Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

# Structural effect of cobalt ions added to a borophosphate-based glass system

R. Lucacel Ciceo[a,b,*], M. Todea[b,c], R. Dudric[a], A. Buhai[a], V. Simon[a,b]

[a] Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania
[b] Interdisciplinary Research Institute on Bio-Nano-Science, Babes-Bolyai University, Cluj-Napoca, Romania
[c] Department of Molecular Sciences, Faculty of Medicine, Iuliu Haţieganu University of Medicine and Pharmacy, Cluj-Napoca, Romania

ARTICLE INFO

*Keywords:*
Vitreous
Crystallites
Local structure
Cobalt ions
XRD, XPS, FTIR, Raman

ABSTRACT

A new melt derived glass system consisting of $Co_2O_3$ added to $40P_2O_5{\cdot}25B_2O_3{\cdot}25CaO{\cdot}10Na_2O$ matrix was investigated in order to evaluate the influence of cobalt ions on the network structure. Multiple techniques, i.e. X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS) were used to characterize the local structure, the nature of the chemical bonding and the surface composition of these samples. The XRD measurements proved the vitreous character of samples with 0 and 3 mol% $Co_2O_3$. At higher cobalt oxide content (5, 7 and 10 mol%) the occurrence of a crystalline phase characteristic to $Co_2P_4O_{12}$ has been observed. The complementary spectroscopic studies (FTIR and Raman) revealed that the incorporation of $Co_2O_3$ enhances the network connectivity and thereby the short range order in samples. Depending on their amount, the cobalt ions differently influence the borophosphate network via the tetraborate/triborate and metaphosphate/pyrophosphate ratios. For the sample containing 10 mol% $Co_2O_3$ the FTIR analysis indicates absorptions assigned to vibrations in $CoO_6$ tetrahedra and suggests the presence of six-coordinated cobalt ions in $Co^{3+}$ valence state. This study has proven that borophosphate based glasses are able to entrap cobalt ions, are sensitive from structural point of view to the amount of $Co_2O_3$ and possess interesting structural peculiarities.

## 1. Introduction

Multicomponent glasses are widely studied since their properties can be controlled by changing the ratio of the components. Borophosphate glasses represent one of the most interesting class of glass materials since their properties highly differ of pure borate and phosphate glasses and recommend them for a quite diverse range of applications, from fast ion conductors in solid-state batteries [1], low-melting glass solders [2], hermetic sealing materials [3,4] to more recently, biomaterials [5–7].

The interest in phosphate based biomaterials comes from their application in bone tissue engineering. In the inorganic phase of the human bone, which is the biological apatite, calcium is present beside phosphorus, so its addition in the compositions considered for bone tissue reconstruction is needed [8–10]. Following recent studies, the boron additions in the phosphate network improves the chemical durability, as well as the thermal and mechanical stability of the glasses [6,7,11]. At the same time, boron itself is a stimulating agent for bone tissue engineering [12–16]. The natrium oxide diminishes the melting temperature of glasses and increases the glass degradability [17–20] so that it is a desirable component of bioglasses.

In order to improve the biological behaviour of bioglasses designed for regenerative medicine applications, a variety of metallic ions such as copper, silver, strontium, gallium, magnesium, zinc and cobalt have been incorporated into different glass compositions [12,21]. Some of these ions stimulate the osteogenesis and angiogenesis process helping the bone formation while some of them confer other properties like antibacterial activity, for example. Low oxygen pressure (hypoxia) plays a vital role in the development and regeneration of skeletal tissue [22–26] and cobalt ions are mimic hypoxia agents, so that their additions in the biomaterial composition is once more motivated [27–29].

In the glass technology the cobalt ions are known to act as nucleating agents that promote the crystallization process. Their influence on the structural characteristics of glasses is influenced by samples composition, synthesis method and parameters. Usually, in vitreous materials cobalt ions exist in two stable valence states, $Co^{2+}$ and $Co^{3+}$. The $Co^{2+}$ ions are disposed in octahedral (six coordinated) and tetrahedral (four coordinated) structural units while the $Co^{3+}$ ions are found in octahedral (six coordinated) units, mainly [30]. The relative variation in the concentration of these structural units strongly influences the structure and the properties of the host glass and/or glass-ceramic.

This study is focused on the structural effect of cobalt ions

* Corresponding author at: Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania.
*E-mail address:* raluca.lucacel@phys.ubbcluj.ro (R. Lucacel Ciceo).

https://doi.org/10.1016/j.jnoncrysol.2017.11.050
Received 3 November 2017; Received in revised form 28 November 2017; Accepted 29 November 2017

incorporation in a new borophosphate based vitreous matrix. The starting composition $40P_2O_5{\cdot}25B_2O_3{\cdot}25CaO{\cdot}10Na_2O$ of the host glass matrix was chosen having in mind the potential application of this glass as borophosphate biomaterial [31], but the structural investigation of materials of such a composition may be useful to extend their practical applications as optical devices or rechargeable batteries. The system was synthesized using the classical melt quenching method. The structural changes imposed by the cobalt ions additions were followed first by X-ray diffraction (XRD), then on the basis of two complementary spectroscopic techniques, infrared absorption and Raman scattering, as well as by X-ray photoelectron spectroscopy (XPS). The spectroscopic results have been used to elucidate the connectivity of the various structural groups such as that of phosphorus – oxygen, boron – oxygen, and mixed units, especially after the addition of $Co_2O_3$.

## 2. Experimental procedure

### 2.1. Samples synthesis

The $40P_2O_5{\cdot}25B_2O_3{\cdot}25CaO{\cdot}10Na_2O$ based composition with different $Co_2O_3$ content, up to 10 mol%, were prepared by conventional melt quenching technique. Appropriate quantities of reagent grade $NH_3{\cdot}H_2PO_4$, $H_3BO_3$, $CaCO_3$, $Na_2CO_3{\cdot}10H_2O$ and $Co_2O_3$ were mixed in an agate mortar. The $xCo_2O_3{\cdot}(100-x)[40P_2O_5{\cdot}25B_2O_3{\cdot}25CaO{\cdot}10Na_2O]$ batches ($x$ = 0, 3, 5, 7 and 10 mol%) were melted in air, in sintered corundum crucibles, in an electric furnace at 1200 °C for 15 min. The melts were quickly cooled at room temperature by pouring and stamping between two copper plates. All samples are transparent, colorless for sample with $x$ = 0 and with different shades of blue for the rest of them. The blue shade intensity increases with the cobalt ions addition. Glass frit was ground to powder in a Retsch Planetary ball mills, type PM 100.

### 2.2. Characterization methods

The structure of the samples was investigated by X-ray diffraction (XRD) using a standard Bruker X D8 Advance diffractometer with a monochromator of graphite for Cu Kα radiation. The XRD patterns were recorded in 2θ range from 10° to 80° with a speed of 2°/min.

X-ray photoelectron spectroscopy (XPS) analysis was carried out on finely powdered samples using a SPECS PHOIBOS 150 MCD system equipped with monochromatic Al Kα source (250 W, $h\nu$ = 1486.6 eV), hemispherical analyser and multichannel detector. The typical vacuum in the analysis chamber during the measurements was in the range of $10^{-9}$–$10^{-10}$ mbar. Charge neutralization was used for all samples. The binding energy (BE) scale was charge referenced to the C 1s photoelectron peak at 284.6 eV. The elemental composition on samples surface was obtained by a standard quantitative XPS analysis of survey spectra acquired at pass energy of 100 eV in the binding energy range 0–1200 eV. The atomic concentrations were estimated from the areas of the characteristic photoelectron lines assuming a Shirley type background. High-resolution spectra were obtained using analyser pass energy of 30 eV. The position and full width at half maximum of photoelectron peaks were estimated by spectra deconvolution with Casa XPS (Casa Software Ltd., UK).

For Fourier transform infrared (FT-IR) measurements identical amounts of glasses 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. The spectra were recorded at room temperature in the 350–4000 $cm^{-1}$ range with a 6100 Jasco spectrometer with a maximum resolution of 0.5 $cm^{-1}$ and signal/noise ratio 42,000:1.

Raman spectra were obtained using multilaser confocal Renishaw InVia Reflex Raman spectrometer (λ = 532 nm). The samples were scanned from 100 to 2000 $cm^{-1}$ wavenumber shift at a spectral resolution of 1 $cm^{-1}$. The data acquisition time was 40 s and averaging was performed over 10 measurements.

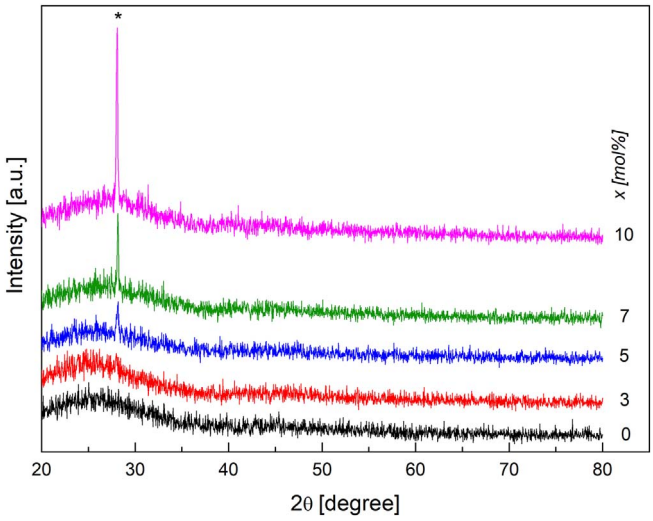


**Fig. 1.** X-ray diffraction patterns of $xCo_2O_3{\cdot}(100-x)[40P_2O_5{\cdot}25B_2O_3{\cdot}25CaO{\cdot}10Na_2O]$ samples.

## 3. Results

According to X-ray diffraction patterns presented in Fig. 1, the cobalt free sample and that with 3 mol% $Co_2O_3$ exhibit vitreous structure. The XRD spectra of samples with $x$ = 5, 7 and 10 mol% $Co_2O_3$ point out a crystalline peak centred at 2θ = 28.10 attributed to the $Co_2P_4O_{12}$ crystalline phase [32,33]. The intensity of this peak progressively increased when the $Co_2O_6$ content increased from 5 to 10 mol%.

In Fig. 2 the XPS survey spectra of the obtained glass and glass-ceramic samples are shown. The survey spectra are quantified in terms of peak intensities and peak positions. All XPS and Auger peaks from the constituent elements of the obtained glasses were clearly identified and marked on the spectra. The results obtained for the atomic concentrations on the outermost layer of samples surface are listed in the Table 1.

Usually, the cobalt ions detection in glasses is done using the Co $2p_{3/2}$ and Co $2p_{1/2}$ doublets observed at about 790 eV and 794 eV. For our samples these peaks were detected as extremely weak, but the peak at 101 eV, assigned to the Co 3s photoelectrons was clearly evidenced. This could be due to Co 2p signal broadening and intensity decreasing noticed in powder samples [34]. We used the Co 3s peak for cobalt in the elemental analyses of the samples. Moreover, increasing the $Co_2O_3$

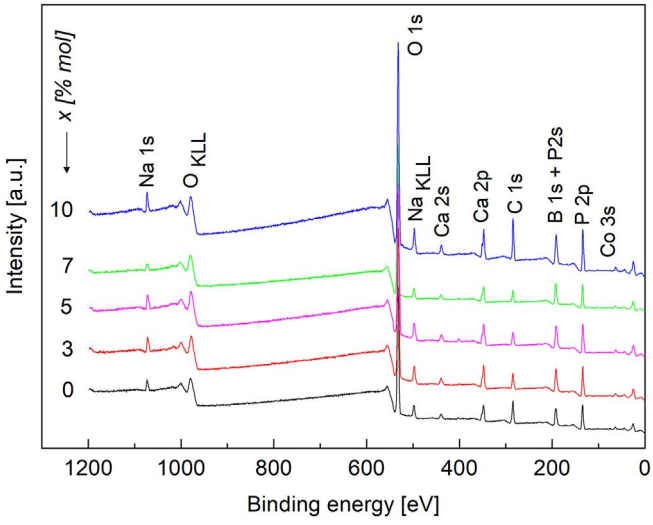


**Fig. 2.** XPS survey spectra of the investigated $xCo_2O_3{\cdot}(100-x)[40P_2O_5{\cdot}25B_2O_3{\cdot}25CaO{\cdot}10Na_2O]$ samples.