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Role of molybdenum ions in lead zinc phosphate glass system by means of dielectric studies

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PbO-ZnF_2-P_2O_5 glasses doped with different mol% (0.1 to 1.0) of MoO_3 have been prepared. Dielectric properties $\epsilon'(\omega)$, tanδ, σ_{AC}, of the synthesized samples were calculated from frequency measurements versus temperature. Space charge polarization was used to analyze the temperature and frequency dispersions of dielectric constant $\epsilon'(\omega)$ and dielectric loss tanδ. Quantum mechanical tunneling model was employed to explain the origin of AC conductivity. The AC conductivity exhibited an increasing trend with increasing concentration of MoO_3 (up to 0.2 mol%) but the activation energy for conduction decreased. The plots of AC conductivity revealed that the relaxation dynamics depends on MoO_3 dopant concentration.

Keywords: *electrical and dielectric properties; quantum mechanical tunneling; AC conductivity; relaxation dynamics*

1. Introduction

In recent years, the study of electrical properties, including dielectric characteristics in glasses plays a significant role in solid state electronic devices [1]. The main applications of glassy dielectrics involve capacitance elements in electronic circuits and electrical insulators. Transition metal ions (TMI) in glasses are beneficial in electrochromic devices, such as smart windows and flat panel displays [2–7]. A small percentage concentration of TMI in oxide glasses resulted in their semiconducting properties [8, 9] and for these glasses the dielectric relaxation effect was due to electron hoping pairs [10].

Phosphate glasses exhibit distinctive physical properties when compared to the other borate and silicate glasses. The phosphate glasses have lower coefficient of thermal expansion, high ultraviolet transmission and comparatively lower melting temperature [11–13]. The semiconductor oxide MoO_3 acts as a conditional glass former as well as a modifier. When phosphate glasses are mixed with this oxide, their physical properties and chemical durability are expected to be improved [14, 15]. The MoO_3 mixed glasses find potential applications in developing alphanumeric displays, microbatteries, gas sensors, and memory devices [16, 17]. The stable oxidation states, Mo^{5+} and Mo^{6+} of MoO_3, are anticipated to change the dielectric properties depending on the composition of glass.

PbO-P_2O_5 glasses are recognized for their stability and moisture resistance. PbO plays a dual

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role: a modifier for Pb–O ionic bond and a glass former for Pb–O covalent bond [18–20]. The addition of ZnF_2 to this type of glass system increases liquidus temperature and corrosion resistance of the glasses [21]. Zn^{2+} cation is responsible for the good glass forming ability.

2. Experimental

Lead zinc phosphate glasses of the composition $(20 - x)PbO\text{-}30ZnF_2\text{-}50P_2O_5{:}xMoO_3$, with $x = 0.1$, 0.2, 0.3, 0.4, 0.8 and 1.0 mol% (labeled as M_1, M_2, M_3, M_4, M_8 and M_{10}) were prepared by the melt quenching method [22, 23]. The chemicals (from Acros Co.) PbO $\geqslant$ 99 %, ZnF_2 $\geqslant$ 99.8 %, P_2O_5 $\geqslant$ 99 % and MoO_3 $\geqslant$ 99 % were weighed and the mixture of the compounds was melted in a platinum crucible in a PID electric furnace at a temperature of 1273 K for one hour. The bubble free liquid melt was transferred into a preheated brass mould and the samples were annealed at 523 K for five hours. The density of the prepared glass samples was measured by the Archimedes principle with distilled water as a buoyant liquid. The actual compositions of the glass samples and other physical parameters such as average molecular weight, ion concentration, mean ion separation distance and polaron radius have been evaluated and tabulated in Table 1.

X-ray diffraction study confirmed the amorphous nature of the prepared glass samples. SEIFERT diffractometer model SO-DEBYE FLUX 202 was used for X-ray diffraction analysis of the prepared samples. Silver coating on both sides of the sample acted as electrodes for measurement of dielectric properties [24, 25]. The dielectric measurements of the samples in the present investigation were performed with HP 4263B LCR Meter in the frequency range of 10^2 Hz to 10^5 Hz and the temperature range of 30 °C to 350 °C. Radart Q-Meter was used for high frequency measurements.

3. Results

Fig. 1 shows the frequency variation of dielectric constant ϵ' and loss tanδ of the $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses. At room temperature and at high frequency of 100 kHz the values of ϵ' and tanδ were found as 9.3 and 0.0074, respectively, for the pure sample M_0. These values have increased with increasing concentration of MoO_3 up to 0.2 mol% (inset of Fig. 1) further, larger dielectric constant values were noted at the low frequency 1 kHz.

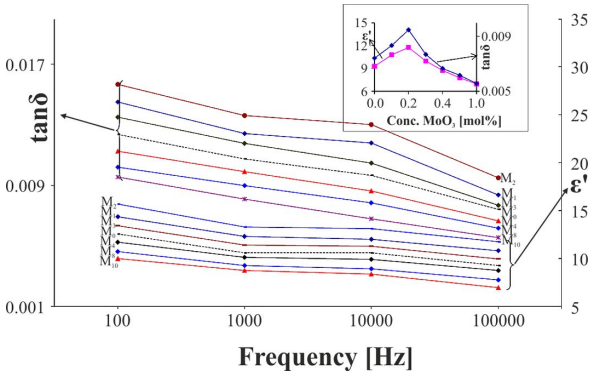

Fig. 1. Variation of dielectric constant and loss tangent with frequency at room temperature for $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses. The inset figure represents the variation of ϵ' and tanδ with the concentration of MoO_3 at 100 kHz.

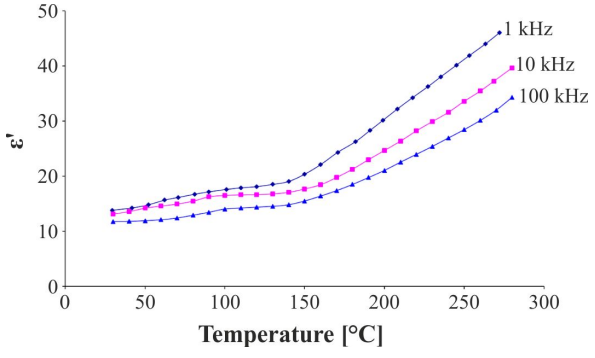

Fig. 2. Variation of dielectric constant of glass M_2 with temperature at different frequencies.

Fig. 2 presents the variation of dielectric constant with temperature at different frequencies for the glass sample M_2. The measured ϵ' values of the sample were found to increase with temperature and the rate of the increase was larger at low frequencies; the other samples also followed the same trend.

Table 1. Data on various physical properties of $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses.

Sample	Glass composition	Density [g/cm^3]	Average molecular weight	Concentration of molybdenum ions N_i [$\times 10^{21}$ ions per cm^3]	Interionic distance r_i [Å]	Polaron radius r_p [Å]
M_0	20.0 $PbO\text{-}30ZnF_2\text{-}50P_2O_5$	2.7018	116.4	–	–	–
M_1	19.9$PbO\text{-}30ZnF_2\text{-}50\ P_2O_5{:}0.1MoO_3$	2.7047	116.5	1.65	7.78	2.95
M_2	19.8$PbO\text{-}30ZnF_2\text{-}50P_2O_5{:}0.2MoO_3$	2.7099	116.6	2.79	7.09	2.86
M_3	19.7$PbO\text{-}30ZnF_2\text{-}50P_2O_5{:}0.3MoO_3$	2.7105	116.7	4.19	6.20	2.50
M_4	19.6$PbO\text{-}30ZnF_2\text{-}50P_2O_5{:}0.4MoO_3$	2.7176	116.8	5.66	5.63	2.27
M_8	19.2$PbO\text{-}30ZnF_2\text{-}50P_2O_5{:}0.8MoO_3$	2.7870	117.2	11.458	4.44	1.79
M_{10}	19.0$PbO\text{-}30ZnF_2\text{-}50P_2O_5{:}1.0MoO_3$	2.8210	117.4	12.356	4.33	1.74

Fig. 3 depicts a comparison of dielectric constant variation with temperature for $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses measured at 1 kHz. The temperature dependent dielectric constant ϵ' is the highest for sample M_2. The variation of dielectric loss (tanδ) with temperature at different frequencies for sample M_4 and comparison of tanδ variation with temperature for $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses have been shown in Fig. 4 and Fig. 5, respectively. The relaxation peak and tanδ values are found to increase with the MoO_3 up to 0.2 mol%. The activation energy AE of the samples has been calculated from equation 1 and tabulated in Table 2. The activation energy of 2.51 eV is the lowest for sample M_2:

$$f = f_o e^{-W_d/KT} \tag{1}$$

where W_d is the activation energy, f is resonance frequency, f_o is a constant, K is the Boltzmann constant and T is temperature.

The AC conductivity of the samples was evaluated from the equation:

$$\sigma_{AC} = \omega \varepsilon' \varepsilon_o \tan\delta \tag{2}$$

The plots of σ_{AC} versus 1/T (evaluated at 100 kHz) for $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses are shown in Fig. 6. The activation energy for conduction in the high temperature region was evaluated from these plots, and collected in Table 2. Fig. 7 presents the isotherms (drawn at 200 °C, 220 °C and 240 °C) of σ_{AC} for $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses at 10 kHz. Fig. 8 shows the X-ray diffraction patterns of the prepared glasses and does not indicate any line of diffraction which confirms the amorphous nature of the glass samples.

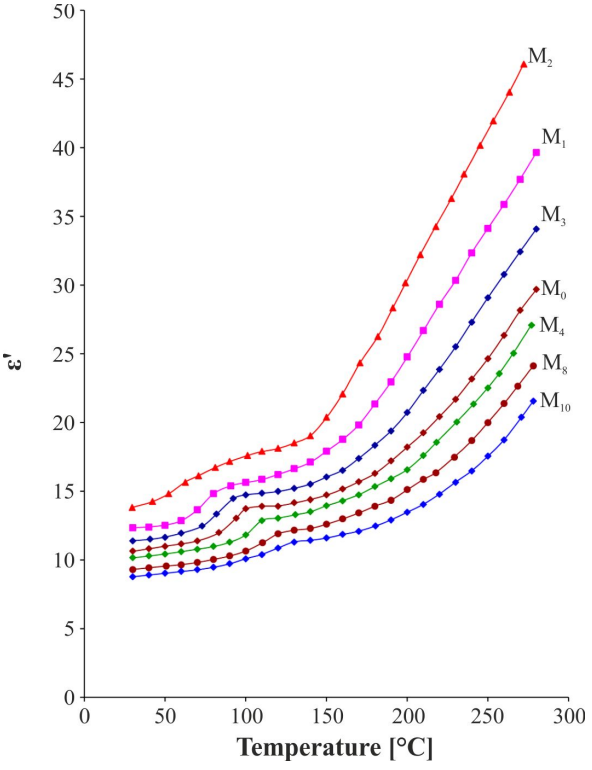

Fig. 3. A comparison of variation of dielectric constant with temperature measured at 1 kHz for $PbO\text{-}ZnF_2\text{-}P_2O_5{:}MoO_3$ glasses.

4. Discussion

Molybdenum, belonging to the intermediate class of glass forming ions, was found to exist in two ionic states, i.e. Mo^{5+} and Mo^{6+}.

Table 2. Dielectric properties of PbO-ZnF_2-P_2O_5:MoO_3 glasses.

Sample	Temp	Dielectric constant			Dielectric loss			AE for dipoles
	[°C]	1 kHz	10 kHz	100 kHz	1 kHz	10 kHz	100 kHz	[eV]
	30	10.62	10.61	09.30	0.011	0.010	0.007	
M_0	100	13.72	12.29	10.38	0.020	0.012	0.009	2.95
	250	24.64	22.68	19.64	0.103	0.087	0.070	
	30	12.33	12.20	10.80	0.012	0.011	0.009	
M_1	100	15.62	14.90	13.11	0.016	0.015	0.018	2.65
	250	34.12	30.46	26.50	0.219	0.210	0.180	
	30	13.28	13.12	11.76	0.014	0.013	0.010	
M_2	100	17.59	16.50	14.04	0.174	0.017	0.016	2.51
	250	40.18	33.61	28.46	0.402	0.397	0.329	
	30	11.40	11.28	09.98	0.011	0.011	0.008	
M_3	100	14.73	13.85	11.58	0.014	0.020	0.011	2.58
	250	29.08	26.76	23.31	0.103	0.087	0.070	
	30	10.15	09.94	08.76	0.011	0.008	0.006	
M_4	100	11.82	10.89	09.51	0.013	0.009	0.007	3.10
	250	22.53	20.16	16.67	0.069	0.055	0.047	
	30	09.30	08.96	07.77	0.009	0.008	0.006	
M_8	100	10.65	09.69	08.35	0.010	0.009	0.007	3.25
	250	20.00	17.68	14.09	0.050	0.034	0.032	
	30	08.77	08.37	06.96	0.008	0.006	0.005	
M_{10}	100	10.09	08.93	09.27	0.009	0.007	0.006	3.42
	250	17.54	14.77	11.90	0.036	0.023	0.021	

Table 3. AC conductivity of PbO-ZnF_2-P_2O_5:MoO_3 glasses.

Sample	Austin $N(E_f)$ [10^{21} eV^{-1}/cm^3]	Butcher $N(E_f)$ [10^{21} eV^{-1}/cm^3]	Pollak $N(E_f)$ [10^{21} eV^{-1}/cm^3]	AE for conduction [eV]
M_0	1.318	0.555	1.339	0.356
M_1	1.530	0.638	1.555	0.332
M_2	1.712	0.714	1.739	0.311
M_3	1.414	0.590	1.437	0.343
M_4	1.228	0.512	1.248	0.408
M_8	1.099	0.459	1.117	0.445
M_{10}	1.027	0.428	1.043	0.489

The structure of phosphate network significantly depends on its oxidation state and position it occupies. Mo^{5+} ions acting as modifier disrupt the phosphate glass network leading to dangling bonds with non-bridging oxygens (NBO), similar to divalent zinc ions [26–31]. The defected dangling bonds cause the relocation of charge carriers, increase the space charge polarization and facilitate the enhancement of dielectric values ϵ', tanδ and σ_{AC}, of PbO-ZnF_2-P_2O_5:MoO_3 glasses up to 0.2 mol% of the dopant.

The measured decrease in dielectric values of the glasses beyond 0.2 mol% suggests a decrease in the concentration of free charge carriers [32, 33].

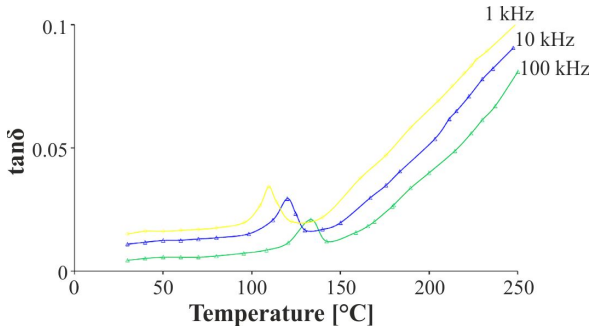

Fig. 4. Variation of dielectric loss with temperature measured at different frequencies for PbO-ZnF_2-P_2O_5 glasses doped with 0.4 mol% of MoO_3.

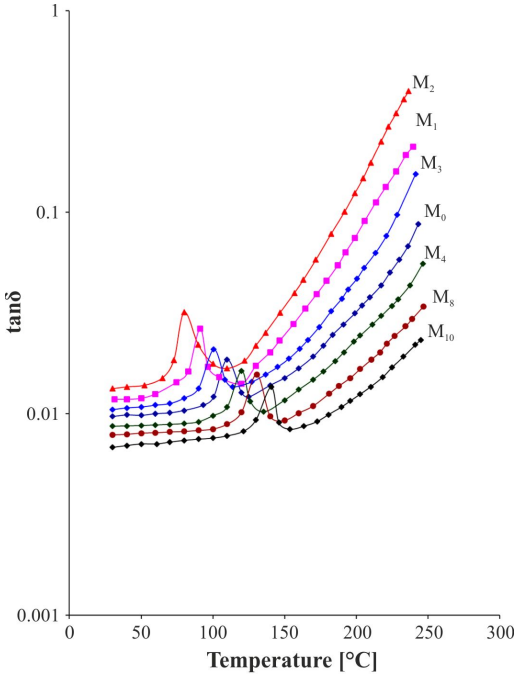

Fig. 5. A comparison of variation of dielectric loss with temperature for PbO-ZnF_2-P_2O_5:MoO_3 glasses measured at 10 kHz.

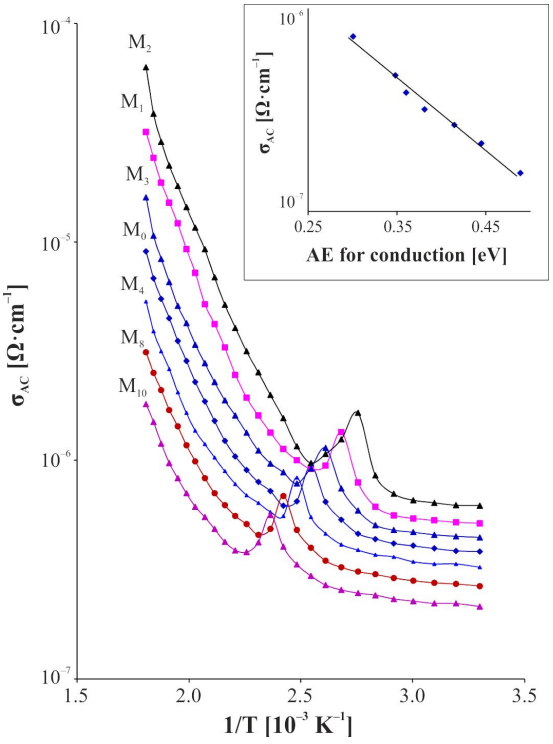

Fig. 6. Variation of AC conductivity with 1/T measured at 100 kHz for PbO-ZnF_2-P_2O_5 glasses doped with different concentrations of MoO_3.

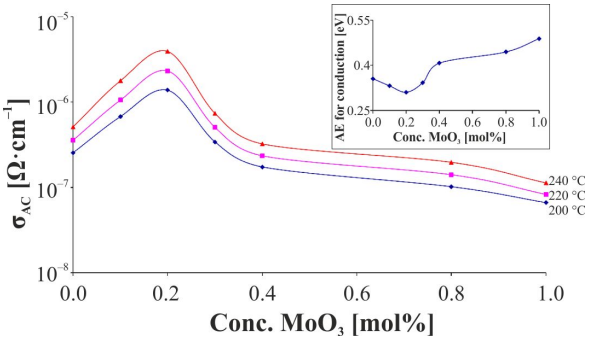

Fig. 7. Variation of AC conductivity with the concentration of MoO_3 measured at different temperatures and at a frequency of 10 kHz for PbO-ZnF_2-P_2O_5 glasses. The inset presents the variation of activation energy for conduction with the concentration of MoO_3.

In other words, the fraction of Mo^{5+} ions in such glass samples is relatively low, hence, there is a reduction in the rate of increase of dielectric constant. The plots of variation of tanδ with the temperature for PbO-ZnF_2-P_2O_5:MoO_3 glasses exhibit dipolar relaxation effects due to Mo^{5+} ions state in $Mo(V)O^{3-}$ [34, 35]. In the present glass system, beyond 0.2 mol% of MoO_3, we have observed a decrease in the intensity of the relaxation peaks and increasing trend of activation energy for dipoles. This observation confirms the existence of Mo^{6+} ions that participate in the glass network forming

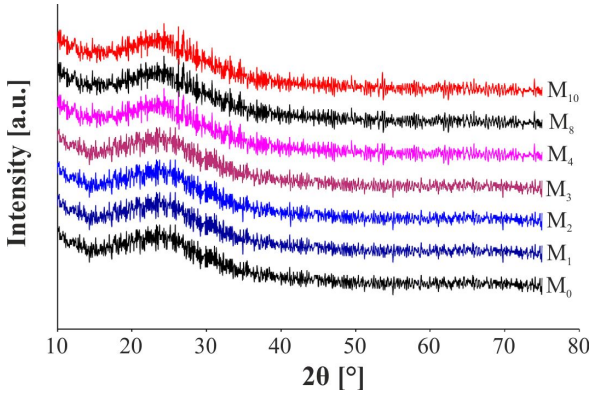

Fig. 8. XRD patterns of PbO-ZnF_2-P_2O_5:MoO_3 glasses.

for the samples from M_3 to M_{10}. A linear relationship between σ_{AC} and AE for conduction (inset of Fig. 6), suggests that the development of conductivity is directly related to the thermally stimulated mobility of the charge carriers [36]. Fig. 6 shows that σ_{AC} is maximum and AE for conduction (in the inset of Fig. 7) is minimum for sample M_2 due to transition from ionic (up to 0.2 mol%) to electronic conductivity (beyond 0.2 mol%) [37].

The active centers for the ionic conduction are due to the gradual increase of the content of modifier Mo^{5+} ions and either mobile electrons or polarons by the transition of $Mo^{5+}$to Mo^{6+}. Quantum mechanical tunneling (QMT) model was adapted to explain the AC conductivity of the present glass system at low temperatures. According to QMT, equation for AC conductivity is:

$$\sigma(\omega) = \eta e^2 K_B T [NE_F]^2 \alpha^{-5} \omega \left[\ln \frac{\nu_{ph}}{\omega}\right]^4 \qquad (3)$$

where NE_F is density of the defect energy states at the Fermi level, α is a decay constant ($\sim$0.485 Å^{-1}), e is a charge of electron, K_B is the Boltzmann constant, ω is an angular frequency, ν_{ph} is phonon frequency (5×10^{12} Hz), T is temperature, η is a constant and its value is given by $\eta = \pi/3$ (Austin et al. [38]), $= 3.66\pi^2/6$ (Butcher et al. [39]), $= \pi^4/96$ (Pollak [40]).

The value of NE_F is observed to be maximal for the glasses mixed with 0.2 mol% of MoO_3 and beyond this range it is found to decrease (Table 3). Such variations are consistent with our prediction that in the glass M_2 there is a predominant existence of molybdenum Mo^{5+} states that act as modifier, whereas in the samples M_3 to M_{10} the fraction of molybdenum is in Mo^{6+} states and these molybdenum ions participate in the glass network forming with MoO_4 structural units.

5. Conclusions

PbO-ZnF_2-P_2O_5:MoO_3 glasses (0 mol% to 1.0 mol%) were synthesized. Dielectric parameters ϵ', tanδ, and σ_{AC}, were measured over a wide range of frequency at low temperature. It has been stated that the space charge polarization plays a vital role in the ϵ' and tanδ of prepared glasses. We have observed an increase in the dielectric constant ϵ', dielectric loss tanδ and AC conductivity σ_{AC} up to 0.2 mol% of MoO_3, suggesting that a major portion of molybdenum ions got reduced to Mo^{5+} state. These ions acted as modifiers, which produced disorder in the glass network and enabled an increase of dielectric constant by contributing to the space charge polarization. The overall analysis indicated that glasses containing up to 0.2 mol% of MoO_3 are more appropriate for attaining good electrical conductivity.

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