EPR and IR structural investigations on xMnO·(1-x)[3P₂O₅·CaO] glass system

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xMnO·(1-x)[3P₂O₅·CaO] glass system with $1 \leq x \leq 5$ mol % was prepared and investgated in order to evidence the structural changes induced by the manganesse ions in the glass network. EPR spectra of these glasses have been recorded in the X-band (9.3 GHz) at room temperature. All the investigated samples exhibit resonance signals which are characteristic to the Mn^{2+} ions. The shapes of the EPR spectra are also changed with the increasing of manganese ions content. IR spectra of these glasses put in evidence that main vibration bands for phosphate glasses because the MnO content is low. The intensity and frequency variations for the characteristic phosphate group vibrations: P-O-P bending and stretching, P = O stretching have been correlated with the changes of the structural units present in these glasses. Both investigation techniques inform about the structural effect of MnO on the calcium-phosphate glass matrix.

1. Introduction

The phosphate glasses are of interest both for various applications [1-4] and from the viewpoint of further insight into the glass structure [5-9]. Specific properties of phosphate glasses can be understood only if the behavior over the entire composition range is known, which is also of interest with regard to changes of certain macroscopic properties.

In order to obtain further information on the local structure in phosphate glasses with manganese ions, the xMnO·(1-x)[3P₂O₅·CaO] glass system with $1 \leq x \leq 5$ mol % have been prepared and investigated by IR and EPR methods.

2. Experimental

xMnO·(1-x)[3P₂O₅·CaO] glass system with $1 \leq x \leq 5$ mol % have been prepared from corresponding quantities of $MnCO_3$, $(NH_4)_2HPO_4$ and $CaCO_3$ of p.a. purity, by melting at 1200 C for 5 min. No crystalline phase was detected by X-ray diffraction analysis. Infrared spectra were obtained in the 400-2000 cm⁻¹ spectral range with a Bruker Equinox Fourier transform-infrared (FT-IR) spectrophotometer by using the KBr pellet technique. EPR measurements were done at room temperature in the X-band (9.46 GHz) with a SEX-2000 spectrometer.

3. Results and discussion

The EPR spectra (Fig. 1) present a symmetric absorption centered at $g \cong 2.0$ owing to Mn^{2+} ions situated in tetragonal distorted octahedral sites and very small absorption centered at $g \cong 4.3$, for x = 1 mol %, characteristic for isolated Mn^{2+} ions in rhombic distorted octahedral environment [10-12].

The $g \cong 2.0$ resonance line is prevalent in the spectrum and shows for $x \leq 3$ mol % the resolved hyperfine structure (h.f.s.) characteristic of the ^{55}Mn (I = 5/2) isotope. The resolved h.f.s. of the spectrum is assigned to isolated Mn^{2+} ions [10-12]. For x = 1 mol % the $g \cong 2.0$ resonance line presents an additional splitting of the h.f.s. sextet owing to a variety of structural units in which manganese ions are disposed, suggesting high fluctuation of the crystal field parameters [13]. The h.f.s. sextet superimposes on a large absorption line, the envelope of all contributions at the resonance absorption having $g \cong 2.0$ caused by a random distribution of Mn^{2+} in the 3P₂O₅·CaO glass matrix.
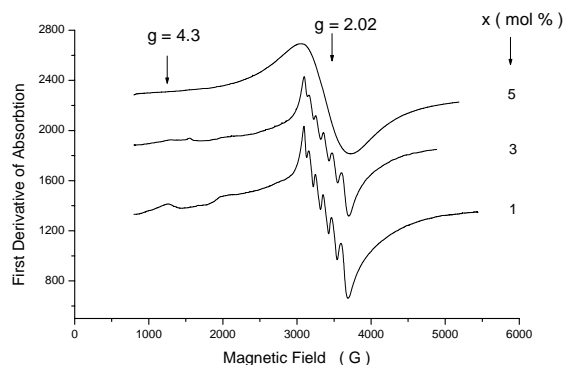

Fig. 1. EPR spectra for xMnO·(1-x)[3P₂O₅·CaO] glasses.

When the MnO content increases (x = 5 mol %) the h.f.s. is smeared out because of the distribution of crystal field parameters and because of dipol-dipol interactions. In Fig. 2 is presented the variation of linewidth with composition. The absorption progressively broadens evidencing dipole-dipole –type interactions between Mn^{2+} ions. These data suggest that the manganese ions are isolated or participate in dipole-dipole interactions.

The IR spectra obtained for the investigated samples are shown in Fig. 3. They consist of large absorption bands typical for the vitreous materials. The bands assignment in the 400-550 cm^{-1} is difficult because of the superposition of the CaO and MnO absorption bands [14]. The broad band at 740-790 cm^{-1} is assigned to P-O-P stretching vibration [15]. The P-O-P bending mode is constantly centered at 900-930 cm^{-1} regardless of the MnO concentration. The PO_4^{3-} units appear at $\sim$ 1040 cm^{-1}. The (P-O)- and P=O bands [11] appear in the 1140-1175 cm^{-1} and 1280-1320 cm^{-1}, respectively. The bending mode of O – H was identified at $\sim$ 1620 cm^{-1} and is directly dependent on MnO concentration. One can assume that the hydroxyl groups act as partial modifiers of the glass network [16].
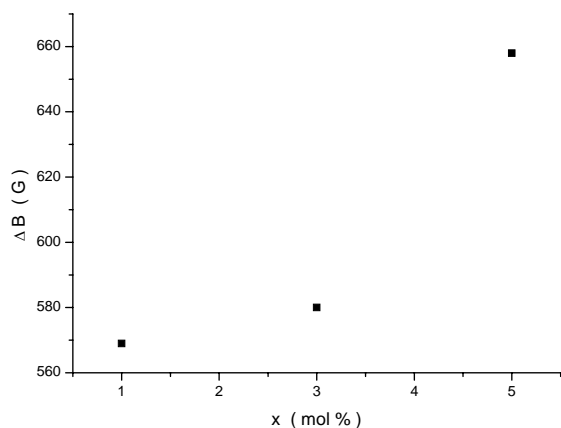

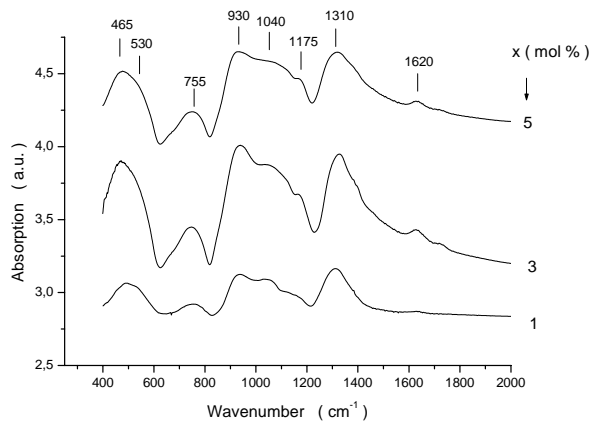*Fig. 2. Composition dependence of the linewidth of the g $\cong$ 2.0 absorption.*

Fig. 3. Infrared spectra of the xMnO·(1-x)[3P₂O₅·CaO] glasses.

4. Conclusions

Results of EPR data and infrared analysis shows that in the investigated glass system the manganese ions are positioned in different structural units of the glass matrix and for x < 5 mol % they are isolated. The intensity and frequency variations for the characteristic phosphate group vibrations have been correlated with the changes of the structural units present in these glasses. The fact that the main resonance is centered around g = 2.02 and exhibits the well-resolved hyperfine structure due to ^{55}Mn proves that almost the entire number of the Mn^{2+} ions are localized in an environment close to the octahedral symmetry.

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