

COMPARATIVE STUDY OF STRUCTURAL AND MAGNETIC PROPERTIES OF $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ AND $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ (MO => As_2O_3 OR GeO_2) GLASS SYSTEMS

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Abstract:

Glasses from $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ system, with $0 \leq x \leq 20$ mol% and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ (MO => As_2O_3 or GeO_2) systems, with $0 \leq x \leq 50$ mol% were prepared and investigated by electron paramagnetic resonance (EPR) and magnetic susceptibility measurements.

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 two resonance lines centered at $g_{\text{eff}} \approx 4.3$, for $0.5 \leq x \leq 20$ mol%, in all investigated systems and at $g_{\text{eff}} \approx 2$, for $x \geq 35$ mol%, in $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ (MO => As_2O_3 or GeO_2) glass systems. The line from $g_{\text{eff}} \approx 4.3$ is due to the isolated Fe^{3+} ions situated in octahedral symmetry rhombic or tetragonal distorted neighborhoods subjected to the effect of an intense crystalline field. The line from $g_{\text{eff}} \approx 2$ is attributed to the isolated Fe^{3+} ions situated in octahedral distorted neighborhoods but also to the Fe^{3+} ions which participate to dipolar and/or superexchange interactions. In order to obtain detailed information regarding the influences of a gradual increase of Fe_2O_3 content on the glass structure, the evolution of the spectra was presented for the investigated systems, considering the dependence of concentration of 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 .

Magnetic susceptibility measurements suggest that in all investigated glass systems, for $x \leq 20$ mol%, the temperature dependence of the reciprocal magnetic susceptibility, follows a Curie law and over this concentration, for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ (MO => As_2O_3 or GeO_2) glass systems, follows a Curie-Weiss law with the negative paramagnetic Curie temperature. Also, from both, EPR and magnetic susceptibility data have shown that the iron ions are present in the

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glasses as isolated species, coupled by dipole – dipole and superexchange interactions.

1. Introduction

During recent years, there has been an increasing interest in the synthesis and investigation of the structure and physical properties of heavy metal oxide glasses containing Bi_2O_3 , due to their high refractive index, high IR transparency and high third order non-linear optical susceptibility [1, 2]. Due to these properties, the bismuthate glasses have wide applications in the field of glass ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors and reflecting windows [1]. Also, the interest in these glasses has increased because their suitability to synthesize high – temperature ceramic superconductors [3]. Dumbaugh et al. [4] concluded that these properties usually come at the expense of glass stability. They studied the glass forming regions of heavy metal oxides (HMO) such as Bi_2O_3 by adding several oxides as As_2O_3 and GeO_2 [4] due to their properties such as those mentioned below. As_2O_3 is a network former with corner – sharing AsO_3 pyramidal units [5]. As_2O_3 based glasses have been identified as the low-loss materials for long-distance optical transmission [6]. These glasses have exceptionally high transmission potential in the far infrared region when compared with the conventional glasses based on B_2O_3 , SiO_2 , P_2O_5 and GeO_2 . They have very high Raman scattering coefficients and are found to be suitable for active fiber Raman amplification [7]. GeO_2 is a typical glass former [8] and germanate glasses have potential use as optical fibers and infrared transmitting windows [9].

Transition metal ions are being extensively used in the present day to probe the glass structure, since their outer d – electron orbital functions have broad radial distribution and due to their high sensitive response to the changes in the surrounding actions [10]. Among various transition metal ions, iron ions have strong bearing on electrical, optical and magnetic properties [11]. The addition of iron ions in the Bi_2O_3 based vitreous network may confer to the investigated glasses semiconducting properties [12].

Electron paramagnetic resonance (EPR) spectroscopy is a method used for characterizing the local structure, dynamics and spatial distribution of paramagnetic species [13]. Structural investigations of glasses performed by means of EPR of transitional metal ions may use Fe^{3+} ($3d^5$, ${}^6\text{S}_{5/2}$) ions as paramagnetic probes. There are several site symmetries appropriate to split the ${}^6\text{S}_{5/2}$ ground state level of the Fe^{3+} ion into three doublets, the EPR spectra being characterized by the $g_{\text{eff}} \approx 4.3$ resonance line arising from the isotropic transition inside one of the Kramers doublets [14 – 18]. Resonance line at $g_{\text{eff}} \approx 2$ may also occur, due to ions distributed in cluster which interact by dipolar and/or superexchange coupling [17 – 20].

Along with the EPR spectroscopy, the magnetic susceptibility measurements provide useful information about the valence state and the interaction involving the iron ions in vitreous materials.

The purpose of this work is to investigate the distribution and interactions of iron ions in the investigated glass systems by electron paramagnetic resonance (EPR) and magnetic susceptibility.

2. Experimental

$x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ systems (where $\text{MO} \Rightarrow \text{As}_2\text{O}_3$ or GeO_2) were prepared by mixing components of reagent grade purity, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, As_2O_3 , GeO_2 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 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.

3. Results and discussion

The EPR spectra of $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$, for $x \leq 20$ mol%, and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ glass systems (where $\text{MO} \Rightarrow \text{As}_2\text{O}_3$ or GeO_2), for $x \leq 50$ mol%, are presented in figures 1 and 2.

The EPR spectra of $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ glasses present, in all compositional range, a single absorption line centered at $g_{\text{eff}} \approx 4.3$. The EPR spectra of $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ glass systems (where $\text{MO} \Rightarrow \text{As}_2\text{O}_3$ or GeO_2), with $0 \leq x \leq 50$ mol%, present two absorption lines at $g_{\text{eff}} \approx 4.3$ and $g_{\text{eff}} \approx 2$. The absorption line centered at $g_{\text{eff}} \approx 4.3$ can be observed for $x \leq 20$ mol% in all investigated systems and 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 [17, 18, 20 – 23]. The absorption line centered at $g_{\text{eff}} \approx 2$ can be observed for $x \geq 20$ mol% in $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ glass systems (where $\text{MO} \Rightarrow \text{As}_2\text{O}_3$ or GeO_2) and may be attributed either to Fe^{3+} species interacting by

dipole-dipole interaction in sites of less distorted octahedral (tetrahedral) field and/or to superexchange coupled pairs [24, 25].

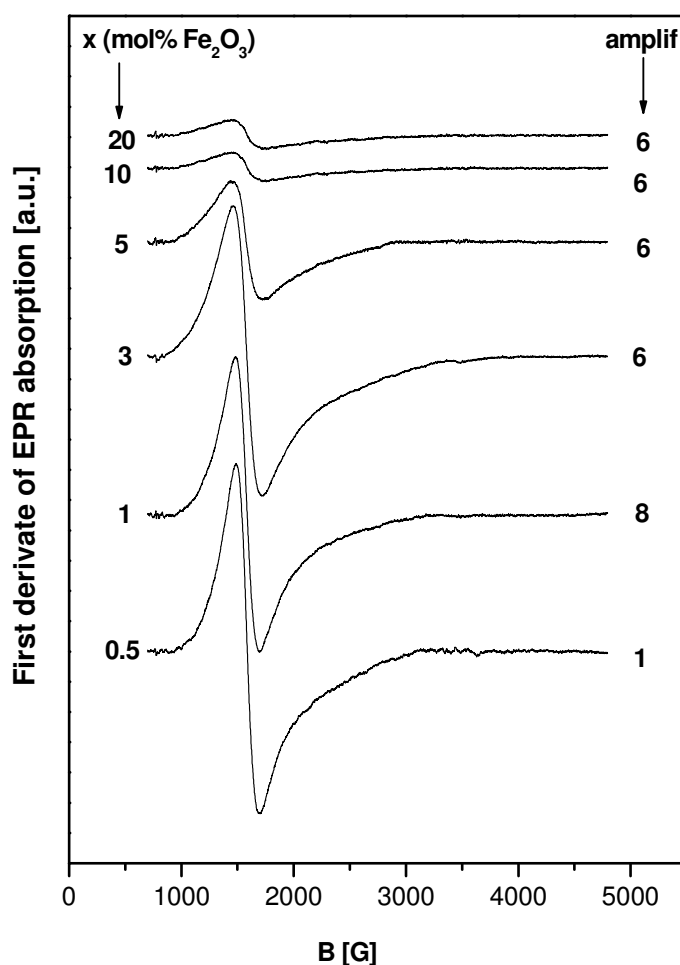
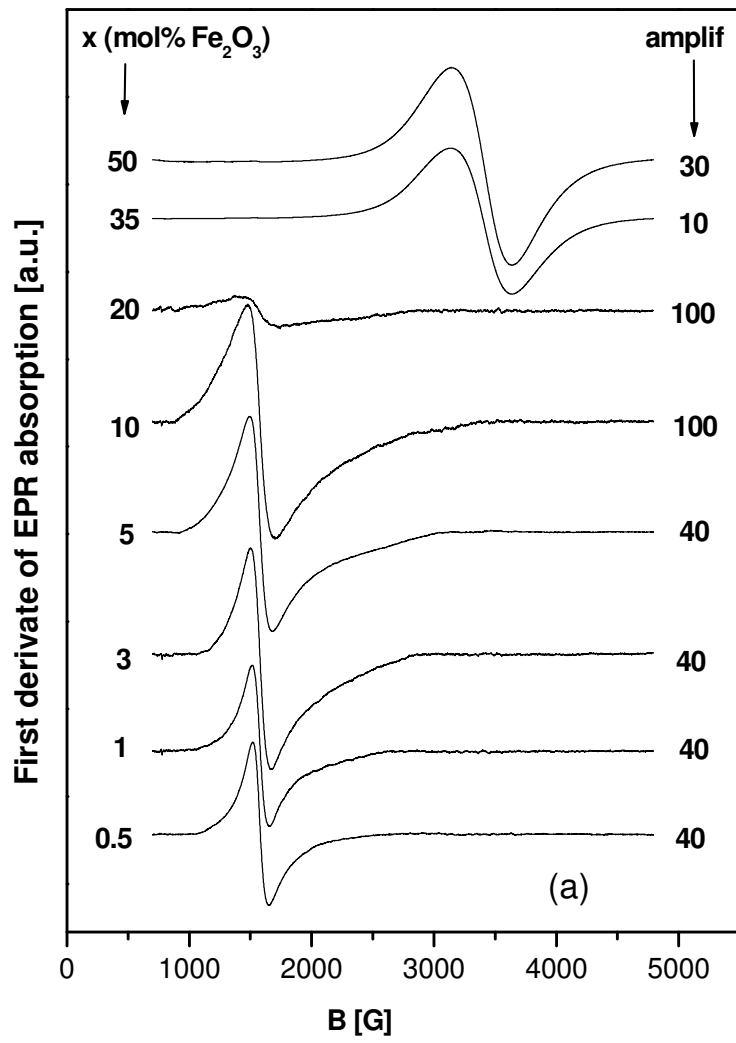


Fig. 1. EPR absorption spectra of Fe^{3+} ions in $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ glasses

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 lines centered at $g_{\text{eff}} \approx 4.3$ and $g_{\text{eff}} \approx 2$ are presented in figure 3 and 4.



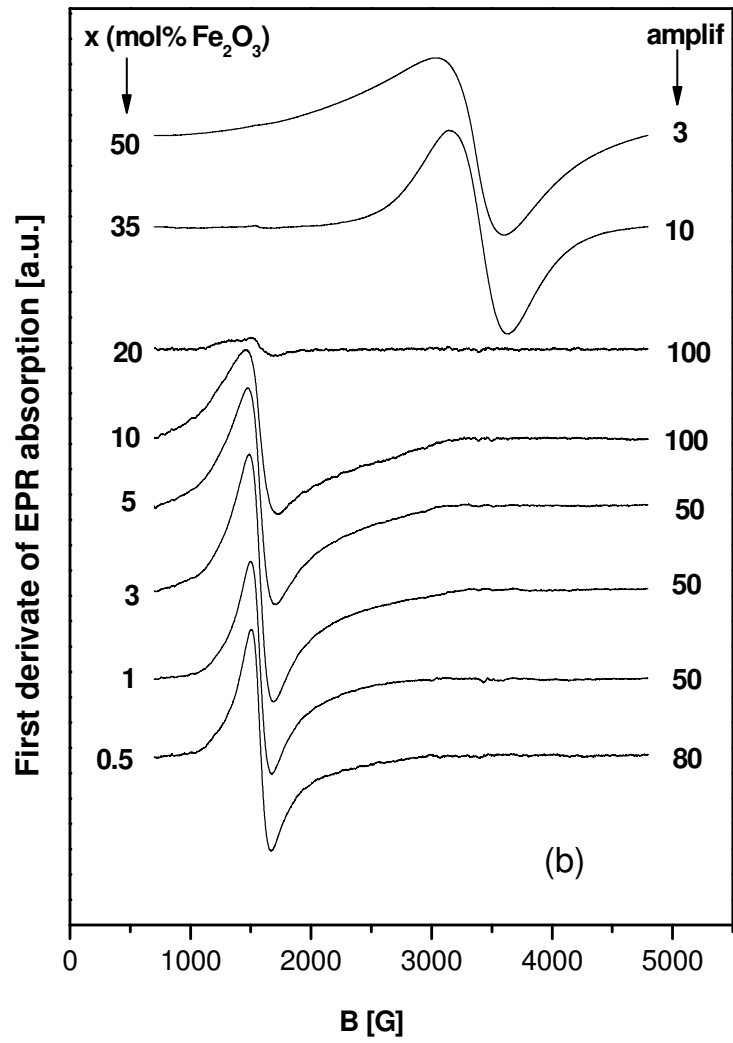


Fig. 2. EPR absorption spectra of Fe^{3+} ions in (a) $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glasses and (b) $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$

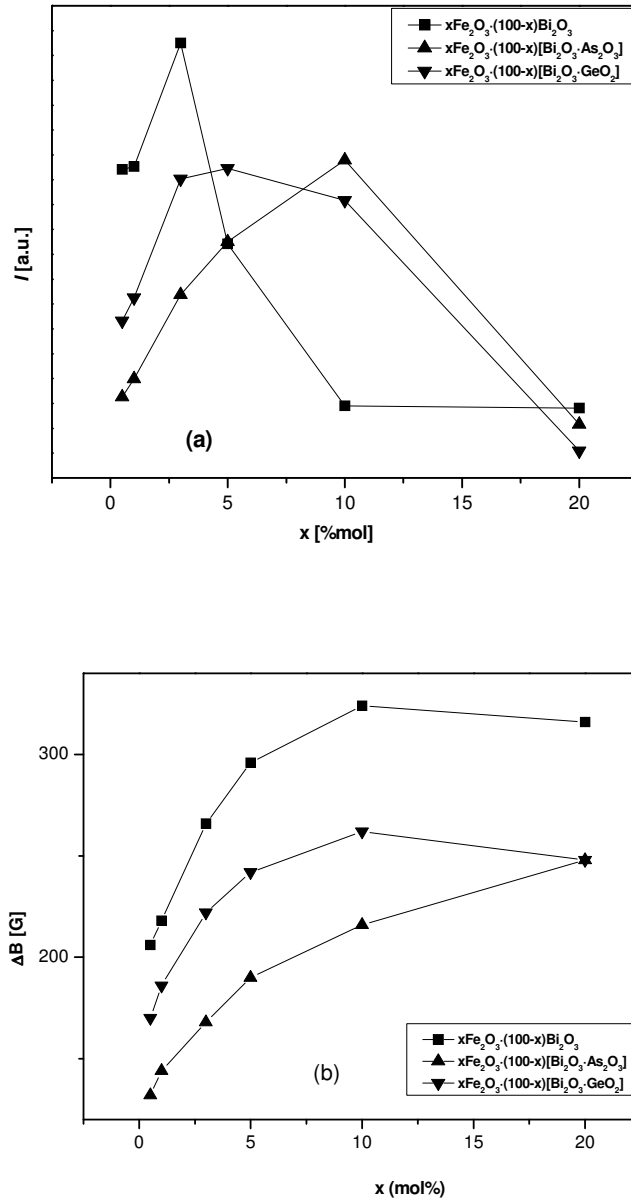


Fig. 3. Composition dependence of the line intensity (a) and the line – width (b) of EPR absorption at $g_{\text{eff}} \approx 4.3$ for $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ systems (where $\text{MO} \Rightarrow \text{As}_2\text{O}_3$ or GeO_2)

The intensity of the resonance line from $g \approx 4.3$ increases up to $x = 3$ mol% for $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ glass system, up to $x = 10$ mol% for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glass system and up to $x = 5$ mol% for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ glass system. This increasing indicates the increasing of the isolated Fe^{3+} ions in glasses. For higher concentration of Fe_2O_3 the intensity of the resonance line from $g \approx 4.3$ decreases (Fig. 3a). This decreasing is due to the destruction of the configuration from the iron ions neighborhoods, which assures their magnetic isolation [22]. The gradual increasing of the iron content in the matrices destroys the local ordering of the Fe^{3+} ions neighborhoods, so the structural units as characteristic entities become less represented. This evolution suggests that, Bi_2O_3 and $\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2$ glass matrix offer more limited possibilities to Fe^{3+} ions to structure their vicinities in defined symmetry unities [26] comparing with $\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3$ glass matrix.

The line – width from $g \approx 4.3$ (Fig. 3b) is increasing and present a line broadening within $1 \leq x \leq 5$ mol% due to increase of the number of Fe^{3+} ions. For $x > 5$ 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 $g \approx 4,3$ absorption is decreasing and favorite the formation of clusters.

The line intensity at $g \approx 2$ (Fig. 4a) can be observed for $x > 20$ mol% in $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ glass systems. Due to the fact that the absorption line from $g \approx 2$ can not be observed for $x \leq 20$ mol% it can be assumed that for these concentrations the iron ions are isolated. For higher concentrations of Fe_2O_3 the iron ions prefer the structural units in which they are distributed as clusters.

The line – width of the $g \approx 2$ absorption line (Fig. 4b), for $x > 20$ mol%, increases up to 35 mol% and then its slope decreases. The evolution of the line – width from $g \approx 2$ suggests that for $x \geq 35$ mol% Fe_2O_3 the iron ions participate at dipolar and/or superexchange magnetic interactions. The $\Delta B=f(x)$ dependence reflect the competition between the broadening mechanisms (dipole-dipole interactions, the interactions between ions in different valence state and structural disorder) and the narrowing ones (superexchange interactions). The prevalence of one type of mechanism or another is a function of the iron content in glasses.

EPR absorption data reflect the structural changes in the investigated vitreous matrices when increasing the iron content. In all investigated systems, for $x \leq 20$ mol%, the iron ions are present only as isolated Fe^{3+} ions. For $x > 20$ mol%, in $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ glass systems, can be observed that the iron ions participate to dipolar and/or superexchange interactions.

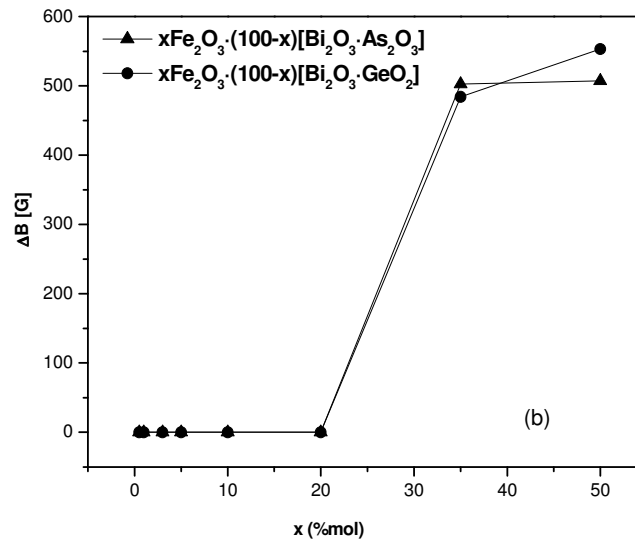
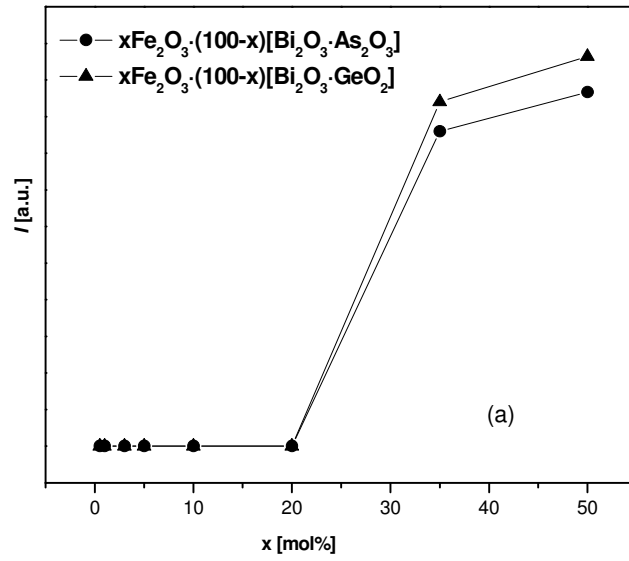


Fig 4. Composition dependence of the line intensity (a) and the line – width (b) of EPR absorption at $g_{\text{eff}} \approx 2$ for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ systems (where $\text{MO} \Rightarrow \text{As}_2\text{O}_3$ or GeO_2)

The magnetic susceptibility data are in good agreement with the EPR result. The temperature dependence of the reciprocal magnetic susceptibility is given in figures 5 – 7. In all investigated systems, for $x \leq 20$ mol%, the Curie law is obeyed, suggesting the existence of magnetic isolated iron ions. For $x > 20$ mol%, in $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glass systems, the reciprocal magnetic susceptibility obeys a Curie-Weiss law with negative paramagnetic Curie temperature (θ_p) characteristic to antiferromagnetic coupled ions by means of superexchange interactions. These interactions are narrowing mechanism of EPR absorption line and explain the slope change of the $\Delta B = f(x)$ curve (fig. 4 (b)).

The composition dependence of θ_p is given in figure 8. The absolute value of θ_p increases for $x > 20$ mol% with the magnetic ions content but their values are relatively small, which indicates that the magnetic interactions between the iron ions are relatively weak. Also it can be remarked that the absolute values of θ_p are higher for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glass system comparative with $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ glass system which suggests that, in the first system, the intensity of the superexchange interactions between the iron ions is higher.

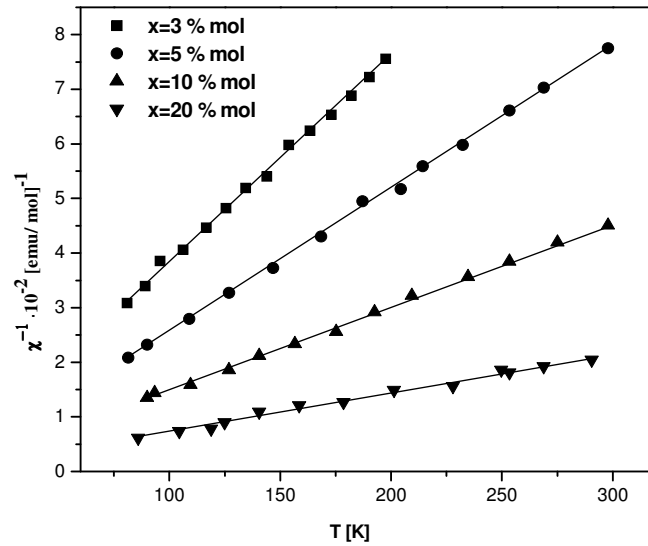


Fig. 5. Temperature dependence of χ^{-1} for $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ glasses with $x \leq 20$ mol%

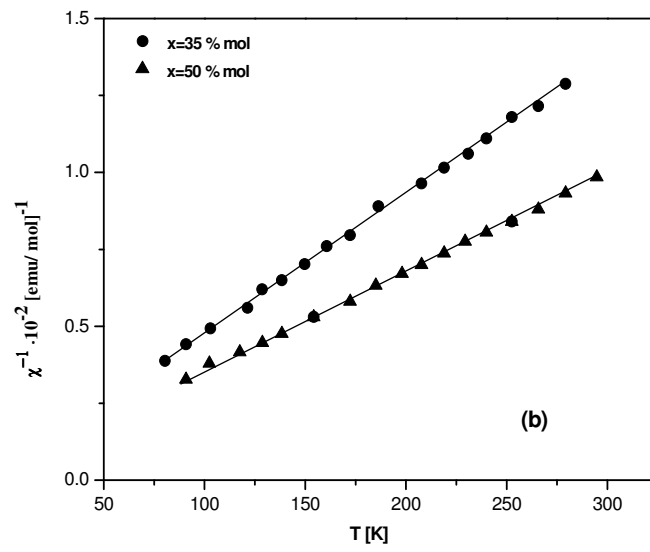
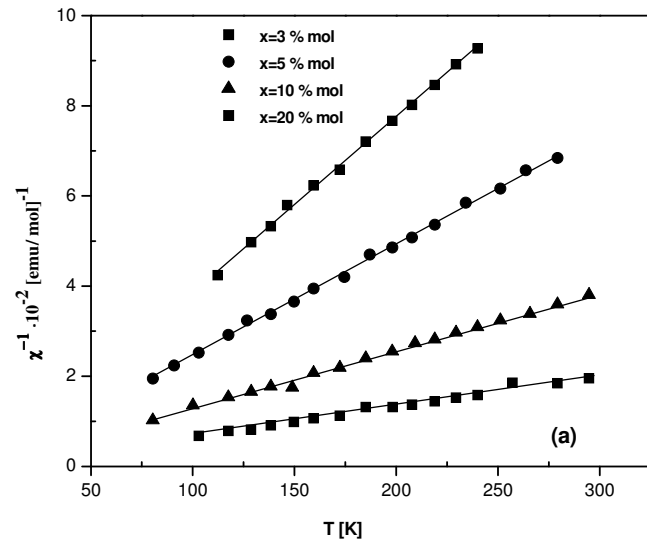


Fig. 6. Temperature dependence of χ^{-1} for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glasses with $3 \leq x \leq 20$ mol% (a) and $x \geq 35$ mol% (b)

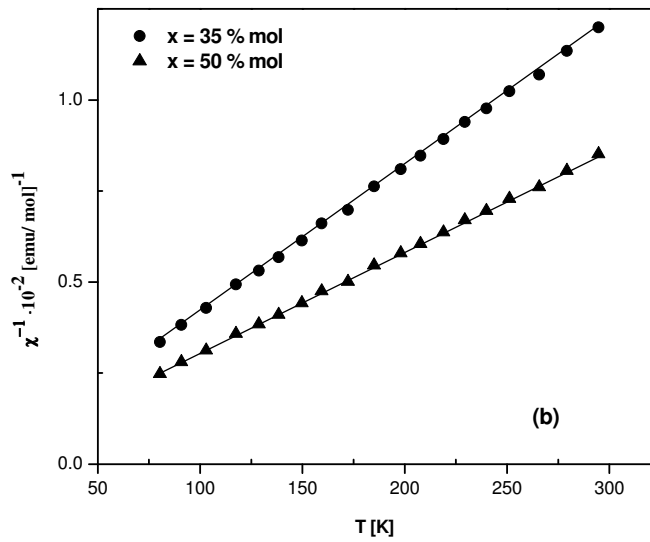
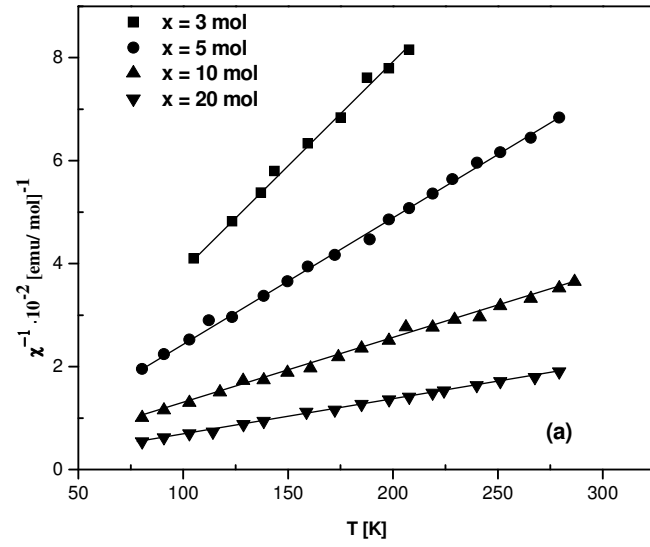


Fig. 7. Temperature dependence of χ^{-1} for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ glasses with $3 \leq x \leq 20$ mol% (a) and $x \geq 35$ mol (b)

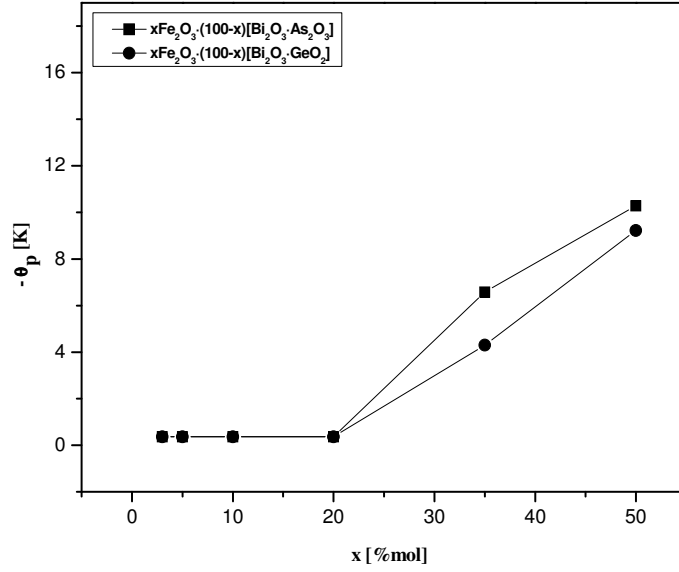


Fig. 8. Concentration dependence of θ_p for $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{MO}]$ systems (where $\text{MO} \Rightarrow \text{As}_2\text{O}_3$ or GeO_2)

The composition dependence of the molar Curie constant and the experimental effective magnetic moments (μ_{eff}) for all investigated systems are presented in Tables 1 – 3. Using the atomic magnetic moment values of free Fe^{3+} and Fe^{2+} ions: $\mu_{\text{Fe}^{3+}} = 5.92\mu_B$ and $\mu_{\text{Fe}^{2+}} = 4.90\mu_B$ [22], it can be estimated in first approximation the molar fraction of these ions in the investigated glasses using the relations:

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

$$x = x_1 + x_2,$$

where $\mu_{\text{eff}} = 2.827 \sqrt{\frac{C_M}{2X}}$, 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.

From Table 1 it can be observed that in $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ glass system, the molar fraction of Fe^{3+} ions is increasing up to 10 mol% then decreases. Due to the fact that the experimental magnetic moment vary between $5.92\mu_B$ at 3 mol % Fe_2O_3 to $4.95\mu_B$ for 20 mol % Fe_2O_3 it can be assumed that in all the studied glasses Fe^{3+} and Fe^{2+} ions coexist. So, from table 1 it can be observed that the molar

fraction of Fe^{2+} ions and the C_M values are increasing with the increasing of Fe_2O_3 content.

In $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ and $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ glass systems (tables 2 and 3) it can be observed that the concentrations of Fe^{3+} and Fe^{2+} ions and also the C_M values are increasing with the increasing of Fe_2O_3 content.

Table 1. Molar Curie constants, effective magnetic moment and molar fractions of Fe^{3+} (x_1) and Fe^{2+} (x_2) ions in $x\text{Fe}_2\text{O}_3 \cdot (100-x)\text{Bi}_2\text{O}_3$ glasses

x [mol% Fe_2O_3]	C_M [emu/ mol]	μ_{eff} [μ_B]	x_1 [mol% $\text{Fe}_2^{3+}\text{O}_3$]	x_2 [mol% $\text{Fe}_2^{2+}\text{O}_3$]
3	26,31	5,92	3	-
5	38,11	5,51	2,87	2,13
10	65,48	5,11	1,9	8,1
20	122,72	4,95	0,89	19,11

Table 2. Molar Curie constants, effective magnetic moment and molar fractions of Fe^{3+} (x_1) and Fe^{2+} (x_2) ions in $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{As}_2\text{O}_3]$ glasses

x [mol% Fe_2O_3]	$C_M \times 10^2$ [emu/ mol]	μ_{eff} [μ_B]	x_1 [mol% $\text{Fe}_2^{3+}\text{O}_3$]	x_2 [mol% $\text{Fe}_2^{2+}\text{O}_3$]
3	25,9	5,87	2,84	0,16
5	40,89	5,71	3,9	1,1
10	77,7	5,57	6,35	3,64
20	151,46	5,5	11,3	8,7
35	210,084	5,36	14,97	20,03
50	304,83	5,31	20,1	29,9

Table 3. Molar Curie constants, effective magnetic moment and molar fractions of Fe^{3+} (x_1) and Fe^{2+} (x_2) ions in $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{Bi}_2\text{O}_3 \cdot \text{GeO}_2]$ glasses

x [mol% Fe ₂ O ₃]	C _M ×10 ² [emu/ mol]	μ _{eff} [μ _B]	x ₁ [mol% Fe ₂ ³⁺ O ₃]	x ₂ [mol% Fe ₂ ²⁺ O ₃]
3	25,47	5,82	2,69	0,31
5	40,89	5,71	3,85	1,15
10	79,3	5,62	6,87	3,13
20	147,13	5,42	9,72	10,28
35	250,06	5,35	14,28	20,72
50	358,01	5,34	20,41	29,59

4. Conclusions

For all investigated glasses, the EPR absorption spectra are due to Fe³⁺ (3d⁵, ⁶S_{5/2}) paramagnetic ions. The evolution of the EPR spectra significantly depends of Fe₂O₃ concentration. The evolution of the EPR parameters with the increasing of iron ions content suggest that, for x ≤ 20 mol%, the iron ions are presented in all investigated glass matrices as isolated Fe³⁺ ions. For higher concentration of Fe₂O₃ the iron ions participate to dipolar or/and superexchange interactions.

The magnetic susceptibility measurements confirm the results suggested by EPR spectroscopy. The type of interactions involving iron ions and their valence states was also determined. For x ≤ 20 mol%, the iron ions are presented in all investigated glass matrices as isolated Fe³⁺ ions, for 35 mol% they participate to dipole – dipole interactions and for higher concentrations they appear as antiferromagnetically coupled pairs of ions, connected by means of superexchange type interactions. The magnetic measurements also suggests the simultaneously presence of Fe³⁺ and Fe²⁺ ionic species.

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