Ultraviolet Transmitting Glass Matrix for Low Power Laser Lens

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The ZnO doped phosphate glass system of chemical composition $(65-x)\text{P}_2\text{O}_5-(25+x)\text{ZnO-10Na}_2\text{O}$, with $(x=10,20,30)$ were prepared using a conventional melt-quench technique. The structural investigation of the glass state was done using the XRD technique. It proved that the obtained materials are amorphous, with no crystal phase present. Their density was measured by the Archimedes method and the molar volume $(v_m)$ was calculated. The density increased and the molar volume decreased, respectively, by increasing the ZnO content.

The optical spectroscopic analyses were performed with a spectrophotometer (JASCO Corp., V-570, Rel-00, Japan) covering the wavelength range from 200 to 2500 nm. The UV transmittance of the glass samples at the wavelength range from (100-400) nm of UVC, UVB and UVA varies from 24 to above 55% and increases with the increasing ZnO dopant content. The refractive index been estimated according to the Clausius-Mossotti method using the ionic refraction. Some characteristic features such as elasto-optic coefficient and susceptibility were derived from the obtained values of refractive index. The results reveal the importance of such glass composition for low cost ultraviolet laser lenses and special ultraviolet optics.

Keywords: Phosphate glass, UV transmittance, optical spectroscopy, laser materials
1. INTRODUCTION

The glasses used by mankind throughout most of our history base on silica. A large number of inorganic glasses, which don’t contain silica, can be obtained. The traditional view is that glass is a solid obtained from a super-cooling liquid. However, it can be manufactured in many ways, including vapor deposition, sol-gel processing of solutions, and by neutron irradiation of crystalline materials [1-3]. The phosphate glasses exhibit some advantageous properties and are considered as promising for the optical applications, such as optical amplifiers, fibers, laser, etc. [4-11]. Phosphate glasses have miraculous properties such as low dispersion, high refractive index, low melting and softening temperatures, high thermal expansion coefficients, high electrical conductivity and large ultraviolet (UV) transmission, comparable to that of silicate glass [12-15]. The limited chemical durability of the phosphate glasses is one of the disadvantages for using them as glass formers. However, adding the transition metals oxide increases their durability. The chemical durability and the melting properties are very important for ultraviolet transmitting glass optical properties. Glasses containing transition metal (TMS) ions have interesting optical and electrical properties, which are due to the presence of TMS ions in several oxidation or coordination states in the glassy matrix [16-22]. ZnO oxide plays a good role for changing the properties of phosphate glass when is added as a modifier. The Zn$^{2+}$ ions occupy the interstitial sites in glass network. They act as an ionic cross linker between different phosphate anions, inhibiting the hydration reaction [23]. Addition of zinc oxide suppresses the crystallization and extends the glass forming region of poly-phosphate glasses [24]. Additionally, zinc is believed to impart antibacterial properties to the material. Ultraviolet (UV) transmitting glasses are important for applications in micro-lithography equipment, special ultraviolet optics and laser systems [25]. Quartz exhibits a much larger dispersion than fluorite. Unfortunately, unlike fluorite, the absorption in quartz becomes quite marked at 2 μ and is very large beyond 3μ. However, for the spectral region from the remote ultraviolet (0.25μ) to 1.7μ in infrared [26] it does not make a problem. Fluoride single crystals and high purity vitreous silica are well-known materials used for high transmittance UV optics (wavelength, λ < 300 nm). However, the practical size of single crystal is limited and melting of high-purity vitreous silica is expensive and difficult [27,28].

The paper focuses on enhancing the ultraviolet transmitting phosphate glass range by using the reagent-grade raw materials. The distinguished chemical, thermal, optical properties of the sodium zinc phosphate glass system were studied. The structural changes with different compositions, to be used for laser systems as low laser lenses, special ultraviolet optics and micro lithography equipment were also considered.
2. EXPERIMENTAL

2.1. Glass preparation
The glass samples composed of \((65-x)P_2O_5-(25+x)ZnO + 10Na_2O\) with \(x=(0,10,20,30)\) were prepared by the conventional melt quenching technique. The pure chemicals were used: \(P_2O_5\) as ammonium dihydrogen phosphate \((NH_4)_2H_2PO_4\), Zinc oxide \((ZnO)\) and \(Na_2O\) as anhydrous sodium carbonate. The powders were completely mixed and crushed using a mortar for 10 min for each sample. Then the batch was melted in a porcelain crucible using muffle furnace at temperature ranging from 900 to 1000 °C for 1 hour. All samples were shaken clockwise to ensure that the material is of high homogeneity. Finally, the casting was quenched and annealed at the temperature range 250-300 °C for 2.5 hours, using two heat preheated brass plates to obtain a thin disk. Then the samples were left to cool at room temperature. The prepared glass samples were annealed to remove the internal stress created during the quenching step.

2.2. Analysis of glass
In this study, to characterize the glass samples, we have performed the measurements of: density, XRD, transmission and absorption. The amorphous state of the glass samples was confirmed by the X-ray diffraction (XRD) on a Brucker Optical spectroscopic system on phosphate doped with ZnO. For XRD measurements a D8-diffractometer was used and Cu-Ka \((k=1.5406 \text{ Å})\) radiation, operating at 40 kV and 30 mA at a rate of 2°/min. The diffraction data were recorded for 2h between 4° and 70°. The optical absorption and the transmission spectra for polished glass samples were recorded in the wavelength range 200–2500 nm and at room temperature using the UV/VIS (JASCO V570) spectrophotometer.

3. RESULTS AND DISCUSSION

The glass samples were characterized by the X-ray diffraction technique to check their amorphous nature. The X-ray diffraction patterns, displayed in Fig.1, show no sharp peaks, confirming absence of the crystal order in the prepared samples. The density was measured using the Archimedes method, using toluene for all prepared glass samples as the immersing liquid, with the staple density of 0.866 g/cm\(^3\) at room temperature. Molar volume was calculated from the obtained density. The density \((\rho)\) and the molar volume \((V_m)\) of glass samples were calculated according to Eqs. (1,2) [29], respectively

\[
\rho = \frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{liq}}} \rho_o \tag{1}
\]
\[ V_m = \frac{M_w \rho_{glass}}{\rho_{glass}} \]  

where \( \rho \) is the sample density; \( \rho_o \) the liquid density; \( W_{air} \), the weight in the air; \( W_L \), the weight in the liquid (toluene), \( V_m \) the molar volume; and \( M_w \) the molar mass of glass.

The calculated values of the density and the molar volume are listed in Table 1. The dependence of density and molar volume on the quantity of ZnO is explained in Fig. 2. The density is found to increase with the increasing ZnO content. The molar volume changes in the opposite direction. This is a natural behavior between the density and the molar volume.

Calculation of the oxygen packing density (OPD) serves basically to measure the straits of packing on the oxide network. The oxygen packing density was calculated using the following relation:

**TABLE 1**

<table>
<thead>
<tr>
<th>ZnO content (mol %)</th>
<th>Density (g/cm³)</th>
<th>Molar volume (cm³/mol)</th>
<th>Oxygen packing density (OPD)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO 25%</td>
<td>2.3419</td>
<td>50.7309</td>
<td>70.963</td>
<td>3.68</td>
</tr>
<tr>
<td>ZnO 35%</td>
<td>2.8118</td>
<td>40.0989</td>
<td>79.803</td>
<td>3.47</td>
</tr>
<tr>
<td>ZnO 45%</td>
<td>2.9848</td>
<td>35.7466</td>
<td>78.331</td>
<td>3.33</td>
</tr>
<tr>
<td>ZnO 55%</td>
<td>3.3139</td>
<td>30.3682</td>
<td>72.444</td>
<td>3.25</td>
</tr>
</tbody>
</table>

**FIGURE 1**

XRD patterns for the glass samples
O\textsubscript{atoms} = \left(\frac{\rho}{Mw}\right)O\

where \(\rho\) is the density; \(Mw\) is the molar volume; \(O\textsubscript{atoms}\) is the number of oxygen atoms.

The calculated values of oxygen packing density for different ZnO contents are given in Table 1. It is obvious that the oxygen packing density decreases with the increasing ZnO content. In this respect, the structure of glass network became less tightly packed and the degree of disorder is increased by increasing the ZnO content, i.e. formation of open structure, which explains the observed results for the molar volume.

Figure 3 shows the optical absorption spectra in the wavelength range (200-2500nm) of the prepared ZnO containing glass samples. It is obvious that the absorbance decreases with the increasing of ZnO content.
Figure 4 displays the optical transmission spectra of the prepared glass samples containing ZnO over the wavelength range (200–2500 nm). The optical transmission increases with the increasing ZnO contents. The results reveal also that all samples exhibit a broad transmission band in UV range. It is well known that the UVC radiation ranges from 100 to 290 nm, UVB from 290 to 320 nm and UVA from 320 to 400 nm, respectively. The present study offers excellent materials with a high transmission in the whole UV range, i.e. UVC, UVB and UVA. The transmission ranges from 29 to 51%. The obtained systems can be perfect for UV transmission applications such as

![Graph showing optical transmission spectra for ZnO doping levels.](image1.png)

**FIGURE 3**
Glass samples absorbance versus wavelength for different ZnO doping levels.

![Graph showing glass samples transmittance versus wavelength for different ZnO doping levels.](image2.png)

**FIGURE 4**
Glass samples transmittance versus wavelength for different ZnO doping levels.
UV-Laser systems as low power laser lenses and in micro lithography equipment.

Table 3 lists the transmission maxima’s of the glass samples for the ultraviolet range, UVA and UVB. All samples are opaque at wavelengths below 200 nm.

Table 4 gives the transmissions of glass samples for the ultraviolet ranges UVA, UVB and UVC. The transmission of the sample glass, containing 25% ZnO increases from 0.2 pct at 200 nm to 27.3 pct at 290 nmv at UVC range. In UVB range the increase is from 27.3 pct at 290 nm to 31.3 pct at 320 nm. In UVA range the increase is from 31.3 pct at 320 nm to 34.7 pct at 400 nm. The transmission of the sample glass containing 35% ZnO increases in UVC range from 6.6 pct at 200 nm to 49.4 pct at 290 nm. For UVB the increase is from 47 pct at 290 nm to 53.2 pct at 320 nm. For UVA these numbers are 53.2 pct at 320 nm to 56.4 pct at 400 nm.

For the glass samples containing ZnO 45% , the transmission increases in UVC range from 7.1 pct at 200 nm to 47.4 pct at 290 nm. In UVB range it increases from 49.4 pct at 290 nm to 52.5 pct at 320 nm. In the UVA range the transmission varies from 52.5 pct at 320 nm to 55.9 pct at 400 nm.

Finally, the transmission of the glass sample containing 55% of ZnO increases from 1.1pct at 200 nm to 44.9 at 290 nm, in UVC, from 44.9 pct at 290 nm to 49.9 pct at 320 nm in UVB and from 49.9 pct at 320 nm to 53.3 pct at 400 nm in UVA range, respectively.

The reflectance $R$, shown in fig 5, was calculated using the following equation

$$A + T + R = 1 \text{ so } R = 1 - A - T$$

where $A$ is absorbance $T$ the transmittance. Knowing the reflectance we can easily calculate the refractive index $n$, shown in Fig. 6, using the following relation [30]

$$R = \frac{(n-1)^2}{(n+1)^2}$$

TABLE 3
Transmission maxima of all glass samples in the ultraviolet range, UVA, UVB.

<table>
<thead>
<tr>
<th>Glass samples</th>
<th>UVA</th>
<th>UVB</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>33.475</td>
<td>30.089</td>
</tr>
<tr>
<td>S2</td>
<td>55.044</td>
<td>51.906</td>
</tr>
<tr>
<td>S3</td>
<td>54.878</td>
<td>50.777</td>
</tr>
<tr>
<td>S4</td>
<td>50.532</td>
<td>48.532</td>
</tr>
</tbody>
</table>

Ultraviolet Transmitting Glass Matrix for Laser Lens
The knowledge of refractive index is very important for any optical material. In glasses, the electronic polarization frequencies are in UV, where they induce a strong absorption, and the molecular polarization frequencies are in the infrared, where they cause multiphoton absorption. In between, the refractive index shows a weak frequency dependence, decreasing with the increasing wavelength (normal dispersion).

The refractive index depends mainly on the chemical composition of glass. However, the refractive index is a function of ion refraction as given by the Clausius–Mossotti relation. In the present study the refractive index is found to decrease with the increasing ZnO content, the main factor that can affect the material refractivity.

The absorption coefficient, shown in Fig 7 for the studied glass samples, can be calculated using the following equation [31]:

$$\alpha(\nu) = \left(\frac{1}{d}\right) \ln \frac{I^0}{I}$$

### TABLE 4
Transmission of all glass samples for the ultraviolet wavelength range: UVA, UVB and UVC.

<table>
<thead>
<tr>
<th>Samples glass system</th>
<th>UVA</th>
<th>UVB</th>
<th>UVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 with ZnO 25%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2 with ZnO 35%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S3 with ZnO 45%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S4 with ZnO 55%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where, $I_0$ and $I$ are the intensities of the incident and transmitted beams respectively, $d$ is the thickness of the glass samples and $\lambda$ is the wavelength.

The optical band gap, $E_g$ of the glass samples was calculated using the following relation [32,33]:

\[
\alpha \nu = B(\nu - E_g)^2
\]  

(7)

where $B$ is a constant, $\alpha$ is the absorption coefficient and $\nu \nu$ is the photon energy. The thickness of the glass specimens was measured using a digital
micrometer gauge. Optical absorption spectra were recorded at room temperature on a UV–vis spectrophotometer, in the wavelength range of 200–2500 nm. However, for non-crystalline systems, it is customary to plot \((\alpha \nu)^{1/2}\) as function of the photon energy \((\nu h)\) in order to find the optical band gap shown in Fig 8, and listed in Table 1. The optical energy gap is found to decrease from 3.68 eV to 3.25 eV with the increasing ZnO content. This can be related to the gradual increase in number of non-bridging oxygen (NBO) atoms.

The permittivity \((\varepsilon)\), and the polarizability \((\Upsilon)\) were respectively calculated using the following equations:

\[
\varepsilon = n^2
\]

(8)
The electric susceptibility \( \gamma \) was calculated using the following equation [29]:

\[
\gamma = \frac{3}{4N\pi} \frac{\varepsilon - 1}{\varepsilon + 2}
\]  

(9)

The permittivity \( \varepsilon \) and the polarizability \( \gamma \) depend on wavelength and are shown, respectively in figs 9,10,11. According to Clausius–Mossotti relation, they decrease with the increasing ZnO content.

The extinction coefficient \( k \) was calculated using the following equation [34]:

\[
k = \frac{\alpha \lambda}{4\pi}
\]  

(11)

where, similarly as before, \( \alpha \) is the absorption coefficient and \( \lambda \) is the wavelength.

The dielectric constant real \( (\varepsilon') \) and imaginary \( (\varepsilon'') \) parts were calculated using the following equations [34-37]:

\[
\varepsilon' = n^2 - k^2
\]  

(12)

\[
\varepsilon'' = 2nk
\]  

(13)

where \( n \) is the refractive index and \( k \) is the extinction coefficient.

The wavelength dependences of the extinction coefficient and the dielectric constants are shown respectively in Figs 12,13,14. According to Clausius–Mossotti, they were diminished by the ZnO dopant.

The elasto-optic coefficient \( P \), displayed in Fig 15, was calculated using the following equation [38,39]:

\[
P \approx \frac{(1 - B)(1 + 2B)}{3}, \text{where } B = \frac{1}{\varepsilon}
\]  

(14)
The Brewster angle and the phase velocity can be calculated, respectively, from the following equations, knowing the refractive index. They are shown in Figs 16 and 17.

\[
\text{The Brewster’s angle } = \arctan\left(\frac{n_2}{n_1}\right)
\]

(15)

FIGURE 9
The Permittivity verses wavelength of the glass samples for different ZnO doping levels.

FIGURE 10
The Electric susceptibility versus wavelength of the glass samples for different ZnO doping levels.
The optical conductivity was calculated from the following relation

\[
\sigma = \frac{\alpha \pi c}{4\pi}
\]

and is displayed in Fig 18 for the studied samples.
In Eq. (17) $\alpha$ is the absorption coefficient, $n$ is the refractive index and $c$ is the speed of light.

The Ion concentration $N_i$ was calculated using the relation:

$$N_i = \frac{x \rho}{M_w} N_A$$  \hspace{1cm} (18)

where $\rho$ is the density; $M_w$ is the molar volume; $N_A$ is the Avogadro’s number.
Knowing Ni one can derive the inter ionic distance (r) using the relation:

$$r = \left( \frac{1}{Ni} \right)^{\frac{1}{3}}$$  \hspace{1cm} (19)

Molar refraction (R) was calculated from the following relation$^{[40,41]}$:

$$R = \sum_i A_i R_i$$  \hspace{1cm} (20)
where $A_i$ is the atomic fraction of each component element, which equals the atomic concentration of each atom per mole divided by the summation of the atomic concentrations of all ions per mole. $R_i$ is the ionic refraction. A table of ionic refractions for various elements is given in Ref. [42].

The atomic concentration for the studied samples was calculated from the relation:

$$N = \frac{\rho NA}{M_w}$$  \hspace{1cm} (21)$$

and is shown in Fig 18.

**FIGURE 17**
The Phase velocity verses wavelength of the glass samples for different ZnO doping levels.

**FIGURE 18**
The Optical conductivity verses wavelength of the glass samples for different ZnO doping levels.
The ion concentration, inter ionic distance and molar refraction are listed in Table 2.

4. CONCLUSIONS

We have studied the effect of zinc oxide on the optical properties of glass based systems of the chemical composition \((65-x) \, \text{P}_2\text{O}_5 \, (25+x) \, \text{ZnO-10Na}_2\text{O}\), with \((x=10,20,30)\). XRD patterns prove the amorphous nature of the obtained samples. The molar volume and density were studied and describe the effect of the ZnO on the phosphate glass. It leads to the increasing of the density and decreasing the molar volume. The transmittance of some glass samples increases by increasing the ZnO contents. At the same time the absorbance decreases. The optical energy gap is found to decrease from 3.68 to 3.25 eV by increasing the ZnO content.

The wavelength dependence of the refractive index and extinction coefficient and some other related optical properties were also studied. The results reveal the importance of using the prepared glass system as low laser lenses and for special ultraviolet optics as well as in micro lithography equipment.

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