

Spectroscopic (FT-IR and Raman) studies on CuO-B₂O₃-PbO-Ag₂O glass systems

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Glasses from $x\text{CuO}\cdot(1-x)[3\text{B}_2\text{O}_3\cdot 0.5\text{PbO}\cdot 0.5\text{Ag}_2\text{O}]$ ($0 \leq x \leq 0.1$) system were prepared and studied by means of FT-IR absorption and Raman scattering. Both spectroscopic techniques provide information regarding the local structure revealing the presence of borate arrangements such as: di-, tri-, tetra-, penta-, ortho-, meta-, pyro-borate and boroxol rings. It was followed the influence of CuO addition on the short-range order (SRO) of the network in order to obtain information concerning the local structure of copper-doped $3\text{B}_2\text{O}_3\cdot\text{PbO}\cdot\text{Ag}_2\text{O}$ glass matrix. The conversion between the tri-coordinated boron atoms and tetra-coordinated ones was also followed.

(Received November 1, 2008; accepted November 27, 2008)

Keywords: Cooper-silver-lead-borate glasses structure, FT-IR, Raman spectroscopy, Short-range order

1. Introduction

Borate based glasses have been widely studied over the years since they are relatively easy to obtain and moreover present interesting structural particularities, due to the existence of the boron anomaly; the boron atom can be placed in the network in tri- or tetra- coordination depending on the concentration of the modifier oxide [1-4].

Oxide glasses containing heavy metals possess an enhanced non-linearity while they are highly transparent in the near-infrared region. Therefore, PbO-B₂O₃ based glasses have many applications as optical lenses, electronic devices, simulated Raman fiber amplifiers (due to their high refractive indices), high resistance against devitrification and low melting temperature [5].

Glasses containing Ag⁺ ions have important technological properties presenting high ionic conductivity with the prospect of producing glasses that are superionic conductors. On the other hand, glasses with small quantities of silver oxide have the desired characteristics for photochromic lenses, solid electrolytes and chemical sensors [6].

The local structure of the B₂O₃-PbO glass system was the subject of many FT-IR, Raman, Mössbauer, density and electrical measurements [5-10]. Up to 50 mol % PbO content it acts as a network modifier leading to the formation of BO₄ units which along with the presence of BO₃ units are placed in borate arrangements such as: di-, tri-, tetra-, and penta-borate groups. On the other hand above 50 mol % PbO there is an increase of the non bridging oxygen's (NBOs); the lattice consists in chain- and ring-type metaborate at the expense of BO₄ units [11].

The addition of copper oxide to the B₂O₃-PbO-Ag₂O ternary glass system is motivated by the fact that CuO gives great fluidity without increasing thermal expansion [12]. In addition, the coexistence of copper in two different oxidation states in the glasses is important for

technical applications, for soldering and integrated circuit (IC) packaging [13].

The aim of the present work is to evaluate the influence of CuO content on the local structure of $x\text{CuO}\cdot(1-x)[3\text{B}_2\text{O}_3\cdot 0.5\text{PbO}\cdot 0.5\text{Ag}_2\text{O}]$ glasses.

2. Experimental procedure

The prepared glass compositions were $x\text{CuO}\cdot(1-x)[3\text{B}_2\text{O}_3\cdot 0.5\text{PbO}\cdot 0.5\text{Ag}_2\text{O}]$ with $0 \leq x \leq 0.1$ copper oxide content. The batch of the mixture of the reagent grade H₃BO₃, PbO, AgNO₃ and CuO was melted in air, in sintered corundum crucibles, in an electric furnace at 950°C for 15 minutes. The melts were quickly cooled at room temperature by pouring them onto stainless steel plates. The FT-IR absorption spectra were recorded with a 6100 Jasco spectrometer, at room temperature, in the 350-4000 cm⁻¹ range using the KBr pellet technique. The Raman spectra were recorded for bulk glasses using a LabRam spectrometer in back-scattering (90°) geometry with a resolution of 4 cm⁻¹ at room temperature using for excitation the green line (514.5 nm) of a Spectra Physics with argon ion laser with an output power of 50 mW.

3. Results and discussion

Various experimental and theoretical studies made on vitreous B₂O₃ expose a network based on BO₃ units, which can be associated to form six-membered boroxol rings. Addition of various glass modifiers to B₂O₃ causes a conversion between BO₃ and BO₄ units, phenomenon also observed for silver-lead-borate glasses [14].

The experimental FT-IR spectra of the glass system are shown in Fig. 1. There are three main absorption regions for the 3B₂O₃·0.5PbO·0.5Ag₂O glass matrix: the first one is between 500 cm⁻¹ and 800 cm⁻¹, the second

appears from 800 cm^{-1} to about 1150 cm^{-1} and the third is situated between 1150 cm^{-1} and 1600 cm^{-1} .

The lower wavenumber domain is dominated by an intense absorption band centered at $\sim 684 \text{ cm}^{-1}$ revealing the presence of the penta-borate groups (B_5O_8^-). In addition, a small band assigned to the vibrations of oxygen bridging one tetrahedral and one trigonal boron ($\sim 760 \text{ cm}^{-1}$) was detected. Two absorption bands having the center at $\sim 915 \text{ cm}^{-1}$ and $\sim 1110 \text{ cm}^{-1}$ can be distinguished under the envelope from the second spectral domain. Generally, these absorption bands are given by the B-O bond stretching vibrations in BO_4 units from di-borate groups ($\text{B}_4\text{O}_7^{2-}$). Regarding the last spectral domain contributions from asymmetric stretching vibrations of B-O bonds from ortho-borate groups (BO_3^{3-}) ($\sim 1210 \text{ cm}^{-1}$) and asymmetric stretching vibrations of $\text{B}\emptyset_3$ and $\text{B}\emptyset_2\text{O}^-$ borate triangles were detected (where \emptyset represents an oxygen atom bridging two boron atoms and O^- a non-bridging oxygen).

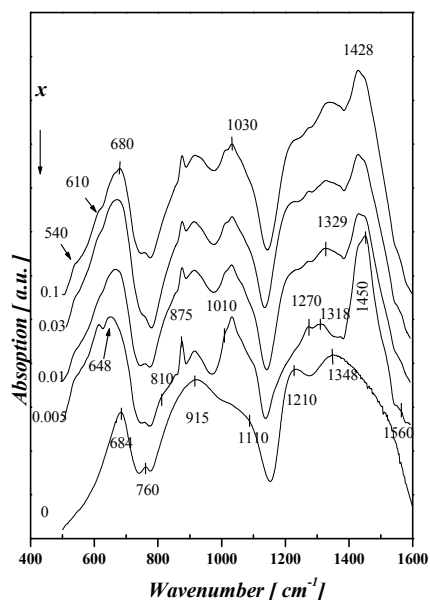


Fig. 1. FT-IR spectra of $x\text{CuO}-(1-x)[3\text{B}_2\text{O}_3-0.5\text{Ag}_2\text{O}-0.5\text{PbO}]$ glass system.

Based on the assignments of the detected infrared bands we propose for the glass matrix a network mainly built by: penta- (B_5O_8^-), di- ($\text{B}_4\text{O}_7^{2-}$), ortho-borate groups (BO_3^{3-}), $\text{B}\emptyset_3$ and $\text{B}\emptyset_2\text{O}^-$ borate triangles. It seems that for this particular glass composition the amount of boron atoms placed in tri-coordinated sites is much higher than the four-coordinated ones.

The addition of copper oxide into the glass matrix affects the existence and also the relative distribution of the borate structural groups as it follows. In the lower wavenumber domain structural changes involving the CuO addition are revealed through the appearance of two new bands centered at $\sim 540 \text{ cm}^{-1}$ and $\sim 610 \text{ cm}^{-1}$ both assigned to the B-O-B bending vibration from various borate segments. This means that CuO enters into the network

and breaks some of the borate arrangements, creating isolate borate segments. The decrease in the band wavenumber position from 684 cm^{-1} to 648 cm^{-1} might be due to a decrease of the B-O bond length or an increase in the chain B-O-B bond angle.

The most significant changes occur in the two last spectral domains (800-1150 cm^{-1} and 1150-1600 cm^{-1}) where are active the vibrations characteristic to borate groups. With the copper oxide addition the wide envelope from the second spectral domain present in the glass matrix spectra, develop in three well defined bands ($\sim 875 \text{ cm}^{-1}$, $\sim 915 \text{ cm}^{-1}$ and $\sim 1030 \text{ cm}^{-1}$) and two shoulders ($\sim 810 \text{ cm}^{-1}$ and $\sim 1110 \text{ cm}^{-1}$). Also, a very small shoulder appears at $\sim 1010 \text{ cm}^{-1}$. These new features ($\sim 875 \text{ cm}^{-1}$, $\sim 1010 \text{ cm}^{-1}$, $\sim 1030 \text{ cm}^{-1}$) are assigned to the B-O bond stretching vibrations of $\text{B}\emptyset_4$ tetrahedra from tri- (B_3O_5^-), tetra- ($\text{B}_8\text{O}_{13}^{2-}$) and penta-borate groups, while the weak band positioned at 810 cm^{-1} comes from di-borate groups.

In the last spectral domain (1150-1600 cm^{-1}) a strong band having two centers at $\sim 1450 \text{ cm}^{-1}$ and $\sim 1428 \text{ cm}^{-1}$ assigned to the B-O $^-$ vibration from meta- ($\text{B}_3\text{O}_6^{3-}$) and pyro-borate groups ($\text{B}_2\text{O}_5^{2-}$) developed with the copper oxide addition. A weak band ($\sim 1270 \text{ cm}^{-1}$) attributed to the stretching vibration of the B-O from ortho-borate groups was also detected in the spectra. It is worth notice that only for small quantity of copper oxide ($x = 0.005$) the center from ~ 1450 is visible; for the rest of the compositional domain ($x > 0.01$) the center from $\sim 1428 \text{ cm}^{-1}$ remains more pronounced. The band positioned at $\sim 1210 \text{ cm}^{-1}$ shows a drastically decrease in intensity only for $x = 0.005$ CuO, increasing in intensity for the rest of the compositional domain. Two shifts toward smaller wavenumber of the band at $\sim 1348 \text{ cm}^{-1}$ were also observed with CuO addition. The first shift is more significant and it appears for $x = 0.005$ CuO concentration (the band is placed at $\sim 1310 \text{ cm}^{-1}$) followed by a smaller shift (the band is placed at $\sim 1329 \text{ cm}^{-1}$) for the rest of the copper oxide concentrations. A small contribution of B-O-H bending mode was detected ($\sim 1560 \text{ cm}^{-1}$) for all x values.

Analyzing the infrared spectra of this glass system it can be conclude that addition of copper oxide implies several rearrangements in the network structure at short range order (SRO) favoring the presence of new structural borate groups namely: tri-, tetra-, meta-, and pyro-borate groups. Following the evolution in intensity of the infrared bands from the last two spectral domains, which slowly decreases it can be said that the controlled addition of copper oxide determine a slight depolymerization process. For all the glass compositions the infrared data indicates that the predominant units in the structure are BO_3 units related to BO_4 one.

Similar to FT-IR, Raman spectra of the glass system presented in Fig. 2 arise mainly from the modified borate network.

The Raman spectrum of the glass matrix $3\text{B}_2\text{O}_3-0.5\text{Ag}_2\text{O}-0.5\text{PbO}$ is dominated by the presence of a multicomponent envelop situated between 1000 and 1600 cm^{-1} . Under this envelop are present bands assigned to $\text{B}\emptyset_2\text{O}^-$ triangles linked to other borate triangular units ($\sim 1490 \text{ cm}^{-1}$), $\text{B}\emptyset_2\text{O}^-$ triangles linked to $\text{B}\emptyset_4^-$ units ($\sim 1360 \text{ cm}^{-1}$), pyro- ($\sim 1260 \text{ cm}^{-1}$) and di-borate groups ($\sim 1115 \text{ cm}^{-1}$). Boroxol rings give rise to a weak band centered at $\sim 800 \text{ cm}^{-1}$, while tri-, tetra- and penta-borates

scatter at $\sim 767\text{ cm}^{-1}$. Supplementary, two broad bands were detected coming from meta-borate rings ($\sim 640\text{ cm}^{-1}$) and isolate di-borate groups ($\sim 460\text{ cm}^{-1}$). Similar to FT-IR data, Raman spectrum reveals the occurrence of the tricoordinated boron placed in various borate arrangements.

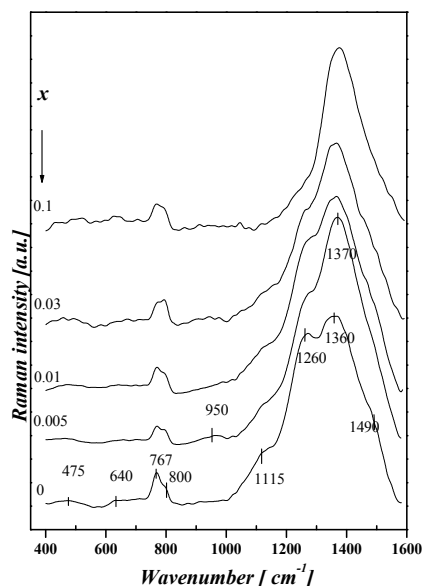


Fig 2. Raman spectra of $x\text{CuO}-(1-x)[3\text{B}_2\text{O}_3-0.5\text{Ag}_2\text{O}-0.5\text{PbO}]$ glass system

As the copper oxide enters in the glass matrix network a new band assigned to the ortho-borate groups ($\sim 950\text{ cm}^{-1}$) and a shift to a higher wavenumber (1370 cm^{-1}) of the band from $\sim 1360\text{ cm}^{-1}$ were detected. Moreover, with the progressive addition of copper oxide the contribution from the pyro-borate groups ($\sim 1270\text{ cm}^{-1}$) becomes smaller comparing to that of $\text{B}\text{O}_2\text{O}^-$ triangles linked to BO_4^- units ($\sim 1370\text{ cm}^{-1}$) which remains the most intense band in the spectra. The copper ions addition implies a progressively decrease of the Raman bands intensities (~ 800 , ~ 1270 and $\sim 1490\text{ cm}^{-1}$) characteristically for borate triangular units placed in different environments denoting the increase of the vitreous network depolymerization degree. A break in the chained di-borate groups evidenced by the decrease in intensity of the band from $\sim 1115\text{ cm}^{-1}$ could be correlated with the formation of more isolated di-borate groups ($\sim 475\text{ cm}^{-1}$ band whose intensity increase for all compositional range). For $x = 0.01$ CuO the glass network arise only from the $\text{B}\text{O}_2\text{O}^-$ triangles linked to BO_4^- units, a small amount of boroxol rings, tri-, tetra-, penta-, meta-, and isolated di-borate groups denoting a progressively disorder of the borate network. Although, the amount of the tricoordinated boron remains higher than the tetra-coordinated one with the copper oxide addition.

4. Conclusions

Several glass compositions, based on $3\text{B}_2\text{O}_3-0.5\text{Ag}_2\text{O}-0.5\text{PbO}$ containing different CuO concentrations were obtained and investigated using FT-IR

absorption and Raman scattering techniques. With the copper oxide addition the infrared data revealed beside the structural groups characteristic for the glass matrix (penta-, di-, ortho-borate groups, BO_3 and $\text{B}\text{O}_2\text{O}^-$ borate triangles) new structural borate arrangements (tri-, tetra-, pyro- and meta-borate groups). For all glass samples the three-coordinated boron atoms number is higher than that of four-coordinated one. The Raman data confirm the structure proposed by the FT-IR measurements and supplementary detects new structural groups, i.e. boroxol rings. Still, FT-IR spectroscopy seems to be a more sensitive technique for the changes that appear in the glass network with the addition of copper oxide denoting a smaller depolymerization degree of the vitreous network than the Raman measurements. The changes induced by copper oxide gradual addition, revealed by both techniques employed in this study, show the vitreous network modifier role of copper ions.

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