The Structural Study of the Ternary Zinc Magnesium Phosphate Glass

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Abstract

Background: Glass in the system (ZnO)x(MgO)100−x(P2O5)100−x (where x = 5, 10, 15, 20 mol %) were prepared by melt quenching technique. The structure of these glass systems has been investigated using FTIR spectroscopy. Objective: The IR spectra of the investigated glasses have been studied in order to understand the characteristic frequency of the vibrational chemical bonds and revealed the network structures of the phosphate glass samples. Results: The results revealed that the absorption band observed in the IR spectra composed of Q1 and Q3 phosphate units in the network glass structure. Conclusion: This study suggests that the changes in the structural of the ternary zinc magnesium phosphate glass related to the addition of Mg cation which acts as network modifier.

INTRODUCTION

Phosphate glasses have received a great deal of attention in many technologies due to their interesting properties such as lower melting temperature, low glass transition temperature (Tg), high thermal expansion coefficient, biocompatibility [14], higher electrical conductivity [11] and unusual trend with respect to their composition difference [7]. However, they typically have poor chemical durability which often limits their usefulness [3,2]. Pure vitreous phosphate is extremely hygroscopic in nature and dissolved rapidly by atmospheric moisture [5]. Thus, several studies have shown that addition of various metal oxides from alkaline, alkaline rare earth and transition group in the phosphate glasses productions improved their chemical durability [3]. The network of phosphate glasses contains a polymeric structure of tetrahedral PO4 units in which only three of the oxygen atoms can be shared with the adjacent bridge while the forth oxygen form a terminal double-bonded (DBO). The addition of metal oxides into the glass network leads a depolymerisation of P-O-P bond and creation of non-bridging oxygen (NBO’s). It has been suggested that the metal oxides provide ionic cross-linking between the NBOs of two phosphate chain and hence, increasing the bond strength and improved the mechanical and chemical durability of the glasses. P-O-M (M = Mg, Zn) bonds in the glass network are more stable towards atmospheric hydrolysis [1]. As the molar ratio of metal oxide to P2O5 increase (MO/ P2O5), the phosphate structural group passes from Q3 to Q2 to Q1 to Q0. The similar network modification occurred in silicate glass upon addition of metal oxides [11]. Later work on binary magnesium phosphate glass exhibit unusual trends in the relationship of their composition/ physical properties such as density and refractive index around the metaphosphate composition [7,12]. This anomalous behavior is related to the Mg-O coordination number (6 or 4) in phosphate structures. Magnesium ion act as network modifier in binary (MgO) (P2O5)1−x glass system over the range x = 0.45-0.60. The abrupt changes in physical properties due to the intermediate range order occurred in the phosphate network [12]. However, according to [8] work, with further addition of MgO content, these atoms tend to participate in the glass forming position. In addition, the structural roles of ZnO in phosphate glass also have been discussed by [13] work. They found that the Zn cation can act both as network modifier and network glass former. ZnO enters the network with ZnO structural unit as a glass forming oxides while octahedrally coordinated as network modifier. In the previous studies, Raman and infrared spectroscopy are among the vibrational method that frequently used for glass structural characterization [1]. In this work, the

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structure of ternary zinc magnesium phosphate glasses is studied by means of IR spectroscopy as interest to obtained further information on the structural role of addition of magnesium ions in ternary glass systems.

Methodology:
Sample Preparation:
Glasses of the (ZnO)30.(MgO)x.(P2O5)100-x system were prepared using ZnO (99.7% purity), MgO (98% purity), and P2O5 (99.9% purity) in suitable proportion. The mixtures were mixed thoroughly in a 50 cm³ alumina crucible with a 15-20 g batch. The crucible was heated in electric furnace for about 1 hour at a temperature of 673 K to remove moisture and allow the phosphate to decompose and react with other batch constituent. Then, the crucible was transferred to the second electric furnace and kept at 1473 K for 2 hour for melting process. Next, the melt were quenched between two preheated stainless steel moulds to form coin shaped glass. Lastly, the resulting glasses were annealed at about 673 K in electric furnace which was left to cool down to room temperature.

X-ray Diffraction Measurements:
The X-ray powder diffraction experiment was carried out on Brukers X-ray powder diffractometer equipped with a CuKα X-ray source and step size 0.02 in the range of 2θ angles between 10°-80°. X-ray diffraction data was used to check for possible crytallinity of the sample.

Infrared Measurements:
The vibration spectra of various glasses were obtained at room tempera
ture using KBr pellet technique in the range 400-4000 cm⁻¹ on Perkin Elmer spectrophotometer. The investigated samples were ground to fine powders and then were mixed with KBr in the ratio 1:9. The mixture was then pressed by using hydraulic pressure. The spectra were measured immediately after preparing the desired disks.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis:
Figure 1 shows the XRD pattern of CZ glasses. All the glass samples with different ternary composition shows the same peak pattern where a broad peak were detected at 2θ values around 20-40°. Thus, the glass samples were confirmed that free from any detectable crystalline phases with the absence of the sharp peak and successfully done.

Fig. 1: XRD pattern of CZ glasses.

<table>
<thead>
<tr>
<th>X</th>
<th>ν(PO₄)</th>
<th>ν₁PO₂</th>
<th>ν₃POP</th>
<th>ν₅POP</th>
<th>(O=P-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1289</td>
<td>1089</td>
<td>914</td>
<td>777</td>
<td>480</td>
</tr>
<tr>
<td>10</td>
<td>1290</td>
<td>1091</td>
<td>917</td>
<td>769</td>
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<td>20</td>
<td>1294</td>
<td>1099</td>
<td>923</td>
<td>776</td>
<td>508</td>
</tr>
</tbody>
</table>

Infrared Spectra:
The IR spectra of the ternary zinc magnesium phosphate glasses with different composition are compared in Figure 2 while their band assignments are listed in Table 1. The FTIR spectra for the glasses reveal the characteristic bands of phosphate which broadened as would be expected for the vitreous and glassy state[4]. As
seen from this figure (based on visual judgement), there were a strong broad peak around 1300cm⁻¹, a broad peak near 1100 cm⁻¹, a peak at 900 and 700 cm⁻¹, and a broad peak near 500cm⁻¹. At high frequency region, the broad bands appear at 3100cm⁻¹ and 3500cm⁻¹. There is also a band exist at lower frequency about 1600cm⁻¹.

![Infrared absorption spectra of the (ZnO)ₓ(MgO)ᵧ(P₂O₅)₁₀₀₋ₓ glass system with x = 5, 10, 15, 20 mol %](image)

**Fig. 2:** Infrared absorption spectra of the (ZnO)ₓ(MgO)ᵧ(P₂O₅)₁₀₀₋ₓ glass system with x = 5, 10, 15, 20 mol %.

Although the sample under investigation does not contain water molecule as unit in the network, but the nature of phosphate glasses is hygroscopic where it would absorb moisture from the surrounding. The appearance of IR band belonging to the H₂O molecules in the structure are shown at high frequency regions. The absorption band of hydroxyl or water groups was revealed at 3000-3600 cm⁻¹. While, a medium band at about 1600 cm⁻¹ can be attribute to the O-H bending vibration.

The strong band observed near 1300 cm⁻¹ was belong to the characteristic of P=O. Previous study has reported that the band found in the frequency range 1230-1390 cm⁻¹ was assigned to the stretching vibration of doubly bonded oxygen. A general view of this band is that it becomes smaller as the MgO content was increased. According to [12] work, this may indicate a decrease in the double bond character. It is also observed that the wavenumber increases with increasing MgO content and shift toward lower wavenumber with changing from ultraphosphate to metaphosphate composition. It is concluded that when investigated samples contained MgO < 20 mol% with fixed 30 mol% ZnO content, magnesium ions act as a network modifier. MgO leads breakdown of some terminal bonds (P=O) and decrease the bond strength. Thus, peak centre is shifted towards lower wavenumber as observed [11]. According to Doweidar [2] work, the assignment of the IR absorption band for the studied glasses is similar to the reported in the literature for different alkali phosphate glasses.

The band near 1090-1100 cm⁻¹ is assigned to asymmetric stretching modes of the two NBO atoms bonded to phosphorus atoms, O-P-O groups or (PO₂)asym. The (PO₂) groups are characteristics of Q₂ unit in phosphate tetrahedral. The band intensity was increase with increasing MgO content due to the increase of Q₂ units. Thus, it shown that the phosphate linkages were shortened as Mg content was increase. However, previous study reported by (Marzouk et al., 2011), the asymmetric stretching vibration of the metaphosphate group, (PO₃) is in the range of 1120-1080 cm⁻¹. Therefore, the (PO₃)asym which is characteristics of Q₁ unit could interfere with the band in the present spectra.

The band appears in the range of 914-920 cm⁻¹ was ascribed to the asymmetric stretching band of P-O-P linkages. The band was shift to higher frequency as the MgO increases. Larger wavenumber is a result of the smaller P-O-P bond angle. While, smaller bond angle were results from shorter phosphate linkages or smaller metal cation size [6]. Thus, depolymerisation of phosphate glass structure had shift the frequency of the IR band. While, the weak absorption band around 760 cm⁻¹ is due to the symmetric stretching vibration of P-O-P linkages. The asymmetric and symmetric stretching vibrations of (P-O-P) linkages observed in the spectra are characteristics of Q₃ and Q₂ groups.

The absorption band in the low frequency region, 470-600 cm⁻¹ is assigned to the harmonics of bending vibration of O=P-O linkages. It has been reported that this band appears in most binary and ternary glasses (Doweidar et al., 2005). On the other hand, according to [9] work concluded that vibration of Zn-O may appear above 400 cm⁻¹. Thus, we can concluded here that this band may superimpose with or mask the vibration of O=P-O linkage [2].
Conclusion:
Glasses of the \((\text{ZnO})_{30}.(\text{MgO})_{x}.(\text{P2O5})_{100-x}\) system prepared by melt quenching technique and their structure was studied by X-ray diffraction and IR spectroscopy. It was found that introduction of metal oxides in phosphate glass induces the creation of non bridging oxygen ions and shorter linkages. The IR spectra of those glasses indicate that the arrangements of the network structural units are affected by the addition of metal oxides. Increasing of \(\text{MgO}\) content leads to a breakdown of double bonded oxygen in phosphate tetrahedral. All the symmetric and asymmetric stretching vibration of \(\text{POP}\) and \(\text{PO}_2\) observed in the spectra are characteristics of \(Q_3\) and \(Q_2\) groups.

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REFERENCES