JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 2, February 2008, p. 243 - 245

Electron paramagnetic resonance study of manganese ions in P_2O_5-TeO_2 glass matrix

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Electron paramagnetic resonance measurements on $xMnO\cdot(1-x)[P_2O_5\cdot TeO_2]$ glasses with $0 < x \leq 35$ mol. % are reported. In all concentration range of studied glasses are evidenced the EPR absorption line centered at $g_{eff} \approx 2.0$ characteristic to the Mn^{2+}. Octahedral symmetric sites, tetragonally distorted, were detected. The progressive clustering of manganese ions was evidenced when the MnO content increased. The line at $g_{eff} \approx 2.0$ have a hyperfine structure for $0 < x \leq 1$ mol%, suggesting the presence of isolated Mn^{2+}. The MnO content dependence of line-width for $g_{eff} \approx 2.0$ resonance line suggest, that for $x > 1$ mol% are present the dipolar and/or superexchange magnetic interactions. It is important to notice that the spectra do not present the $g_{eff} \approx 4.3$ absorption line characteristic for Mn^{2+} isolated ions.

(Received September 25, 2007; accepted February 7, 2008)

Keywords: Tellurite-phosphate glasses, Manganese ion, EPR

1. Introduction

Structural characteristic and properties of vitreous system containing manganese ions may be revealed by means of EPR. Manganese ions used as paramagnetic probes may provide valuable information about the structural units evolution, the type and strengths of bondings, the valence state and the involved magnetic interactions [1-5].

Glasses such as borate [5- 8], silicate [9- 11], phosphate [11], tellurite [12, 13], bismuthate [14, 15], chalcogenide [16, 17] and halide [18, 19] doped with manganese ions were investigated by means of EPR absorption spectra, for different content of these ions. Generally, the absorption spectra consist of resonance lines centered at $g_{eff} \approx 2.0$, $g_{eff} \approx 4.3$ and $g_{eff} \approx 3.3$ values. The $g_{eff} \approx 2.0$ was generally attributed to isolated paramagnetic centers in octahedral symmetric sites slightly tetragonally distorted or to exchange-coupled pair ions [5]. There are also strongly distorted sites of Mn^{2+} ions in octahedral vicinities subjected to strong field effects, given rise to absorption at $g_{eff} \approx 4.3$ and $g_{eff} \approx 3.3$ values [10, 18].

Glasses of the system $xMnO\ (1-x)[P_2O_5$-$TeO_2]$ with $0 < x \leq 35$ mol% were studied by using the EPR spectroscopy. For exploring the structure of these glasses, Mn^{2+} ions were chosen as paramagnetic probe in order to obtain information on the distribution and valence states of these ions in the oxide glasses.

2. Experimental

The starting materials used in the present study were of reagent grade purity $MnCO_3$, $(NH_4)HPO_4$ and TeO_2. The samples were prepared by weighing the components, mixing the powder and melting it in sintered corundum crucibles at 1250 ^oC for 5 minutes. The melts were poured very quickly onto stainless-steel plates. The X-ray patterns were characteristic for the vitreous systems. No crystalline phases were evidenced up to 35 mol% of MnO.

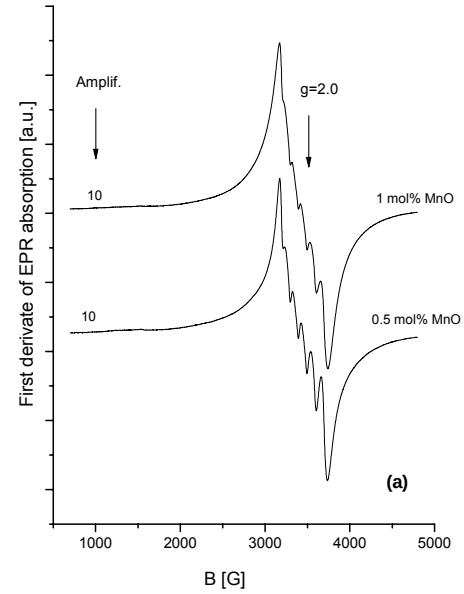
The EPR measurements were realized at room temperature, at X-band (9.45 GHz), with 100 kHz field modulation, using an ADANI Portable EPR PS 8400 type spectrometer. The same quantities of powdered samples were studied in fused tubular holders of the same caliber.

3. Results and discussion

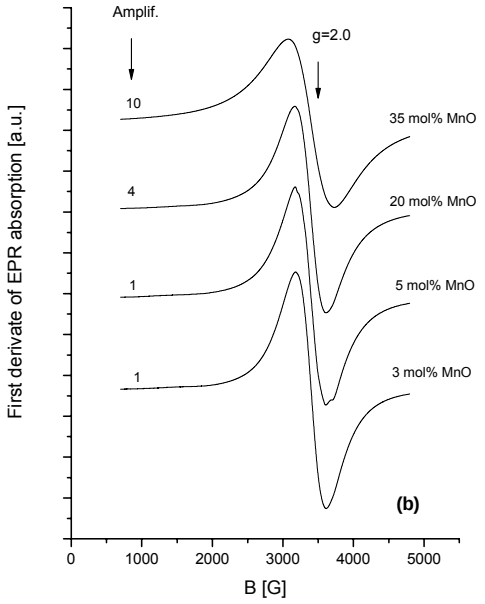
Recorded EPR spectra show resonance line due to the Mn^{2+} ($3d^5$, $^6S_{5/2}$) paramagnetic ions for all range of concentration. The structure of the spectra strongly depends on the manganese content of the samples. The EPR spectra are presented in Fig. 1. The detected spectra for all the samples consist in one resonance line centered $g_{eff} \approx 2.0$, their shape and intensity depending on the manganese content.

The $g_{eff} \approx 2.0$ was generally attributed to isolated paramagnetic Mn^{2+} ions in octahedral symmetric sites slightly tetragonally distorted or to exchange coupled pairs of these ions [14]. Depending on concentration, our samples show an evolution of the vitreous matrix structure from structural units involving Mn^{2+} in well definited vicinities having certain symmetry, to structural aggregates containing clustered ionic formations. This evolution was revealed by the changes in the $g_{eff} \approx 2.0$ absorption line when increasing the Mn^{2+} ions concentration

For $x \leq 1$ mol% the $g_{eff} \approx 2.0$ absorption line shows hyperfine structure (hfs) characteristic to the ^{55}Mn (I=5/2) isotope. The resolution depends on the Mn^{2+} ion concentration as can be seen in Fig. 1(a). The resolution of the line is loosing with the increasing of the concentration due to the ligand field fluctuation in the manganese ion surrounding [15, 16].



a



b

Fig. 1. EPR absorption spectra of Mn^{2+} ions in xMnO · (100-x)[P_2O_5-TeO_2] glasses (a) 0.5 ≤ x ≤ 1 mol% MnO, (b) 3 ≤ x ≤ 35 mol% MnO.

The hyperfine sextet is due to isolated Mn^{2+} in high symmetric sites that are separated well enough from each other to avoid dipolar interactions. The g factor and hyperfine coupling constant values and the well resolved hfs, support this statement and also show the predominantly ionic character of the bonding between Mn^{2+} and O^{2-} ions generating the octahedral symmetric ligand field. There are week axial distortions superimposed on this field varying in intensity and orientation from the vicinity of manganese ion to another [17, 18]. The hfs sextet superimposes on a large absorption line, the envelope of all contributions at this absorption having $g_{eff} \approx 2.0$. The hyperfine coupling constant, A, was approximated as separation between the lines of the central pair of the hfs sextet. For the sample having 0.5 mol% MnO this parameter was estimated as A ≈ 93 Gs. Data available on the EPR of Mn^{2+} ions in glasses show that g and *A* parameters are less sensitive to variation of local environmental of these ions as compared to the crystal field parameters *D* or *E* [19, 20]. Computer simulation of EPR spectra for various borate glasses [21] explains the additional splitting of the $g_{eff} \approx 2.0$ hyperfine sextet as due to large distributions of *D* and *E* of the fine structure parameters.

For x ≥ 3 mol% the EPR resonance line centered at $g_{eff} \approx 2.0$ does not have hfs, (Fig. 1(b)).

The concentration dependence of the intensity, *J*, obtained as an integral of the area under the corresponding EPR signals and the line-width, ΔB, for the line at $g_{eff} \approx 2.0$ is presented in figures 2 and 3. For x ≤ 3 mol% the intensity of the resonance line increases very slowly. The increasing is more pronounced for x > 5 mol% (Fig. 2).

The line-width from $g_{eff} \approx 2.0$ is increasing almost linear until x ≤ 10 mol %, which suggests that the Mn^{2+} ions are involved in dipolar interaction responsible for the EPR line broadening (Fig. 3). At higher concentration of MnO, the line-width dependence on MnO content reduced its slope and is constant. These mean that for a higher content of manganese the dipolar broadening is balanced by narrowing mechanism due to negative superexchange interaction between the manganese ions of antiferromagnetic type. The achieved doping level of the samples imposes the progressive clustering of manganese.

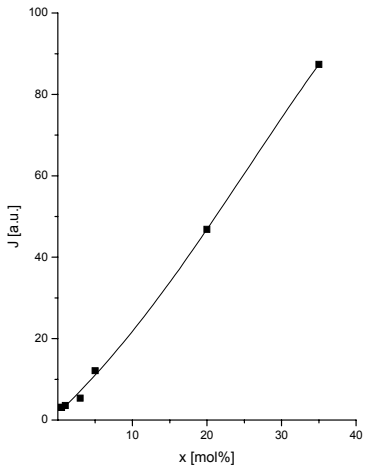


Fig.2. Concentration dependence of the g≈2.00 intensity line for the xMnO (100-x)[P_2O_5-TeO_2] glasses

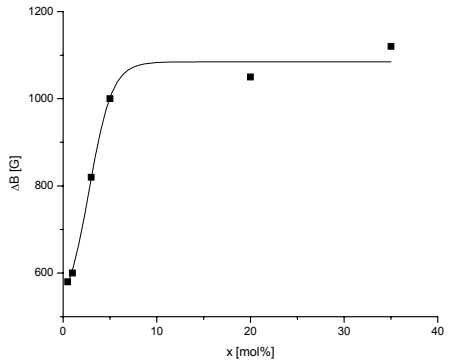


Fig. 3. Concentration dependence of the g≈2.00 line-width for the xMnO (100-x)[P_2O_5-TeO_2] glasses

It is noticed that the line at $g_{eff} \approx 4.3$ did not appeared for all concentration range of MnO. It means that in our samples there are not strongly distorted sites of isolated Mn^{2+} ions in octahedral vicinities subjected to strong crystal field effects.

The structure of our glasses shows an evolution depending of the manganese content of the samples from structural units involving isolated and dipolar coupled Mn^{2+} ions in well defined vicinities, to structural units containing clustered magnetic ions. In these clusters, the Mn^{2+} ions are coupled by superexchange interactions, of antiferromagnetic type. The change in the shape and ΔB of $g_{eff} \approx 2.0$ absorption line when the MnO content increases revealed this evolution.

4. Conclsions

Glasses of the xMnO (1-x)[P_2O_5-TeO_2] system were obtained within $0 \leq x \leq 35$ mol%.

The EPR investigation of Mn^{2+} ions in the P_2O_5-TeO_2 glass matrix revealed influences of the MnO content. Also, the distribution of the Mn^{2+} ions on different types of structural units depends on the MnO content. Up to 5 mol% there are isolated or dipolar coupled ions in well structured vicinities, having tendencies of associate in cluster formations. For higher concentration of Mn^{2+} ions, the magnetic interactions of Mn^{2+} ions in clusters are of antiferromagnetic type.

The $g_{eff} \approx 4.3$ absorption line is not evidenced in the EPR spectra.

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