Research Article

Effect of Manganese Ions on Spectroscopic and Insulating Properties of Aluminophosphate Glasses

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The melt-quenching technique was used to produce 39CdO–10Al2O3–(51–x)P2O5–xMnO glasses (x = 0, 0.1, 0.2, 0.3, and 0.4 wt.%). Various stability factors were calculated and presented from DTA analysis. The stability of the glass network appears to increase with the increase of MnO concentration, according to the findings. IR spectral analysis of these glasses exhibited several symmetrical and asymmetrical bands due to phosphate groups. The observed change in these band intensities with the rise in MnO concentrations, ranging from 0.1 wt.% to 0.4 wt.%, shows an increase in the stability of the glass network. Optical absorption analyses of these glasses revealed an absorption band that shifted from 500 to 488 nm as the concentration of manganese oxide (MnO) increased from 0.1 wt.% to 0.4 wt.%, indicating that Mn2+ ions were gradually converted into Mn3+ ions. EPR spectra of these glasses were characterized by two signals due to Mn2+ and Mn3+ ions. Observations on these signal intensity variations revealed an increase in stability of the glass network with the increase of MnO concentration from 0.1 wt.% to 0.4 wt.%. Parameters, which describe the insulating characteristics, for example, dielectric constant, , dielectric loss, tan δ, and AC conductivity , were determined in relation to frequency (10^3 Hz to 10^5 Hz) and temperature (20°C to 400°C) and presented in the dielectric analysis of these glasses.

1. Introduction

The dielectric constant, loss tan, and AC conductivity, as well as the dielectric breakdown strength of the glasses, are used to determine their insulating character and understand the structural features over such a wide frequency and temperature range [1]. In recent years, a number of studies have investigated a number of inorganic glasses under this way, resulting in useful information [1–3].

Phosphate glasses may be used for a variety of uses, including bone transplantation, hazardous waste containment, high electron conductors, laser host components, low-temperature seals, metallic seal materials, bioglasses, diametric purposes, and solid state electrolytes, among others [4–7]. They have significant physical properties, such as a low melting temperature, high heat transfer coefficient, high ultraviolet transmission, lower glass transition temperature, minimum softening temperature, high ionic conductivity, and biocompatibility [8]. Addition of Al2O3 to phosphate glasses improves their chemical durability and modifies their physical properties for more commercial applications [9, 10].
Transition metals-doped glasses have interesting optical, luminescent, semiconducting, memorizing, and photoconducting properties [11, 12]. Manganese ion is an intriguing transition metal ion although it can be present in a number between valence states (Mn$^{2+}$ and Mn$^{3+}$) of different glass matrices [13]. The quantitative characteristics of modifiers and glass formers, size of both ions in the glass structure, field strength, and mobility of the modifier cation, among some other factors, determine the amount of manganese contained in the glass in different forms and valence states [14]. Mn$^{2+}$ has an electronic configuration of 3d$^5$, which corresponds to a half-filled d shell. The impact of manganese on the thermal, physical, structural, and optical properties of glasses has been the subject of numerous studies [15, 16]. Moreover, manganese ions are well known to have a significant impact on the electric, magnetic, and optical properties of glasses; there seem to be numerous important studies on manganese ions’ environment in different inorganic glass systems available [17].

The main objective of this paper is to integrate manganese ions and their impact on structural integrity (namely, different band positions ranges between 487 and 1215 cm$^{-1}$; optical band gap energy) and insulating character of CdO-Al$_2$O$_3$-P$_2$O$_5$: MnO glasses through a thorough investigation of dielectric constant $\varepsilon$, loss tan $\delta$, and AC conductivity $\sigma_{ac}$ within the spectrum of frequency 10$^3$ Hz to 10$^5$ Hz as well as within the temperature range 20–400°C.

2. Experimental Works

Glasses with compositions 39CdO-10Al$_2$O$_3$-(51-x) P$_2$O$_5$: xMnO (0–0.4 mol %) were made using the traditional melt quenching techniques, and the samples were labeled as CAPM$_0$: 39CdO-10Al$_2$O$_3$-51 P$_2$O$_5$; CAPM$_1$: 39CdO-10Al$_2$O$_3$-50.9 P$_2$O$_5$: 0.1 MnO; CAPM$_2$: 39CdO-10Al$_2$O$_3$-50.8 P$_2$O$_5$: 0.2 MnO; CAPM$_3$: 39CdO-10Al$_2$O$_3$:50.7 P$_2$O$_5$: 0.3 MnO; and CAPM$_4$: 39CdO-10Al$_2$O$_3$:50.6 P$_2$O$_5$: 0.4 MnO, respectively. Subsequently, the glasses were made using a technique called rapid melt quench, by which the amorphous solid is formed during the melt-quenching process through the gradual toughening (i.e., rise in viscosity) of a melt.

In this experiment, the glasses were made using the melt-quenching method. The starting materials CdO, Al$_2$O$_3$, P$_2$O$_5$, and MnO that were used in the making of the present glass systems were of analar grade (greater than 99.9% purity). After polishing, the final glasses’ measurements were 1.0 cm $\times$ 1.0 cm $\times$ 2.0 cm. For this dielectric analysis, various parameters, namely, dielectric constant $\varepsilon$, dielectric loss tan $\delta$, and AC conductivity $\sigma_{ac}$, were investigated over a broad temperature spectrum and also as a function of wavelength. All these parameters, which were used in this analysis, were measured using LCR Meter (Hewlett-Packard Model-4263B).

3. Results and Discussion

3.1. Results. From the measured values of density $d$, average molecular weight $M$, and refractive index $n_d$ of CdO-Al$_2$O$_3$-P$_2$O$_5$: MnO glasses, various other physical parameters, such as manganese ion concentration $N_i$, mean manganese ion separation $R_i$, polaron radius $r_p$, molar volume $V_m$, electron polarizability $\alpha_e$, reflection loss $R$, and molar refractivity $R_M$, were calculated and presented in Table 1.

The dopant ion concentration ($N_i$) could be obtained from

$$N_i \left( \text{ions/cm}^3 \right) = N_A M \left( \text{mol} \% \right) \frac{d}{M} \quad (1)$$

The calculated values of $N_i$, the interionic distance $r_i$ and polaron radius $r_p$ of dopant ions can be evaluated by the following equations [17]:

$$r_i (\text{Å}) = \left( \frac{1}{N_i} \right)^{1/3} \quad (2)$$

$$r_p (\text{Å}) = \frac{1}{2} \left( \frac{\pi}{6 N_i} \right)^{1/3} \quad (3)$$

Using the refractive index of the glass, the theoretical dielectric constant ($\varepsilon$) was determined:

$$\varepsilon = n_d^2 \quad (4)$$

The Fresnel formula was used to calculate the reflection loss from the glass surface based on the refractive index:

$$R = \left[ \left( \frac{n_d - 1}{n_d + 1} \right)^2 \right] \quad (5)$$

The following formula was used to calculate the molar refractivity $R_M$ for each glass:

$$R_M = \left[ \left( \frac{n_d - 1}{n_d + 2} \right)^2 \right] \cdot V_m \quad (6)$$

Using the following formula, the electronic polarizability $\alpha_e$ was determined:

$$\alpha_e = \frac{3(n_d^2 - 1)}{4\pi N_i(n_d^2 + 2)} \quad (7)$$

The number of manganese ions per unit volume is given by the symbol $N_i$.

3.1.1. Differential Thermal Analysis (DTA). As shown in Figure 1, the glass transition temperature $T_g$, which is between 492 and 523°C, causes an inflection in the spectra and differential thermal analysis (DTA) traces of pure and MnO-doped CdO-Al$_2$O$_3$-P$_2$O$_5$, through which glasses were observed at temperatures ranging from 30 to 1000°C. The crystallization temperature $T_c$ at 698°C to 750°C causes a well-defined exothermic effect, which is accompanied by a well-defined endothermic effect, and melting temperature
due to the endothermic effect in the range of 945°C to 956°C. Based on the observed values of \(T_g\), \(T_c\), and \(T_m\), various stability factors of glasses, namely, \(T_g/T_m\), \((T_c – T_g)/T_g\), and \((T_c – T_g)/T_m\) and the glass forming capacity parameter, which was developed by Hruby, \(K_{g1} = (T_c – T_g)/(T_m – T_c)\), were calculated and are presented in Table 2.

The difference of various stability parameters, \(T_g/T_m\), \((T_c – T_g)/T_g\), \((T_c – T_g)/T_m\), and \(K_{g1}\), with MnO concentration is depicted in the inset of Figure 1. These curves display a growing trend in the stability factors in MnO concentrations increasing from 0.1 wt.% to 0.4 wt.% implying that the glass network becomes more stable as MnO concentration rises.

3.1.2. IR Studies. Figure 2(a) represents the room temperature recordings of pure infrared spectra and manganese oxide-doped CdO-Al\(_2\)O\(_3\)-P\(_2\)O\(_5\) glasses. Different IR bands corresponding to phosphate and aluminate structural groups appear in the glass matrix as the concentration of manganese oxide increases. Table 3 shows the data on different band positions from the IR spectra of these glasses.

For this specific network of glasses, the infrared transmission spectra were recorded for glasses as shown in Figure 3, and the conventional bands were caused due to the following:

(i) The O-P-O symmetric stretching vibrations in the range of 1198–1214 cm\(^{-1}\) (band 1)
(ii) The asymmetrical stretching of PO\(_4^{3-}\) groups in the region between 995 cm\(^{-1}\) and 1047 cm\(^{-1}\) (band 2)
(iii) The asymmetrical bending vibrations of P-O-P groups in the range of 896–915 cm\(^{-1}\) (band 3)
(iv) The vibrations of AlO\(_4\) groups in the region between 700 cm\(^{-1}\) and 750 cm\(^{-1}\)

The frequency of the band 1 (symmetrical band) changes towards lower frequency as the MnO concentration in the glass matrix increases from 0.1 wt.% to 0.4 wt.%, according to the IR-Spectra. Bands 2 and 3 (symmetrical bands) change towards higher frequency as strength decreases, suggesting a decrease in asymmetric stretching and increase in symmetrical stretching in phosphate units, indicating increased polymerization/stability of the glass network. In the presence
of some MnO concentration in the glass network, however, no shift in the band location of AlO4 groups is observed. The difference between symmetrical and asymmetrical band intensities for pure and MnO-doped CdO-Al2O3-P2O5 glasses is depicted in Figure 2(b).

3.1.3. Optical Absorption Studies. Figure 3(a) shows the optical absorption spectra of various materials CdO-Al2O3-P2O5: MnO glasses. The spectra of MnO-doped glasses exhibit two absorption bands resulting from Mn2+ transition (around 500 nm) $^{6}A_{1g}(S) \rightarrow ^{4}T_{1g}(G)$ and Mn3+ transition (around 490 nm) $^{5}E_g \rightarrow ^{5}T_{2g}$.

There is a change in band positions from 500 to 488 nm as the concentration of MnO rises from 0.1 wt.% to 0.4 wt.% suggesting the incremental conversion of Mn2+ ions into Mn3+ ions.

The optical band gap $E_{opt}$ can be decided based on Urbach plot $\alpha(hv)^{1/2}$ versus hv, which is related by

$$\alpha(v) = \alpha_0 \left[\frac{hv - E_{opt}}{hv}\right]^{2},$$

where $\alpha_0$ is a constant that is proportional to the length of the band tailing and $E_{opt}$ is the optical band gap energy [12].

Finally, MnO concentrations were increased from 0.1 wt.% to 0.4 wt.%.. The observed band positions and measured optical band gaps for these glass series indicate a development in the glass network and an insulating character. A similar trend was also observed from other studies (namely, DTA, IR, and EPR) of CdO-Al2O3-P2O5: MnO glasses.

Table 2: Data on DTA analysis of CdO-Al2O3-P2O5: MnO glasses.

| Glasses | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $T_g/T_m$ | $(T_c-T_g)/(T_m-T_g)$ | $(T_c-T_g)/T_g$ |
|---------|------------|------------|------------|-----------|------------------------|-----------------|
| CAPM_0  | 493.0      | 698.0      | 945.0      | 0.5216    | 0.829                  | 0.415           |
| CAPM_1  | 499.0      | 712.0      | 951.0      | 0.5236    | 0.883                  | 0.426           |
| CAPM_2  | 505.5      | 723.5      | 953.0      | 0.530     | 0.945                  | 0.430           |
| CAPM_3  | 511.5      | 732.0      | 954.0      | 0.536     | 0.993                  | 0.431           |
| CAPM_4  | 523.6      | 750.0      | 956.0      | 0.547     | 1.099                  | 0.432           |

Table 3: Data from the infrared spectra of different band positions CdO-Al2O3-P2O5: MnO glasses.

| Glasses | O-P-O units (cm$^{-1}$) band 1 | PO$_4^{3-}$ units (cm$^{-1}$) band 2 | P-O-P units (cm$^{-1}$) band 3 | AlO$_4$ units (cm$^{-1}$) |
|---------|--------------------------------|---------------------------------|-------------------------------|--------------------------|
| CAPM_0  | 1214                           | 995                             | 896                           | 726                      |
| CAPM_1  | 1210                           | 1005                            | 903                           | 726                      |
| CAPM_2  | 1207                           | 1020                            | 907                           | 726                      |
| CAPM_3  | 1204                           | 1033                            | 911                           | 726                      |
| CAPM_4  | 1198                           | 1047                            | 915                           | 726                      |

Figure 2: (a) IR spectra of CdO-Al2O3-P2O5: MnO glasses. (b) Variation of symmetrical and asymmetrical band intensities for pure and MnO-doped CdO-Al2O3-P2O5.

Figure 3(b) presents Urbach plot of CdO-Al2O3-P2O5: MnO glasses. Data on various band positions from the optical absorption spectra are shown in Table 4.
3.1.4. EPR Studies. Figure 4 shows the EPR spectra of CdO-Al2O3-P2O5: MnO glasses registered at room temperature. The spectra are characterized by two intense resonance signals; one of them is roughly oriented at $g = 2.01$ (signal 1) with a six-line hyperfine structure typical of independent Mn$^{2+}$ ions, and the other is focusing at $g = 4.3$ (signal 2), which is a characteristic of isolated Mn$^{3+}$ ions.

As MnO concentration is increased from 0.1 wt.% to 0.4 wt.%, the strength of signal 2 increases at the expense of signal 1, indicating that Mn$^{2+}$ ions are converted to Mn$^{3+}$ ions. As the MnO concentration is raised from 0.1 wt.% to 0.4 wt.%, there is a transformation of Mn$^{2+}$ ions into Mn$^{3+}$ ions observed in the current glass method, which is indicative of increased covalent nature over that of ionic. Furthermore, this suggests that the glass polymerization increases with improved stability with MnO concentrations increasing from 0.1 wt.% to 0.4 wt.% in the glass matrix.

3.1.5. Dielectric Studies. Figures 5(a)–5(c), respectively, show the variations of dielectric loss tan $\delta$, dielectric constant $\varepsilon$, and AC conductivity $\sigma_{ac}$ of CdO-Al2O3-P2O5: MnO glasses with temperature (20°C to 400°C) measured as a function of different frequencies at 1kHz, 10kHz, and 100kHz.

Dielectric constant $\varepsilon$ is observed to increase with temperature (with glass) at any frequency for all glasses; in addition, the value of the dielectric constant decreases as the MnO content rises from 0.1 wt.% to 0.4 wt.%. However, at any given temperature and MnO content in the glass network, it was observed that the dielectric constant reduces as the frequency is increased (Figure 5(a)). A similar trend is observed for dielectric loss tan $\delta$ variations (Figure 5(b)). The ac conductivity $\sigma_{ac}$ of these glasses is calculated using the following at various temperatures:

$$\sigma = \omega \varepsilon_0 \varepsilon \tan \delta,$$

where $\varepsilon_0$ is the vacuum dielectric constant for various frequencies.

The graph of log $\sigma_{ac}$ against $1/T$ is depicted in Figure 5(c) for all glasses at different frequencies. $\sigma_{ac}$ of these glasses is found to increase with temperature and frequency; in addition, it is observed that $\sigma_{ac}$ increases with rises in MnO content from 0.1 wt.% to 0.4 wt.% (Figure 3). Similar results were reported for MnO containing various glass matrices [3, 18]. Data on dielectric constant, dielectric loss, and AC conductivity of CdO-Al2O3-P2O5: MnO glasses at 1kHz, 10kHz, and 100kHz for temperatures 20°C and 400°C are presented in Table 5.

3.2. Discussion. In general, glass properties are determined by its composition and, to a large degree, its structure. Aluminophosphate glasses doped with MnO are a mixture of network formers and modifiers with a complex composition [4, 5, 9, 10, 19]. P$_2$O$_5$ is a well-known network former composed of PO$_4$ structural units, in which one of the four oxygen atoms in the PO$_4$ tetrahedron is doubly bonded to the phosphorous atom [15]. By bridging oxygen atoms, the PO$_4$ tetrahedrons are joined together in chains or rings by covalent bonding. Cross bonds between metal cations and
two nonbridging oxygen atoms of each PO₄ tetrahedron connect neighboring phosphate chains [14]. It is well known that adding a modifier oxide such as CdO to a P₂O₅ glass matrix causes the conversion of sp₂ planar PO₃ units to more stable sp³ tetrahedral PO₄ units, as well as the formation of nonbridging oxygen atoms [20].

bands observed at \( \sim 1200 \text{ cm}^{-1} \) and \( \sim 1040 \text{ cm}^{-1} \) result from symmetrical straining vibration (\( v_s(O-P-O) \)) groups of nonbridging oxygen in phosphate chain and normal vibrational mode of asymmetric straining (\( v_{as}(PO_4^{3-}) \)) group vibrations, respectively [20, 21]. Another band in the vicinity of 895 to 980 cm\(^{-1} \) due to P-O-P bending vibration that corresponds to tendency of asymmetric straining of phosphate group [20] was also observed.

Three conventional phosphate bands were visible in the spectra of these lenses due to (i) O-P-O group symmetric straining vibrations in the range 1198–1214 cm\(^{-1} \) (band 1), (ii) PO₄³⁻ group asymmetrical straining vibrations in the range 995–1047 cm\(^{-1} \) (band 2), and (iii) P-O-P group asymmetrical bending vibrations in the range 896–915 cm\(^{-1} \) (band 3). In addition, a band due to AlO₄ group vibrations with a fixed band position at 726 cm\(^{-1} \) was observed for all glasses. From the IR spectral studies of these glasses, it was observed that as the MnO concentration rises from 0.1 wt.% to 0.4wt.% in the glass matrix, the frequency of the symmetrical band (band 1) of phosphate units shifts towards a reduction in frequency as its intensity increases, and the asymmetrical bands 2 and 3 migrate towards higher frequencies as their intensities decrease, while they shift towards lower frequencies as their intensities decrease. This suggests a reduction in the degree of asymmetric stretching and increase in symmetrical stretching in phosphate units, MnO concentrations were increased from 0.1wt.% to 0.4 wt.%, and there is also a rise in polymerization or stability in the glass network. However, there is no observed change in the band position of AlO₄ groups at any concentration of MnO in the glass network.

Spectra of optical absorption MnO-doped two distinct absorption bands can be seen in the glasses resulting from Mn²⁺ transition (around 500 nm) \( ^{5}A_{1g}(S) \rightarrow ^{4}T_{1g}(G) \) and Mn³⁺ transition (around 490 nm) \( ^{5}E_g \rightarrow ^{5}T_{2g} \). The band at 500 nm arises from intraconfigurational transitions due to Mn²⁺ ions [14, 22]. These detected bands due to Mn²⁺ ions were hidden, beyond 0.1 wt.% of MnO concentration. Due to the presence of Mn³⁺ ions, a new strong absorption spectrum with a limit at around 490 nm has emerged [15, 18, 23, 24]. It was observed that the optical band gap increases as the concentration of manganese oxide (MnO) increases from 0.1 wt.% to 0.4 wt.%, whereas the Urbach energy decreases, which indicates improvement in the insulating character and hence the glass network’s strength.

Electron spin resonance gives information about the condition of valence of TM ions, local environment, and the essence of their interactions [25]. Since many of those Mn²⁺ compounds were octahedral and have a top spin structure with five unpaired electrons, they have a top spin arrangement, and an ESR signal with a \( g \) value close to the free electron value of 2.0023 is predicted [7,25]. Signal at \( g \sim 2.01 \) due to Mn²⁺ ions shows an octahedral symmetrical environment with the bond dominantly ionic [15, 25, 26].

In the present study, at room temperature, the EPR spectroscopy of all these glasses was recorded by E11Z Varian X-band (\( \nu = 9.5 \text{ GMZ} \)) ESR Spectrometer. The spectra are characterized by two intense resonance signals; one of them is centered at approximately \( g = 2.01 \) (signal 1) with a six-line hyperfine sequence that is typical of independent Mn²⁺ ions, and the other is centered at \( g = 4.3 \) (signal 2), which is a characteristic of isolated Mn³⁺ ions.
Dielectric constant, $\varepsilon$

| Temperature, °C | 1kHz | 10kHz | 100kHz |
|----------------|------|-------|--------|
| 20             | 8    | 8     | 6      |
| 210            | 11.6 | 17.2  | 11.6   |
| 400            | 15   | 13.3  | 11.6   |

Dielectric loss, $\tan\delta$

| Temperature, °C | 1kHz | 10kHz | 100kHz |
|----------------|------|-------|--------|
| 20             | 0.0017 | 0.00315 | 0.00085 |
| 210            | 0.0013 | 0.002  | 0.00085 |
| 400            | 0.00085 | 0.00315 | 0.00085 |

Figure 5: Continued.
The presence of a resonance signal at $g = 2.01$ is because of the existence of the Mn$^{2+}$ ion in an area similar to octahedral symmetry. As MnO concentration is increased from 0.1 wt.% to 0.4 wt.%, the strength of signal 2 increases at the cost of signal 1, which is a sign that Mn$^{2+}$ ions are being converted to Mn$^{3+}$ ions. These samples’ spectra are identical to those recorded for manganese ions doped in a variety of glass systems [15, 18, 27].

Ionic, dipolar, electronic, and space charges all contribute to a material’s dielectric constant. Polarization is determined by the purity and perfection of the lenses [1, 28]. At very low temperatures, the effect of space charge polarizations is negligible, but it is within the low frequency range, and there is a significant difference [28]. The dipolar alignment effects in the glasses can be observed at up to 106 Hz. Retrieving our information, we find that $\varepsilon$ is slightly frequency-dependent even at room temperature for pure as well as MnO-doped glasses. This is because of the dielectric constant and loss being influenced by space charge polarization. For temperature changes of around 400°C, for many solids, the reduction within the electronic dielectric constant is found to be less than 3% [29]. The defects in glasses can only increase $\varepsilon$ and $\tan \delta$. As the temperature rises, space charge polarization becomes more dominant and therefore increases [1, 28, 29]. As this form of polarization decreases with frequency, the change in $\varepsilon$ and $\tan \delta$ at higher frequencies and temperature is lower [30–38].

The values increased by up to 0.5% with the addition of MnO, and $\tan \delta$, $\sigma_{ac}$, and $\varepsilon$ are found to decrease at any temperature and frequency. Modifiers, such as octahedral Mn$^{2+}$ ion, weaken the glass network by creating paths for free ions to migrate through, accumulating space charge and increasing disorder. The space charge polarization increases as the glass network becomes weaker, resulting in a reduction in dielectric parameters (i.e., MnO concentration ranging from 0.1 to 0.4). In MnO-doped glasses, the decrease of these parameters in this concentration range suggests that the Mn$^{3+}$ ions present in these glasses (as demonstrated by measurements of optical absorption) establish cross-linkages, where Al-O-Mn bonds are formed by combining a portion of AlO$_3$ unit ions with a portion of AlO$_3$ unit ions. This is also logical because Al$^{3+}$ and the oxidation state of Mn$^{3+}$ ions are nearly identical, and their ionic radii are nearly similar (0.51 Å and 0.66 Å, respectively). As a result of these cross-links, the space charge polarization of glasses with MnO concentrations decreases, resulting in lower dielectric parameter values. As a result of increased concentration of MnO in the lenses, the existence of the tan variation often supports that the bulks of the magnesium oxide in the glasses CAPM_1 and CAPM_2 are in the Mn$^{2+}$ state, which acts as modifiers, and in the

![Graph](image-url)
Table 5: Data on dielectric constant, dielectric loss, and AC conductivity of CdO-Al\textsubscript{2}O\textsubscript{3}-P\textsubscript{2}O\textsubscript{5}: MnO glasses at 1 kHz, 10 kHz, and 100 kHz for temperatures 20°C and 400°C.

| Glass      | 20°C  | 400°C | 20°C  | 1 kHz | 400°C | 20°C  | 1 kHz | 400°C | 20°C  | 1 kHz | 400°C | 20°C  | 1 kHz | 400°C | 20°C  | 1 kHz | 400°C | 20°C  | 1 kHz | 400°C |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| CAPM_0     | 9.96  | 21.92 | 0.002014 | 8.44 | 19.8 | 0.001567 | 8.44 | 19.8 | 0.001567 | 8.44 | 19.8 | 0.001567 | 7.38 | 42 | 7.36 | 16.86 | 0.00098 | 0.00147 | 40.2 | 242 |
| CAPM_1     | 9.68  | 20.69 | 0.00195 | 8.18 | 16.65 | 0.001531 | 8.18 | 16.65 | 0.001531 | 8.18 | 16.65 | 0.001531 | 6.99 | 32.46 | 7.13 | 14.23 | 0.000963 | 0.00169 | 38.345 | 172.4 |
| CAPM_2     | 9.36  | 18.86 | 0.00187 | 7.88 | 14.36 | 0.001507 | 7.88 | 14.36 | 0.001507 | 7.88 | 14.36 | 0.001507 | 6.629 | 24.8 | 6.95 | 12.07 | 0.000948 | 0.00192 | 36.78 | 129.7 |
| CAPM_3     | 9.1   | 16.48 | 0.00178 | 7.67 | 12.64 | 0.001467 | 7.67 | 12.64 | 0.001467 | 7.67 | 12.64 | 0.001467 | 6.286 | 19.6 | 6.76 | 10.54 | 0.000929 | 0.00217 | 35.06 | 99.68 |
| CAPM_4     | 8.74  | 14.68 | 0.000908 | 7.34 | 11.26 | 0.001422 | 7.34 | 11.26 | 0.001422 | 7.34 | 11.26 | 0.001422 | 5.827 | 15.9 | 6.54 | 9.41 | 0.000908 | 0.00250 | 31.1445 | 77.38 |
glasses CAPM_3 and CAPM_4, they are in the Mn$^{3+}$ state, which act as formers.

4. Conclusion

The conclusions drawn from different physical studies and spectroscopic properties of CdO-Al$_2$O$_3$-P$_2$O$_5$: MnO glasses are summarized as follows.

(i) The increase of MnO content from 0.1 wt.% to 0.4 wt.% improved glass network stability in the temperature range of 30–1000°C, according to DTA traces registered in the temperature range of 30–1000°C.

(ii) With the improvement due to MnO content increase from 0.1 wt.% to 0.4 wt.%, the IR spectra measured at room temperature showed a rise in the symmetrical bands' intensity (band 1) at the expense of asymmetrical bands (bands 2 and 3); the observed trend indicates that the glass network's stability has improved.

(iii) The gradual transformation of Mn$^{2+}$ ions into Mn$^{3+}$ by increasing MnO concentrations from 0.1 wt.% to 0.4 wt.% was observed in EPR spectra measured at room temperature, indicating an enhanced covalent atmosphere of manganese ions as well as an improvement in the consistency of the glass network.

(iv) The MnO production was increased from 0.1 wt.% to 0.4 wt.% with an improvement in MnO content percent, and optical absorption spectra showed a shift in the concentration of Mn$^{3+}$ ions at the cost of Mn$^{2+}$ ions, as well as a rise throughout the optical band gap; the observed pattern shows an increase in insulating character and thereby the stability of the glass network.

(v) At 105 Hz, the dielectric constant of glass $\varepsilon_{dc}$ (pure glass) is determined to be 7.36 at room temperature and it was frequency-oriented, with lower frequencies having comparatively higher values. With an improvement in MnO concentration of up to 0.4 wt.%, the dielectric constant value decreases with introduction of MnO. The variance of dielectric loss of frequency at different temperatures reveals a consistent pattern across all glasses.

(vi) The space charge polarization increases as the glass network becomes weaker, resulting in higher measures of dielectric parameters. As more Mn$^{3+}$ is added to the network of glasses, the space charge polarization decreases, resulting in a decrease in the measures of the dielectric parameters of the glasses.

(vii) For all types of glasses at different frequencies, $\delta_{ac}$ of these glasses is found to increase with temperature and frequency; in addition, it is observed that as $\delta_{ac}$ decreases, MnO content was increased from 0.1 wt.% to 0.4 wt.%. This indicates that high proportion of Mn$^{2+}$ in glass CAPM_1 (taking modifier positions) and high proportion of Mn$^{3+}$ in glass CAPM_4 (when glass former position high insulating character was considered).

(viii) Finally, the results from various studies made on CdO-Al$_2$O$_3$-P$_2$O$_5$: MnO glasses reveal an improved stability of the glass network with increase in MnO content from 0.1 wt.% to 0.4 wt.%. 

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

This study was performed as a part of the employment of the authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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