Original Article

Glass-forming compositions and physicochemical properties of degradable phosphate and silver-doped phosphate glasses in the P₂O₅–CaO–Na₂O–Ag₂O system

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ABSTRACT

Phosphate and silver-doped phosphate glasses are potential candidates for use as degradable biomaterials and as antibacterial materials as well. The present investigation explores the glass-forming compositions (GFC), physical properties and degradation rates of both phosphate glasses in the P₂O₅–CaO–Na₂O ternary system and silver-phosphate glasses derived from it by introducing Ag₂O in replacement of Na₂O. The glasses were prepared using the traditional melting-annealing technique applied in glass making industry. Bulk glasses were prepared without using any special precautions or specific conditions (contrary to previous studies) which can prevent crystallization or segregation of silver particles from the melt. A wide glass formation domain with ≥40 mol% P₂O₅ was determined in the ternary P₂O₅–CaO–Na₂O system. However, up on Ag₂O addition, the amount of Ag₂O that can exist in the glass and remains amorphous was limited to 2 mol% as ensured from X-ray diffraction (XRD). The compositions with ≥60 mol% P₂O₅ and 0.5, 1 or 2 mol% Ag₂O formed transparent and colorless silver phosphate glasses. Whereas, the compositions with ≤55 mol% P₂O₅ did not form glasses and showed immediate partial crystallization and separation of silver particles. Thereafter, the structure of representative glasses was studied by FT-IR and UV–vis absorption spectroscopy. Finally, as silver ions function as antibacterial metal ions, the amounts of silver ions released from silver phosphate glasses were measured by atomic absorption spectrometry (AAS).

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1. Introduction

Dissolution studies conducted on various types of melt-derived glasses in aqueous solutions have led to the development of degradable glasses which can show gradual lixiviation of their constituents [1–4]. These degradable glasses are based on several types of glass compositions such as phosphate and borate glasses [5–7]. The phosphate glasses in the P2O5–CaO–Na2O system, in which P2O5 acts as the network former, are typical example of degradable glasses. Interestingly, these glasses can be prepared by melting together precursors of phosphorous, calcium and sodium oxides at relatively low temperatures between 800 and 1200 °C [5]. Furthermore, their chemical composition can be tuned to obtain glasses with different degradation rates suitable to the targeted end application. Therefore, bioreadsorbable phosphate glasses containing phosphorous and calcium in their composition are potential candidates as biomaterials for bone regeneration [8–11]. Moreover, in vitro and in vivo studies revealed low cytotoxicity and good biocompatibility of such glasses in hard and soft tissues [12,13].

Degradable phosphate glasses also offer interesting features as reinforcement phases for composite biomaterials [14–16] and drug delivery systems [17]. Also as fibers for potential use in tissue engineering particularly for any tissue with a medium to high anisotropy such as muscle and ligament [11,18–21]. Furthermore, silver-containing phosphate glasses are used as antibacterial materials [20,22] and recently as favorable matrices for laser writing in photonics [23,24]. Indeed, there is much recent interest in silver-containing glasses for use in technological applications e.g. laser optical data recording and photonics [25–28]. However, the preparation of melt-derived silver-containing glasses is not an easy task. Actually, silver oxide has limited solubility in glass melts and it may require melting under oxidizing conditions [29–31]. The oxidative state in glass melt could prevent reduction of the Ag+ ions to metallic Ag0 atoms at elevated temperatures [32]. Hence, silver-containing silicate glasses are mostly produced at low temperatures by sol–gel method [33–36]. However, it is much desirable to produce silver-containing glasses using easily scalable and cost effective method. Meanwhile, compared to silicate glasses, phosphate and borate glasses have better ability to accommodate heavy metal oxides and remain amorphous [37,38]. Nevertheless, the amounts that can be incorporated depend on the glass composition and the nature of the heavy metal oxide [39]. Thus, determining new silver containing melt-derived glass-forming compositions and studying their physicochemical properties are highly attractive for their possible use in biomedical applications.

To this end, herein we determined and discussed glass-forming compositions and the Ag2O contents that could exist in the system P2O5–CaO–Na2O using the traditional melting–annealing method applied in glass making industry. Therefore, bulk glasses were prepared without using any special conditions or specific precautions (such as rapid quenching, rapid melt-pressing or melting in oxidative environment) that were used in previous studies [40–43]. Such conditions are utilized to prevent glass crystallization and/or segregation of metallic silver particles from the glass melt. Finally, some of the prepared glasses were investigated in terms of their physical properties, degradation rates, silver ions release rates and glass structure.

2. Materials and methods

2.1. Preparation and melting of batches

The precursors used in each batch preparation were of pure grade. P2O5 was introduced as NH4H2PO4 (99.0% Merck), CaO as CaCO3 (99.5% SRL), sodium oxide (Na2O) as Na2CO3 (99.5% SRL) and Ag2O as AgNO3 (99.9% SRL). The appropriate amounts of batch constituents equivalent to 50 g were accurately weighed, thoroughly mixed and then transferred to porcelain crucibles. The chemical composition (mol%) of the prepared batches are given in Fig. 1. The batches were initially heated at about 350–550 °C for removal of byproducts (e.g. H2O, NH3, NO2, and CO2) and minimizing the evaporation tendency of P2O5. The batches were then melted in the range of 800–1200 °C using an electrically heated furnace (Carbolite CWF1200 electric furnace). The melting time was continued for <2 h depending upon the chemical composition. The melt was then cast on a preheated stainless steel plate in the form of rectangular rods which subsequently annealed in a muffle furnace maintained at temperature in the range 200–450 °C for 20 min. The glass samples were then left overnight to cool slowly to room temperature and then kept in a desiccator for further uses.

2.2. Density measurements

The density (\( \rho \)) values were determined on bulk glasses by the Archimedes’s method using o-xylene as buoyant liquid. The measurements were conducted according to the standard test method for density of glass by buoyancy (ASTM C693). The glass sample mass was measured both in air (\( M_a \)) and after immersion in o-xylene (\( M_i \)). The density was calculated from the following equation: \( \rho = M_i / (M_a - M_i) \times 0.86 \), 0.86 is the density of o-xylene (g/cm³). Measurements of masses of three different glass pieces were performed for each glass sample and the average density was calculated. The molar volume \( (V_m) \) of each glass composition was calculated from the corresponding value of density using the formula: \( V_m = \Sigma c_i M_i / \rho \), \( c_i \) is the molar fraction and \( M_i \) is the molar mass of the \( i \)-th component.

2.3. Glass degradation and silver ions release

The degradation of powdered phosphate and silver-doped phosphate glasses (particle size: 0.3–0.5 mm) was performed in aqueous medium at 37 °C. The degraded amounts were calculated from the measurements of the initial (before test) and final (after test) dry weights. The dissolution rates of glasses were obtained from the slope of the linear fit of the degradation plot. Furthermore, the release of silver ions during the degradation of silver-doped phosphate glasses was determined by atomic absorption spectrometer (AAS, GBC Avanta \( \Sigma \), Australia).
2.4. Glass structure characterization

The amorphous structure of silver-doped phosphate glasses was confirmed by powder X-ray diffraction (XRD, Bruker D8 Advance) using Cu Kα radiation (λ = 0.15418 nm) generated at 40 kV and 40 mA. Scans were performed with a step size of 0.02° and a step time of 0.4 s. FT-IR absorption measurements (400–4000 cm⁻¹) were also performed on powdered silver-doped phosphate glass samples contained in KBr discs using an infrared spectrometer (Jasco FT-IR 6100). Finally, UV–vis absorption spectra (200–1000 nm) of polished silver-doped phosphate glass samples (3 cm × 1 cm × 2 mm) were obtained using UV–vis spectrometer (T80+, PG instruments Ltd.).

3. Results

The glass forming compositions and glass forming domains in P₂O₅–CaO–Na₂O (named here as FCN) and P₂O₅–CaO–Na₂O–Ag₂O (named here as PCNA) systems are shown in Fig. 1. The results of glasses preparation in the PCN system revealed that the compositions with ≥40 mol% P₂O₅ formed clear, transparent and homogenous glasses. However, the compositions with 35 mol% P₂O₅, exhibited spontaneous crystallization on increasing CaO content and it was not possible to obtain fully transparent glasses. Therefore, the glass formation domain in the PCN system started at contents of P₂O₅ ≥ 40 mol%. Meanwhile, the results of glasses preparation in the PCNA system showed that the compositions with ≥65 mol% P₂O₅ and 0.5, 1 or 2 mol% Ag₂O formed transparent and colorless silver phosphate glasses. However, it was not possible to prepare glasses form the compositions with ≤55 mol% P₂O₅. These compositions showed immediate partial crystallization and separation of metallic silver particles. Off note, from the compositions with 60 mol% P₂O₅ and 2 mol% Ag₂O, only three compositions (namely I₅Ag₂, I₄Ag₂ and I₃Ag₂) formed transparent and colorless silver phosphate glasses. Only the I₁Ag₂ has very faint yellow color. The preparation of homogenous silver phosphate glasses form compositions I₂Ag₂, I₁Ag₂ and I₄Ag₂ (located inside rectangular as shown in Fig. 1(b)) was not possible because of metallic silver separation. Therefore, a glass formation domain with ≥60 mol% P₂O₅ and 0.5–2 mol% Ag₂O was determined in the PCNA system.

The measured densities (summarized in Table 1) and the calculated molar volumes of all glasses prepared in the PCN system are shown in Fig. 2. The densities varied in the range from 2.38 to 2.71 g/cm³, whereas the molar volumes changed from 49.55 to 34.92 cm³/mol. Fig. 2(a) shows that the replacement of Na₂O by CaO at fixed P₂O₅ contents resulted in an increase in density while, the molar volume changes inversely to the density behavior (Fig. 2(b)). The densities and molar volumes of the Ag₂O-doped glasses are depicted in Fig. 3. The densities changed from 2.41 to 2.61 g/cm³, whereas the molar volumes varied from 49.098 to 42.81 cm³/mol. Fig. 3(a)–(c) revealed that the replacement of Na₂O by Ag₂O (or where P₂O₅ was replaced by Ag₂O in the binary glass, G₇) caused almost linear increase in density and the glasses with higher amounts of Ag₂O possess higher densities. Meanwhile, the increase in Ag₂O contents resulted in decreased molar volumes as displayed in Fig. 3(d)–(f).

The degradation of phosphate glasses containing 40–60 mol% of P₂O₅ are illustrated in Fig. 4. The glasses showed increased degradation degrees (represented by weight loss) with increasing degradation time in aqueous medium as depicted in Fig. 4(a)–(h). Furthermore, the degradation rates (summarized in Table 1) were found to decrease with increasing the replacement of Na₂O by CaO at fixed P₂O₅ contents as shown in Fig. 4(i). Similarly, silver-doped phosphate glasses showed degradation during immersion in aqueous medium and the degradation increased with increasing degradation time as seen in Fig. 5(a)–(c). The degradation rates of PCNA glasses were also found to slightly
concentrations increased with increasing the degradation time as represented in Fig. 6(a)–(c) and the silver ions release rate was found to increase with increasing Ag₂O contents (Fig. 6(d)).

XRD patterns of representative silver phosphate glasses with 2 mol% Ag₂O are displayed in Fig. 7. The XRD spectra did not showed any sharp diffraction peaks and just showed halo patterns. FT-IR and UV–vis spectra of representative undoped and silver doped phosphate glasses are also shown in Fig. 8 and Fig. 9, respectively. The FT-IR spectra showed main absorption bands at ~470, 750, 911 and 1300 cm⁻¹ (band positions are indicated on the spectra). Moreover, the UV–vis spectra revealed UV absorption peak at about 230 nm with red shift due to the Ag⁺ ions while increasing their contents. Of note, there is an absorption band centered at ~340 nm only noted in the spectra of I₃Ag₂.

4. Discussion

Glass forming ability accounts for the vitrification capability of a melt when cooled from a temperature above the melting point to its glass transition temperature [43]. In binary systems such as CaO–P₂O₅ and Na₂O–P₂O₅, glass formation occurs only up to 55 mol% CaO and 60 mol% Na₂O, respectively [44]. Uo et al. [40] prepared various compositions of PCN glasses as thin sheets using the melt-rapid quenching technique. The glass formation domain obtained in the current work (≥40 mol% P₂O₅, determined using normal melting–annealing method for preparation of bulk glass samples) was compared to the one conducted by Uo et al. (≥35 mol% P₂O₅) in which rapid melt quenching was used for preparation of glass thin sheets [40]. Interestingly, the two glass regions are quite close to each other which could indicate that the rapid cooling does not have significant effect on the region of glass formation for the PCN system. This may support that the glass formation in the ternary system PCN is affected by the percent of P₂O₅ and other modifiers [40]. According to Walter et al. [45] decreasing the P₂O₅ content makes the phosphate-based glasses more resistant to moisture attack but restricts the glass formation area. Furthermore, the glass formation domain found here is in agreement with glass formation ranges in other systems,
namely $X_2O\cdot YO\cdot P_2O_5$ (X: monovalent cation, Y: divalent cation) \cite{40,44}. Thus it is evident that in the $X_2O\cdot YO\cdot P_2O_5$ system, glass formation is not affected by the type of the modifier and only the contents of $P_2O_5$, $YO$ or $X_2O$ are the determining parameters of the glass formation ability \cite{40,44,45}.

Glass formation was observed at $\geq 60$ mol% of $P_2O_5$ and 0.5–2 mol% $Ag_2O$ in the PCNA system. However, at contents $\leq 55$ mol% of $P_2O_5$, immediate partial crystallization and separation of metallic silver particles were observed. Here, silver-doped glass compositions were melted by the traditional method of glass making and without using any certain conditions. Actually, it is known that the preparation of silver-containing glasses requires melting under oxidizing conditions in order to achieve an oxidative state in the glass melt and thus to prevent a reduction of the $Ag^+$ to metallic $Ag^0$ \cite{32}. Ahmed et al. \cite{43} used $AgNO_3$ as a precursor to introduce $Ag_2O$ into phosphate glass with molar composition of $5P_2O_5\cdot 30CaO\cdot 20Na_2O$. However, they did not produce homogeneous transparent glasses and instead large brown streaks (due to reduction of the silver ions to metallic silver atoms) were obtained. These results are consistent with our determined glass forming compositions. However, when Ahmed et al. \cite{43} used silver sulfate ($Ag_2SO_4$) with some special precautions, clear transparent silver-doped glasses were produced. Indeed, at elevated temperatures $Ag_2O$ is easily reducible oxide and decomposes at temperatures above 280°C \cite{46}. Actually, silver may exist in glass structure as $Ag^+$ or $Ag^0$ \cite{24,28,46,48}. Furthermore, other $Ag$ species would exist as $Ag_6^{2+}$ or $Ag_8^{4+}$ clusters as recently reported by Marquestaut et al. \cite{24}. Moreover, $Ag_2O$ has different solubilities in glass melts depending on their nature and such solubility is a key factor for successful production of silver-doped glasses \cite{37–39}. Silver solubility in silicate melts is very low as silver has been found as nanoparticles or as colloidal species \cite{29,30}. However, silver solubility in phosphate melts is relatively high e.g. zinc phosphate glasses with 4% of molar $Ag_2O$ was successfully fabricated using a conventional elaboration method \cite{24}.

Addition of $Ag_2O$ over its solubility limit in glass melt could result in reduction of $Ag^+$ to atomic silver and it is difficult to solubilize more amounts of $Ag_2O$ beyond the solubility limit \cite{37}. Actually, the solubilization of $Ag_2O$ in glass melts is greatly influenced by glass composition, melting temperature, and oxygen pressure \cite{38,39}. Therefore, selection of glass composition is a key parameter as $Ag_2O$ behaves as a basic oxide and thus it becomes very stable in acidic glass melts \cite{37–39}. However, $Ag_2O$ can exist in glass melts in a stable form at a limited content even at high temperatures. Therefore, the production of $Ag_2O$ containing glass which has attracted much interest for its antibacterial activity is possible.

Changes in glass density could indicate to striking changes in glass structure such as degree of compactness and variations in dimensions of the interstitial spaces \cite{49}. Furthermore, the molar volume ($V_m$), which compares volumes occupied by one mole of glass, is an effective tool for determining the compactness of the glass structure. Molar volume is more sensitive to changes in glass structure than density as it normalizes for atomic masses of glass components.

For density of phosphate glasses, the compaction degree of phosphate structural units depends on the chain length and the branching extent in the glass structure. Therefore, the presence of long phosphate chains and much branching groups would result in low density and loosely glass structure \cite{50}. In this work, the replacement of $Na_2O$ by $CaO$ at

![Fig. 3](image-url)
constant $P_2O_5$ content resulted in a smooth and a gradual increase in density as shown in Fig. 1(a). This behavior could be attributed to differences in atomic masses between Na$^+$ and Ca$^{2+}$. Moreover, the field strength of Ca$^{2+}$ is higher than that of Na$^+$ which makes the phosphate chains bound tighter and leads to increase in density. The smooth trend observed in the density-composition relationship would indicate that the studied glass compositions did not exhibit any striking structural changes at any particular glass composition. The decrease in molar volume upon increasing CaO content is consistent with the replacement of the bigger Na$^+$ cations with the smaller Ca$^{2+}$ cations which shorten the chain length and make the glass structure more compact. The density of PCN glasses increases as Ag$_2$O replaces Na$_2$O. This increase could be ascribed to the differences in molar masses of Na$_2$O (62 g/mol) and Ag$_2$O (231.77 g/mol). The Ag$_2$O addition to phosphate glasses resulted in decrease in molar volume. This would indicate to the presence of enough spaces for Ag$^+$ ions in the glass network and its incorporation decreased these spaces.

The weight loss during the degradation of phosphate and silver phosphate glasses in aqueous media is nearly proportional to the degradation time. It increases in a linear way as shown in Figs. 4 and 5. This weight loss behavior indicates to network dissolution rather than selective leaching of modifier cations. The degradation rates phosphate glasses (Fig. 4(i)) decreased with increasing CaO contents. This behavior is due to Ca$^{2+}$ cations which can cross-link two different chains in phosphate glass structure. These Ca$^{2+}$ cross-links strengthen the phosphate structure and decrease the degradation rate. Bunker et al. [1] showed that the calcium phosphate glasses are made up of long chains in which Ca$^{2+}$ ions form cross-links between non-bridging oxygens of two phosphate chains. The degradation rates of phosphate glasses were also found to slightly decrease (at fixed contents of $P_2O_5$ and CaO) as Ag$_2$O replaces Na$_2$O up to 2 mol% Ag$_2$O (Fig. 5(d)). This could be attributed to that the P–O–Ag groups are more stable and more resistant to water attack compared to the P–O–Na groups. Furthermore, Ag$_2$O has lower solubility in water compared to that of Na$_2$O [51]. The silver ions release profiles (Fig. 6) showed sustained release of silver ions with concentrations range (summarized in Table 2) effective to kill bacteria [52]. Actually, very low concentrations of silver ions are very potent in killing bacterial [53–56].

The amorphous structure of silver-doped glasses has been ensured from the XRD patterns. Fig. 7 revealed broad halo pattern and the absence of sharp diffraction peaks relevant to crystalline materials. The chemical structure of silver
Fig. 5 – Degradation of silver-doped phosphate glasses in aqueous media (a–c) as a function of time and changes of degradation rates (d) upon replacement of Na₂O by Ag₂O.

Fig. 6 – Silver ions release profiles of silver-doped phosphate glasses during their degradation in aqueous media (a–c) as a function of time and changes of silver ions release rates (d) upon replacement of Na₂O by Ag₂O.
phosphate glasses was also investigated by FT-IR spectroscopy (Fig. 8). The FT-IR spectra showed typical bands of phosphate glasses. The band at ~470 cm⁻¹ is due to the O–P–O units, δ (PO₂⁻) of (PO₂⁻)ₙ groups, and the shoulder at 530 cm⁻¹ is assigned to fundamental bending vibrations of O=P–O [57]. The shoulder at ~660 cm⁻¹ only found in the spectra of I₅ and I₆ may be attributed to PO₃⁻ units [58]. The band at 750 cm⁻¹ is attributed to P–O–P linkages, ν₂ (P=O–P) modes [57–59]. It shifts to lower wavenumbers with increasing the amounts of Ag₂O which acted as a network modifier and made breakage of cyclic P–O–P bonds in the glass structure. The band at ~910 cm⁻¹ is due to P–O–P asymmetric stretching vibrations [57]. The shift of the band at 900 cm⁻¹ to higher frequencies [3] indicates to increased covalency of the P–O–P bonds and strengthening of glass structure. The band at ~1300 cm⁻¹ indicates to the existence of amounts of Q² units which is feature of ultraphosphate glass structure and it originates from ν₂ (P=O) modes [57–61]. Ag–O–P bonds are formed upon substitution of Na₂O by Ag₂O, which replace Na–O–P bonds. The Ag–O bond is more coherent than the Na–O bond since the electronegativity of Ag (1.93 on Pauling scale) is greater than that of Na (0.93 on Pauling scale). The FT-IR spectra of silver phosphate glasses provided evidence of increased covalent nature of the bond between the non-bridging oxygens with Ag⁺ ions to form P–O–Ag units. The band near 910 cm⁻¹ shifts to higher wave numbers as Na₂O substituted by Ag₂O. As Ag⁺ ions replace Na⁺ ions, the P–O–P bond strength increases since Ag⁺
ions have higher field strength than Na\(^+\) ions. This correlates well with the determined degradation rates which decreased with increasing AgO\(_2\) amounts. Finally, the structure of silver-doped glasses has been studied by UV–vis spectroscopy (Fig. 9). Actually, UV–vis spectra could be helpful in the confirmation of silver states in the glass matrix since atomic Ag in a glass matrix absorbs in the visible region while ionic Ag\(^+\) absorbs in the UV region. The strong band at ~210 nm is originated from electronic absorption of the host glass matrix. Electronic transitions involving Ag\(^+\) ions produce absorption bands between 200 and 230 nm [62,63]. However, electronic transitions involving Ag\(^+\) atoms and molecular silver clusters produce bands in the range of 250–350 nm [24–28]. Therefore, the band at 230 nm which showed red shift to ~245 nm due to increased AgO\(_2\) contents could be assigned to electronic transitions involving Ag\(^+\) ions. Interestingly, a broad and very weak band centered at ~340 was only noticed in the UV–vis spectrum of the I\(_2\)/Ag\(_2\) glass composition. The I\(_2\)/Ag\(_2\) glass composition was homogenous, transparent and very faint yellow in color (as visually observed). Thus this band is probably ascribed to electronic transitions involving metallic silver atoms Ag\(^0\) or molecular silver clusters [24–28,63]

5. Conclusion

Degradable phosphate and silver-doped phosphate glasses were successfully produced using the traditional melting–annealing method applied in glass making industry. Bulk glasses were prepared without using any special conditions or specific precautions (such as rapid melt-quenching, rapid melt-pressing or melting in oxidative environment) that is required for preventing crystallization and/or segregation of metallic silver particles from the melt. The production of these degradable and antibacterial glasses is highly demanded for biomedical applications. The proposed glasses are considered potential candidates as bioresorbable materials for bone regeneration and/or as additives for manufacture of antibacterial composite materials.

Fig. 9 – Representative UV–vis spectra of silver-doped phosphate glasses, (a) 60P\(_2\)O\(_5\)–20CaO–(20–x)Na\(_2\)O–xAg\(_2\)O and (b) 60P\(_2\)O\(_5\)–30CaO–(10–x)Na\(_2\)O–xAg\(_2\)O, x = 0, 0.5, 1 and 2 mol%.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


Shih PY, Yung SW, Chin TS. FTIR and XPS studies of P₂O₅–Na₂O–CuO glasses. J Non-Cryst Solids 1999;244:211.


