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Study the effect of Mn^{2+} ions on the ac electrical properties of some iron doped phosphate glasses

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Abstract:

Oxide glasses doped with transition metal ions are of high interest because of their variant applications in both science and technology fields. However, the normal melt quench method have used to prepared some iron doped phosphate glasses according the following molecular formula: (65-x) mol% P_2O_5 - 20 mol% Na_2O - 15 mol% Fe_2O_3 - x mol% MnO, Where x= 0, 5,10, 20, 25. The room temperature Mössbauer Effect ME Spectra used to characterized the glassy state homogeneity of these glasses. ME spectra show, for all glasses, no magnetic field participate which mean good glassy state formation. The ac electrical transport properties were also measured, as function of temperature up to 500k. It was found that the ac conductivity increased with the gradual increase of Mn^{2+} cations, while the electrical activation energy decreased.

I. Introduction

Studies of the magnetic and electrical properties of transition metal ions in glass have made it possible not only to interpret the energy levels involved in the observed transitions and the type of conduction mechanisms, but also to provide evidence on the chemical and structural environment about the metal ion center [1]. One of the first detailed investigations of glassy materials incorporating transition metal ions was under taken by sands [2]. It is well known that glasses containing transition metal ions (TMI) exhibit electronic conductivity [3,4]. Transition metal oxides, for instance NiO or Fe_2O_3, when mixed with glass formers like P_2O_5, SiO_2 form stable glasses in a comparatively wide range of compositions. A general condition for this semiconducting behavior is the ability of transition metal ions to co-exist in more that one valence state, So that the conduction can take place by a transfer of electrons from a low to a high valence state. This provides on opportunity for investigation of the effect of charge carrier concentration of their electrical, magnetic and dielectric properties [5]. In the present work glass samples of different composition were prepared to study the Mossbauer, ac conductivity and dielectric constant

II. Experimental techniques

The glass samples were prepared having the following compositions: (65-x) mol % P_2O_5. 20 mol % Na_2O. 15 mol % Fe_2O_3. x mol% MnO., Where x= 0, 5, 10, 20 and 25. These samples were investigated from the structural point of view, applying Mössbauer effect and ac electrical transport properties as well. The glass batches were ground and mixed well using a gate mortal. Then they were melted in porcelain crucibles using an electric muffle furnace at 1000oC for two hours. Melts were stirred to get complete mixing and homogeneity. The ME measurements were performed, at room temperature, using 20 mCi ^{57} Co radioactive source in Rh matrix. A constant acceleration transceducer interfaced to a based PC-MCA; metallic iron was used for calibration. The ac conductivity measurements were obtained by using RLC bridge (Stanford model SR 720 RLC meter) at temperature range from room temperature up to 500k, at four different frequencies o.12, 1, 10 and 100kHz.

III. Results and discussion

3.1 Mössbauer spectra

Fig.(1) shows the ME spectra of the studied glasses, at room temperature. For each sample, ME spectrum can be interpreted as an overlapping of three absorption peaks indicate the existence of three paramagnetic phases. ME parameters reveal that Fe^{3+} ions have occupied both tetrahedral and octahedral coordination states, while Fe^{2+} ions have occupied, only, octahedral coordination states. Also, it was found that the Fe^{2+} fraction increases with the gradual increase of the MnO content, which mean that the MnO caused Fe^{3+} to transformed to Fe^{2+}. Like behavior can be attributed to the decrease in the non-bridging oxygen fraction [6]. Noticeable fluctuations in the quadruple splitting (QS) and isomer shift (IS) values have been observed. Such fluctuations, somehow, indicate that the electric field gradient of the lattice have been varied as a result to the random structure that usually presented in amorphous materials and glasses.

3.2 AC conductivity

During any experiment to measure the ac conductivity the measured conductivity σ_m is usually expressed as

$$\sigma_m = \sigma_{dc} + \sigma_{ac}$$

Where ω is the angular frequency, σ_ω is the frequency dependent conductivity measured under an ac field and σ_{dc} is the dc conductivity. The dc and ac conductivity as a function of T can be studied according to the following relation:

$$\sigma = \sigma_o\, e^{(-W/kT)} \qquad \text{(Where W is the activation energy)}$$

The results of the temperature dependence of ac conductivity at a fixed frequency (1 kHz) as a function of temperature for various compositions (x= 0, 5, 10, 20, 25) are presented in Fig. (2). From the figure it is clear that the conductivity increases approximately linearly as the absolute temperature was increased. This indicates that the conductivity may be thermally activated process from different localized states in the energy gap [7]. Also, it can be observed that, the conductivity shows weak frequency dependent at high temperature, while at low temperature it shows strong frequency dependent as shown in Fig.(3). This may be due to the type of the conduction mechanism, which at low temperature is linearly electronic and at high temperature the participation of ions, as well as electrons, in the conduction process take place.

3.3 Dielectric constant

The dielectric constant (έ) temperature dependence was studied for the investigated glass system at different compositions at 1kHz as shown in Fig. (4). This figure shows that, the dielectric constant of the present glasses increases with increasing MnO content, which leads to an increase of the ion motions and increases the dielectric constant. Moreover, the variation of the dielectric constant is large at low frequency. This behavior can be attributed to the fact that the orientational polarization is related to the thermal motion (vibration) of molecules [8] and / or it can be attributed to the space charge polarization due to the bonding defects in the structure [7]. Fig. (5) shows that the dielectric constant decreases as the frequency was increased. This behavior may be due to the fact that as the frequency increased the orientational polarization decrease, since it takes more time than the electronic and ionic polarization [7]. A very important quantity is the loss factor (tan δ), which measures directly the phase difference due to loss of energy within a sample at a particular frequency. The observed dielectric loss (tan δ) may be due to two main contributions, a part which is thermal-activated relaxation of Debye-type freely rotating dipoles in which the thermal energy is the only type of excitation. The second part at higher temperature which increases with temperature and is due to electrical condition in which there is an electron- phonon interaction [9]. The dielectric loss of the glass sample is shown in Fig.(6) as a function of temperature for different concentration of MnO at fixed frequency (1 kHz). It was observed that the dielectric loss decreases as the concentration of MnO increase. On the other hand, the temperature dependence of the tan δ at different frequencies (0,12, 1, 10 and 100 kHz) at fixed composition (25 mol%) was shown in fig.(7), since the tan δ as a function of both temperature and frequency is a useful practical quantity, which it is independent of the samples geometry.

Generally, it is observed that all studied samples (tan δ) shows a relaxation peak at a certain temperature $T_{m.}$ This peak is shifted to a higher temperature as the frequency was increased, indicating the dielectric relaxation character of the dielectric loss of the studied glasses [7]. This behavior can be attributed to the frequency dependence of the orientational polarization [10]. Fig.(8) shows the variation of ac conductivity with the MnO concentration at a fixed temperature (423k) for 0.12 kHz. It can be seen that the conductivity increases with increasing MnO content. On the other hand the activation energy exihibits the opposite behavior of the conductivity, which it may help to detect structural changes consequent on increasing Mn^{2+} ions content. This reveals that addition of Mn^{2+} ions to the glass increases the conductivity as a result of the non-bridging oxygen ions increase with increasing MnO and increase the conductivity.

IV. Conclusion

In the present work we have reported the ac conductivity, dielectric constant and Mossbauer spectra were carried out on (65-x) mol % P_2O_5 . 20 mol % Na_2O . 15 mol % Fe_2O_3 . x mol% MnO., Where x= 0, 5,10, 20, 25. The Mossbauer spectra measurements showed three absorption peaks, which indicates the presence of ferrous and ferric cations. Also, it was found that, slight fluctuation in Qs and IS values indicating slight variations in the electric field gradient due to glass as well as slight structural changes affect the wave function of the s-electron density of the iron ions. Moreover, by increasing MnO content the conductivity increases because of the decrease of Fe^{2+} fraction, as confirmed from Mossbauer data.

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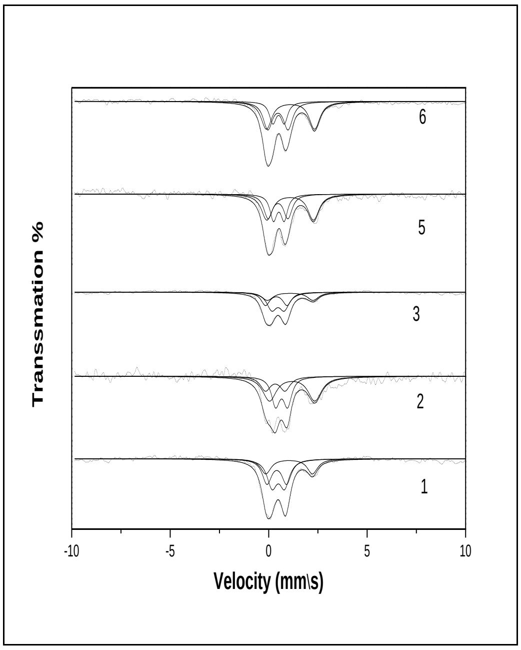

Fig.1 Mössbauer chart of the studied system

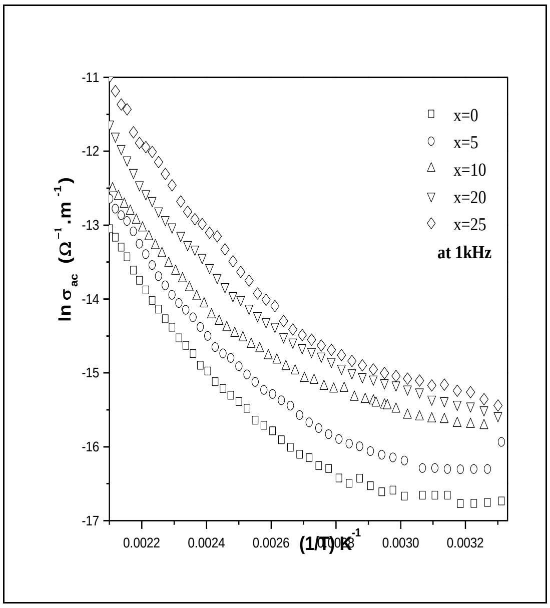

Fig.2 ac conductivity as a function of temperature for the studied system at a fixed frequency

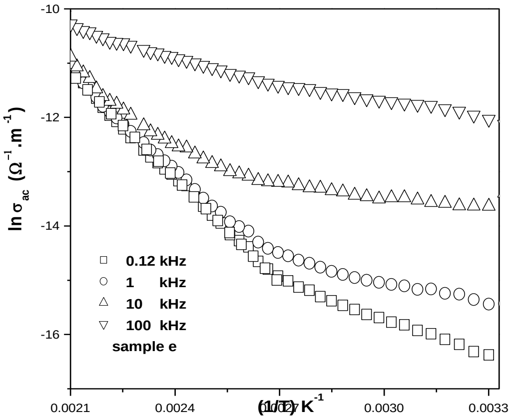

Fig.3 Ac conductivity as a function of temperature at four different frequencies for x=25 sample.

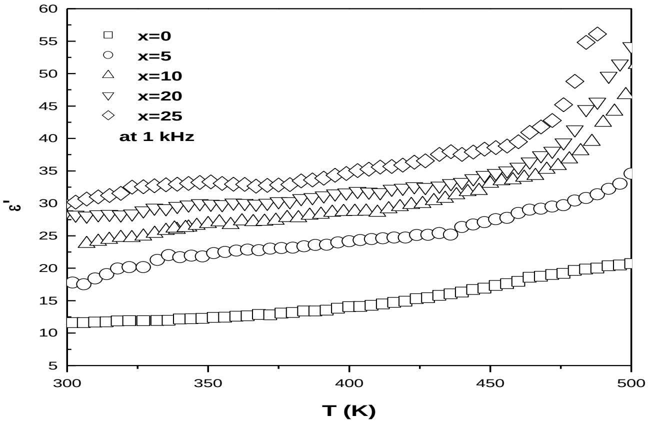

Fig.4 Dielectric constant as a function of temperature at four different frequencies.

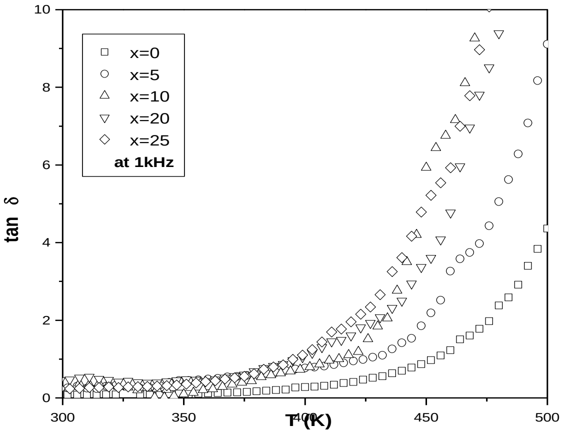

Fig.5 Loss factor as a function of temperature at four different frequencies for x=25 sample

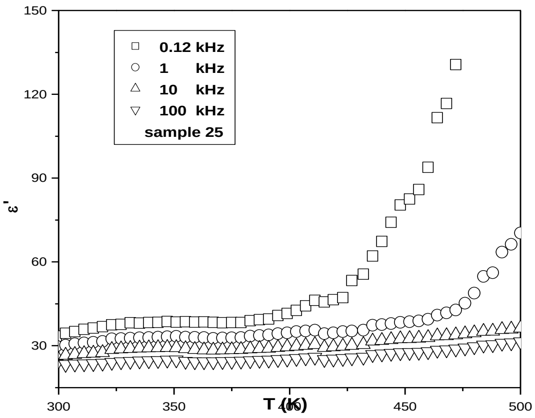

Fig.6 Dielectric constant as function of temperature at four different frequencies.

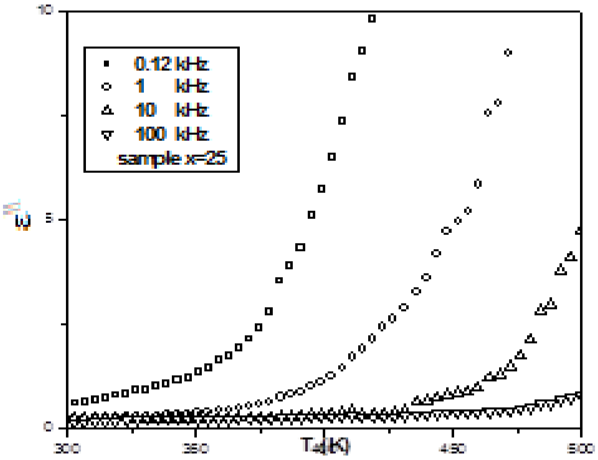

Fig. 7 Dielectric loss as a function of temperature at four different frequencies for x=25 sample.

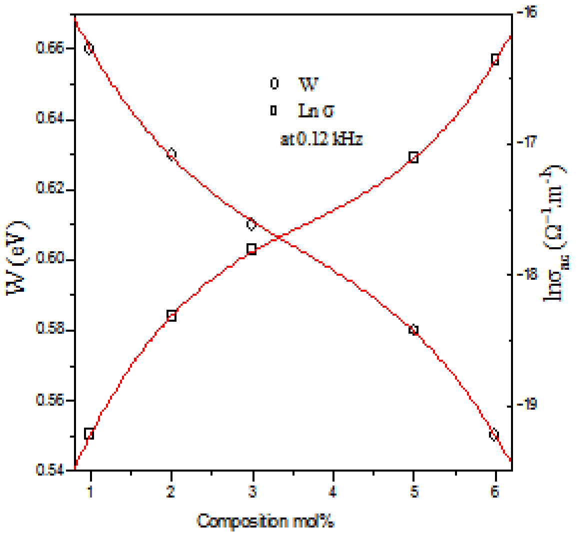

Fig.8 Ac conductivity as a function of structure