STRUCTURAL INVESTIGATIONS OF $xFe_2O_3 \cdot (100\text{-}x)[Bi_2O_3 \cdot CdO]$ SYSTEM BY EPR AND MAGNETIC SUSCEPTIBILITY MEASUREMENTS

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Abstract:
Samples from $xFe_2O_3 \cdot (100\text{-}x)[Bi_2O_3 \cdot CdO]$ system, with $0 \leq x \leq 50$ mol%, were prepared and investigated by X – Ray diffraction, electron paramagnetic resonance (EPR) and magnetic susceptibility. The influences of a gradual increase of Fe_2O_3 content on the glass structure and magnetic interactions that involve iron ions have been discussed.
The XRD patterns show a vitreous state for $x < 35$ mol% Fe_2O_3. The local structure in glasses was revealed by means of EPR using Fe^{3+} ($3d^5$; $^6S_{5/2}$) ions as paramagnetic probes. The shape of the EPR spectra consist in a single resonance absorption line centered at $g_{eff} \approx 4.3$ which appears in all compositional range. The line from $g_{eff} \approx 4.3$ is due to the isolated ions situated in octahedral symmetry rhombic or tetragonal distorted neighborhoods subjected to the effect of an intense crystalline field. Magnetic susceptibility measurements suggest that for $x \leq 20$ mol%, the temperature dependence of the reciprocal magnetic susceptibility follows a Curie law. Also, from both, EPR and magnetic susceptibility data have shown that the iron ions are present in these glasses as magnetic isolated species coupled by dipole – dipole interactions.

1. Introduction

The structural study of bismuthate glasses became recently very useful due to the unconventional role of Bi_2O_3 as glass-former and to their interesting properties [1 – 3].

Nowadays, due to their high sensitive response to the changes in their surrounding, the transition metal ions are extensively used to probe the glass

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structure [4]. A method used to characterize the local structure, dynamics and spatial distribution of paramagnetic species is Electron Paramagnetic Resonance (EPR) spectroscopy [5]. EPR of Fe^{3+} ($3d^5$, $^6S_{5/2}$) ions may provide useful information concerning the structural details of the vitreous matrix revealed by their distribution on different structural units building the network, their coordination and the valence state.

In addition, the magnetic susceptibility measurements provide information about the valence state and the interaction involving the transition metal ions.

The purpose of this study is to obtain, by EPR spectroscopy and the magnetic susceptibility measurements, information about the valence state and the interaction involving the iron ions in $Bi_2O_3 \cdot CdO$ glass matrix.

2. Experimental

Glasses from $xFe_2O_3 \cdot (100\text{-}x)[Bi_2O_3 \cdot CdO]$ system were prepared by mixing components of reagent grade purity, $Bi(NO_3)_3 \cdot 5H_2O$, $CdCO_3$ and Fe_2O_3, in suitable proportions to obtain the desired compositions. The mixtures were melted in sintered corundum crucibles, introduced in an electric furnace Carbolite RF 1600, directly at $1250^°$ C and kept for 5 minutes at this temperature. They were quickly cooled at room temperature by pouring onto stainless steel plates.

The structure of samples was analyzed by means of X-ray diffraction, using powders, with a Bruker D8 Advanced diffractometer. As reference the latest database of ICDD – International Center for Diffraction Data was used. The XRD patterns for two of most representative samples from $xFe_2O_3 \cdot (100\text{-}x)[Bi_2O_3 \cdot CdO]$ system are presented in figure 1. For x < 35 mol%, the XRD patterns presents a broad diffuse scattering at low angles which indicates a long – range structural disorder characteristic to vitreous solids. For x ≥ 35 mol% the vitreous and the crystalline phase coexist. They were identified as $Bi_{1.5}Cd_{0.5}O_{2.75}$ (reference number: 40-0315, compound name: cadmium bismuth oxide) and Fe_3O_4 (reference number: 89-0951 (C), compound name: magnetite). Because this study is referring to a glass system, only the samples from 0 to 20 mol% Fe_2O_3 will be discussed afterwards.

The EPR spectra were obtained at room temperature with an Adani Portable EPR Spectrometer PS8400 in X-frequency band (9,4 GHz) and a field modulation of 100 KHz. For these measurements, equal quantity of powders from the investigated samples, closed in glass tubes, were used.

Magnetic susceptibility measurements were performed on a Faraday type balance in the 80 – 300 K temperature range. The sensitivity of the equipment was 10^{-7} emu/g.
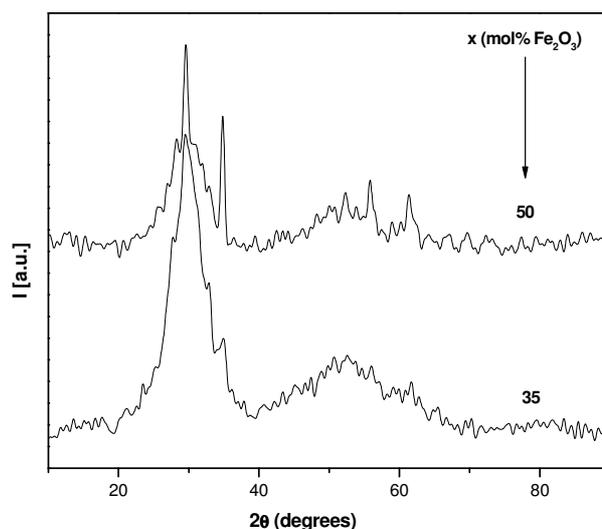
Fig. 1. XRD patterns of $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ glasses for $x \geq 35$ mol%

3. Results and discussion

The EPR spectra of $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$, for $x \leq 20$ mol%, are presented in figure 2.

The EPR spectra of $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ glasses present, in all compositional range, a single absorption line centered at $g_{eff} \approx 4.3$ which is due to isolated Fe^{3+} ions situated in sites of distorted octahedral symmetry (rhombic or tetragonal) subjected to the effect of an intense crystalline field [6 – 15].

The evolution of the spectra is easier to follow considering the dependence of concentration on the EPR parameters, i.e. the line – intensity (obtained as an integral of the area under the corresponding EPR signal), J and the line – width, ΔB. The corresponding variations of these parameters for the resonance line centered at $g_{eff} \approx 4.3$ are presented in figure 3.

The intensity of the resonance line from $g_{eff} \approx 4.3$ increases up to $x = 10$ mol% and then decreases (Fig. 3a). This increasing indicates the increasing of the isolated Fe^{3+} ions in glasses. The decreasing of this resonance line with the increasing of iron ions content is due to the destruction of the configuration from the iron ions neighborhoods, which assures their magnetic isolation [10]. The gradual increasing of the iron content in $Bi_2O_3 \cdot CdO$ matrix destroys the local ordering of the Fe^{3+} ions neighborhoods, so the structural units as characteristic entities become less represented.
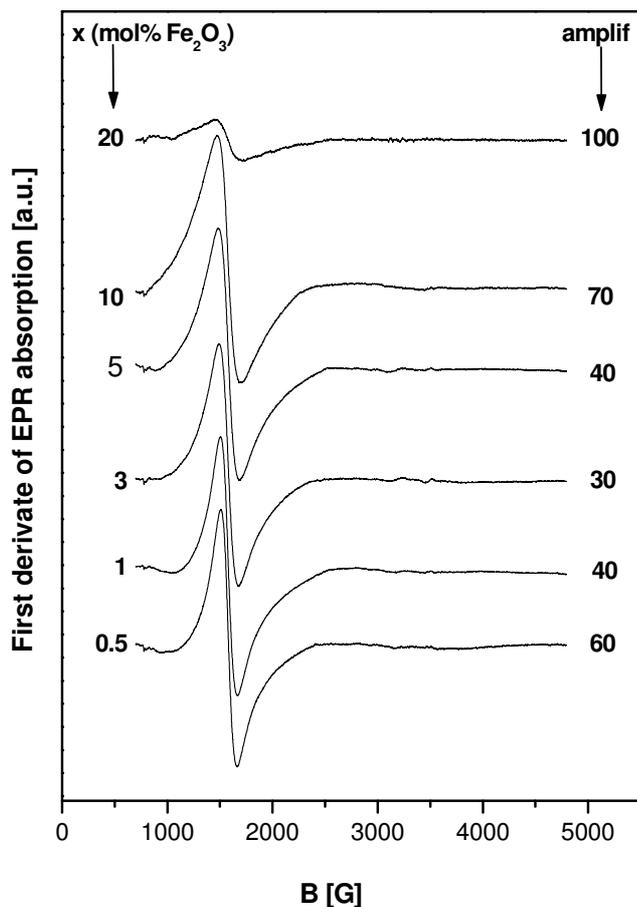
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Fig. 2. EPR absorption spectra of Fe^{3+} ions in $xFe_2O_3 \cdot (100\text{-}x)[Bi_2O_3 \cdot CdO]$ glasses

The line – width from $g_{eff} \approx 4.3$ (Fig. 3b) show a line broadening within $1 \leq x \leq 10$ mol% due to increase of the number of Fe^{3+} ions. For $x > 10$ mol% the increasing of ΔB is progressively attenuated due to the decreasing of Fe^{3+} ions and to the structural disorder in glasses with the increasing of Fe_2O_3 content. For higher concentration of Fe_2O_3 the possibilities of Fe^{3+} ions to structure their vicinities in coordination with oxygen ions is decreasing, so the participation of Fe^{3+} ions to $g_{eff} \approx 4,3$ absorption is decreasing and favorite the formation of clusters.
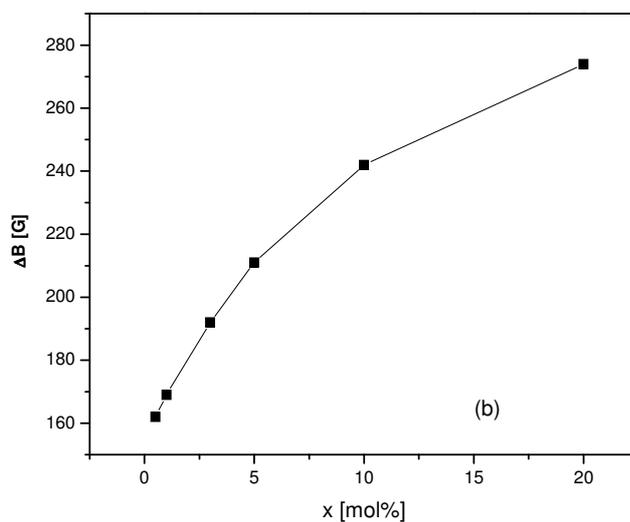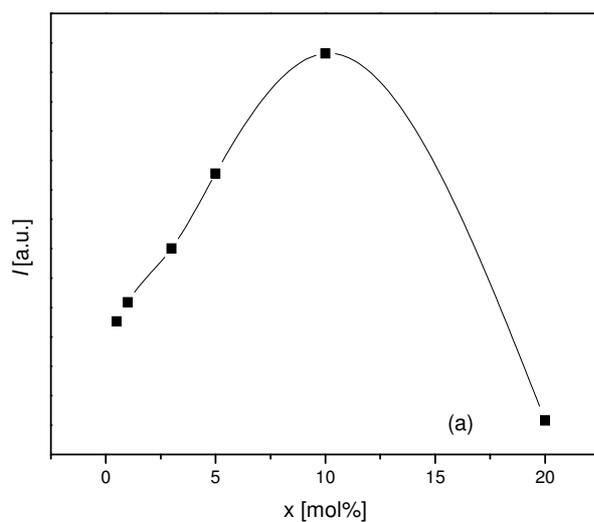
Fig. 3. Composition dependence of the line intensity (a) and the line – width (b) of EPR absorption at $g_{eff} \approx 4.3$ for $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ glasses

The magnetic susceptibility data are in good agreement with the EPR result. The temperature dependence of the reciprocal magnetic susceptibility is given in figure 4. It can be observed that for $x \leq 20$ mol%, the Curie law is obeyed,

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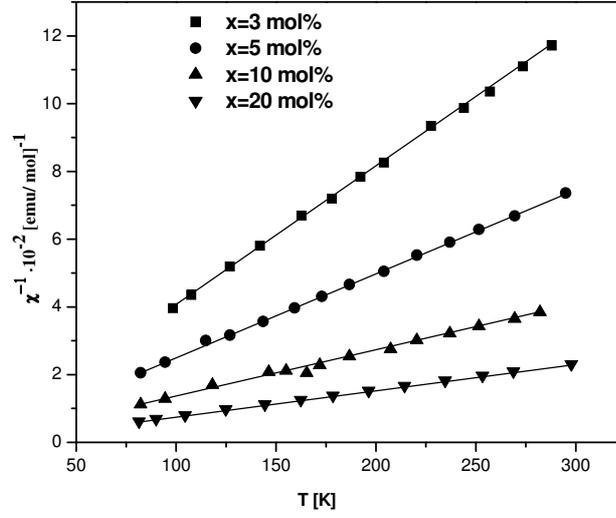suggesting the existence in the studied glasses of isolated Fe^{3+} ions.

Fig. 4. Temperature dependence of χ^{-1} for $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ glasses with $x \le 20$ mol%

The composition dependence of the molar Curie constant and the experimental effective magnetic moments (μ_{eff}) for all investigated systems are presented in Table 1. Using the atomic magnetic moment values of isolated Fe^{3+} and Fe^{2+} ions: $\mu_{Fe3+} = 5.92\mu_B$ and $\mu_{Fe2+} = 4.90\mu_B$ [10], it can be estimated in first approximation the molar fraction of these ions in the investigated glasses using the relations:

$$x \cdot \mu_{eff}^2 = x_1 \cdot \mu_{Fe^{3+}}^2 + x_2 \cdot \mu_{Fe^{2+}}^2 ,$$

$$x = x_1 + x_2 ,$$

where $\mu_{eff} = 2.827\sqrt{\dfrac{C_M}{2x}}$, is the experimental magnetic moment, x_1 and x_2 are the molar fraction of iron ions in Fe^{3+} and Fe^{2+} valence states. Due to the fact that the experimental magnetic moment vary between 5.71 μ_B at 3 mol % Fe_2O_3 to 5.05 μ_B for 20 mol % Fe_2O_3 we assume that in all the studied glasses Fe^{3+} and Fe^{2+} ions coexist.

From Table 1 it can be also observed that in $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ glass system, the molar fraction of Fe^{3+} ions is increasing up to 10 mol% then decreases with the increasing of Fe_2O_3 content. The molar fraction of Fe^{2+} ions and the C_M values are increasing with the increasing of Fe_2O_3 content.

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Table 1. Molar Curie constants, effective magnetic moments and molar fractions of Fe^{3+} (x_1) and Fe^{2+} (x_2) ions in $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ glasses

x [mol% Fe_2O_3]	C_M [emu/ mol]	μ_{eff} [μ_B]	x_1 [mol% $Fe_2^{3+}O_3$]	x_2 [mol% $Fe_2^{2+}O_3$]
3	23.96	5.71	2.34	0.66
5	40.19	5.66	3.64	1.36
10	73.69	5.42	4.87	5.13
20	127.78	5.05	2.7	17.3

4. Conclusions

The XRD patterns of $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ system confirm the presence of a vitreous state for $0 \leq x \leq 20$ mol%.

The EPR absorption spectra for all investigated glasses are due to Fe^{3+} ($3d^5$, $^6S_{5/2}$) paramagnetic ions. The shape of the spectra and the values of the EPR parameters of the resonance lines depend of Fe_2O_3 concentration.

Considering the dependence of concentration on the EPR parameters, i.e. the line – intensity, J and the line – width, ΔB it can be concluded that in $xFe_2O_3 \cdot (100-x)[Bi_2O_3 \cdot CdO]$ glass system the iron ions are present as isolated ions situated in octahedral symmetry rhombic or tetragonal distorted neighborhoods subjected to the effect of an intense crystalline field.

The magnetic susceptibility measurements confirm the results suggested by EPR spectroscopy.

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