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LOCAL STRUCTURE AND BIOLOGICAL EFFECTS OF VITREOUS CALCIUM-SODIUM-PHOSPHATE SYSTEM CONTAINING IRON

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Iron phosphate glasses have found in the last time technical and biomedical application due to their specific properties. The relationship between composition and structure for the glass system (100-x)[$50P_2O_5 \cdot 30CaO \cdot 20Na_2O$]$\cdot xFe_2O_3$, $0 \leq x \leq 20$ mol % Fe_2O_3 has been studied. X-ray diffraction, Raman and infrared spectroscopy have been used to evidence the structural changes induced by iron addition to sodium-calcium-phosphate host glass. The biological effect of the cations released from these glasses into nutrient medium of plants was tested on Phaseolus vulgaris c.v Ardeleana.

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1. Introduction

Phosphate glasses are of large interest due to their unique properties that recommend them as potential candidates for solid state electrolytes, laser glasses, host for nuclear waste storage or as biomaterial for tissue engineering [1,2,3]. The addition of iron oxide to calcium-sodium-phosphate glasses was found to increase their chemical durability and to suppress the tendency for crystallization on cooling or reheating [4]. Furthermore it was evidenced that the change from bridging oxygens to non bridging oxygens with the increasing of iron oxide content affects various glass properties [5].

The aim of this study was to obtain by means of Raman and IR spectroscopic methods information regarding the structural changes in samples belonging to (100-x)[$50P_2O_5 \cdot 30CaO \cdot 20Na_2O$]$\cdot xFe_2O_3$ glass system and to evidence the influence of the cations released from these samples into nutrient medium of plants on their growth, as potential fertilisers.

2. Experimental set-up

Glass samples of composition (100-x)[$50P_2O_5 \cdot 30CaO \cdot 20Na_2O$]$\cdot xFe_2O_3$, $0 \leq x \leq 20$ mol % Fe_2O_3, were prepared using as starting materials reagent grade chemicals Fe_2O_3, $NH_4H_2PO_4$, $CaCO_3$, $Na_2CO_3 \cdot 10\ H_2O$. The mixtures were melted in air, in sintered corundum crucibles introduced into an electric furnace Carbolite RF 1600 directly at 1200 ^oC, maintained for 15 minutes at this temperature. The melts were quickly undercooled at room temperature by pouring and pressing between two stainless steel plates. Bulk samples were ground using an agate mill. The (XRD) data were collected on a Bruker D8 Advance powder diffractometer in the plate geometry, using Cu K_α radiation. The Raman measurements of the glass samples were performed on a Dilor Labram system

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equipped with a 100 × 0.80 NA microscope objective. For all measurements it was used a grating with 1800 lines/mm and an external laser with an emission wavelength of 514 nm. In the recording of the micro-Raman spectra a power of 150 mW incidents on the sample has been employed.

Fourier transform infrared (FTIR) measurements were made by employing the KBr pellet technique. The glasses were ground into a fine powder with a mass of 0.005 g. This amount was then mixed with 0.2 g purified KBr powder [6]. The FTIR spectra were recorded on a Bruker Equinox 55 spectrometer with spectral resolution of 2 cm^{-1}.

The biological effect of these glass samples, which could be used as fertiliser[1] was tested on the growth of Phaseolus vulgaris seedlings. Seeds were put to germinate in Linhardt-dishes on moist filter paper at 25 ºC in the dark. The treatment was applied for 48 hours. The seedlings from the first and the second dishes containing 50 and 100 mg matrix mixed with 25 ml distillated water were used as reference. In the others dishes were introduced 50 mg and 100 mg powder glass with $x = 3$, 5, 10 or 20 mol % solvated in 25 ml distillated water. The biological effect on the plant growth was estimated by measurements of root, hypocotyl and epycotyl length, after 24, 48 and 72 hours.

3. Results and discussion

The X-ray diffraction (XRD) patterns on investigated samples consist of a broad line typical of vitreous systems. The patterns do not evidence any narrow line of crystalline phases.

The Raman and IR spectra recorded on as prepared glasses are displayed in Fig. 1. Using the literature data has done the assignment of the vibrational modes. Raman and IR spectra were recorded only from the samples with $x \leq 10$ mol % Fe_2O_3 because for $x = 20$ the sample becomes fluorescente. In phosphate glasses the basic structural units are PO_4 tetrahedra connected by corners. Pure vitreous P_2O_5 has a three-dimensional network build up with PO_4 tetrahedra connected by three of their four corners. The fourth one is occupied by terminal double-bonded oxygen. The addition of other oxides to P_2O_5 may result in breaking some P-O-P links and occurrence of more terminal oxygens. Depending on the number of the bridging oxygens the phosphate tetrahedra can be described as Q^i where i represents the number of the bridging oxygens and can have a value of 0, 1, 2, 3. A framework built up with Q^3 denotes a fully polymerization structure, while Q^2 unit given only a two-dimensional structure based on chains or rings. Q^1 means two tetrahedra connected by a corner and Q^0 means isolated tetrahedral [7].

By inspecting the Raman spectra (Fig. 1) one can see that the addition of iron oxide determine the appearance of a few structural changes. The band that occurs about 164 cm^{-1} for $x = 10$ mol % is attributed to the vibrational mode dominated by the motion of the iron ions. It was shown that the decrease in amplitude of the band around to 690 cm^{-1}, which is assigned to the P-O-P stretching vibrations of the long-chain species, is caused by the increase of the number of very short phosphate chains [8]. The band at 690 cm^{-1} is no longer visible for $x = 10$ mol % Fe_2O_3, because it is shifted at 730 cm^{-1}. This latter band, which is attributed to the symmetric stretching P-O-P vibration, could belong to very short chain phosphate units or ring structures. The presence of the prominent band at 1069 cm^{-1} for $x = 5$ and at 1067 cm^{-1} for $x = 10$ mol % shows an increase of the non-bridging oxygens (PO_2) number. The band, which appears at 1197 cm^{-1} in the spectrum recorded for $x = 10$, is attributed to the (PO_2) symmetric stretching vibration of non-bridging oxygens involving iron ions, in Q^2 units. The number of Fe-O-P bonds increases while the number of P-O-P bonds decreases [9].

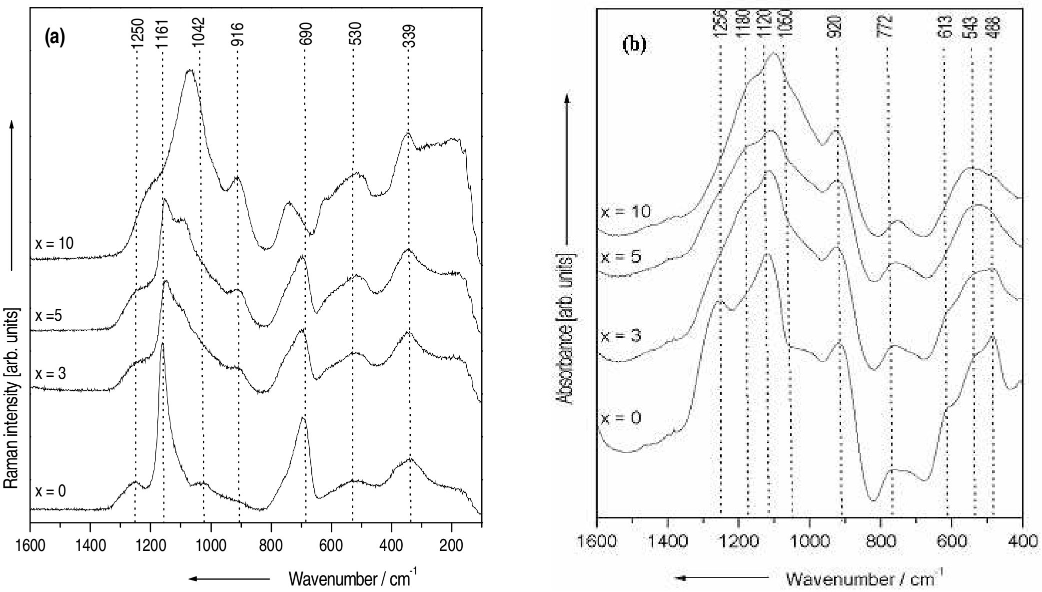

Fig. 1. (a) Raman and (b) FT IR spectra of (100-x)[$50P_2O_5 \cdot 30CaO \cdot 20Na_2O$]$\cdot xFe_2O_3$, glass samples.

The changes observed in the Raman spectra are confirmed by the changes appeared in the FT-IR spectra (Fig. 1b). They indicate the existence of a depolymerisation process of the phosphate network with the Fe_2O_3 addition. The strong band around to 920 cm^{-1} is due to the asymmetric stretch of $(PO_4)^{3-}$ anions.

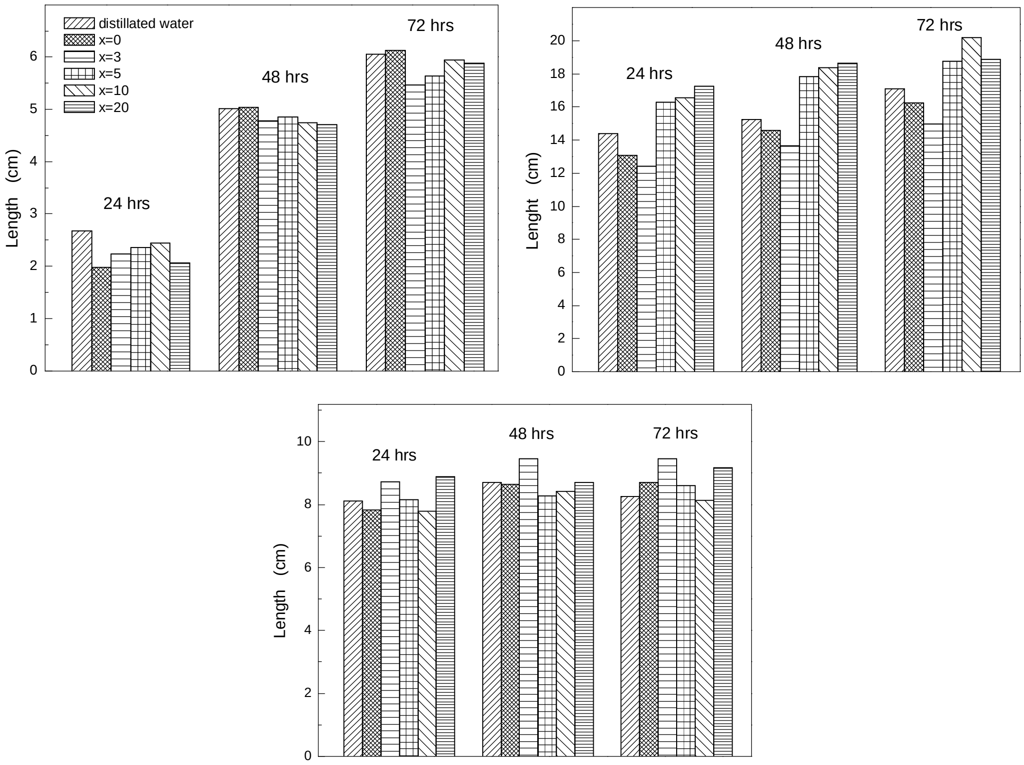

Fig. 2. Length of (a) epycotyls, (b) roots and (c) hypocotyls for seedling grown in nutrient media including dissoluted calcium-sodium-phospate glasses with iron.

The band at 1120 cm^{-1} assigned to P-O$^-$ bond vibration reveals the rupture of P-O-P bonds by addition of iron, which acts as a network modifier [10]. IR bands located between 1250 and 1300 cm^{-1} are attributed to vibrations of PO^{2-} group and one remarks that they decrease in intensity as Fe_2O_3 content increases. These results indicate the appearance of a depolymerisation process of the phosphate network caused by iron oxide addition.

The biological effect of the cations released from these glasses in aqueous nutrient medium of Phaseolus vulgaris seedlings was investigated by measuring the length of roots, epycotyls and hypocotyls. The results displayed in Fig. 2 show different effect on different seedling parts. One remarks a relative increase in hypocotyl and root length, and an inhibitory effect with respect to epycotyl growth. At the same time for roots is observed a favorable effect with increasing iron content in the first 48 hours, while after 72 hours the most pronounced effect is not obtained for the samples with highest iron content (x = 20) but for that with x = 10. For hypocotyls the most fertilising composition corresponds to x = 3 mol % Fe_2O_3.

By correlating the spectroscopic results with the data regarding the biological effect on seedlings growth one can consider depolymerisation tendency of glass network by iron addition that could appear because the P-O-P bonds are probably replaced by P-O-Fe^{2+} and P-O-Fe^{3+}. This effect may stimulate the growth of hypocotyl and root, but has an inhibitory effect of epycotyl. It seems like the high content of iron oxide presents toxicity for epycotyl. During the time it is possible to appear two leaching stages relative to the incipient dissolution of glas samples. In the first stage the lowest release rate is obtained from the sodium-phosphate matrix (x = 0), and from the samples with low CaO content. In the second stage the cations release is proportional to CaO content. Knowles et al. [11] observed that the increasing of the amount of CaO mol % resulted in a decrease in solubility.

The initial stage of the aqueous reactions always results in the leaching of alkali and alkaline earth species from the surface of the glass to create a P_2O_5 rich surface layer. It is generally believed that in the initial stage of the leaching reaction, the contact of water with the glass surface leads to an exchange of alkali and alkaline earth ions in the glass with hydrogenated ions in the aqueous environment. (i.e. ion exchange or interdiffusion mechanism). Another mechanism proposed is based on the diffusion of molecular water into the glass and its chemisorbtion at the non-bridging oxygens sites where alkali and alkaline earth species reside in the glass [12].

4. Conclusions

The Raman and IR results obtained from the investigated samples indicate that the addition of iron oxide to calcium-natrium-phosphate host glass leads to a partial replacement of P-O-P bonds with P-O-Fe and implicitly to a depolymerisation of the glass network. The cations released from these glass samples into nutrient medium of tested plants cause different biological effects that lead to growth of hypocotyl and root and exert an inhibitory effect on epycotyl growth.

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