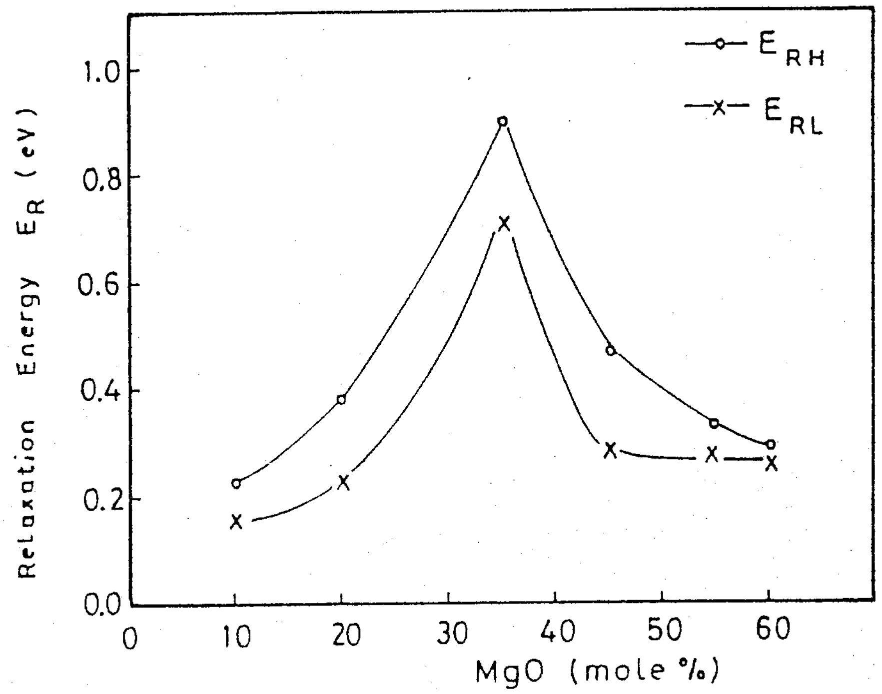

Fig. (9): Variations of the relaxation energy with MgO content where E_{RH} represents activation energy for high temperature range (375-573 K) and E_{RL}, for low temperature range (293-375 K).

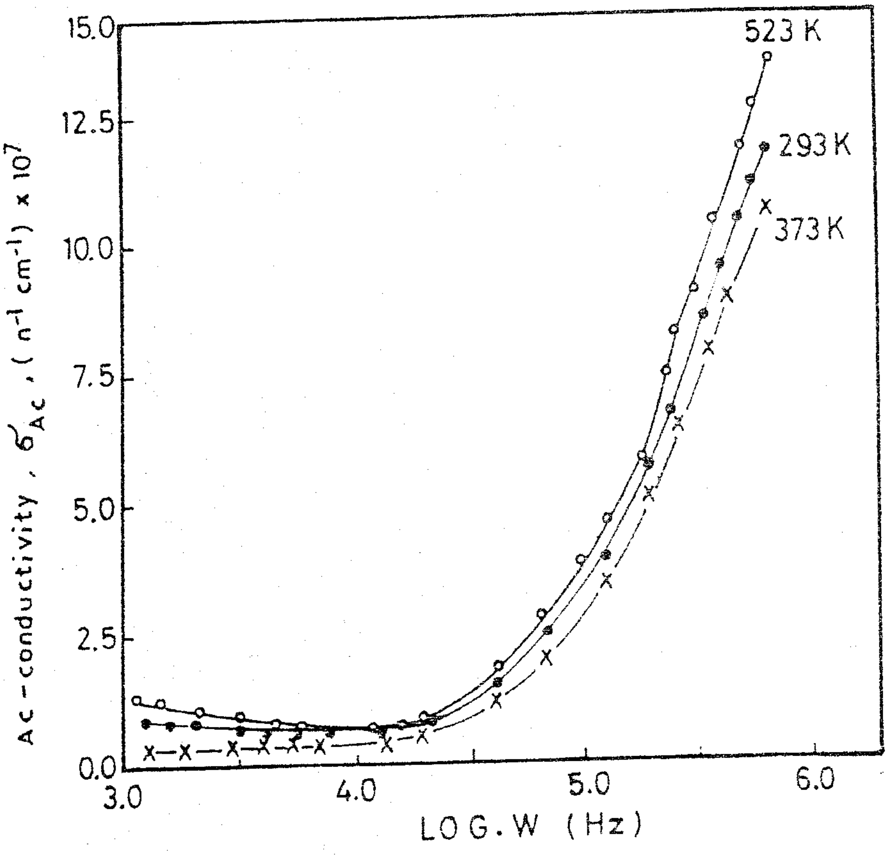

Fig. (10): Dependence of AC-conductivity on frequency at different temperatures, for a 55 mole % MgO glass sample.

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التوصيل الكهربى وثابت العزل لزجاج فوسفات الماغنسيوم

انور عبد الرحمن حجازى

قسم الفيزياء – كلية العلوم – جامعة المنوفية

الملخص العربى

فى هذه الدراسة تم تحضير عينات مختلفة التركيز من زجاج فوسفات الماغنسيوم وقد تم قياس كل من ثابت العزل والممانعة والتوصيل الكهربى لهذه العينات عند درجات حرارة مختلفة فى المدى من ٢٩٣ كيلفن إلى ٥٧٣ كيلفن وأيضا تم حساب الموصلية الكهربية لهذه العينات عند ترددات مختلفة من (٠,١ كيلو هرتز إلى ١٠٠ كيلو هرتز) وكذلك عند تردد يساوى صفر . وقد دلت النتائج على أن التوصيل الكهربى لهذه العينات هو توصيل أيونى وأن قيم هذه النتائج تعتمد على التركيزات المختلفة لأيون الماغنسيوم فى الزجاج . وقد أمكن تقسيم مدى التركيزات إلى منطقتين تبعا للإرتباطات المختلفة لأيون الماغنسيوم .