

**dc and ac conductivities of the  $y\text{Li}_2\text{O}-(1-y)[0.35(\text{MoO}_3)_2-0.65(\text{P}_2\text{O}_5)]$  glasses**

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Glass formation and properties of glasses containing  $\text{Li}_2\text{O}$  and  $\text{MoO}_3$  oxides have been investigated to determine the influence of lithium oxide  $\text{Li}_2\text{O}$  in phosphomolybdate glasses. Conductivity spectra have been taken on  $y\text{Li}_2\text{O}-(1-y)[0.35(\text{MoO}_3)_2-0.65(\text{P}_2\text{O}_5)]$  glasses at various temperatures in the frequency range  $10^{-2}\text{Hz} - 1\text{MHz}$ . The frequency dependent conductivity is found to display the universal dynamic response behaviour widely observed in disordered solid electrolytes. Contrary to some ion conducting glasses, no typical conductivity scaling was observed for these glasses.

*Key words : phosphate, molybdenum, glasses, electrical conductivity.*

**I. INTRODUCTION**

The semiconducting properties of transition metal oxides (TMO) were discovered in 1937 by de Boer and Verwey [1]. Although the charge carriers are electrons, their mobility is of the same order of magnitude as the mobility of ions in highly conducting solid electrolytes. Therefore, a description of the electronic properties of transition metal oxides is not possible in terms of standard band theory. The experimental findings can, however, be explained by introducing the concept of small polarons. Many TMO form vitreous materials when melted with  $\text{P}_2\text{O}_5$ . These glasses usually show deviations from the stoichiometric composition. The transition metal ions exist in different valence states, and conduction is achieved by the hopping of small polarons from low to high valence states. Selecting molybdenum as a transition metal, electric properties of glasses within the  $\text{Li}_2\text{O}-\text{MoO}_3-\text{P}_2\text{O}_5$  system have been reported recently by us [2-4]. The aim of the present work is to determine the effect of alkali oxide  $\text{Li}_2\text{O}$  on the electrical conductivity on phosphomolybdate glasses with another P/Mo ratio..

**II. EXPERIMENTAL**

Glasses of different compositions were prepared by mixing appropriate amounts of lithium carbonate with molybdenum and phosphorus oxides of analytical grade, before transferring to a platinum

crucible. The mixtures were heated in an electric furnace first at about 650 K, then the mixture was melted at 1100-1200 K for several hours, with frequent stirring, to ensure homogeneity. The melt was then poured on a stainless steel plate preheated at 450 K. Finally, the vitreous samples were annealed for 6 h at 550 K.

The amorphous character of the resulting solid was tested by x-ray diffraction analysis. A structureless spectrum was obtained for an amorphous sample.

Both a.c. and d.c. electrical measurements were performed in order to define electronic and ionic contributions to the total conductivity. Electrical conductivity measurements were carried out by the complex impedance method using a 1260 Solartron frequency response analyser. The samples were pellets of 0.8 cm diameter and ca. 0.2 mm thickness, on which gold electrodes were deposited by vacuum evaporation. The frequency range used as  $10^{-2}-10^6$  Hz, the measurements being made between room temperature and 520 K in several temperature cycles. In all cases, no recrystallisation is detected by x-ray diffraction

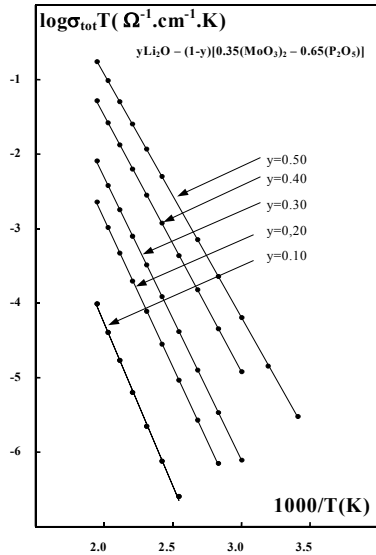
**III. RESULTS AND DISCUSSION**

### III.1 dc data

The temperature dependence of the conductivity (Figure 1) between 273 and 520 K exhibits an Arrhenius type variation and the conductivity evolves as a temperature function

$$\sigma T = \sigma_0 \exp\left(-\frac{\Delta E_\sigma}{kT}\right).$$

The Cole-Cole plots in the whole frequency range for compositions in the alkali poor region ( $y < 0.20$ ) contained only a semi-circle. By contrast the impedance plots for compositions in the alkali rich region ( $y > 0.20$ ) consisted of a semi-circle at higher frequencies, accompanied by a straight line at lower frequencies, characteristics of an interfacial impedance. Such an interfacial impedance is attributable to ionic adsorption and charge transfer at the interface between the ionic conductor and the metallic electrodes [5].



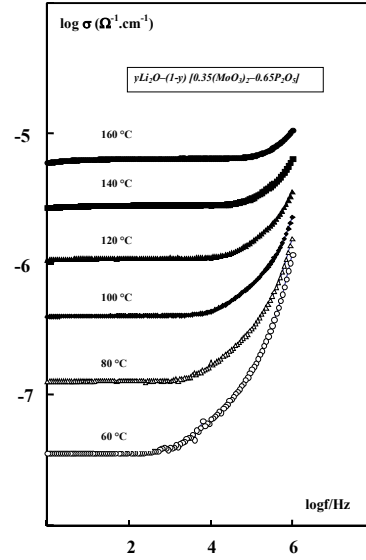
**FIGURE 1** : Temperature dependence of conductivity for the glasses under study. The curves are a fit of the data to the Arrhenius equation.

We may, therefore, conclude that for the glasses under study, electronic conductivity is predominant for  $y < 0.20$  and ionic one for  $y > 0.20$ . Similar results have been obtained by us in an earlier work [3]. As the matter fact, the investigation of the effect of  $\text{Li}_2\text{O}$  on the electrical properties of molybdenum-phosphate glasses having P/Mo ratio equal to 1.5 shows two regions in which the glasses manifest different electrical behaviour.

### III.2 ac data

From the experimental data (Figure 2) in a limited frequency region it is noted that the overall frequency dependence of conductivity (or the so called 'universal dynamic response', UDR, of ionic conductivity) could be approximated by the following simple relation :

$\sigma(\omega) = \sigma_{dc} + A\omega^\beta$ , where  $\omega (= 2\pi f)$  is the angular frequency.



**FIGURE 2** : a typical frequency dependent conductivity obtained for the glasses under study ( $y = 0.40$ ).

The UDR of the glasses is often analysed in terms of the complex modulus formalism. The advantage of the electric modulus is that it discriminates against electrode polarisation and other interfacial effects in solid electrolytes [6]. For a given temperature and a frequency, the real part,  $M'$ , and the imaginary part,  $M''$ , of the  $M^*$  complex modulus ( $M^* = M' + jM''$ ) can be calculated from

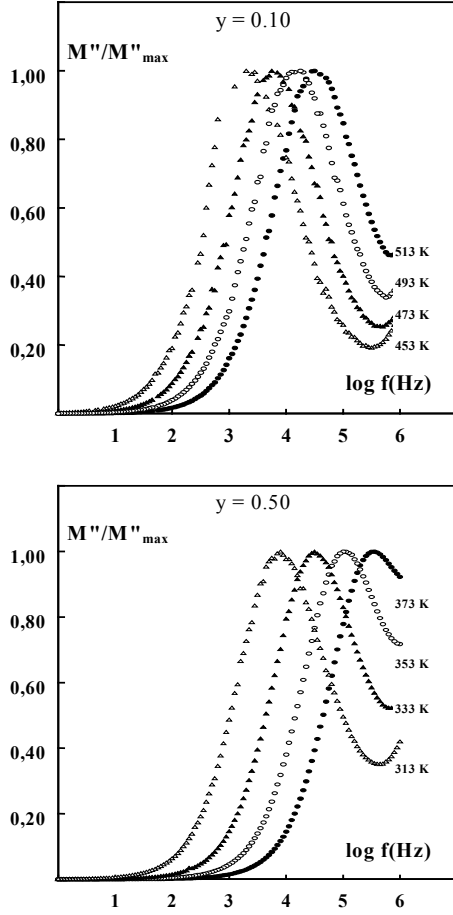
the complex impedance data ( $Z^* = Z' - jZ''$ ) by the following relations :  $M' = \omega C_0 Z''$  and  $M'' = \omega C_0 Z'$

Typical plots of  $M''/M''_{max}$  spectrum at any given temperature shows an asymmetric peak (Figure3). The  $M''/M''_{max}$  curves are non-symmetric, in agreement with the non-exponential behaviour of the electrical stretched exponential Kohlrausch function: [7-9]:

$$\phi(t) = \phi_0 \exp\left(-\left(\frac{t}{\tau_\sigma}\right)^\beta\right)$$

The  $\tau_\sigma$  and  $\beta$  parameters of that stretched exponential function are respectively the conductivity relaxation time and the Kohlrausch exponent. The full width at half maximum (FWHM) of the  $M''/M''_{max}$  spectrum is clearly

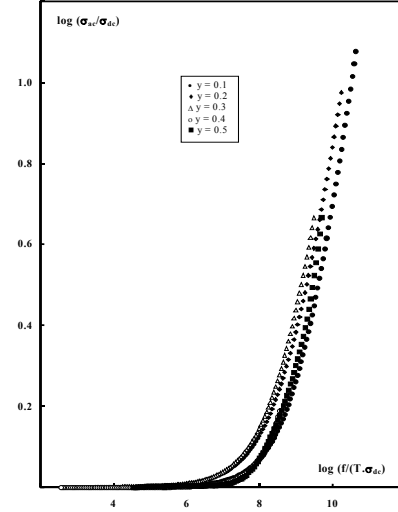
greater than the breath of a Debye-peak (1.14 decades) and it results in a value of  $\beta = \frac{1.14}{FWHM}$  for the Kohlrausch parameter.



**FIGURE 3** : Imaginary part of the electric modulus versus frequency for the glasses corresponding to  $y = 0.10$  (electronic behaviour) and  $y = 0.50$  (ionic conductor).

The  $\beta$  values which are smaller than unity are consistent with the ac conductivity in the glasses under study exhibiting a dispersion. Such a dispersion can be influenced by both disorder of the glassy network and interactions between charge carriers. Such an assumption is clearly supported by the results of Monte Carlo simulations [10].

In Figure 4 we represent master curves of the frequency-dependent conductivities of glasses containing different amounts of lithium oxide. As seen from this figure, the individual master curves are very similar in shape although the lithium content of the glasses is varied. The positions of these curves on the scaled



**FIGURE 4** : Conductivity master curves of  $y\text{Li}_2\text{O}-(1-y)[0.35(\text{MoO}_3)_2-0.65(\text{P}_2\text{O}_5)]$  glasses.

frequency axis ( $\frac{f}{T\sigma_{dc}}$ ) are, however, different.

This kind of behaviour has also been observed for sodium germanate  $x\text{Na}_2\text{O}-(1-x)\text{GeO}_2$  glasses [11], and  $y\text{Li}_2\text{O}-(1-y)[0.40(\text{MoO}_3)_2-0.60(\text{P}_2\text{O}_5)]$  glasses [3]. For lithium phosphomolybdate glasses, under study, the position depends on composition in a more complicated manner. Such a deviation from the ( $\frac{yf}{T\sigma_{dc}}$ ) scaling could be related to the composition dependence of the root mean square displacement of the mobile lithium ions [3].

#### IV. CONCLUSION

The glasses belonging to the series  $y\text{Li}_2\text{O}-(1-y)[0.35(\text{MoO}_3)_2-0.65(\text{P}_2\text{O}_5)]$  have been prepared. Electrical conductivity data have been examined using both the electric modulus  $M^*$  and the ac conductivity representations. At low values of  $y$ , the glasses have mainly electronic behaviour. At high values of  $y$ , ionic conductivity prevails. The master curves of frequency-dependent conductivities of glasses containing different amounts of lithium oxide have the similar shape. However, their positions depend on the chemical composition in a complicated manner. We suggest that the electrical conductivity in the glasses under study could not be scaled in an easier fashion.

#### Acknowledgment

The authors gratefully acknowledge financial supports from the mixed Moroccan-Tunisia committee under grant 04/MT/21.

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