Raman and EPR studies of calcium-phosphate glasses doped with manganese ions

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Abstract. The structure of xMnO (1-x)[2.5P₂O₇ CaO] glass system with 1 ≤ x ≤ 10 mol % was prepared and investigated by Raman and EPR spectroscopy. The characteristic Raman bands of these glasses due to the stretching and bending vibrations were identified and analyzed by increasing of MnO content. 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. All the investigated samples exhibit EPR signals which are characteristic to the Mn²⁺ ions. The shapes of spectra are also changed with the increasing of manganese ions content.

1. Introduction

Phosphate glasses have been of large interest for a variety of technological applications due to several unique properties such as high thermal expansion coefficient, low viscosity, UV transmission or electrical conduction [1]. Important biological applications for calcium phosphate glasses exist. Also, it was demonstrated that they are biocompatible as bones and dental implants [2, 3].

The properties that make phosphate glasses candidates for so many applications are related to their molecular – level structure [4]. The basic building blocks of amorphous phosphates are the P-tetrahedra [4]. They result from the formation of sp³ hybrid orbital by the P outer electrons (3s³3p³). The fifth electron is promoted to a 3d orbital where strong π – bonding molecular orbital are formed with oxygen 2p electrons. These tetrahedra link through covalent bridging oxygens to form various phosphate anions. The tetrahedra are classified using the Qⁿ terminology, where “n” represents the number of bridging oxygen per tetrahedron [5]. Specific properties of phosphate glasses could 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.

The understanding of the glasses structure on different length scales remains difficult mainly due to the lack of periodicity inherent to glasses. Only the suitable correlation of experimental data obtained from several investigations provided by different methods allows the finding of helpful structural information.
In order to evidence the structural changes induced by MnO in the phosphate glass network, a xMnO·(1-x)[2.5P2O5·CaO glass system was prepared and investigated by means of Raman and EPR spectroscopy.

2. Experimental
xMnO·(1-x)[2.5P2O5·CaO] glass system with 1 ≤ x ≤ 10 mol % have been prepared from corresponding quantities of MnCO3, (NH4)2HPO4 and CaCO3 of p.a. purity, by melting at 1200 C for 5 min. The molten liquid was poured onto a cooper plate and pressed with another one very quickly to preserve the local disorder characteristic to the liquid state.

The Raman spectra were collected at room temperature using a JASCO NRS-3300 micro-Raman Spectrometer with an air cooled CCD detector in a backscattering geometry and using a 600/mm grating. The microscope objective used for the studies was 100X. As excitation, it was used a 785 nm laser line with the power at the sample surface of 85 mW.

The EPR experiments were performed at room temperature in the X-band (9.46 GHz) on a Bruker ELEXSYS E500 spectrometer.

3. Results and discussion
The Raman spectra of the investigated samples are displayed in figure 1. It can be observed that their shapes are changed with the increase of MnO content. On the other hand the majority of the bands are large and asymmetric and they present some shoulders.

![Figure 1. Raman spectra of xMnO-(1-x)[2.5P2O5·CaO] glasses.](image)

The most important bands observed in our glasses are: ~ 660 cm⁻¹ assigned to the P-O-P symmetric stretching vibrations; ~ 1170 cm⁻¹ due to the symmetric stretching motions of two non-bridging oxygen (NBO) atoms bonded to phosphorous atoms (PO2) in the Q² phosphate tetrahedron; ~ 1300 cm⁻¹ due to the P=O symmetric stretching vibrations of the Q⁰ species [6-11]. For high content of MnO (x ≥ 5 mol %) a new band appear at ~ 900 cm⁻¹ due to the (PO₄) symmetric stretching vibrations of the Q⁰ species [9]. The increase of Q⁰ groups is due to the breaking of phosphate chains [8].

The asymmetric 660 cm⁻¹ band assigned to P–O–P symmetric stretching vibrations of the long-chain phosphate glasses is shifted to 702 cm⁻¹ due to the decreasing of phosphate chains lengths [10-14]. The shift of this band may be also attributed to a change in the in-chain P–O–P bond angle as an effect of the MnO network modifier on the glass structure [14, 15]. The higher wavenumber of the P–
O–P symmetric band is a result of the smaller P–O–P bond angle, characteristic for shorter phosphate chain length [6, 7].

Recorded EPR spectra show resonance line due to the Mn$^{2+}$ ($3d^5$, $6S_{5/2}$) paramagnetic ions for all range of concentration. The structure of the spectra strongly depends on the manganese content of the samples. The EPR spectra are presented in figure 2. The EPR spectra observed in the calcium phosphate glass matrix consist of a well resolved sextet centered at $g = 2.0$ with a broad background signal underneath the sextet and very small absorption centered at $g = 4.3$, which is characteristic for isolated Mn$^{3+}$ ions in rhombic distorted octahedral environment, as shown in figure 2.

![EPR spectra for xMnO-(1-x)[2.5P$_2$O$_5$-CaO] glasses.](image)

The $g = 2.0$ resonance line is known to arise from the central $M_s = -1/2 \rightarrow +1/2$ transition where $M_s$ is the effective spin component. The six-line multiplet results from the hyperfine interaction of the electron spin with the $^{55}$Mn nucleus ($I = 5/2$). This isotropic signal at $g = 2.0$ is due to Mn$^{2+}$ ions in an environment close to octahedral symmetry.

The hyperfine structure (hfs) superimposes on a large absorption line. It could be considered as the envelope of all contributions at the resonance absorption having $g = 2.0$ caused by a random distribution of Mn$^{2+}$ in the 2.5P$_2$O$_5$-CaO glass matrix. When the MnO content increases ($x = 5$ mol %) the hfs is smeared out due to both, the distribution of crystal field parameters and the dipole-dipole interaction. The $g = 2.0$ linewidth increases with the MnO content until $x = 5$ mol % due to the increase of the dipolar interaction between the Mn$^{2+}$ ions. The reduction in the increase tendency of the $g = 2.0$ linewidth for the $5 \leq x \leq 10$ mol % compositional range, indicates the possible presence of superexchange interactions between the Mn$^{2+}$ ions (table 1) [17].

| X (mol %) | $\Delta H$ (G) | $I_{EPR} \times 10^{10}$ (a.u.) |
|----------|----------------|-------------------------------|
| 1        | 527            | 3.3742                        |
| 3        | 540            | 7.9008                        |
| 5        | 578            | 43.8666                       |
| 10       | 565            | 22.4684                       |

In table 1 is also presented the absorption line intensity, $I_{EPR}$, (obtained after the integration of the area under the corresponding signal) for the investigated samples. In the concentration range $1 \leq x \leq 5$ mol %, the increase of MnO content in the samples determines an increase of $I_{EPR}$. Since the signal
intensity is proportional to the number of EPR active species involved in the resonance absorption, the observed increase of $I_{EPR}$ reflects an increase of the concentration of Mn$^{2+}$ ions involved in other structural vicinities. For the concentrations higher than $x = 5$ mol %, the increase of the MnO content determines a corresponding decrease of the line intensity. It could be due to the decrease of the number of Mn$^{2+}$ ions and probably, to the appearance in the investigated glasses of the Mn$^{3+}$ ions which do not manifest in EPR spectra at room temperature [18].

4. Conclusions

The glass network structure of the investigated sample is mainly formed by P-O-P symmetric stretching vibrations; (PO$_4$) in the Q$^2$ phosphate tetrahedron and P=O symmetric stretching vibrations. For higher content of MnO, due to the (PO$_4$) symmetric stretching vibrations of the Q$^0$ species a new band appears. The vibrational spectral features indicate a depolymerization process of the phosphate network with increasing of the manganese content. This process implies an increase of the number of non-bridging oxygen.

The EPR investigations performed on these glasses have indicated the presence of two signals: an isotropic one at $g = 2.0$ which is due to Mn$^{2+}$ in an environment close to the octahedral symmetry and a very small absorption centered at $g = 4.3$ which is characteristic for isolated Mn$^{2+}$ ions in cubic symmetric sites slightly tetragonally or rhombically distorted. In the samples with up to 5 % mol MnO, the isolated Mn$^{3+}$ ions in well structured vicinities and the dipolar coupled ones were identified. For higher concentrations, the superexchange interaction between the Mn$^{2+}$ ions could be present and probably, Mn$^{3+}$ ions appear in the investigated glasses.

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