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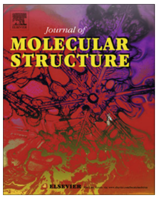

Copper ions influence on lead–phosphate glass network

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HIGHLIGHTS

- High-copper content $2PO_2O_5{\cdot}PbO$ vitreous system has been prepared.
- Q^n units ratio strongly depends on CuO content.
- Cu may have a possible former role over 20 mol%.
- The (P=O) shift, is explained through the existence of two types of P=O groups.

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ABSTRACT

The structure of $x\mathrm{CuO}{\cdot}(1-x)[2P_2O_5{\cdot}\mathrm{PbO}]$ glass system with $0 \leqslant x \leqslant 50$ mol% was investigated by Raman spectroscopy. The characteristic bands of these glasses were identified and analyzed by increasing CuO content. A deconvolution of each Raman spectrum was made in order to make a better identification and assignment of all bands which appear in these spectra Thus, by determining the number of all independent components it was possible to carry out a quantitative analysis of the spectra and also to find the concentration distribution of these components across the investigated glass system. By adding CuO, the symmetric vibration of P—O—P bond in Q^2 groups shifts to higher frequencies due to the depolymerization of long phosphate chains and the bands attributed to $(PO_2)_{asym.}$ stretching and $(P{=}O)_{sym.}$ stretching vibrations shift to lower frequencies due to the linking of P—O bond to cooper ions. The UV–visible optical absorption results suggest that Cu ions act as a modifier in the studied glasses and may have a possible former role over 20 mol%. Beside this, cooper can be considered as a color center in this glass system.

1. Introduction

Phosphate glasses containing transition metal ions have unique properties which offer them many technical applications in electrochemical, electronic and electro-optical devices [1,2]. However, these glasses have a relatively poor chemical durability that often limits their use [3]. Several studies have shown that chemical durability of phosphate glasses can be improved by the addition of various oxides such as PbO and Fe_2O_3 [4,5] which lead to the formation of P—O—Pb and P—O—Fe bonds and thus to the increase of durability [6,7]. It was suggested that the addition of CuO to phosphate glasses lead the formation of Cu—O—P bonds which increase the cross-link density in the glass network.

The basic structural units of phosphate glasses are PO_4 tetrahedra which are described in the so-called Q^n terminology, where "*n*" represents the number of bridging oxygens (BOs). In this formalism, the pure phosphate glasses are formed by Q^3 tetrahedra with three BOs and one double bonded oxygen P=O, forming a three-dimensional cross-linked network. In ultraphosphate glasses both Q^2 and O^3 structures are present, while in metaphosphate glasses prevailed Q^2 tetrahedra which form long chains or rings. Beside these, small phosphate groups like: pyro Q^1 and orthophosphate Q^0 could also be present in the glass structure [8].

In previous studies the vibrational spectra analysis of glasses, were mainly qualitative, based on the assignment and shift of infrared absorption bands. There are also studies focused on the chemical durability improvement of phosphate glasses by addition of oxides like PbO, CuO or Fe_2O_3 were made. In this work, we paid attention to the quantitative analyses of the Raman spectra by using the deconvolution method to determine the relative concentration of structural units and thus, to analyze the role of cooper oxide versus its concentration. Deconvolution of Raman spectra can be considered a useful tool to extract information about phosphate glass structure rather than the traditional analysis of Raman spectra.

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The xCuO·(1 − x)[2P$_2$O$_5$·PbO] glass system with $0 \leqslant x \leqslant 50$ mol% was prepared and characterized by Raman spectroscopy and UV–visible optical absorption in order to understand the role of CuO in the local structure. The objective of the present work is to study the compositional dependence of the different structural units which appear in these glasses with the increasing of the cooper oxide content by maintaining the P$_2$O$_5$/PbO ratio constant.

2. Experimental

The starting materials used in the present investigation were (NH$_4$)$_2$HPO$_4$, PbO, CuO of reagent grade purity. The samples were prepared by weighting suitable proportions of each component, powder mixing and mixture melting in sintered corundum crucibles at 1250 °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 steel plate.

Raman spectra were measured with a Horiba Jobin Yvon Micro-Raman spectrometer (LabRam-HR) equipped with an integral Olympus BX 41 microscope and Peltier-cooled CCD detection, using the 632.8 nm line of a He—Ne laser (1.5 mW) for excitation. The spectra were recorded in the 1400–200 cm^{-1} range of Raman shifts at 1.3 cm^{-1} spectral resolution.

Optical response of samples was studied by using UV–Vis absorption spectra recorded from a JASCO V570 UV–Vis-NIR Spectrophotometer equipped with absolute reflectivity measurement JASCO ARN-475 accessory. The transformation of reflectance spectra in absorbance spectra were obtained with an intern soft of apparatus.

The deconvolution procedure was made with OriginPro 8.5. 1 computer program using a Gaussian type function. The procedure gave us the possibility to make a quantitative analysis of the spectral bands in order to find out the concentration distribution of the components in the glass mixture. The experimental spectrum was first normalized to the most intense band and then the relative intensities of each observed band were calculated which allow their comparison. The relative intensity is considered to be proportional with the relative aria of a fitted peak reported/divided to the total aria of all considered peaks.

3. Results and discussion

Experimental Raman spectra of the xCuO·(1 − x)[2P$_2$O$_5$·PbO] glass system with $0 \leqslant x \leqslant 50$ mol% are presented in Fig. 1. Because most of the Raman bands are large and asymmetric a deconvolution of each Raman spectrum was made in order to give a better assignment of the vibrational bands and to quantitative estimate the evolution of each structural group (Fig. 2). The line broadening is caused once by different position of Cu ions and on the other hand by variations of the local field symmetry. The line type that we used in the deconvolution procedure was the Gaussian one, because it is commonly assumed that the broadening of Raman lines give rise to use Gaussian line shapes [9–15]. In Table 1 are presented the: wavenumber, assignments and relative intensities of each Raman band.

The band centered at about 470 cm^{-1} may be correlated with Pb—O stretching vibration in [PbO$_4$] structural units [16,17], whereas the free PO$_4$ tetrahedron – T_d – symmetry – has vibrational normal modes that give usually in aqueous solution frequencies around ~567 cm^{-1} and ~938 cm^{-1} [18]. With the addition of CuO, the number of PO$_4$ units strongly increases, fact that is related to the drastic depolymerization of phosphate network.

In his way the P—O—P symmetric stretching vibration of the long-chain phosphate glasses appears in Raman spectra around 665 cm^{-1}. By addition of cooper oxide, this band shifts to a higher wave number as an effect of the phosphate chain lengths decreasing [19,20]. On the other hand, this shift could be an effect of the cooper oxide addition on the glass network by changing the in-chain P—O—P bond angle [20,21]. The band at 752 cm^{-1} assigned to (P—O—P) asymmetric stretching vibration [22] decreases in intensity and shifts to 784 cm^{-1} due to the increase in covalent character of P—O—P bond. The ~1012 cm^{-1} line is the stretching mode of the PO$_3$ symmetric chain-end groups [23] and appears in Raman spectrum only at very high cooper content (x = 50%). At high concentration of CuO (x = 50%) two new bands at 1012 cm^{-1} and 604 cm^{-1} assign to the stretching mode of the PO$_3$ symmetric chain-end groups [23] and to symmetric stretching vibration of P—O in Q^0 [24] groups respectively appear and they are consistent with the depolymerization of phosphate network.

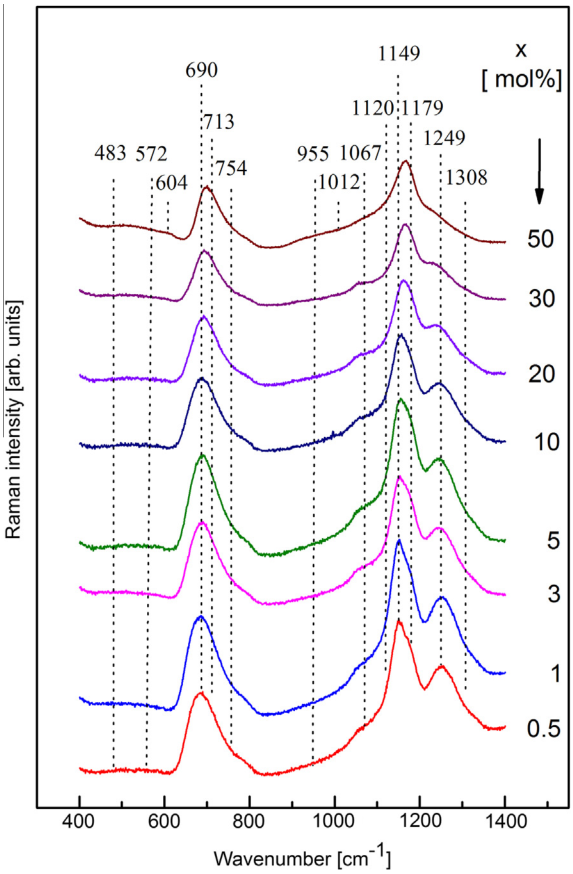

Fig. 1. Experimental spectra of xCuO·(1 − x)[2P$_2$O$_5$·PbO] glass system.

The (PO$_3$)$^{2-}$ end-of-chain asymmetric stretching vibrations are present in our spectra at about 1046–1071 cm^{-1} range [25]. The concentration of (PO$_3$)$^{2-}$ groups increases when the long chains of the metaposphate are replaced by the small phosphate units. The intensity increase of the band located around 1113 cm^{-1}, assigned to the (PO$_3$) symmetric stretching vibration in Q^1 units [25] is due to the strong depolymerization of phosphate network by cooper oxide addition, but it can arise from the overlapping of this band with those arising from the overlapping of this band with the band corresponding to P—O—Cu stretching mode [26].

The band from ~1149 cm^{-1}, attributed to (PO$_2$) symmetric stretching vibration increases as CuO is added to phosphate network. The increase in the concentration of PO$_2$ groups and the creation of non-bridging oxygen atoms in the glass network are necessary to accommodate the valence and coordination requirements of the incorporated cooper ions [8]. A band around 1180 cm^{-1} has been attributed to "strained" (PO$_2$) symmetric