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Dedicated to Professor Dr. Cozar Onuc on His 70th Anniversary

STRUCTURAL CHANGES INDUCED BY ACTINIDES INCORPORATION IN SODA-PHOSPHATE GLASSES

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ABSTRACT. Soda-phosphate glasses incorporating uranium and thorium were investigated with respect to structural effect of UO_3 and ThO_2 content added to P_2O_5-Na_2O glass matrix, as well as to the structural effect of the self-irradiation of the actinide containing glass samples. XRD analysis proves the amorphous state of the as-prepared samples up to 20 mol %. FTIR results support the depolymerisation of the phosphate glass network by progressive increase of the amount of actinide oxide incorporated in the host glass. The self-irradiation determines the occurrence of structural defects evidenced by EPR analysis.

Keywords: *phosphate glasses; self-irradiation; structure.*

1. INTRODUCTION

Oxide glasses have potential application as suitable materials for the embedding and safe storage, i.e., for the immobilization and long-term confinement of nuclear wastes [1-4]. The property of these materials is to retard the release of radionuclides to the biosphere until their radioactivity is reduced to negligible levels. The introduction of radioactive isotopes in glass matrices will induce structural changes in the glass network. The soda-phosphate matrices enter as components of vitreous systems proposed for nuclear waste disposal [5]. The structural modification of the glass matrices induced by the incorporated radioisotopes may afect their stability and storage properties.

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This paper reports on structural changes occured in a soda-phosphate glass matrix hosting uranium and thorium, as evidenced by X-ray diffraction, infrared spectroscopy, and electron paramagnetic resonance spectroscopy.

2. EXPERIMENTAL

Glass samples incorporating up to 20 mol % UO_3 and ThO_2 in $2P_2O_5\ Na_2O$ glass matrix were prepared by melting of $(NH_4)_4HPO_4$, $Na_2CO_3{\cdot}10H_2O$, UO_3 and $Th(NO_3)_2{\cdot}4H_2O$, respectively, used as precursors of P_2O_5, Na_2O, UO_3 and ThO_2 oxides, respectively. The corresponding mixtures of reagents were melted at 1250 ^oC and quickly undercooled at room temperature by pouring in stainless crucibles.

The samples density was measured at room temperature using the Arhimedes method with decationized water as immersion fluid. X-ray diffraction analysis was carried out with Shimadzu LabX XRD-6000 diffractometer, using Cu K_α radiation (λ = 1.5405 Å) with Ni-filter. The measurements were performed in 2θ geometry, with a scanning speed of 5^o/min, for 2θ angles ranging between 10^o and 100^o. The operation voltage was 40 kV and the current was 30 mA. Fourier transform infrared (FTIR) spectra were recorded at a resolution of 4 cm^{-1} with a Bruker Equinox 55 spectrometer, at room temperature. Electron paramagnetic resonance measurements were performed at room temperature with a JEOL JES-3B spectrometer operating at 9.4 GHz (X-band).

3. RESULTS AND DISCUSSION

Density measurements indicate an increase of density values from 2.2 g/cm^3 for the host matrix to 2.5 g/cm^3 for the sample with 20 mol % actinide oxide. These values are not only on the account of samples composition, but they are also influenced by the degree of structural compactness due to geometrical configuration modifications in the glass network related to the coordination change of the former ions and the variation of dimensions of the interstitial holes [6]. The addition of UO_3 or ThO_2 leads to the increased breaking of the P-O-P bonds in the phosphate structural units and implicitely to the decrease of the number of bridging oxygens.

The XRD patterns of the as-prepared samples (Fig. 1) attest their vitreous state. For barium borosilicate glasses containing ThO_2 samples prepared at 1000 ^oC [3] three sharp peaks superimposed over the broad pattern were recorded at 27.6^o, 45.8^o and 54.3^o which are characteristic of crystalline ThO_2 [JCPDS - file card 42-1462] and denote a partial phase separation of ThO_2 in the glass matrix. The higher melting temperaure of our ThO_2-P_2O_5-Na_2O system impeded such a phase separation up to x = 20 mol % ThO_2.

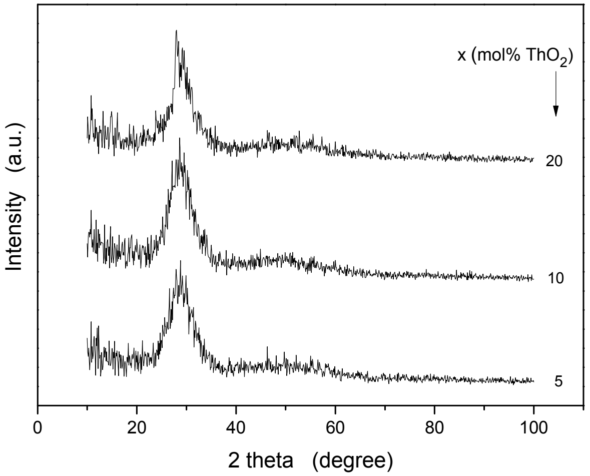

Fig. 1. XRD patterns of xThO$_2$·(100-x)[2P$_2$O$_5$·Na$_2$O] samples

The FTIR spectra recorded from thorium containing samples (Fig. 2) consist of large absorption bands typical for the vitreous samples. The main absorption bands are centered around 485, 540, 615, 770, 920, 1120 and 1260 cm^{-1}. Absorption bands assignable to ThO$_2$ [7] are not detected. All these bands recorded in the spectral range up to 1300 cm^{-1} are assigned to vibrations of P–O bonds in $(PO_4)^{3-}$ structural units. The $(PO_4)^{3-}$ tetrahedra interconnected to form the phosphate glass network may occur as Q^3, Q^2, Q^1 and Q^0 species according to the number of the bridging oxygens in (PO$_4$) units, expressed by *n* in this Q^n notation.

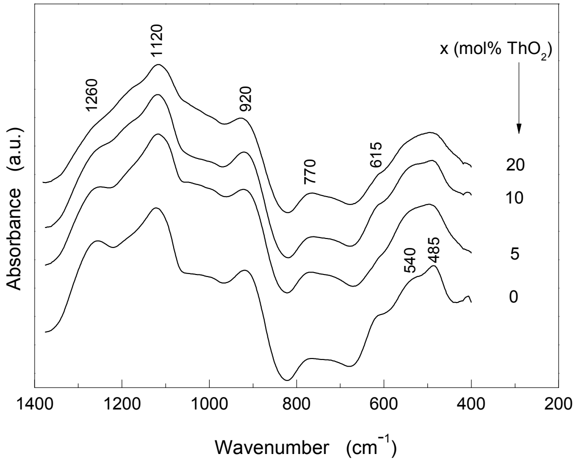

Fig. 2. FTIR spectra of xThO$_2$·(100-x)[2P$_2$O$_5$·Na$_2$O] samples

The progressive addition of thorium influences the position of the infrared absorption bands, mainly a shift of 770 cm^{-1} band to lower wavenumbers is observed, as well as the broadining of all bands due to the increase of the structural disorder by enhancement of non-bridging oxygens on account of bridging oxygens shared by the phosphate tetrahedra. This structural change implies to a certain extent the glass network depolymerisation of ThO_2 hosting material.

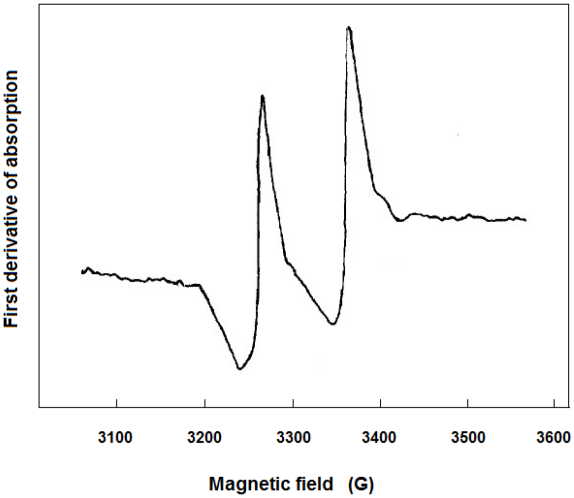

Fig. 3. EPR spectrum recorded from the sample containing 5 mol % UO_3.

The EPR spectra of as prepared samples embedding radioactive nuclides contain no resonance signal, but already after storage for a week an EPR signal (Fig. 3) arising from defects of electron trapped at a non-bridging oxygen vacancy type is observed [8]. The doublet structure is due to the interaction of the electron with the nearest of the neighboring phosphorus nuclei.

4. CONCLUSIONS

The investigation of $xUO_3\cdot(100-x)[2P_2O_5\cdot Na_2O]$ and $xThO_2\cdot(100-x)[2P_2O_5\cdot Na_2O]$ systems with $0 \leq x \leq 20$ mol % followed the structural changes in the glass matrix induced by increasing content of actinide oxide and by the inside delivered radiation. Actinides incorporation in P_2O_5-Na_2O glass matrix up to 20 mol % preserves the vitreous state of the as prepared samples. Nevertheless, actinide oxide addition causes the depolymerisation of the phosphate glass network as proved by FTIR spectroscopic results. Due to the self-irradiation owing to radioactive decay of the actinides, structural defects of oxygen vacancy type were evidenced by EPR spectroscopy.

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