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Structural study of $xK_2O \cdot (100 - x)[P_2O_5 \cdot CaO]$ glass system

Adriana N. Regos · R. Ciceo Lucacel ·
I. Ardelean

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Abstract The P_2O_5–CaO glasses with incorporation of K_2O were investigated using X-ray powder diffraction, infrared absorption, and Raman scattering. These measurements give information about potassium–calcium phosphate glasses related vibration modes and the nature of the bond between P, K, and Ca ions and surrounding oxygen atoms within the glass network. Thermal analysis DTA and GTA were also made to study behavior under different temperature regimes and to see chemical changes with time and temperature of these glasses. The evolution of the absorption bands, with the increasing of K_2O, shows the significant distortions of the phosphate groups. Beginning with $x = 35$ mol% in Raman spectra appear new bands and the existing one disappear. But from Raman spectra we can see that the increasing of potassium oxide content leads to the appearance of gradually depolymerization process of the calcium phosphate network.

Introduction

Phosphate glasses have a large interest for many technological applications due to the high refraction index and thermal expansion coefficient, low melting temperature and viscosity, these glasses present transmission in UV. The roles of phosphate-based glasses in the usage of raw material for optical instruments, for glass fibers, for implant and in clinical dosimetry have paid attention in the recent years. [1–10].

According to the model proposed by Lippma et al. [1] for silicate glasses, applied to the phosphate glasses by Wazer [2] the structure of phosphate glass is formed by four types of structural units Q^n, where n represents the number of bridging oxygen atoms ($n = 0,1,2,$ and 3). In the case of phosphorous oxide glass, only the Q^3 units are present in the vitreous network. However, the relatively poor chemical durability of the phosphates glasses often limits their usefulness. Recent studies show that the chemical durability can be improved by properly adding small amounts of one ore more oxides, such as Al_2O_3, B_2O_3, PbO, CaO, Na_2O, ZnO, TiO_2, and Fe_2O_3 to the phosphate glasses [10–18].

Phosphate glasses are composed of PO_4 tetrahedra which can be bonded to one (Q^1), two (Q^2), or three (Q^3) other tetrahedra through the formation of P–O–P bonds at the corners of the tetrahedra PO_4^{3-}. The addition of metal cations such as Ca^{2+} to the glass in the amount of one metal cation to the P_2O_5 unit changes the characteristics of the network from the three-dimensional random network of P_2O_5 to long chain of PO_4 tetrahedra. The classical picture of these glasses maintains that as higher concentrations of metal cations are added, the infinitely long phosphate chains are shorted, Q^1 terminal groups ($-PO_3^{2-}$) are thus formed by breaking bridging oxygen in the metaphosphate chain [1–19].

On the basis of stoichiometric considerations, Van Wazer [19] has described the average chain length (n) in the terms of the mole ratio of the metal cation to P_2O_5. For the glasses of interest here, the relevant mole ratio is that of

A. N. Regos (✉) · R. C. Lucacel · I. Ardelean
Faculty of Physics, Babes-Bolyai University, Cluj Napoca
400084, Romania
e-mail: dadrianad@yahoo.com

R. C. Lucacel
e-mail: raluca.lucacel@phys.ubbcluj.ro

I. Ardelean
e-mail: ioan.ardelean@phys.ubbcluj.ro

CaO to P_2O_5 and is given the notation $R = [CaO]/[P_2O_5]$. The average chain length is related to R according to the following equation:

$$R = [CaO]/[\ P_2O_5] = (n + 2)/n.$$

In our study, we have a glass matrix $[P_2O_5 \cdot CaO]$ were mole ratio is $R = 1$, which is close to the mineral phases of bone and teeth. Numerous investigators demonstrated that it was possible to fabricate calcium phosphate glasses that were biocompatible [4, 20, 21]. Raman spectral studies of metaphosphate glasses ($R = 1$) presented by Jeanne E. Pemberton et al. [22] in their study of calcium phosphate glasses with varying CaO concentration reveal a medium—to strong intensity band at 690–700 for γ_s (POP) vibration, a strong band at 1168–1178 for γ_s (PO_2) vibration, and a medium-to-weak band at 1260–1280 cm for the γ_{as} (PO_2) vibration [22–25].

Potassium is one of twelve essential salts that can found in all body fluids and the ninth most common element by mass (0.2%) in the human body. Only minerals like calcium and phosphorus are more abundant, while sodium and chloride are each only about 2/3 of the potassium content. Potassium cations are important in neuron (brain and nerve) function, and in influencing osmotic balance between cells and the interstitial fluid, with their distribution mediated in all animals. Potassium is also important in preventing muscle contraction and the sending of all nerve impulses in animals through action potentials. By nature of their electrostatic and chemical properties, K^+ ions are larger than Na^+ ions, and ion channels and pumps in cell membranes can distinguish between the two types of ions, actively pumping or passively allowing one of the two ions to pass, while blocking the other [26]. The development of potassium–calcium phosphate glasses having K^+, Ca^{2+} and potassium ions represents one of possible solution to use as biomaterials.

The technological importance of these glasses requires a detailed understanding of the molecular and structural chemistry associated with the synthetic stage and final products of these systems. For explaining some structural aspects of the phosphate glasses infrared (IR) and Raman spectroscopy have been intensively used [20, 22, 23, 26–30].

The present study purposes to prepare calcium phosphate glasses containing potassium oxide and to investigate their structure through various methods (X-ray diffraction, FT–IR absorption, and Raman scattering). Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) was also used to study the thermal proprieties of these glasses and the influence of K_2O to the thermal properties of glass matrix.

Experimental

Glasses from $xK_2O \cdot (100 - x)[P_2O_5 \cdot CaO]$ system with $0 \leq x \leq 50$ mol% were prepared by mixing components of reagent grade purity : $(NH_4)_2HPO_4$, $CaCO_3$, K_2CO_3 in suitable proportions to obtain the desired compositions. The mixtures melted in sintered corundum crucibles, introduced in an electric furnace directly at 1200 °C, and kept for an hour at the same temperature. When time expired, they quickly cooled at room temperature by pouring onto steel plates to avoid crystallization process. The prepared glass samples were used for further studies without any treatments.

The structure of samples was analyzed by means of X-ray diffraction using a Bruker D8 Advanced X-ray diffractometer with a graphite monochromatic for CuK_{α} radiation with $\lambda = 1.54$ Å. The diffractograms were performed in a 2θ degree range 10°–90° with a speed of 2.4°/min. The pattern obtained did not reveal any crystalline phase in all samples.

The FT–IR spectra have been recorded at room temperature in the frequency range 400–1700 cm^{-1} using an infrared spectrometer (FT–IR 615 Fourier Transform). The measurements were made by the KBr disc technique in which discs were prepared by mixing and grinding a small amount of glass powder (1%) with anhydrous KBr powder and then pressed under vacuum and pressure of 10 ton/cm^2 into disc (1.2 cm in diameter).

The Raman spectra were performed by HR Lab Raman Horiba Jobin–Yvon equipped with a 10× microscope objective. For all measurements, it was used an external laser with an wavelength of emission 532 nm and a power of 5 mW incidents on the samples has been employed. The Raman spectra were obtaining from points on the surface of the sample.

The DTA and thermogravimetry (DTA–TG) were carried out on Stanton Redcroft STA780 apparatus with a heating rate of 10 K/s in argon flow using Al_2O_3 as a reference material.

All measurements were performed at room temperature.

Results and discussion

Figure 1 shows X-ray diffractographs of all studied samples of glasses. There were no sharp peaks thus indicating the absence of formation of any crystalline phases. This confirms amorphous character of these glasses which were colorless and transparent.

FT–IR absorption spectroscopy was used to detect changes in the structure of $P_2O_5 \cdot CaO$ glasses as a result of introducing K_2O in these glasses and to obtain essential

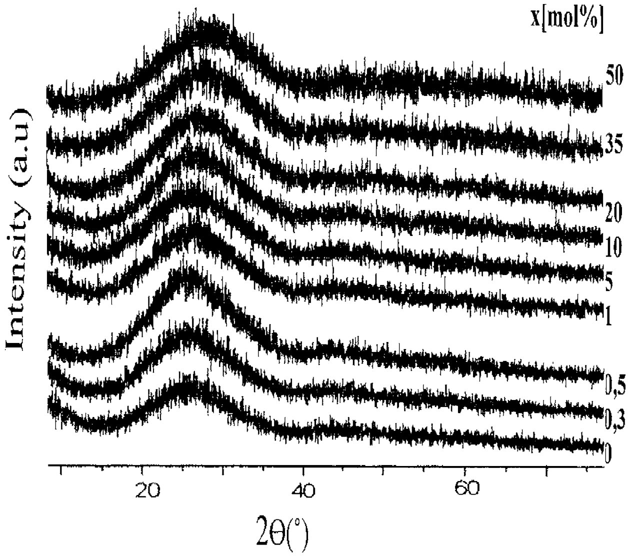

Fig. 1 X-ray diffraction patterns of glasses with $x = 0, 0.3, 0.5, 1, 5, 10, 20, 35$, and 50 mol%

information concerning the arrangement of the phosphate structural units in the calcium phosphate glass network.

The infrared absorption spectra were obtained for the $x\mathrm{K_2O}{\cdot}(100-x)[\mathrm{P_2O_5}{\cdot}\mathrm{CaO}]$ glasses with $0 \le x \le 50$ mol% and the recorders on investigated samples are present in Fig. 2.

The FT–IR spectra of $[\mathrm{P_2O_5}{\cdot}\mathrm{CaO}]$ glass matrix showed in 300–700 cm^{-1} bands at: ~520, ~740, ~912, ~1125, ~1270, 1400 and ~1640 cm^{-1}. The large band with maxim at ~520 cm^{-1} is characteristic for the fundamental O=P–O bending vibrations [3–7]. Band at ~740 cm^{-1} is attributed to a P–O–P stretching vibrations from Q^2 units and band at ~1400 cm^{-1} may be due to a P–O^- bond stretching vibrations combined with a lattice mode [5–9] (Table 1).

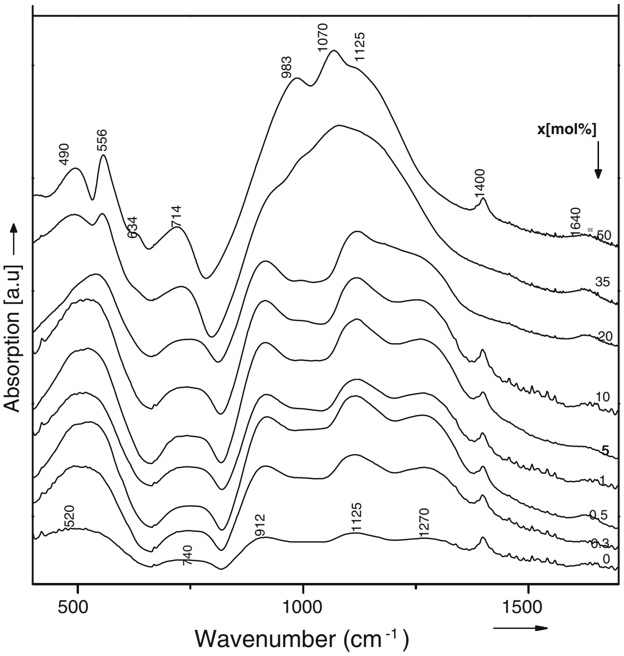

Fig. 2 FT–IR spectra of $x\mathrm{K_2O}{\cdot}(100-x)[\mathrm{P_2O_5}{\cdot}\mathrm{CaO}]$ glass system

The band at ~912 cm^{-1} belongs to asymmetrical bending vibrations of P–O–P. This band is well visible in spectra only when $x \le 20$ mol% and indicates a network with short chains and pyrophosphate groups [3–6].

It has been suggested that the band at the highest wave number : ~1270 cm^{-1} is caused by the P=O double stretching bond from Q^2 species and the band at ~1125 cm^{-1} is due to $\mathrm{PO_3}^{2-}$ asymmetric and symmetric vibrations (Q^1) [5, 6]. This band (1125 cm^{-1}) shows a higher intensity evolution with increasing of $\mathrm{K_2O}$.

All spectra glasses showed a very weak band at ~1640 cm^{-1} attributed to the bending vibrations of the free H_2O molecules [10–14]. The presence of these water molecules in our glasses was probably because the mixtures had absorbed some water during the preparation of samples.

However, Raman spectroscopy of ultra and meta sodium phosphate glasses has shown that the P=O only exists in ultraphosphate compositions [7], so the peak at ~1270 cm^{-1} must be due to another molecular vibrations. On the other hand, the authors of works [8, 9] say that the peaks at ~1270 and ~1125 cm^{-1} are due to the asymmetrical and symmetrical stretching of the non-bridging $(\mathrm{PO_2})^-$ units.

We can see that for potassium oxide content greater than 10 mol% the intensity of the P=O (~1270 cm^{-1}) absorption band starts to decrease up to the disappearance, we

Table 1 FT–IR bands assignment for $x\mathrm{K_2O}{\cdot}(100-x)[\mathrm{P_2O_5}{\cdot}\mathrm{CaO}]$ glass system, $0 \le x \le 50$ mol%

v (cm^{-1})	Attribution
~490	Symmetric and asymmetric bending mode of the $\mathrm{PO_4}^{3-}$ groups
~520	Bending vibrations of fundamental O=P–O
~556	Symmetric and asymmetric bending mode of the $\mathrm{PO_4}^{3-}$ groups
~714	Asymmetric stretching vibrations of P–O–P linkages
~740	Bending vibrations P–O–P bonds associated to Q^2 units
~912	Asymmetrical bending vibrations of P–O–P bonds
~983; ~1070	Symmetrical stretching vibrations of the $\mathrm{PO_4}^{3-}$ ions
~1125	Asymmetrical and symmetrical stretching of $\mathrm{PO_3}^{2-}$ (Q^1)
~1270	P=O double stretching bond Q^2 groups
~1400	Stretching vibrations P–O^- bond combined with a lattice mode
~1640	Bending vibrations of free H_2O molecules

attributed this to the increasing replacement P=O by P–O–K bridging units.

Major changes with the addition of potassium oxide are present in the 850–1300 cm^{-1} range, involving the evolution of the intensity and relative area under the absorption bands in this wave number domain especially for 35 mol %. This big large band give evidence of some ionic content in the xK$_2$O·(100 − x)[P$_2$O$_5$·CaO] glass system, the partial break down of the supposedly covalent vitreous network at high potassium oxide content. Also the intensity of this large band reaches a fairly strong maximum for 35 mol% K$_2$O in the region 1030–1120 cm^{-1} when breakdown of the covalent vitreous network into small ionic groups (PO$_4^{3-}$, P$_2$O$_7^{4-)}$ might be expected [11]. To confirm that are bands at ~983 and ~1070 cm^{-1} which appear at 50 mol % K$_2$O and have been ascribed to two of the normal vibrations modes of the PO$_4^{-3}$ ions [12, 14].

An important remark regards the appearance for high content of potassium oxide a two well definite band: at ~490 and ~556 cm^{-1} associated with symmetric and asymmetric bending mode of the PO$_4^{3-}$ tetrahedra (Q^0) [13, 30].

In addition of K$_2$O, a weakening of P=O might be expected when this link is broken by network forming cations. For 50 mol%, the phosphate units are more isolated in the structure since in IR absorption spectra appear new bands: at ~490 and ~556 cm^{-1} in first part and at ~983 and ~1070 cm^{-1} in the second part of spectrum. Finally, a new band peaking at ~634 cm^{-1} appears in the IR spectra characteristic to pyrophosphate glasses (Q^1) [15–19, 27].

The evolution of the absorption bands with the increasing of K$_2$O show the significant distortions of the phosphate groups in studied glasses.

Figure 3 shows the Raman spectra of all investigated glasses. For [P$_2$O$_5$·CaO] matrix spectra evidence the follow six bands: ~340, ~540, ~1030, ~1162 and ~1250 cm^{-1} (Table 2).

The most intense band at ~1162 cm^{-1} in the spectrum has attributed to the symmetric and asymmetric stretching vibrations of (PO$_2$)$^-$ groups from Q^2 units. The less intense band at ~700 cm^{-1} was assigned to the asymmetric stretching vibrations of P–O–P linkages in Q^2 and Q^1 structural units [15, 16].

The large band situated at 400–600 cm^{-1}, with maxim at ~540 cm^{-1}, associated with phosphate polyhedra is well observed only for glass matrix and corresponds to the symmetric stretching of P–O– bonds and O–P–O bending modes [11, 18]. The intensity of this band decrease up to disappearance because of forming of new units.

Bues and Gehrke [17] attributed in glass metaphosphate the well defined band observed at ~340 cm^{-1} to the (PO$_2$)$^-$ and chain O–P–O bending vibrations.

Table 2 Raman bands assignments for xK$_2$O·(100 − x)[P$_2$O$_5$·CaO] glass system, 0 ≤ x ≤ 50 mol%

ν (cm^{-1})	Attribution
~340	(PO$_2$)$^-$ of the Q^2 species and chain O–P–O bending vibrations
~422	Bending vibrations of O–P–O from Q^0 units
~452	Bending vibrations of O–P–O
~540	Symmetric stretching of P–O– bonds and O–P–O bending modes
~561	Symmetric stretching of P–O– bonds
~609	Symmetric stretching of the P–O– bonds
~700	Asymmetric stretching vibrations of P–O–P linkages in Q^2 and Q^1
~762	P–O–P symmetric stretching in Q^1 units
~974	Symmetric stretching vibrations of P–O bonds of the PO$_4^{3-}$ (Q^0)
~1030	P$_2$O$_7$ groups γ_s(PO$_3^{2-}$)
~1044	Symmetric stretching vibrations of (PO$_3$)$^{2-}$ (Q^1)
~1093	Asymmetric vibrations of (PO$_3$)$^{2-}$ from end of phosphate chains
~1162	Symmetric and asymmetric stretching vibrations of (PO$_2$)$^-$ groups from Q^2
~1250	Vibrations of P=O bonds existed in Q^2 units

Other bands (two shoulders) appear at ~1030 cm^{-1} typical of P$_2$O$_7$ group with γ_s(PO$_3^{2-}$) and ~1250 cm^{-1} due to the asymmetric vibrations of P=O bonds existed in Q^2 groups [16, 19].

The intensity of the strong band at ~1162 cm^{-1} decreases with increasing of potassium oxide content and almost vanishes at $x = 35$ mol%. Similar behavior shows the band from ~700 cm^{-1}. These changes are accompanied by appearance of new bands at ~1044 and ~762 cm $^{-1}$ assigned to (PO$_3^{2-}$) symmetric stretching (Q^1) and P–O–P symmetric stretching (Q^1) [8, 28].

The spectrum of glass with maximum K$_2$O content shows the progressive development of a new band at ~974 cm^{-1} corresponding to the symmetric stretching vibrations of P–O bonds of the orthophosphate PO$_4^{3-}$ units (Q^0) [27]. This band is dominant in spectrum while all the other bands founded under this concentration, decrease in intensity with increasing x and finally vanish.

As shown in Fig. 3, the spectrum of 0.5·K$_2$O·0.5 [P$_2$O$_5$·CaO] glass exhibits two broad bands (low intensity) at ~609 and ~422 cm^{-1} which are assigned to the symmetric stretching of the P–O bonds and respectively to O–P–O bending modes of the orthophosphate PO$_4^{3-}$ units (Q^0). For higher potassium oxide content, it appears that, the modifier oxide (K$_2$O) favors the presence of O–P–O bending modes and symmetric stretching of P–O–, information revealed by bands from ~452 and ~561 cm^{-1}.

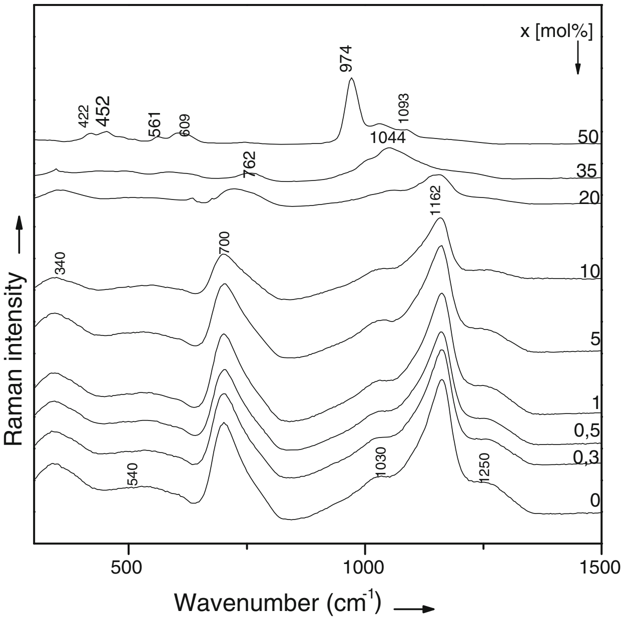

Fig. 3 Raman spectra of $xK_2O·(100 - x)[P_2O_5·CaO]$ glass system

And also at this concentration appears a high wave number band at ~1093 cm^{-1} assigned to the asymmetric vibrations of $(PO_3)^{2-}$ from end of phosphate chains [20, 22, 26, 28–30].

All these variations in the Raman spectra suggest a change in the covalent character between P and O bonds, which is induced by the presence in calcium phosphate glasses structure of potassium cations.

For $x = 20$ and 35%mol studied glasses present the most high grad of disorder as can be observed in Raman spectra. This fact makes evident the distortions that glass network suffers as a result of the incorporation of potassium oxide in studied samples.

Differential thermal analysis is a method used to study the thermal properties, method in which the difference in temperature between a sample and inert referent substance is measured and both are subjected to an identical temperature program.

DTA curves of matrix glass samples and other two with K_2O content ($x = 5$ and 20) are shown in Fig. 4. The features of the DTA lines do not permit clearly to specify the glass transition temperature T_g (which is the onset of the endothermic peak) for all three samples, but the bottom curves in Fig. 4 indicates that this temperature should be at about 303 °C for $P_2O_5·CaO$, 270 °C for $5K_2O·95[P_2O_5·CaO]$ and 200 °C for $20K_2O·80[P_2O_5·CaO]$.

From DTA lines, it is also possible to determine the crystallization temperature T_C. In the matrix case, we observe a well definite exothermic peak at 480 °C as a result of the formation of crystalline phases during the heating. For the other two samples, the exothermic peak is observed at 548 and 546 °C. The endothermic effects for studied samples are about 645 °C ($x = 0$); 637 °C ($x = 5$), and 628 °C ($x = 20$) corresponds to the beginning of the melting samples and indicates melting temperature T_m. To note that T_g and T_m decrease with potassium oxide content: T_g 303 → 270; 200 °C and T_m 645 → 637; 628. This phenomenon can be explained by the fact that potassium has a low melting point (63.38 °C) compared to phosphorus (280.5 °C) and calcium (842 °C). With the introduction of potassium oxide in glass matrix increases the amount of potassium atoms at the expense of calcium and phosphorous.

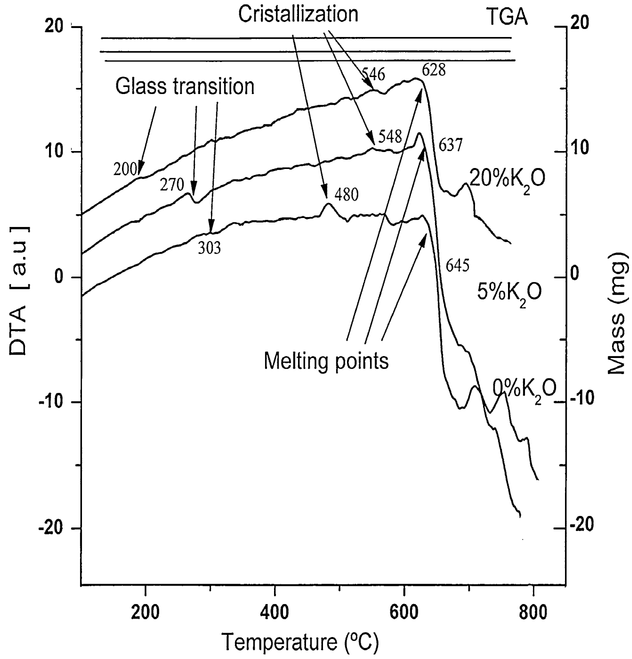

Fig. 4 DTA and TGA curves of the investigated phosphate glasses

The thermal stability of the same three samples was also investigated by TGA measurements. Thermal gravimetric analysis was used to measure the losses of weight as the temperature of the samples is increased. TGA curves glass samples are shown in Fig. 4. The TGA curves are constant for all samples ($m_1 = 17.28$ mg; $m_2 = 17.91$ mg; $m_3 = 19.09$ mg) during the heating process. No weight loss of mass was observed in any studied samples for their temperature range between 100 and 800 °C.

Conclusions

Homogeneous glasses of $xK_2O·(100 - x)[P_2O_5·CaO]$ system were obtained for $0 \leq x \leq 50$ mol%. X-ray diffraction analysis detected no crystalline phase.

FT–IR and Raman spectroscopy are used in order to analyze the local structure and to identify the contributions of each component on the glass network.

From FT–IR, it can be observed that the network structure of the studied glasses consist of randomly connected $(PO_4)^{3-}$, $(PO_3)^{2-}$, and $(PO_2)^{-}$ structural units.

Addition of potassium oxide causes the broken of the infinite metaphosphate chains resulting initially in a distribution of shorter species with $(PO_3)^{2-}$ terminal groups, following by creation of pyrophosphate $P_2O_7^{4-}$ and finally orthophosphate PO_4^{3-} units. Also from DTA curves we observed that the increasing potassium oxide content in glass matrix lead to decreases of the transition temperature (T_g) and melting temperature(T_m) of studied samples (Fig. 4).

The investigation of Raman spectra of glass matrix shows that the increasing of potassium oxide content leads to the appearance of gradually depolymerization process of the calcium phosphate network.

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References

1. Lippma E, Magi M, Samoson A, Enghelhardt G, Grimmer AR (1980) J Am Chem Soc 102:4889
2. Van Wazer JR (1958) Phosphorus and its compounds. Interscience Publishers Ltd, London
3. Moustafa YM, Egili KE (1998) J Noncryst Solids 240:144
4. Dai WD, Kawaoe NK, Lin XT, Dong J, Chen GP (2010) Biomaterials 31(8):2141
5. Arzeian JM, Hogarth CA (1991) J Mater Sci 26(19):5353. doi:10.1007/BF01143233
6. Salim MA, Khattak GD, Fodor PS, Wenger LE (2001) J Noncryst Solids 299:185
7. Brow RK, Kirkpatrick RJ, Turner GL (1990) J Noncryst Solids 116:39
8. Exarhos GJ, Miller PJ, Risen WM (1974) J Chem Phys 60:4145
9. Metwalli E, Brow RK (2001) J Noncryst Solids 289:113
10. Timar-Gabor A, Ivascu C, Vasiliniuc S, Daraban L, Ardelean I, Cosma C, Cozar O (2011) Appl Radiat Isot 69:780
11. Rao KJ, Sobha KC, Kumar S (2001) Proc Indian Acad Sci Chem Sci 113:497
12. Miller FA, Wilkins CH (1952) Anal Chem 24:1253
13. Sun J, Li Y, Li L, Zhao W, Lei Li, Gao J, Ruan M, Shi J (2008) J Noncryst Solids 354:3799
14. Higazy AA, Brige B (1985) J Mater Sci 20:2345. doi:10.1007/BF00556064
15. Koo J, Bae BS, Na HK (1997) J Noncryst Solids 212:173
16. Vedeanu N, Cozar O, Ardelean I, Filip S (2006) J Optoelectron Adv Mater 8:1135
17. Bues W, Gehrke HW (1956) Z Anorg Allgem Chem 288:367
18. Shih PY, Yung SW, Chin TS (1999) J Noncryst Solids 244:211
19. Van Wazer JR (1958) Phosphorous and its compounds. Interscience, New York
20. Ciceo Lucacel R, Hulpus AO, Simion V, Ardelean I (2009) J Noncryst Solids 355:425
21. Ahmed AA et. al. (2011) Solid State Sci. doi:10.1016/j.solidstatesciences.2011.02.004
22. Pemberton JE, Latifzadeh L, Subhash JP, Risbud H (1991) Chem Mater 3:195
23. Wei TY, Hu Y, Hwa LG (2001) J Noncryst Solids 288:140
24. Efimov AM (1997) J Noncryst Solids 209:209
25. Peng YB, Day DE (1991) Glass Technol 32:166
26. Lockless SW, Zhou M, MacKinnon R (2007) PLoS Biol 5:121
27. Byun JO, Kim BH, Hong KS, Jung HJ, Lee SW, Izyneev AA (1995) J Noncryst Solids 190:288
28. Ilieva D, Jivov B, Bogachev G, Petkov Ch, Penkov I, Dimitriev Y (2001) J Noncryst Solids 283:195
29. Karakassides MA, Saranti A, Koutselas I (2004) J Noncryst Solids 347:69
30. Le Ssaout G, Simon P, Fayon F, Blin A, Vaills Y (2002) J Raman Spectrosc 33:740