EPR Structural Investigations on Ag_2O-B_2O_3-CaO-P_2O_5 Vitreous System

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Abstract
Glass samples from vitreous system 1.5Ag_2O98.5%[0.47B_2O_3(0.53-x)CaOxP_2O_5] with $0 \leq x \leq 0.08$ have been obtained by undercooled method. The magnetic species existing in glass powders have been highlighting by mean of electronic paramagnetic resonance (EPR). The resonance linewidth analysis reveal the interactions between magnetic ions.

Keywords: EPR, glass, silver

1. Introduction

In the last two decades various materials such as: glass, glass ceramic, have been investigated in order to obtain useful structures for medical application [1]. Glass samples based on different glass formers oxide, have been studied, due their possible biocompatibility. The glass based on boron oxide (B_2O_3), provide many medical applications depends on the introduced modifiers oxide (Cao, Na_2O) content and transitional ions in glass matrix. The borate network structural units were described by Kamitsos et. al.[2]. Other glass former phosphorus oxide (P_2O_5), gives a high biocompatibility to the material, especially when the calcium oxide is introduced in batch composition. The glass properties can be modify by introducing transitional metal ions (TMO). On the basis of EPR measurements the vicinity and the coordination of silver ions in glass have been revealed [3].
Silver can be found in two natural states $^{107}Ag^0$ and $^{109}Ag^0$, but during the melting process can form many silver ions as well as aggregates such as Ag^+, Ag^{2+}, Ag_2^+. In glass structure silver ions (Ag^+,Ag^{2+}) can link to the open glass units through the ionic bond B-O^- Ag^+ being randomized in glass bulk [4] or the introduced silver oxide (Ag_2O) by its subsequent ions can “run” in the glass inside the melt towards the surface and form metallic silver aggregates.
The main goal of this study was to obtain a bioactive glass homogeneous doped with silver ions, as well as to reveal the main sites occupy by the magnetic ions in the glass and in the surface as well.

2. Materials and methods

The oxide glass of the 1.5%Ag_2O 98.5% [0.47B_2O_3 (0.53-x)CaO xP_2O_5] system with $0 \leq x \leq 0.08$ mol % have been prepared using start materials: Ag_2O, $CaCO_3$, P_2O_5, H_3BO_3 of reagent grade purity. The mixtures were melted in air, at 1250°C, in sintered corundum crucibles, and kept for 15 min. at this temperature. The melts were quickly cooled to room temperature by pouring onto stainless-steel plates.
The EPR measurements of powder samples were carried out in the X-band (~ 9.79 GHz) at room

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temperature using a Bruker E-500 ELEXSYS spectrometer. To avoid the alteration of the glass structure due to the ambient conditions, especially humidity, samples were poured immediately after preparation and enclosed in tubular holders of the same caliber. Equal quantities of samples were studied.

3. Results and discussion

Electronic paramagnetic resonance (EPR) spectra of the investigated vitreous system 1.5% Ag_2O 98.5%[0.47B_2O_3 (0.53-x) CaO xP_2O_5] (Fig. 1) show typical absorption lines for introduced ions (Ag) and impurities (Fe^{3+}) at ~ 3390 Gs (g ≈ 1.99), ~ 3260 Gs (g ≈ 2.05), 1580 Gs (g ≈ 4.3) and a small and broad line at around 2460 Gs for all investigated P_2O_5 concetrations.

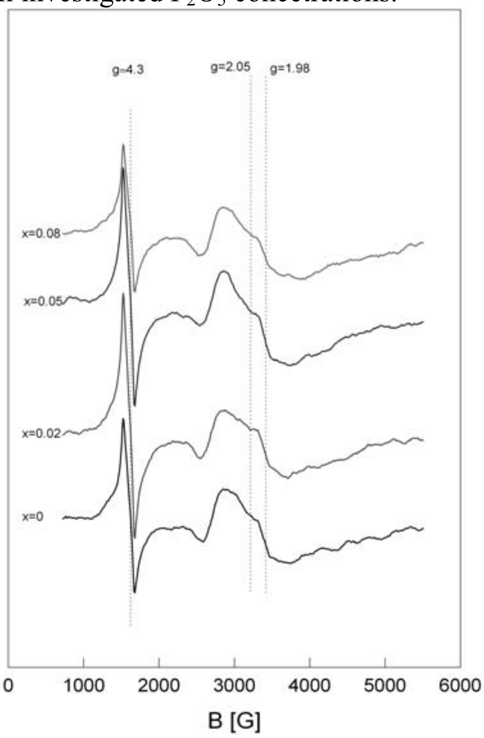

Figure .1 EPR absorption spectra of vitreous 1.5% Ag_2O 98.5%[0.47B_2O_3 (0.53-x)CaO xP_2O_5]

The existing resonances give informations about the interactions between ions, into glass bulk useful when describing physical properties in biological fluids or simulated body fluids (SBF).
The line at g ≈ 4.3 was attributed to iron ions (Fe^{3+}) situated in octahedral symmetry in isolated sites. Depending on the cooling rate, the environment around existing ions, could be distorted with different degree. In the investigated glass the isolated Fe^{3+} impurities are situated in rhombic or tetragonal distorted sites. In addition of iron ions, silver ions or aggregates can give rise to EPR absoption lines. The identification a specific type of EPR silver center is difficult, because in undercooled melt, silver can forms many species. EPR spectroscopy can highlight Ag^0 and Ag_2^+ in glass structure [3, 5], the second aggregaes being formed when Ag^0 is attached to an ions Ag^+ . Several studies [6] described the Ag^{2+} EPR signals at around g ~ 2.003 and also around g ~ 2.24.

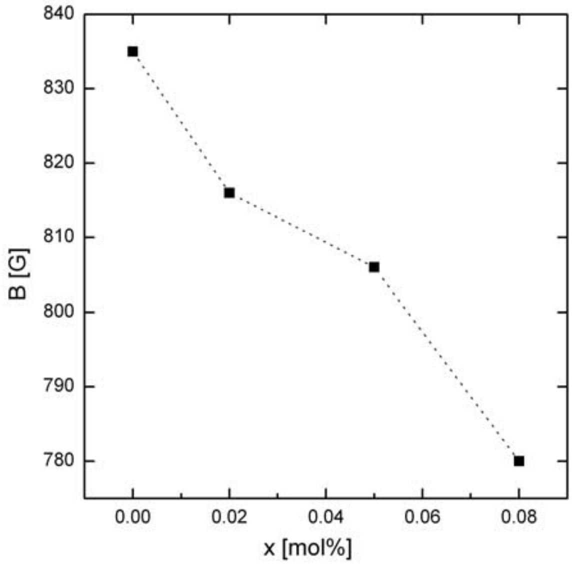

Figure 2. The linewidth of g ~ 2.05 absorption

The line width of the absorption lines is a direct measure of the magnetic interactions between ions who give rise to one specific absorption.
In Figure 2 we plotted the dependence of linewidth at g ≈ 2.05 on the P_2O_5 ratio in glass matrix. The line decrease with 60 G when the P_2O_5 increase with 8 mol% in base glass B_2O_3 – CaO-P_2O_5, revealing the changes in the magnetic ions intractions.

4. Conclusions

Silver containing B_2O_3-CaO-P_2O_5 glass matrix have been prepared by undercooled method at room temperature.
The EPR absorption lines belong to Ag^{2+}, Ag^0 species and Ag_2^+ particles distributed in the glass matrix as well as Fe^{3+} impurities present in the glass.
The line with decreases describe the changes in magnetic interactions between magnetic species into the glass bulk.

Acknowledgements

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