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Effect of selenium addition on network connectivity in P_2O_5-CaO-MgO-Na_2O glasses

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ABSTRACT

A new glass system $xSeO_2(1-x)[40P_2O_5$-30CaO-20MgO-$10Na_2O]$ with nominal concentration of SeO_2 ranging between 0 and 20 mol% was obtained by melting method. The amount of selenium determined on samples surface is much lower than that expected according to the added SeO_2 amount, and this is due first to selenium volatility during melting. The Fourier transform infrared and Raman results evidence the glass network depolymerisation induced by progressive addition of selenium. The depolymerisation effect occurs more pronounced on samples surface than in their inside, as indicated by X-ray photoelectron spectroscopy analysis with respect to the dependence of bridging and non-bridging oxygens on selenium content.

1. Introduction

Selenium containing bioactive glasses with potential applications in tissue engineering attracted interest in the attempt to combine the scaffold properties of the bioactive glasses with the properties of selenium that is an essential component of glutathione peroxidase antioxidant enzyme preventing the cell degeneration of tissues [1–4]. The behavior of these materials strongly depends on their structural properties.

Structural order in the phosphate glasses can be described using Q^n terminology, where n is the number of bridging oxygens connecting PO_4 units per PO_4 tetrahedron [5–7]. The addition of alkali and alkaline earth cations and the lowering of phosphorus content can depolymerize the glass network [8–10].

The aim of the present study was to obtain $xSeO_2(1-x)[40P_2O_5$-30CaO-20MgO-$10Na_2O]$ glasses where in the nominal amount of SeO_2 was progressively increased up to 20 mol%, and further to analyse their local structure, particularly the effect of selenium addition to P2O5-CaO-MgO-Na_2O glasses on the glass network connectivity.

2. Experimental

Glass samples of $xSeO_2(1-x)[40P_2O_5$-30CaO-20MgO-$10Na_2O]$ system prepared with up to 20 mol% SeO_2 were obtained by conventional melt quenching technique. Compositionally corresponding amounts of reagent grade $NH_3{\cdot}H_2PO_4$, $CaCO_3$, $(Mg\ CO_3)_4$, $Mg(OH)_2{\cdot}5H_2O$, $Na_2CO_3{\cdot}10H_2O$ and SeO_2 were thoroughly mixed and melted for 20 min at 1200 °C in air, in sintered corundum crucibles, in a Carbolite 1600 furnace, and thereafter the melts were quickly cooled at room temperature by pouring and stamping between copper plates.

The samples structure was investigated by X-ray diffraction using a with a Shimadzu XRD-6000 diffractometer with graphite monochromator (CuK_α radiation, $\lambda = 1.54$ Å).

X-ray photoelectron spectroscopy (XPS) analysis was performed using a SPECS system at a pressure in the analysis chamber $< 5 \times 10^{-9}$ mbar. XPS spectra were obtained using monochromatic Al Kα radiation. The spectra were corrected for the charging effect. Because the samples have been exposed to the atmosphere an adventitious carbon contamination was detected. The binding energies were referenced to the C 1s XPS peak (284.6 eV) of contamination/adventitious carbon. Surveys were recorded in steps of 1 eV and high resolution spectra with 0.05 eV steps. Analysis of the data was carried out with Casa XPS software [10,11].

The samples were investigated by Fourier transform infrared spectroscopy in KBr pellets, using a JASCO 6200 FTIR spectrometer (number of scans, 256; resolution 4 cm^{-1}; range 4000–400 cm^{-1}). Identical amounts of glass samples were powdered and mixed with KBr in order to obtain thin pellets containing approximately 1 wt% glass powders. The pellets thickness was about 1.5 mm.

Raman spectra were obtained using multilaser confocal Renishaw InVia Reflex Raman spectrometer ($\lambda = 532$ nm). The samples were scanned from 100 to 2000 cm^{-1} wavenumber shift at a spectral

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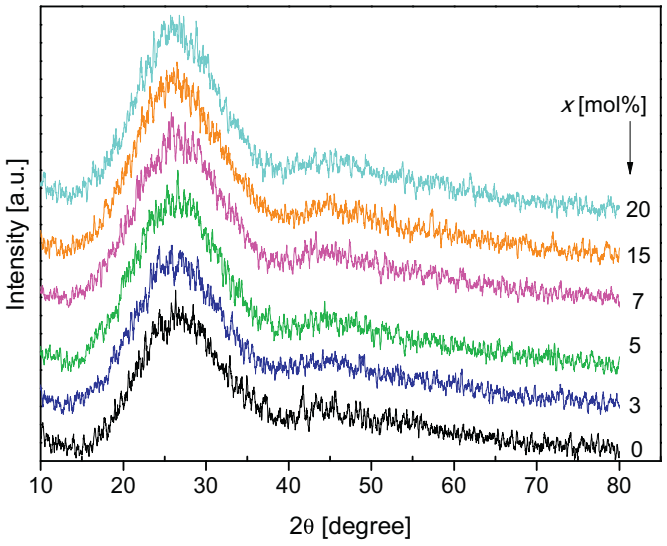

Fig. 1. X-ray diffractograms recorded from $xSeO_2(1-x)[40P_2O5\text{-}30CaO\text{-}20MgO\text{-}10Na_2O]$ system.

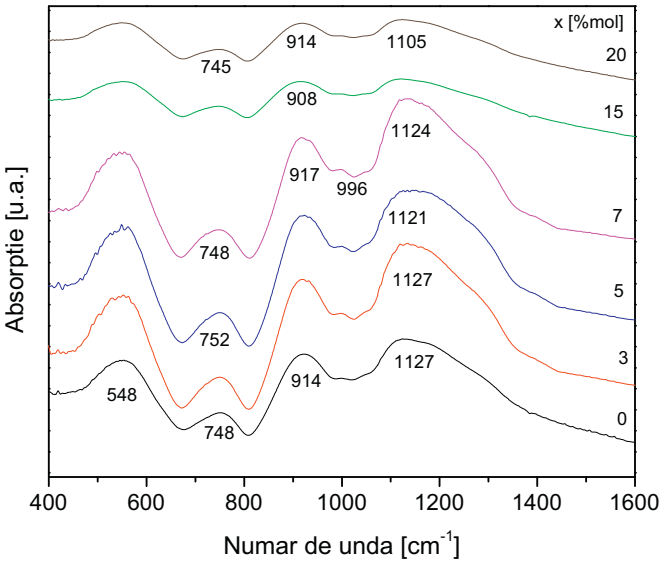

Fig. 3. FTIR spectra of $xSeO_2(1-x)[40P_2O_5\text{-}30CaO\text{-}20MgO\text{-}10Na_2O]$ samples.

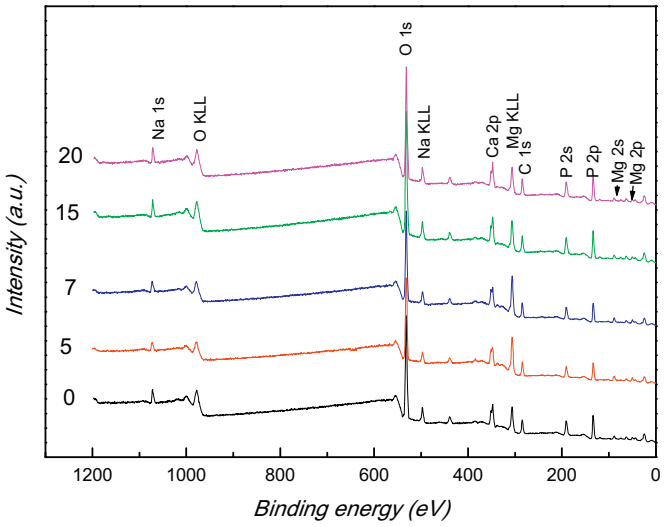

Fig. 2. XPS survey spectra of $xSeO_2(1-x)[40P_2O_5\text{-}30CaO\text{-}20MgO\text{-}10Na_2O]$ samples.

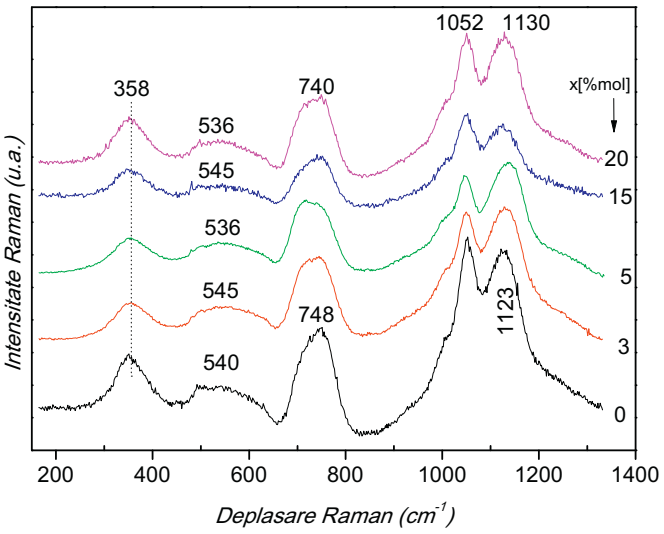

Fig. 4. Raman spectra of $xSeO_2(1-x)[40P_2O_5\text{-}30CaO\text{-}20MgO\text{-}10Na_2O]$ samples.

resolution of 1 cm^{-1}. The data acquisition time was 40 s and averaging was performed over 10 measurements.

3. Results and discussion

The large X-ray diffraction patterns prove the amorphous state of $xSeO_2(1-x)[40P_2O5\text{-}30CaO\text{-}20MgO\text{-}10Na_2O]$ samples for all compositions (Fig. 1).

The elemental composition on the outermost layer of the samples, as evidenced by X-ray photoelectron spectroscopy from analysis of survey spectra (Fig. 2) excluding the carbon contamination, differs from the expected/calculated bulk composition (Table 1), and this result could be related not only to surface particularities but also to the high selenium fugacity/volatility [12].

The effect of selenium addition to P_2O_5-CaO-MgO-Na_2O host glass on glass network connectivity was investigated using spectroscopic

Table 1
Elemental surface concentrations (at.%) on the outermost layer of $xSeO_2(1-x)[40P_2O5\text{-}30CaO\text{-}20MgO\text{-}10Na_2O]$ samples.

x [mol%]	Elemental concentration [at.%]											
	XPS data						Nominal bulk concentrations					
	O	P	Ca	Mg	Na	Se	O	P	Ca	Mg	Na	Se
0	53.9	23.3	9.5	10.8	2.5	–	63.41	19.51	7.32	4.88	4.88	–
5	52.6	23.6	9.9	11.3	2.6	–	63.53	18.79	7.04	4.70	4.70	1.24
7	53.2	22.3	10	11.6	2.8	0.1	63.59	18.49	6.94	4.62	4.62	1.74
15	54.2	21.4	8.9	13.0	2.3	0.2	63.79	17.28	6.48	4.32	4.32	3.81
20	53.8	22.1	9.4	11.5	2.4	0.8	63.92	16.50	6.19	4.12	4.12	5.15