

P₂O₅-CaO-Li₂O glass system - a possible ESR dosimeter

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Phosphate-based glass materials have potential use as biomaterials, because of their chemical composition similarity to the natural bone. In this paper we present an IR, Raman and ESR study on glass systems such as P₂O₅-CaO-Li₂O, where the proportion of P₂O₅ remains constant at 50 mol % and those of Li₂O and CaO modify from 10 to 40 mol %. The IR and Raman spectra allow us to identify the structural units which appear in the structural network of these phosphate glasses and also the network modifier role of Ca²⁺ and Li⁺ ions. The ESR spectra of the gamma irradiated samples with a ⁶⁰Co source, are characterized by the hyperfine doublet of ³¹P isotope (I= 1/2). By representing the ESR signal intensity versus the absorbed doses in the range 100-1500 Gy, a linear dependence was obtained, which proves that the glass system P₂O₅-CaO-Li₂O could be successfully used in the clinical dosimetry and industry.

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1. Introduction

Phosphate glasses are often used as biomaterials, because of their chemical composition similarity to that of natural bone. Simple phosphate glasses do not have enough chemical durability for applications. Since the discovery of bioglass™(BG) by Hench [1], much research has focused on glasses and biomedical glasses for their diversified applications [2-4].

This paper presents a systematic study of the P₂O₅-CaO-Li₂O glass system, with purpose to develop a suitable material for ESR dosimetry.

The network of phosphate glasses contains a polymeric structure dominated by linkages between PO₄ tetrahedra. In the case of vitreous P₂O₅, these groups are connected to adjacent units by three of their four vertices; one place is occupied by a terminal, double-bonded oxygen atom (DBO).

Many authors have proposed the formation of different phosphate structural groups (units) during the reorganization processes accompanying the addition of some modifier oxides (Na₂O, Li₂O, CaO etc.). They assumed that the doubly bonded oxygens (DBO) remain and a one to one correspondence exists between the number of alkali added and the number of non-bridging oxygens (NBO) created [5-7].

The structures of binary phosphate glasses are described by so-called Q^s groups model. The phosphate structural groups (Fig. 1a) pass from Q³ to Q² to Q¹ to Q⁰ as the ratio M₂O/P₂O₅ = R passes from 0 to 1, 2 and finally to 3 [5,8].

The P₂O₅-CaO-Li₂O glasses consist of a polymer like structure of regular tetrahedrons based on PO₄ groups linked by the vertices and interrupted by the glass modifier ions Ca²⁺ and Li⁺ that enter into the glass network modifier positions acting locally as charge compensators (Fig 1b). The relative amount of individual

units, at each alkali oxide content, adjust themselves to satisfy the simultaneous equilibria.

Several authors have applied IR and Raman spectroscopies to explain some structural aspects of phosphate glasses [9-13]. In most of those studies analyses of IR spectra of glasses were qualitative based on the assignment and shift of infrared absorption bands.

Glass dosimeters are important means for the various different high-dose level applications, e.g. for medical, industrial and food irradiation purposes.

The ESR technique has shown to be considerably promising for high dose gamma measurements. It is a non-destructive technique that consists in the application of physical principles based on the number of unpaired spins created on irradiation (holes and electrons trapped at different sites in the glass structure). ESR spectroscopy is currently employed in dosimetry and several materials are suitable for this purpose. Among these, some calcium-phosphate types of glasses were chosen because its composition is similar to that of bones [4-11,14].

The radiation induced hole centers in alkali phosphate glasses are characterized by the ESR hyperfine doublet of ³¹P isotope (nuclear spin= 1/2) and were studied by different authors [15-17]. They found that the efficiency of the generation of electron and hole centers depends on the glass composition and is almost independent of the type of ionizing radiation source.

2. Experimental

The starting materials used in the present investigation were (NH₄)₂HPO₄, CaCO₃ and Li₂CO₃ of reagent grade purity. The samples were prepared by weighing suitable proportions of the components, powder mixing and mixture melting in sintered corundum crucibles at 1250^o C for 5 min. The mixtures were put into the furnace directly at this temperature. The obtained glass-samples were

quenched by pouring the molten glass on a stainless steel plate. The structure of these glasses was studied by means of X-ray diffraction and no crystalline phase was detected.

The FT-IR absorption spectra of the glasses in the 400-1500 cm^{-1} spectral range were obtained with an Equinox 55 Bruker spectrometer. The IR absorption measurements were done using the KBr pellet technique. The FT-Raman spectra were recorded with a Bruker FRA 106/S Raman accessory attached to the Bruker Equinox 55FT-IR spectrometer equipped with an InGaAs detector working at room temperature. The FT-Raman spectra were recorded in backscattering geometry with a resolution of 1 cm^{-1} . In order to obtain good quality spectra, the samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture.

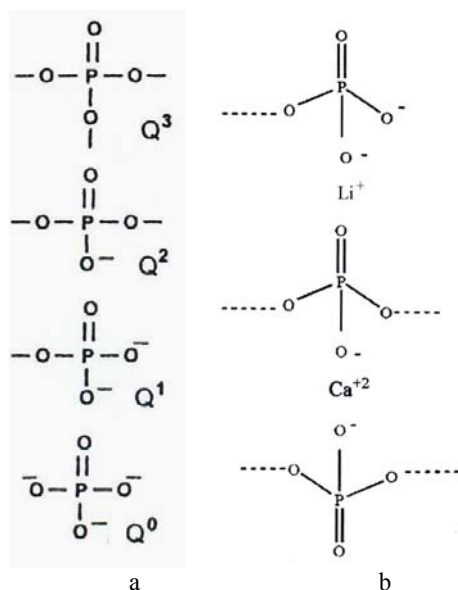


Fig.1. Q^n groups model of phosphate glasses (a) and the glass modifier role of Ca^{2+} and Li^+ cations (b).

The ESR spectra were obtained at room temperature with an Adani Portable EPR Spectrometer PS8400 in X-frequency band (9.4 GHz) and a field modulation of 100 KHz. For these measurements, equal quality of powders from the investigated sample, closed in glass tubes, were used.

The samples were protected from sunlight, fluorescent lamps, and other light sources and stored in the dark. They were irradiated to specific absorbed dose levels with a Gamma - ^{60}Co source type BAHABA Center - India with a 2.4 Ci activity and a dose fluence of 7.5 Gy/h. After irradiation, the samples were stored for ≈ 24 h to eliminate transient signal.

For each sample the initial ESR signal (before irradiation), S_1 , and final (after irradiation), S_2 , were recorded and the dosimeter response was defined as $R = S_2 - S_1$.

3. Results and discussion

a) IR and Raman spectra

Typical infrared spectra of studied glasses are shown in Fig. 2. As seen from this figure, the frequencies of predominant absorption peaks (based on visual judgment) are characterized by two broad peaks near 500 cm^{-1} , two weak peaks around 750 cm^{-1} , three peaks in the 900-1100 cm^{-1} region, a weak peak at 1160 cm^{-1} and a strong broad peak around 1270 cm^{-1} . IR analyses reveals that the low frequency envelope around 500 cm^{-1} consists from two component bands at ~ 487 and ~ 544 cm^{-1} . The band at about 487 cm^{-1} is assigned as the bending vibrations of O-P-O units, $\delta(\text{PO}_2)$ modes of $(\text{PO}_2)_n$ chain groups, and the band at ~ 544 cm^{-1} is described as a fundamental frequency of (PO_4^{3-}) or as harmonics of P=O bending vibrations [4, 9, 10]. The bands from 727 cm^{-1} and 785 cm^{-1} may be attributed to the symmetric stretching vibrations of P-O-P rings [18]. The variation of the frequency of P-O-P bonds with increasing Li_2O content is in consistent with breakage of cyclic P-O-P bonds in the glass when the lithium oxide act as network modifier and both bands are shifted towards lower frequency. The absorption band at ~ 905 cm^{-1} is attributed to asymmetric stretching vibrations of P-O-P groups linked with linear metaphosphate chain [6, 9,10], while that at 1020 cm^{-1} is attributed to asymmetric stretching of P-O-P groups, $\nu_{\text{as}}(\text{P-O-P})$ modes, linked with small metaphosphate rings as cyclotriphosphate $[\text{P}_3\text{O}_9^{3-}]$ or smaller rings. The band at ~ 1100 cm^{-1} is assigned to asymmetric stretching of PO_2^- group, $\nu_{\text{as}}(\text{PO}_2^-)$ modes [9, 18]. The considerable shift in the position of this band toward lower wave number (1098 cm^{-1}) and the increase in its relative area with increasing Li_2O content may be considered as an indication for the formation of the terminal phosphate groups, PO_3^{2-} . The weak band at ~ 1160 cm^{-1} is a good indication for the formation of terminal PO_3^{2-} groups and P-O-P with chain structure. The occurrence of a continuous breakdown of the ring type structures into short arrangements such as small metachains and terminal phosphate groups upon network depolymerization may also account for this behaviour. This development decreases the average length of phosphate chain structures. The broad IR features at 1275 cm^{-1} is attributed to the stretching of the doubly bonded oxygen vibration, $\nu_{\text{as}}(\text{P=O})$ modes [6, 9].

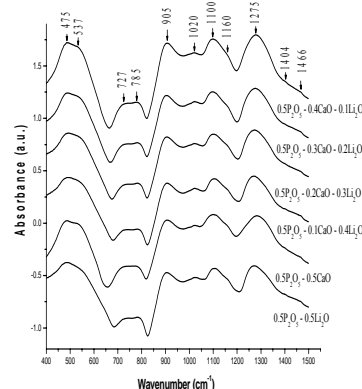


Fig. 2. IR spectra of P_2O_5 -CaO- Li_2O glass system.

It is known that the Raman spectra of phosphate glasses can be divided in two regions around ~ 700 cm⁻¹ and ~ 1200 cm⁻¹ [12,13]. The bands from ~ 700 cm⁻¹ corresponds to bridging stretching modes and that at ~ 1200 cm⁻¹ is ascribed to the terminal P=O stretching vibrations. According to Lines et al. [20] the signals located at ~ 100 cm⁻¹ are due to the well-known boson peaks. Also, the bands observed in the wavenumber regions between 200 and 600 cm⁻¹ are due to complicated internal vibrations such as the skeletal deformation vibrations of phosphate chains and PO₃ deformation vibrations of pyrophosphate segments [21].

The Raman spectra of our glasses present five bands (Fig.3) first at 84 cm⁻¹ and 118 cm⁻¹ due to well-known boson peaks [20], second at ~ 310 cm⁻¹ attributed to skeletal deformation vibrations of phosphate chains and PO₃ deformation vibrations of pyrophosphate segments [21], third at ~ 698 cm⁻¹ attributed to the symmetric stretching mode of P-O-P bridging oxygens, (POP)_{sym}, between Q³ phosphate tetrahedra, the fourth at ~ 1174 cm⁻¹ attributed to the symmetric stretching mode of O-P-O non-bridging oxygens, (PO₂)_{sym}, indicating the formation of Q² phosphate tetrahedra and the fifth bands at ~ 1257 cm⁻¹ attributed to the symmetric stretch of the P=O terminal oxygens, (P=O)_{sym} [12, 22].

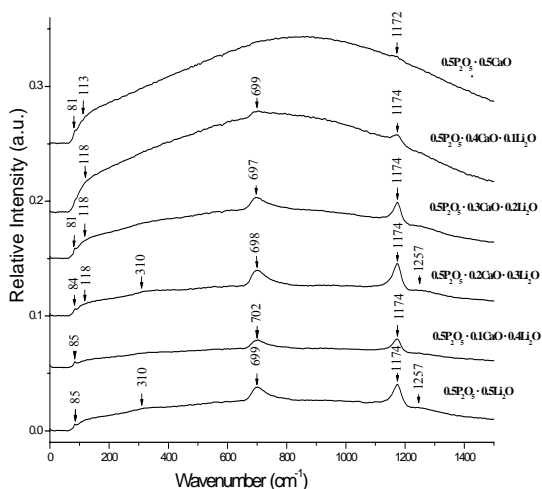


Fig. 3. Raman spectra of P₂O₅-CaO-Li₂O glass system.

The bands from 698 cm⁻¹ and 1174 cm⁻¹ are specific to phosphate glasses, but the assignment of the band centered at ~ 1257 cm⁻¹ represented a problem. Based on several studies of v-P₂O₅ found in literature, Hudgens et al. [22] studied the structure of lithium ultraphosphate glasses. It was observed that the band assigned to P=O terminal oxygens, centered at ~ 1390 cm⁻¹, decreases in wavenumber to ~ 1260 cm⁻¹ with the increasing of the alkali oxide from 20 to 50 mol% and became indistinguishable from the (PO₂)_{asym} mode of a Q² tetrahedron. The explanation was that this decreasing in wavenumber is due to an increase in average length of the

P=O bond resulting from π -bond delocalization on the Q³ tetrahedra [22].

The shape of the Raman spectrum obtained for 0.5P₂O₅ - 0.5CaO sample suggests that it has a more disordered structure than glasses with Li₂O.

b) ESR spectra

The ESR spectra of typical gamma irradiated glass powder samples measured at room temperature are shown in figure 4 and are characterized by a doublet centered at $g=2.023\pm 0.002$ ascribed to phosphorous oxygen hole center (POHC). The term POHC designates the defect responsible for a well-known ESR spectrum in irradiated phosphate glasses characterized by an approximately g tensor with $g \sim 2.009 \pm 0.002$ and a small, nearly isotropic ³¹P hyperfine interaction (~ 40 G) [3, 15]. The g value of the doublet is larger than that of the free spin, consistent with the nature of the hole center.

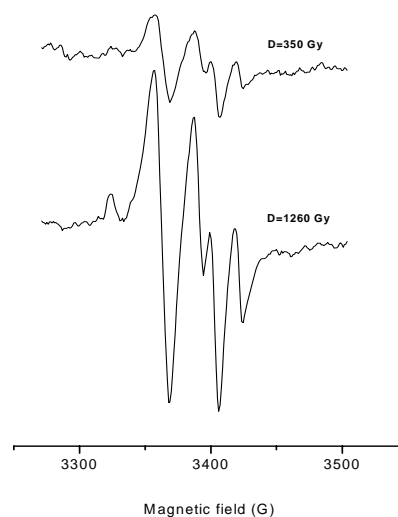


Fig. 4. ESR spectra at room temperature of 0.5P₂O₅ - 0.4CaO - 0.1Li₂O sample γ -irradiated at different dose

Weeks and Bray [19] demonstrated the existence of at least three ³¹P hyperfine doublets of large splitting (70-140 G) in various phosphate glasses subjected to γ -radiation.

Crystalline phosphorus pentoxide P₂O₅ has a structure in which one of the oxygen ions is only bound to a phosphorus ion while the remaining three oxygen ions may either be bonded to another phosphorus ion as bridging oxygens (BO) or they can be at the end positions of the chain, as non-bridging oxygens (NBO).

In crystalline materials two types of oxygen vacancies can be formed, one type by the removal of an oxygen from the non-bridging site and one type by removal of an oxygen from the bridging site. These two types of oxygen vacancies might be expected to occur in P₂O₅ glass since, on average, the same number of BO and NBO per phosphorus ion are expected to be present in the glass as in the crystalline material.

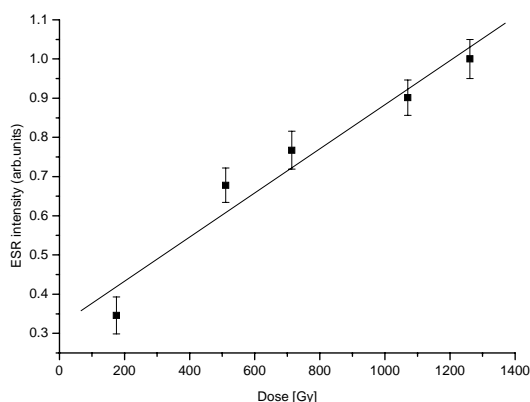


Fig. 5. A linear dose response relationship for $0.5P_2O_5 - 0.4CaO - 0.1Li_2O$ glasses as a function of the irradiated dose.

The observed relationship between absorbed dose and the peak-to-peak height of the ESR first derivative line suggests a linear function in the dose range of $100-10^3$ Gy (Fig. 5). The slope of this line is sufficiently high in order to these glass samples be elected as suitable for dosimetric purpose.

4. Conclusion

In this work, we have undertaken to obtain some information that could contribute to the development of a method for estimating the absorbed dose using a $P_2O_5-CaO-Li_2O$ glass system samples as a dosimeter up to 1.5 kGy gamma dose level. We have chosen this composition because of its stability and low solubility.

IR and Raman spectra allowed us to identify the structural units from the studied phosphate glasses. The presence of the modifier Ca^{2+} and Li^+ cations plays an insignificant role on the structure of phosphate network and are manifest in the spectra only by two IR weak peaks at 1404 cm^{-1} and 1466 cm^{-1} .

The linear relationship between absorbed dose and ESR signal intensity in the range of 100 Gy to 1.5 kGy suggests the possibility of used this glass system for dose measurements.

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