

Structural Studies on Ag₂O-P₂O₅ Glasses

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Abstract

Silver phosphate glasses of general formula $x\text{Ag}_2\text{O}\cdot(100 - x)\text{P}_2\text{O}_5$ have been investigated over compositional range from $x = 40$ to 62.5 mol%. The local structure around phosphorus atom has been studied via ³¹P nuclear magnetic resonance. The distribution of $[\text{PO}_4]_n\text{Q}^n$ species as a function of composition has been shown to slightly deviate from the simple binary alkali phosphate model. An anomalous behavior has been recorded and interpreted in terms of mixed ring-chain effect in metaphosphate composition. The splitting of NMR spectra into sub resonances is assigned to different binding sites characterizing Q¹ ring and Q¹ chain structure. Higher Ag₂O concentration (≥50 mol%) leads to formation of phosphate groups with specific resonance peaks which are mainly related to pyro and orthophosphate species. The rate of change of the chemical shift of the ³¹P NMR depends on the bond type, which in turn reflects the extent of double bonding between phosphorus and oxygen atoms. Increasing concentration of Q⁰ with increasing Ag₂O content leads to decreasing quantities of bridging and double bonds. As a consequence, specific symmetric resonance peak of higher intensity and chemical shift (Q⁰) is a feature of silver rich glasses (orthophosphate). The latter species is therefore proposed to compose of separated membered rings, which cause deshielding of phosphate units. XRD and EDP studies have shown that, amorphous phosphate network is the dominant structure of glasses containing ≤ 55 mol% Ag₂O. Some ordered and well crystallized phases are formed at higher Ag₂O concentration. Increasing non-bridging oxygen atoms is shown to have the main effect on crystallization behavior. Orthophosphate composition is the most crystalline one among the other compositions (ultra, meta- and pyro-phosphate). Presence of orthophosphate species which typically contains highest concentration from isolated Q⁰ units is the main reason for building up crystalline Ag₃PO₄ phosphate phase.

Keywords

Nuclear Magnetic Resonance, Chemical Shift, Phosphate Species, Orthophosphates

1. Introduction

It was known that P_2O_5 consists of a three dimensional (3-D) network of trigonally connected tetrahedral PO_4 units with a $P = O$ unit [1] [2] [3] [4]. Depending on the number of bridging oxygen atoms in Q^n species ($n = 3, 2, 1, 0$), the phosphate tetrahedral units can be described by containing high concentration of Q^3 species in glasses of lower modifier content [2] [3] [4] [5]. Addition of modifier oxide degrades the 3-D network through generation of nonbridging oxygens (NBO). Continuous increasing of fraction of NBO with increasing modifier oxide was interpreted in terms of an increasing long-chain PO_2 groups in the glass [2] [3] [6] [7] [8] [9] [10]. This mechanism causes a structural transition from a 3-D network of interconnected PO_4 groups to a 1-D chain structure of intermediate-range order. This denotes a degradation and transformation of a fully polymerized neutral unit (Q^3) of extremely high shielded structure to new phosphate units ($Q^2 - Q^0$) of higher NBO concentration. Specifically, Q^2 is based on chains and rings and it has one negative charge. Q^1 means two tetrahedral units connected by a corner. Finally, Q^0 is referred to isolated and less shielded phosphate tetrahedral units with three negative charges.

The structure of phosphate glasses strongly depends on specific structural factor namely R which represents modifier (M) to phosphor (P) ratio in the glass composition [10] [11] [12]. The metaphosphate (Q^3) glasses have relatively low R values (<1). The pyrophosphate glasses have intermediate R (~ 1). This composition is consisting of Q^1 as the major structural units. The orthophosphate glasses typically have the highest R (>1) and contain isolated Q^0 units.

Incorporation of metal oxide or alkali oxide in phosphate glasses [10] [13] [14] [15] is commonly consumed in breaking down of the P-O-P linkages and formation of P-OM (M: metal) bonds. The prevalence of particular Q^n unit depends on the nature and concentration of the cations present in the glass [15] [16].

Many of previous studies were carried out on phosphate glasses modified by alkali or alkaline earth oxides in the region of ultra, meta and pyrophosphate [2] [3] [17] [18] [19]. On the other hand, limited reports on modification by Ag_2O , particularly in pyro- and orthophosphate regions, have been considered before. Therefore, this work is devoted to shed light on structural role of Ag_2O in enriched modified glasses. In addition, we make use of the advantage of the high resolution modern NMR spectroscopy to report on anomalous behavior of metaphosphate glass, which to our knowledge, has not been reported before.

2. Experimental Work

Binary silver phosphate glasses in the system, $xAg_2O \cdot (100 - x)P_2O_5$, where $40 \leq x \leq 62.5$ mol% have been prepared by mixing $AgNO_3$, and $NH_4H_2PO_4$ as starting raw materials. $NH_4H_2PO_4$ was heated in a porcelain crucible at $300^\circ C$ for 30 min in order to evaporate ammonia and water. Then $AgNO_3$ was added and the mixture was melted at temperature between $900^\circ C$ and $1100^\circ C$, depending on the composition. The melt was swirled severally to attain homogeneity. The glass

samples were obtained by pouring the melt onto flat plate. The glasses were kept in a desiccator until required.

X-ray diffraction (XRD) was used to examine the amorphous nature of the samples. The patterns were obtained by using a Burker D8 Advance powder XRD instrument. It is fitted with a Vantech super speed position sensitive detector and a Cu K α X-ray tube with a Gobel mirror. Measurements were made over the range 4° to 70° in 2 θ scale.

The internal micro structural features of glass samples were investigated using a transmission electron microscope TEM model JEOL-JEM-2100, Japan equipped (EDP) with an electron diffraction pattern unit. TEM investigations were performed at an electron acceleration voltage of 200 Kv.

Infrared spectra of the glasses were measured by a Mattson 5000 FTIR spectrometer in the range 400 and 2000 cm⁻¹. The measurements were carried out on powdered samples which is mixed with KBr (1 wt%), and then compressing the mixtures to form pellets for measurements.

The distribution of Qⁿ of phosphate unit obtained from ³¹P NMR spectra of selected glasses (x = 40, 50, and 62.5 mol%). The investigations were carried out using JEOL RESONANCE GSX-500 High Resolution Solid state MAS NMR spectrometer. The spectra were obtained at high external magnetic field (11.747T), at a frequency of 160.47 MHz and spinning rate of 40 MHz.

3. Results and Discussions

X-ray diffraction patterns of glasses in xAg₂O·(100-x)P₂O₅ system are shown in **Figure 1** and **Figure 2**. Broad pattern characterizes vitreous nature of the invest-

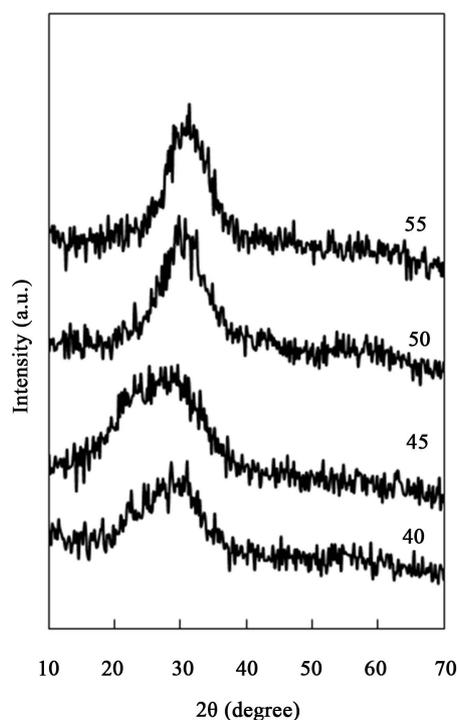


Figure 1. XRD patterns of glasses containing 40, 45, 50 and 55 mol% Ag₂O.

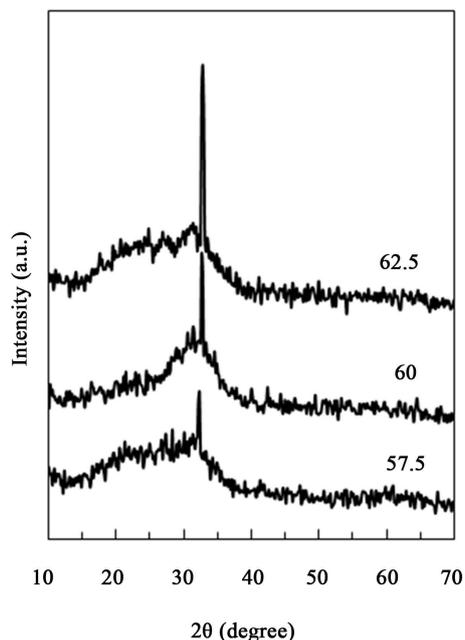


Figure 2. XRD patterns of glasses containing 57.5, 60 and 62.5 mol% Ag_2O .

tigated glass is obviously observed between $2\theta = 18^\circ - 38^\circ$. This amorphous nature is dominated in glasses of 40, 45, 50 and 55 mol% Ag_2O , **Figure 1**. On the other hand, significant changes were observed in Ag_2O rich glasses (>55 mol% Ag_2O). XRD patterns which are shown in **Figure 2** contain sharp diffraction peaks superimposed on the wide hump of the glassy network. Specifically, X-ray diffraction patterns of the sample containing 57.5, 60 and 62.5 mol% Ag_2O are characterized by presence of the intense sharp peak centered at $2\theta = 31.9^\circ$. Presence of these diffraction lines may indicate formation of more ordered species that characterize metaphosphate (Ag_2PO_3), pyrophosphate $\text{Ag}_4\text{P}_2\text{O}_7$ and orthophosphate Ag_3PO_4 units distributed in the main phosphate network [14] [15] [16]. $\text{Ag}_4\text{P}_2\text{O}_7$ is the most dominant phase found particularly in pyrophosphate glass network containing 57.5 mol% Ag_2O . X-ray diffraction data obtained for the resulting glass were found to be fitted with those reported for $\text{Ag}_4\text{P}_2\text{O}_7$ [JCPDS Cards File No. 11-0637]. Increasing intensity of the sharp peak with increasing Ag_2O may reflect an important feature for the studied glasses. This feature could be attributed to formation of ($\text{Ag}_4\text{P}_2\text{O}_7$) pyrophosphate and Ag_3PO_4 orthophosphate crystalline phases [JCPDS Cards File No. 89-7399]. The principal peak at 31.9° (triplet) for reflections (211), (112) and (300) is the main diffraction pattern.

Additional evidence for the formation of an $\text{Ag}_4\text{P}_2\text{O}_7$ and Ag_3PO_4 crystalline phases in silver rich glasses was also found by examination through TEM and EDP (**Figure 3**). It appears from EDP that there is a certain degree of crystallinity in glass of 62.5 mol% Ag_2O . The feature appeared in EDP is in agreement with that obtained from XRD of the same glass, since sharp single diffraction is clearly evidenced from both XRD and EDP patterns, **Figure 3(a)**. The remain glass network seems to be in amorphous state as represented by EDP (b), **Figure 3**.

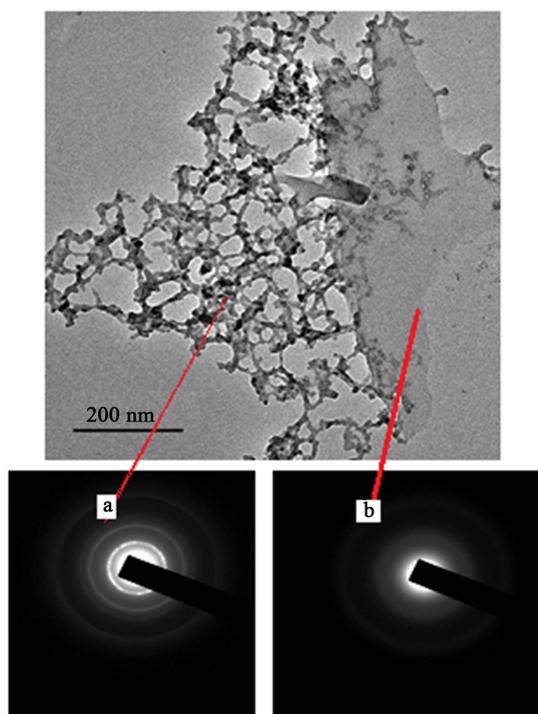


Figure 3. TEM and EDP of Ag₂O rich glass (62.5 mol% Ag₂O).

Formation of high concentration of non-bridging oxygen (NBO) in silver rich glasses are considered as the main reason for building crystallized phosphate species as resolved by both XRD and TEM. When the glass network is constructed from symmetric type of units such as orthophosphate (in 62.5 Ag₂O glass), symmetric and ordered phase enriched with NBO species are also constructed [11] [16]. This consideration is clearly verified from both XRD and EDP of glass containing 62.5 mol% Ag₂O, since one resolved XRD peak (Figure 2) and single diffraction of electron patterns (Figure 3(a)) are clearly evidenced to represent Q⁰ in orthophosphate Ag₃PO₄ crystalline units.

³¹P MAS-NMR Spectroscopy

NMR spectra of phosphorus nuclei are very complicated due to several interconnected side bands which in some cases dilute the real spectra [15] [20]. Present NMR technique has succeeded in dealing with a problem or difficulty which comes from signal of side bands. In this regard, high spinning frequency (21 kHz) and high external magnetic field (11.74 T) are both carefully applied during time scan of measurement. Therefore, side bands free NMR spectra of isotropic chemical shift are simply obtained. Then anisotropic distribution of both side bands and chemical shift are not probable in present study. Only real isotropic chemical shift of NMR spectra free from side bands is obtained.

Figure 4 shows ³¹P NMR spectra of glasses containing 40, 50 and 62.5 mol% Ag₂O. These spectra represent glasses in selected compositions which are found in metaphosphate (40 mol%), pyrophosphate (50 mol%) and orthophosphate (62.5 mol%) extremes. It can be shown from Figure 4 and Table 1 that there are

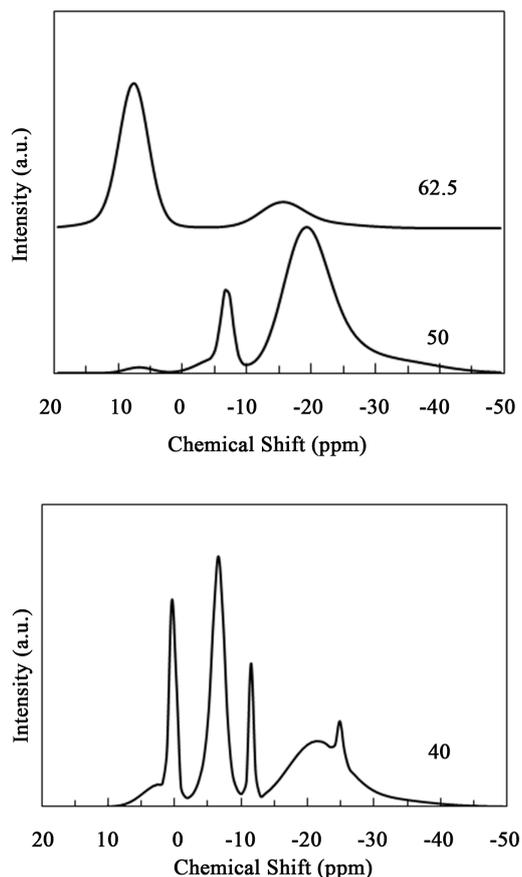


Figure 4. ^{31}P NMR spectra of binary $x\text{Ag}_2\text{O}\cdot(100 - x)\text{P}_2\text{O}_5$ glasses ($x = 40, 50$ and 62.5 mol%).

Table 1. The approximate chemical shift ranges for different types of phosphate tetrahedra in silver phosphate glasses.

Composition mol%	Q^3 ppm	Area %	Q^2 ppm	Area %	Q^1 ppm	Area %	Q^0 ppm	Area %
					-11.5		-	0
$40\text{Ag}_2\text{O}-60\text{P}_2\text{O}_5$	-24.9	9.6	-21.25	31.5	-6.6	58.8	-	0
					0.25		-	0
$50\text{Ag}_2\text{O}-50\text{P}_2\text{O}_5$	-	-	-18.8	84.18	-6.87	14.19	6.75	1.6
$62.5\text{Ag}_2\text{O}-37.5\text{P}_2\text{O}_5$	-	-	-19.12	9.34	-15.4	14.58	7.57	76.07

apparent differences in peak position, intensity and relative area under the resonance spectra during transition from one composition to another. Significant changes in these parameters are observed with increasing $\text{Ag}_2\text{O}/\text{P}_2\text{O}_5$ molar ratio. The position of peaks are shown to move toward less shielded phosphate units, since spectra of less negative chemical shift are observed with increasing Ag_2O concentrations. Both type and concentration of phosphate different species can be defined by analyzing the resonance spectra via band integration as well as deconvolution. **Figure 5** shows deconvoluted NMR spectra of glasses containing 50 and 62.5 mol% Ag_2O , as examples.

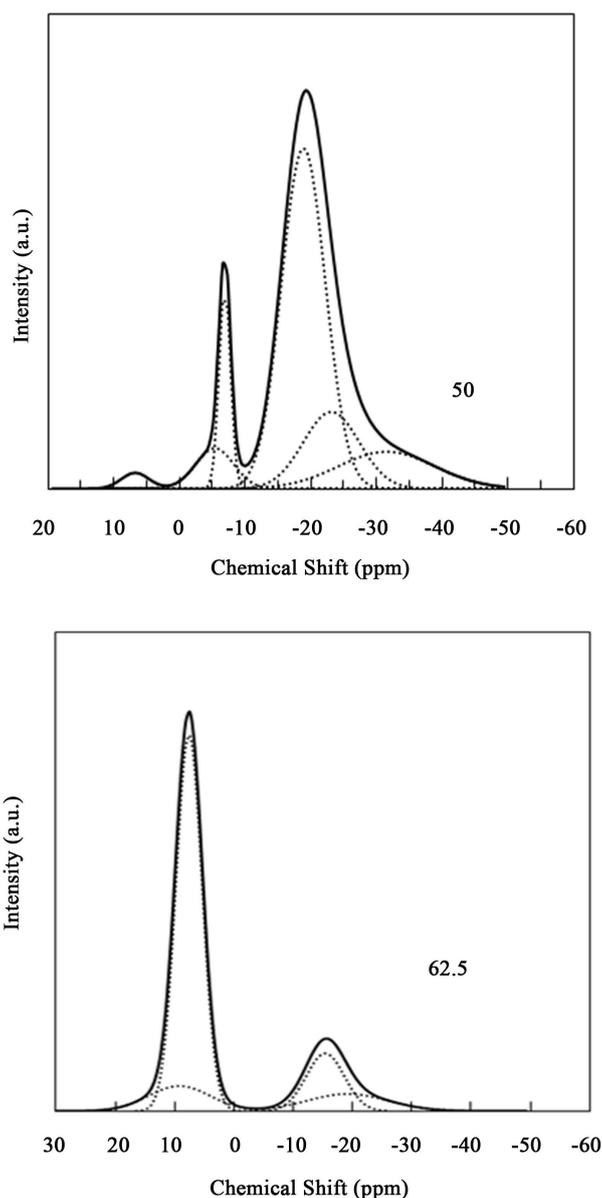


Figure 5. Deconvoluted NMR spectra of 50 and 62.5 mol% Ag_2O glasses.

Based on analyzed data, **Table 1**, mixtures composed of few ultraphosphate and relatively high concentration from metaphosphate species are the main distributed units in matrix of glass of 40 mol% Ag_2O . In this case, PO_4 groups with limited quantity of Q^3 and dominant Q^2 and Q^1 types are the structure species which build up metaphosphate phase. On the other hand, phosphate units containing mixture of Q^2 and (Q^1) are the representative building units for pyrophosphate composition (50 mol% Ag_2O). Finally NMR spectra of orthophosphate network reveal that both Q^1 and Q^0 are the main components of orthophosphate composition. The latter type is dominant feature of crystallization of glass containing 62.5 mol% silver oxide.

Generally, three resolved isotropic resonance line spectra were appeared between 0 ppm and -12 ppm for glass of 40 mol% Ag_2O . The resonance at 0, -7

and -12 ppm are assigned to composite signals from the three phosphorus nuclei of the mixed meta and pyrophosphate groups (formally non-equivalent but accidentally having degenerate chemical shifts). One of the resonance lines is due to Q^1 in ring site, the other in chain site and the third characterized units of double bond and or P-OH groups [19] [20] [21] [22]. On the other hand, based on NMR observations, orthophosphates and end groups of polyphosphates are not probable to be formed in this glass (40 mol%). This is because they resonate a different frequency (more chemical shift) than chain containing meta phosphates species [22]. Based on NMR chemical shift, it can clearly suggest that a change in hydration state has also to be involved [21] [22]. For example, anhydrous silver pyrophosphate resonates around 1 ppm, while the signal from pyrophosphate containing dihydrogen or P-OH bonds is observed at -8 to -12 ppm. It can be seen from **Figure 3** and **Table 1** that positive chemical shift differences of more than 8 ppm to higher frequency are observed on going from central resonance of sample containing 40 mol% Ag_2O to end resonance of glass of 62.5 mol% Ag_2O .

It was confirmed previously that changes in modifier to phosphorus ratio has an effective influence on both structure and properties of glasses [14] [21] [22]. For the values $R = 0, 1, 2,$ and 3 , only specific type of structural unit can exist as the main structure; Q^3, Q^2, Q^1 and Q^0 unit, respectively. The NMR spectra shown in **Figure 4** are correlated to great extent with values of R . For the region $0 < R < 1$ (40 mol% Ag_2O , $R = 0.67$ as an example), only a mixture of Q^3 and Q^2 units are found as metaphosphate species. For the region $R = 1$ (50 mol% Ag_2O), only Q^2 and Q^1 and limited concentration from Q^0 units are found. In this situation, the concentration of Q^2 is still higher than that of $Q^1 + Q^0$. For the region of $R > 1$ (62.5 mol% Ag_2O , $R = 1.6$), Q^0 and Q^1 types are found and there is no any traces from Q^2 can be detected. Specifically, Q^0 is the dominant with relative concentration of (0.79) which means that 79% from the total Q^n is found in Q^0 . This high percentage of Q^0 lent support that major phosphate units are found in orthophosphate type [23]. As a consequence, respectively, metaphosphates with no (Q^0), pyrophosphate with limited Q^0 and orthophosphate with dominant concentration of (Q^0) are the main species in the investigated glasses of 40, 50 and 62.5 mol% Ag_2O . Because of the high concentration of NBO in glass of 62.5 mol% Ag_2O , silver orthophosphate Ag_3PO_4 species are the main crystal phase which is additionally identified by XRD and EDP pattern of this glass.

As discussed, Ag_3PO_4 structural species are shared with significant higher relative concentration (79%) in glass formation. At this composition, the phosphatetetrahedral units containing four NBO's and no BO's are formed in glass of 62.5 mol% Ag_2O . Any further addition of modifier to this composition would result in limiting depolymerization of the phosphate network. Therefore the 62.5 mol% Ag_2O is the maximum limit of glass modification, beside it contains some of specific crystallized species from silver orthophosphate Ag_3PO_4 . These peculiarities may lead one to recommend some of the studied glasses to be used in the field of biomedical applications [24] [25]. This may because, it contains

Ag_3PO_4 apatite phase which play the role of bioactivity. Surprising, this apatite phase is constructed in its crystalline counterpart which would in turns promotes their interaction with living cells. In addition, silver in apatite phase is important as antibacterial and antifungal agent, particularly when is used in dental applications.

4. FTIR Spectroscopy

The movement from a high cross-linked Q^3 structure, to chain-like Q^2 network, to depolymerized Q^1/Q^0 glasses with increasing Ag_2O concentration can be monitored by a variety of other spectroscopic probes [22]-[27]. In pure vitreous P_2O_5 and in glass of high contents of P_2O_5 , the basic structure entities are PO_4 tetrahedra forming predominantly three-dimensional network (3D) with Q^3 type of structural units [7] [9]. Addition of modifier, part of 3D-network would depolymerize and 2D chain structure is simultaneously formed (Q^2 structural units). NMR Data of present glasses indicated that, the fraction of 3D network structure decreases quickly and chain structure created by Q^2 units dominates to the network of the glass containing 50 mol% Ag_2O . More addition of Ag_2O at expense of P_2O_5 the two dimensional chain structure decreases and ring like structure containing mainly Q^1 and Q^0 units are formed. Based on this information, the following observations can be extracted from FTIR spectra upon increasing Ag_2O content. From **Figure 6** it can observe that:

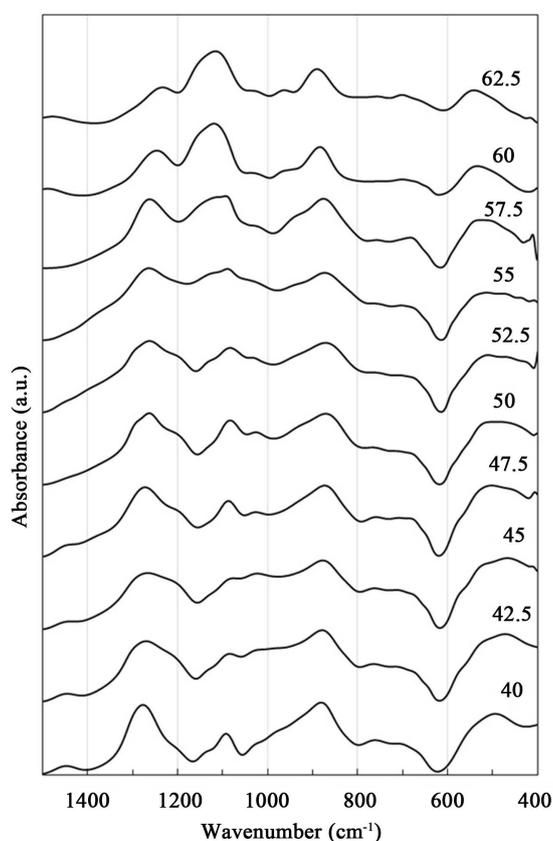


Figure 6. FTIR spectra of $x\text{Ag}_2\text{O}(100 - x)\text{P}_2\text{O}_5$ glasses.

1. The intensity and area of the band centered at about 1290 cm^{-1} , attributed to the absorption of $\text{P}=\text{O}$ and (PO_2) in Q^2 chains [10] are both decreased quickly with increasing Ag_2O content. This leads that the long chain is reduced, and thus the structure of phosphate glasses is composed from shorter chain of Q^1 and/or isolated tetrahedral (Q^0) structural unit [9] [27] [29].
2. The wide humplies in the region between $800 - 1200\text{ cm}^{-1}$ becomes narrower and shifted to higher wavenumber. The intensity and band area are both changed with increasing Ag_2O concentration. For the last composition, its centering at (1140 cm^{-1}) indicates increasing number of Q^0 and Q^1 units [28] [30].
3. The area and intensity of the broad band in the region $620 - 830\text{ cm}^{-1}$ showed decreasing trends and its center (ca 680 cm^{-1}) becomes narrower. It is referred to the stretching vibration of oxygen atoms in P-O-P bridges [29] [30]. Decreasing area of this band leads to decreasing concentration of bridging oxygen linked between two phosphorus ions. This leads to increasing NBO in phosphate network.

Both NMR and FTIR data imply mainly considerable fragments or depolymerization of the phosphate network with an increase of Ag_2O content. This is in harmony with the work presented by Hoppe [31], since it was concluded that the network depolymerization is the dominant principle in modified phosphate glasses.

We consider that Ag_2O as a glass modifier enters the glass by breaking up the P-O-P bonds and may introduce coordination defects along with NBO atoms in the studied glasses. This leads that the long chain is lowered, and thus the structure of P_2O_5 glasses would involve shorter chain of Q^1 and/or isolated tetrahedral (Q^0) structural unit [26] [30] [31].

The areas of absorbance spectra of the “nonbridging” in Q^2 stretching mode (Ca 1300 cm^{-1}) decreases upon increasing Ag_2O contents reaching its minimum value at 62.5 mol% Ag_2O . This decreasing behavior may lead to progressive depolymerization of the phosphate network, as well as the increase in the average bond length of P-non-bridging oxygens presented by the band between 950 and 1200 cm^{-1} . **Figure 7** presents a correlation between different Q^n upon Ag_2O addition. This behavior showed some few increment in Q^2 species with increasing Ag_2O concentration then it abruptly decreases. A reverse behavior is seen in which it can be realized that the total NBO concentration in Q^1 and Q^0 increases at the expense of Q^2 structural species. The above observation is greatly correlated with that derived from both NMR and XRD results which are discussed above, since a decrease in the average p-bond character of the P-O-P upon increasing Ag_2O concentration is additionally confirmed.

5. Conclusion

Different phosphate glasses in meta, pyro and orthophosphate compositions have been studied by distinguished techniques. The structure of silver phosphate is slightly deviated from the alkali phosphate. This is considered due to the

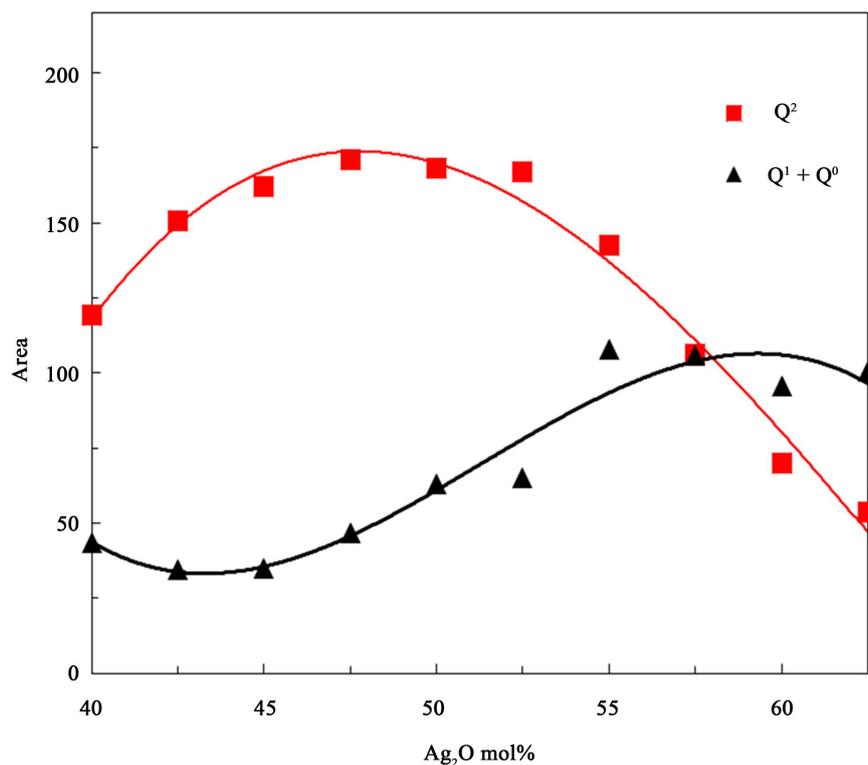


Figure 7. Representative relation between determined area of both Q^2 and $(Q^1 + Q^0)$ via Ag_2O content.

difference in field strength between silver and alkali ion. X-ray and electron diffraction pattern of metaphosphate composition revealed the amorphous nature of investigated network. Pyro and orthophosphates are documented to contain some crystallized species which are correlated with increasing NBO concentration. Using the advantage of the more recent NMR spectroscopy (11.74 T), the anomalous feature found in silver metaphosphate composition has been explored for first time. Regarding this unique feature, no previous studies have been reported.³¹P NMR spectra of the studied silver metaphosphate composition showed three splitting peaks of the same unit of phosphate species (Q^1) which was not evidenced in alkali metaphosphate. The diverse of spectra is diminished with increasing Ag_2O to P_2O_5 ratio and well resolved specific peaks characterized Q^1 and Q^0 are obtained. FTIR analyzed data have demonstrated the inverse relation between quantity of NBO in Q^2 and in other lower species ($Q^1 + Q^0$). NBO species reach their highest concentration in glass of 62.5 mol% Ag_2O . The concentration of NBO in this situation is high enough to construct Ag_3PO_4 apatite units which promote the biomedical application of the glass under investigation.

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