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STRUCTURAL INVESTIGATIONS OF AG_2O-B_2O_3-CAO-P_2O_5 GLASS AND GLASS-CERAMIC SYSTEM

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ABSTRACT. The paper investigated the $1.5Ag_2O\cdot98.5[0.47B_2O_3(0.53\text{-}x)CaOxP_2O_5]$ system prepared in vitreous state using the rapid melt quenching method. In order to obtain glass-ceramic samples, the glass was heat treated to 650ºC during 6 hours. The structural units BO_3 and BO_4 which build the vitreous network and the modifications occurred following partial crystallization were clearly highlighted by Raman and IR spectroscopy. The analysis by X-ray diffraction showed the vitreous features of the samples before the heat treatment and reveals that the crystalline phase developed into the vitreous matrix is $Ca_{10}(PO_4)_6(OH)_2$. The structural changes before and after the heat treatment have been investigated considering the B_2O_3/P_2O_5 ratio.

Keywords: *glass, glassceramic, phosphorous oxide, silver*

INTRODUCTION

The boron oxide was generally studied [1-4] due to its capacity to build vitreous network. The main structural units in glass were identified and has been demonstrated that the boron may be tetra- and three coordinated. The oxide matrix on B_2O_3 are used in tissue engineering as structural scaffold for cell growth that are to be implanted into the body, having direct clinical implications in cartilage, skin and vascular system restoration [4].

The oxide glass containing silver oxide are used in the infections treatment, due to their bacteriostatic and bactericide properties [5], but also in implantology, these two aforesaid properties are also beneficial in this last mentioned medical field. Due to the silver properties, these materials are considered as a separate class of oxide materials, being difficult to obtain, because metallic silver separates in drops on the surface of the new formed glass, during cooling process. The glass doped with Ag^+ can be prepared using the surface ionic exchange method, sol-gel method [6] and using rapid melt quenching method [7].

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The vitreous materials based on phosphorus are widely used [1, 8] for growth stimulation of bone tissues, leading to the formation of hidroxyapatite (HA) layer between the organic tissue and inorganic material. The presence of vitreous network modifiers as CaO in the vitreous material structure helps the formation of bioactive glass which can be used in implants [9] without "non-self" rejection or in stimulation of bone tissue regenerations. The bond between inorganic and organic component is stronger than the bone itself.

The Raman and IR spectroscopy are extremely sensitive techniques for the structural analysis and for the modifications occurring after the heat treatment, allowing the identification of structural units [10] in vitreous structure and for detecting of (HA) formation on the surface of material tested "in vitro" conditions.

The aim of this paper was to obtain a vitreous oxide material based on B_2O_3 which to homogenous include silver ions in a molar content as large as possible and its structural characterization using Raman and IR spectroscopy in order to identify the structural units which are formed in the new materials. The paper is an investigation of vitreous network structure changes occurred following the modification of the molar ratio of two classical forming compounds of vitreous network B_2O_3 and P_2O_5. Also the possibility that their structural units participate together to the formation of vitreous network has been studied. The research aims to obtain a new system, useful in medical area to deliver sufficient ions content for having bactericide and bacteriostatic effect and to build (HA) layer in contact with bone tissue.

RESULTS AND DISCUSSION

X-ray powder diffraction patterns for the thermally untreated samples are shown in Figure 1. One can see that the all investigated samples are in amorphous state. The samples with $x = 0$ and 0.02 are characterized by two halos which are specific to amorphous samples, the most intense maximum being located at 29.6° (2θ). The relation between the most frequently occurring interatomic distance R and the position of the strongest observable maximum is given by the relationship [11]: $R = \frac{5\lambda}{8\sin(\theta)}$, where λ is the wavelength of X-ray beam and θ is the diffraction angle. From this relation R= 3.76Å for samples $x = 0$ and $x = 0.02$.

For samples with $x \geq 0.05$ a new halo appears for 2θ ~21.7° value. The frequently corresponding interatomic distances for this maximum is R = 5.11Å. The appearance of an additional maximum at a smaller angle suggests a supplementary order between atoms corresponding to some larger distances.

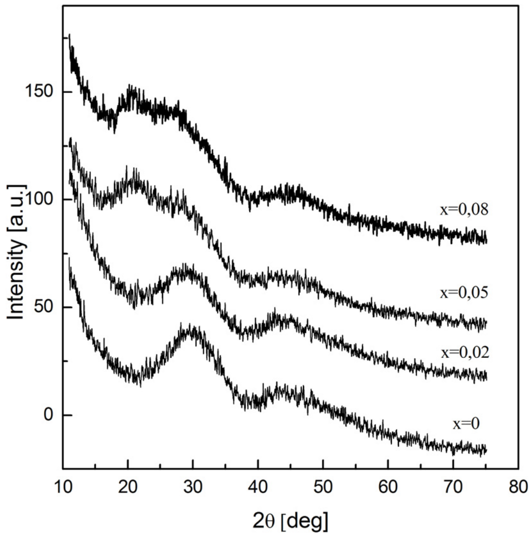

Figure 1. X-ray powder diffraction patterns for the thermally untreated samples of 1.5%Ag_2O 98.5%[$0.47B_2O_3(0.53-x)CaOxP_2O_5$] system

The X-ray powder diffraction patterns for heat treated samples are presented in Figure 2. The samples with x = 0 and x = 0.02 contain only amorphous phase, while samples x = 0.05 and x = 0.08 contain both crystalline and vitreous phase. The crystalline phase was identified as being $Ca_{10}(PO_4)_6O$, as listed in PDF 89-6495, which crystallizes in hexagonal system having the following [12] lattice parameters: a = 9.432 Å and c = 6.881 Å. One can remark that for the samples which have an additional halo at 21.7° (2θ) before heat treatment, after heat treatment they contain both crystalline and amorphous phase. CaO reacts with B_2O_3 and P_2O_5 the two classical vitreous network formers depending on their optical basicity [13], thus it is natural that the crystalline state containing PO_4 to be formed.

The IR spectra of vitreous samples (Figure 3) from the oxide system $1.5Ag_2O98.5[0.47B_2O_3(0.53-x)CaOxP_2O_5]$ with $0 \leq x \leq 0.08$ mol% content in glass matrix, present absorption bands in the spectral domain 1600-400 cm^{-1}. The wide bands structure points to the structural disorder within the system itself, i.e., for each molar ratio among its components.

As shown [14] the glass exclusively based on B_2O_3 is composed of boroxol rings which form a vitreous network [15], with local order and of BO_3 triangles. The vitreous structure based on boroxol rings is maintained also depending on the quantity and type of the network modifier oxide introduced in the starting matrix up to 25% molar content.

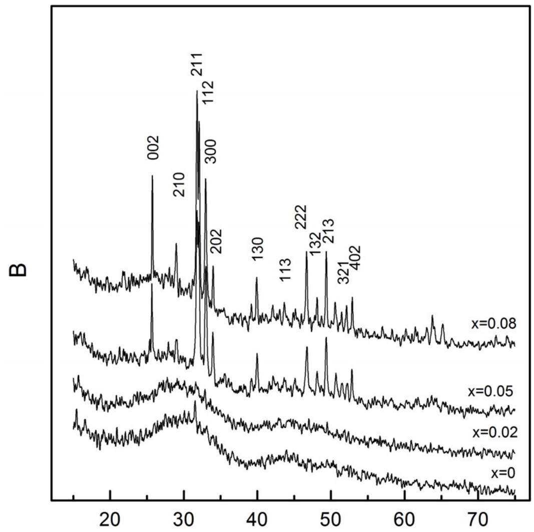

Figure 2. X-ray powder diffraction patterns for the thermally treated samples of 1.5%Ag_2O98.5%[0.47B_2O_3(0.53-x)CaOxP_2O_5] system

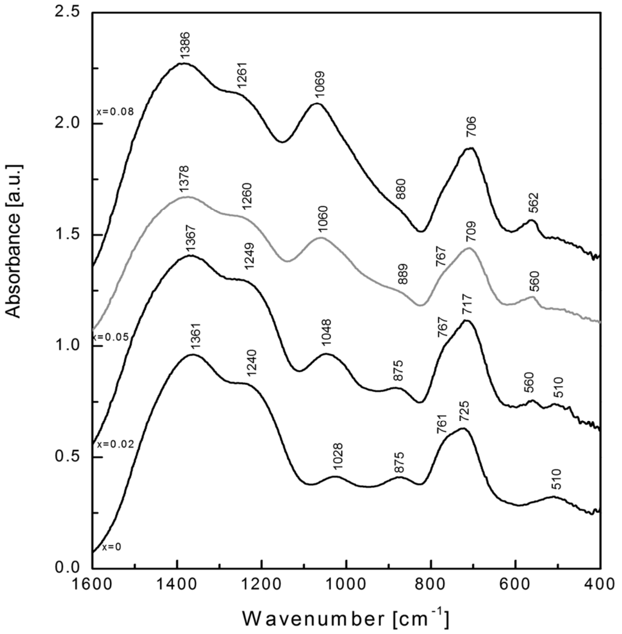

Figure 3. IR spectra of 1.5%Ag_2O 98.5% [0.47B_2O_3(0.53-x)CaO xP_2O_5] vitreous system

In the investigated vitreous system 1.5%Ag_2O98.5%[0.47B_2O_3 (0.53-x)CaOxP_2O_5], one expects the occurrence of the bands characteristic to other borate units, resulting for the fragmentation of the network, together with the modification of the oxides ratio. These are as follow diborate ($B_4O_7^{2-}$), tetraborate ($B_8O_{13}^{2-}$), pentaborate ($B_5O_8^-$) etc. and the boron atoms will exist in both three- and four-coordinated states.

The samples with $x \leq 0.02$ reveal identical absorption bands in the entire spectral range with the exception with the small wave numbers range 400-600 cm^{-1}. Thus, if in x = 0 and x = 0.02 spectra, there is a wide IR band at ~510 cm^{-1}, in x = 0.02 sample a new band at ~560 cm^{-1} appears, in the same spectral domain. The band at ~510 cm^{-1} was assigned to the B-O-B bending vibration [16], this vibration type being more possible when there are no boroxol rings B_3O_6 in glass structure.

While the P_2O_5 content increases in the B_2O_3-CaO-P_2O_5 matrix, the intensity of the band at ~560 cm^{-1} increases without modifying its spectral position and the broad band at 510 cm^{-1} become invisible in spectra. The band at ~560 cm^{-1} was assigned to the characteristic bands of bending vibration of P-O-P linkage in basic units of phosphate glasses [17-19].

Around 700 cm^{-1} it is the domain of B-O-B bending vibrations in borate networks [20] and the IR band at ~706 cm^{-1} was assigned to B-O-B linkage in borate networks [13], this vibration may be assigned to a certain linkage between two trigonal boron atoms [21]. The intensity and width of this band depend on the matrix composition and its position shifts towards smaller wave numbers with the increase of P_2O_5 in the oxide matrix, which demonstrate that the borate network has a limited vibrational freedom in the presence of phosphate groups.

The band has a shoulder at 761 cm^{-1} (x = 0) that decreases in intensity, being included in the line assigned to B-O-B vibration (~700 cm^{-1}), was attributed to the O_3B-O-BO_4 linkage bending vibrations [22, 23], while to the B-O bond stretching vibration in BO_4^- units, was associated with the band at ~870 cm^{-1} [17].

The wide band at ~1028 cm^{-1} becomes more clearly defined and more intense as the P_2O_5 molar content increases into the oxide matrix and move towards larger wave numbers. This is the characteristic of BO_4 units, specifically to the stretching vibration of B-O bond in BO_4 tetrahedron [24]. Once with the further addition of the P_2O_5 content (the number of BO_4 units increases) the band moves towards larger wave numbers, for x = 0.08 reaching to ~1080 cm^{-1}, last frequency is also assigned to $(PO_3)_{as}$ vibrations [25]. This band movement assigned to boron towards larger wave numbers shows that the borate network is more fragmented and has a larger freedom of motion.

The binary glass based on boron contains triangular BO_3 units besides BO_4 tetrahedron units. These can be comprised in BO_3^- orthoborate dimmer units and the band at ~1240 cm^{-1} is assigned for them [26]. This band intensity decreases once with the reduction of molar ratio B/P into the matrix, but for $x > 0.02$ has the same intensity with the BO_4 units typical band.

For larger wave numbers there is a wide band at ~1366 cm^{-1}. The band line width remains unchanged in the whole composition domain researched and was attributed to asymmetric stretching mode of borate triangles BO_3 occurring in complex units [26].

The modification of CaO/P_2O_5 ratio into the oxide matrix leads to modification of the ratio between three coordinate boron (1240 cm^{-1}) and tetracoordinate boron (1080 cm^{-1}) and isomerisation occurs in boron based species.

Due to the formation of Ag-O covalent bond in the glass, the absorption band appears at ~620 cm^{-1} [16]. This peak is absent here, thus we cannot establish that these bonds are forming, or their number is very small and have no influence upon the glass network vibration.

The influence of heat treatment (t = 650°C) upon vitreous samples from $1.5\%Ag_2O98.5\%[0.47B_2O_3(0.53-x)CaOxP_2O_5]$ system cannot be observed in all spectra of the investigated samples. Thus for $x \le 0.02$ the samples IR spectra are identical with those of the samples of vitreous system (Figure 4).

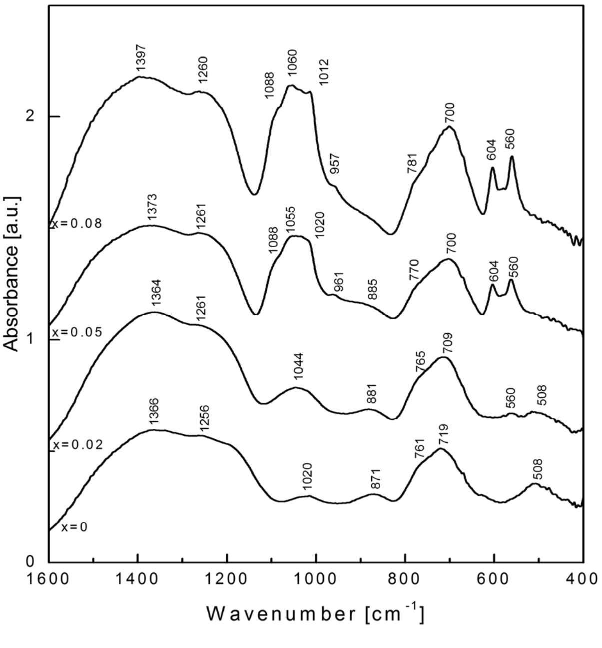

Figure 4. IR spectra of $1.5\%Ag_2O98.5\%[0.47B_2O_3(0.53-x)CaOxP_2O_5]$ heat treated system

For $x \geq 0.05$ the heat treatment effect is obvious in IR spectra, due to the occurrence of a new band at ~604 cm^{-1} near the band at ~560 cm^{-1} and disappearance of the band at 508 cm^{-1}. The band at ~560 cm^{-1} and at ~604 cm^{-1} was assigned to the bending vibrations of the P-O-P phosphate structural units occurring in oxide glass [17]. In this compositional domain the band at ~560 cm^{-1} is more intense and narrow than the one appearing at the same wave number in the vitreous structures and the band at ~604 cm^{-1} is localized. The shape of the two bands reveals the appearance of the structural order at distance and of the crystalline phases containing P_2O_5 as shown by the X-rays.

Following the thermal treatment, the spectral domain $\nu \in$ [850-1100] cm^{-1}, assigned to the B-O bond bending vibrations from BO_4 units, is restructured through the occurrence of a significant number of bands into the samples sensitive to thermal treatment.

The IR band at ~961 cm^{-1} is due to the groups containing BO_4 units [21] especially in diborate groups.

Thus, starting from the same concentration of P_2O_5 in the vitreous matrix, in the spectral range, three IR bands are revealed: at ~1020 cm^{-1}, ~1055 cm^{-1} and ~1088 cm^{-1}, which replace the wide band at ~1020 cm^{-1} ($x = 0$). According to Gaafar [17] this spectral domain is associated with the B-O bond stretching vibrations of BO_4^- tetrahedral (830-1120 cm^{-1}).

In the IR spectra we are expecting the occurrence of the bands due to the isolated tetrahedral ionic PO_4^{3-} (Q^0) units or PO_4^{2-} (Q^1) for any molar content of P_2O_5 in glass, reason for which we assigned the band at 1088 cm^{-1} to the Q^1 units [27].

Bands restructuring in the spectral domain 1000-1080 cm^{-1} and the occurrence of a narrow bands at ~560 cm^{-1} and ~604 cm^{-1}, lead to conclusion that the structural local order is established by the occurrence of crystalline volume domains and the formation of glass-ceramic structures.

The spectral domain specific to the BO_3 structural units stretching vibrations remains unchanged, the groups containing trigonal boron are unaffected by thermal treatment.

The Raman spectra (Figure 5) of the samples of $1.5\%Ag_2O\cdot98.5\%[0.47B_2O_3(0.53-x)CaOxP_2O_5]$ vitreous system are dominated in intensity by two bands located into the 900-1100 cm^{-1} spectral interval. Thus, if the sample $x = 0$ has a wide band centered around the ~960 cm^{-1} value, more intense than any other spectrum band, the sample with $x = 0.02$ reveals two bands in this spectral range at ~992 cm^{-1} respectively at ~960 cm^{-1}. The Raman band at ~960 cm^{-1} was associated to the borate groups [28, 29], and the separation occurs due to the vibrations caused by the groups containing phosphorus.

The band at 992 cm^{-1} was assigned to symmetric stretching vibrations of the final units PO_3^{2-} (Q^1 species) connected to a borate ring, through B-O-P linkage and/or to the orthophosphate ions PO_4^{3-} (Q^o species) [20, 23]. Because the band at ~992 cm^{-1} becomes the most intense and narrow line in the spectra, with the increase of x, one may say that the number of B-O-P linkages increases in the vitreous network with the increase of the available phosphorus quantity into the glass composition.

Isolated ions PO_4^{3-} are responsible for the band at ~952 cm^{-1} [20] this one being assigned to $P\text{-}O^-$ bond vibrations in Q^o species.

These two aforesaid bands are well defined and narrow comparing with the other bands occurring in Raman spectra which reveals the existence of several well defined P_2O_5 structural units.

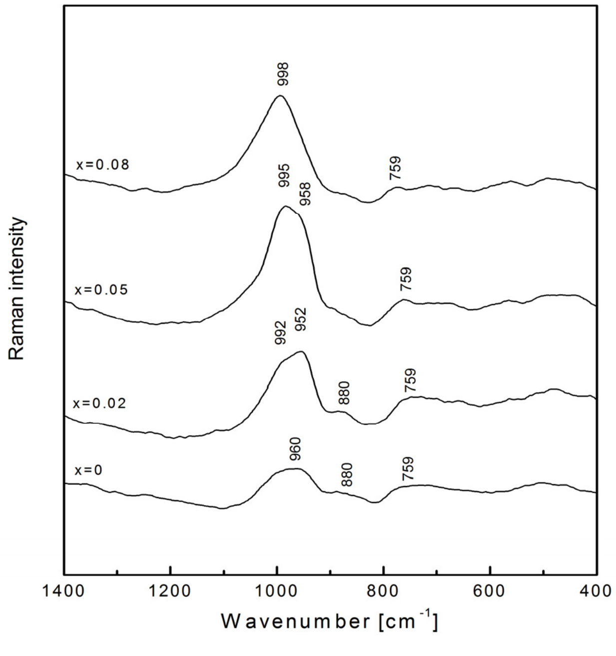

Figure 5. Raman spectra of $1.5\%Ag_2O\ 98.5\%[0.47B_2O_3(0.53\text{-}x)CaOxP_2O_5]$ vitreous system

The absence of Raman band at 806 cm^{-1} indicate the absence of boroxol rings in the glass structure [15], this band is usually assigned to the breathing vibrations of this ring and the result is in good agreement with IR spectral data.

In the spectral range 765-785 cm^{-1} a relative wide band may be observed for all the investigated samples, which was assigned [11] to symmetrical vibrations B-O-B which involves the displacement of oxygen atoms in boroxol ring only, where one or two BO_3 triangles were replaced by BO_4 tetrahedral units or as shown [13] the band at 780 cm^{-1} has to be correlated with the BO_4 units vibrations.

The wide Raman band centered at ~470 cm^{-1} (x=0) was assigned to diborate groups and BO_4 groups lost by the network [22].

After heat treatment of investigated oxide system significant changes of Raman spectra can be observed (Figure 6).

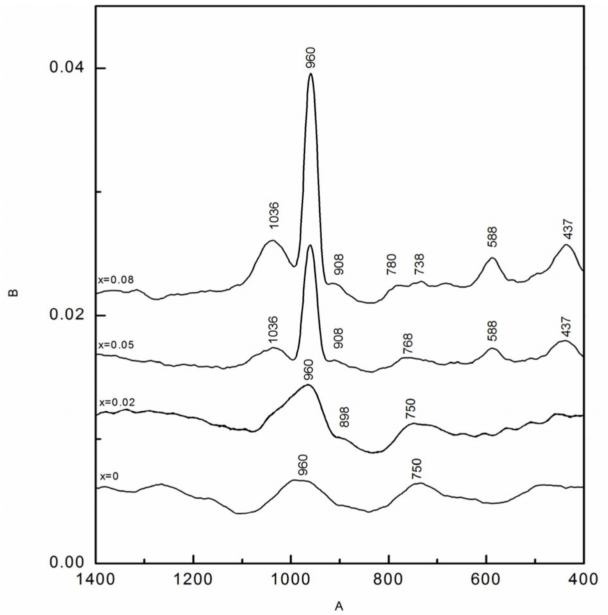

Figure 6. Raman spectra of 1.5%Ag_2O 98.5%[$0.47B_2O_3(0.53\text{-}x)CaOxP_2O_5$] heat treated system

At x = 0 in the spectral range $\upsilon \in$ [900-1100] cm^{-1} a wide band assigned to orthoborate units [30] appears, although it is characteristic for pure borate glass, its origin could not be precisely determined [23]. The band at ~960 cm^{-1} becomes more intense and sharp with the increase of P_2O_5 molar content and the simultaneous presence of Raman bands at ~429 cm^{-1}, ~587 cm^{-1} reveals that the PO_4^{3-} ions vibrations appear into the glass [31] starting with x = 0.02.

The gradual sharpening of Raman band ~959 cm^{-1} assigned to (Q^o species) and its increase in intensity represents a spectroscopic confirmation that the system crystalline domains are due to the structural units that involves P_2O_5 and also that the crystalline units number increases as well as the glass structure changes in glass-ceramics.

The PO_4^{3-} may react with the calcium oxide and form individual groups. The Raman band at 587 cm^{-1} was assigned to the symmetric stretching vibrations of $P\text{-}O^-$ [13] bonds and appears just once in vitroceramic samples.

In the whole investigated concentration range $0 \leq x \leq 0.08$, the structural units building the borate glass network, orthoborate at ~900 cm^{-1} and dipentaborate [21] at ~759 cm^{-1}, maintain their position and intensities which proves that the heat treatment affect only phosphate units.

After the heat treatment a new band at ~1035 cm^{-1} appears in the Raman spectra, being assigned to the stretching mode of PO_3 symmetric vibrations (chained end groups) [20, 32]. The band becomes narrow at further addition of P_2O_5 into the matrix and has an increased intensity.

In the Raman spectra of heated samples, starting with x = 0.05, on these frequencies the bands become narrower and the boron ones, diminish for investigates Ca/P ratio.

The structural modifications highlighted by the Raman spectra following the heat treatment support the results obtained by means of IR spectroscopy, meaning that the tendency of the vitreous system for crystallization increases as much as the P_2O_5 concentration increases, starting with x = 0.05.

CONCLUSIONS

The X-rays diffractogram revealed that the researched system samples are non-crystalline (vitreous) in the whole composition system researched. The heat treatment at 650°C for 6 h determined the appearance of crystalline islands with the following composition: $Ca_{10}(PO_4)_6(OH)_2$.

Glasses from $1.5\%Ag_2O\ 98.5\%[0.47B_2O_3(0.53\text{-}x)CaOxP_2O_5]$ system were prepared with high modifier glass oxide content. The IR spectra reveal the existence of BO_3 and BO_4 groups in different structural units for all the investigated glasses and glass-ceramics. Raman spectra showed the crystallization of isolated PO_4^{3-} units as well as the formation of B-O-P linkages. Structural changes for $x \geq 0.04\%$ induced by heat treatment are revealed by both spectroscopic techniques.

EXPERIMENTAL

The oxide glass of the $1.5\%Ag_2O\ 98.5\%[0.47B_2O_3(0.53\text{-}x)CaO\ xP_2O_5]$ system with $0 \leq x \leq 0.08$ mol% have been prepared using start materials: Ag_2O, $CaCO_3$, P_2O_5, H_3BO_3 of reagent grade purity. The mixtures were melted in air at 1250°C, in sintered corundum crucibles, and kept for 15 min. at this temperature. The oxide glasses were partially crystallized by heat treatment of the samples at 650°C in a single step.

X-ray powder diffraction data were obtained with Bruker D8 Advanced Diffractometer equipped with Si monochromator for incident beam in order to obtain only Cu Kα radiation.

The obtained materials were grinded as powder and mixed with KBr in order to obtain 0.3 mm thick discs using the tablet forming technique. The FTIR spectra characteristic for the vitreous samples and the heat samples were recorded using a JASCO 6100 spectrometer in the spectral domain 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

The FT-Raman spectra were recorded in backscattering geometry with a FRA 106/S (Bruker) Raman accessory equipped with nitrogen cooled Ge detector. The 1064 nm Nd:YAG laser was used as excitation source, and the laser power was set at 300 mW. The FT-Raman spectra were recorded with a resolution of ~4 cm^{-1}.

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