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Magnetic clusters development in $(100 – x)[4Bi_2O_3 \cdot PbO]xGd_2O_3$ glasses

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Electron paramagnetic resonance(EPR) at room temperature and magnetic measurements in the temperature range 5 K-300 K at various magnetic field between 1 T and 9T for $(100 – x)[4Bi_2O_3 \cdot PbO]$ xGd_2O_3 glasses(x = 1; 5; 10 and 20 mol%) are reported. The magnetization curves were fitted with the phenomenological equation proposed by Gaj et al. [3], $M = M_S B_{7/2} [g\mu_B SH / k_B T_{eff}]$, where M_S is the phenomenological saturation parameter, $B_{7/2}$ is the Brillouin function for the spin S = 7/2 and $T_{eff} = T – T_0$ is an effective temperature, M_S and T_0 being treated as adjustable parameters. The negative value of T_0 indicates that the magnetic interactions between the Gd ions are antiferromagnetic of short range as superexchange via oxygen ions. The values of the saturation parameters M_S for all thermal untreated and treated samples are smaller than the expected value for the free Gd^{3+} ions. Gd^{3+}- EPR spectra are the superposition of the well known U–type spectrum, containing prominent features with $g_{eff} \approx 5.9$, 2.85 and 2.0 and of a resonance line at $g_{eff} \approx 4.8$. The line width of the absorption at $g_{eff} \approx 5.9$ increases with x concentration at low Gd_2O_3 concentration, but decreases very rapidly when approaching the concentration x= 20mol%. These results may be explained if one consider that the majority of Gd ions behave as free Gd^{3+} ions, while the others as antiferromagnetically coupled pairs Gd^{3+} - O - Gd^{3+} in the form of magnetic clusters whose sizes depend on the Gd_2O_3 concentration in the glasses.

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1. Introduction

The magnetic properties of glasses containing transition metal ™ or rare earth (RE) ions are mainly determined by the degree of local order/disorder and by the existence of molecular aggregates or magnetic clusters formed from TM – O – TM or RE – O – RE coupled pairs [1,2]. Electron paramagnetic resonance (EPR) and magnetic measurements at high magnetic fields give information about the nature and the strength of the magnetic interactions and about the presence of the magnetic clusters in the investigated glasses, contributing in this way to a better understanding of the correlation between the magnetic properties and the structure [3,4].

Glasses with a high content of heavy metals, like Bi_2O_3 and PbO, are intensively investigated due to their properties such as high density, high refractive index, excellent IR transmission and high polarisability [5-7], properties already exploited in applications such as thermal and mechanical sensors [8], wave – guides in non – linear optics [9], scintillation detectors in high – energy physics [9].

Our previous magnetic susceptibility measurements on $(100 – x)[4Bi_2O_3 \cdot PbO]$ xGd_2O_3 glasses, in the temperature range (80 – 300) K, pointed out smaller values for the effective magnetic moments of Gd ions in comparison with the expected value for the free Gd^{3+} ions, i.e., 7.94 μ_B. The dependence of the experimental magnetic moment as a function of x is linear with a negative slope. Furthermore, the paramagnetic Curie temperatures for all these glasses are negative and decrease with increasing Gd^{3+} content [1]. Decreased values of the magnetic moment of Gd were also reported for other glasses [2] and even in pure Gd_2O_3 , a stable oxide which undergoes antiferromagnetic ordering below about 3.9 K [10].

The aim of this paper is to infer the existence of magnetic clusters in $(100 – x)[4Bi_2O_3 \cdot PbO]$ xGd_2O_3 glasses using magnetic measurements at low temperatures and high magnetic fields and EPR measurements at room temperatures, this being in good agreement with other findings on glasses containing transition metal ™ or rare earth (RE) ions and with the molecular simulations of a model liquid showing the glass transition when it becomes very dense, and /or very cold [11].

2. Experimental

Vitreous samples of $(100 – x)[4Bi_2O_3 \cdot PbO]$ xGd_2O_3 with x = 1, 5, 10 and 20 mol% were obtained by quickly undercooling melts from 1100 ºC to room temperature by pouring them onto a stainless steel plate and pressing with a plate of the same material. The starting materials used to prepare the samples were analytically pure reagents $(BiO)_2CO_3$, PbO, and Gd_2O_3. The suitable mixtures were melted in sintered corundum crucibles in an electric furnace, in air, at 1100 ºC for 10 min. Pieces of each sample were also thermal treated at 500 ºC for 8.5 hours.

EPR spectra were recorded at room temperature using a 9.3 GHz Bruker spectrometer, type EPS 380.

The magnetization was measured at temperatures between 5 K and 300 K in magnetic fields up to 9 T using an Oxford – Instruments magnetometer.

3. Results

Example of the high-field magnetization data is given in Fig. 1 for a thermal treated sample with x = 20 mol%. Similar curves were obtained for all thermal untreated and treated samples.

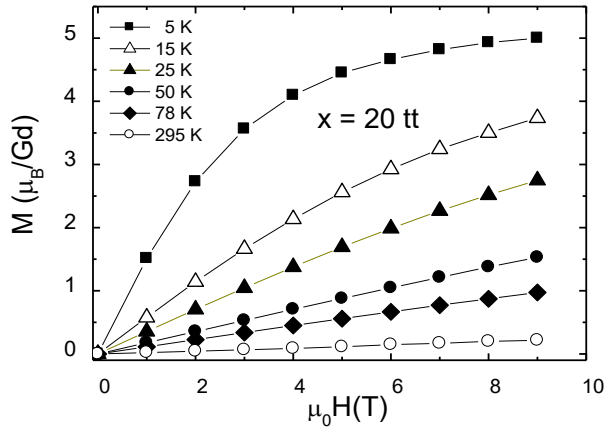

Fig. 1. Magnetization versus magnetic field for (100 – x) [4Bi2O3 · PbO] xGd2O3 thermal treated glass(tt) with x = 20 mol%.

The magnetization curves were fitted with the phenomenological equation proposed by Gaj et al [12]:

$$M=M_S B_{7/2}[g\mu_B SH/k_B T_{eff}] \quad (1)$$

where M_S is the phenomenological saturation parameter, $T_{eff} = T - T_0$ is an effective temperature and $B_{7/2}$ is the Brillouin function for the spin S = 7/2 given by

$$B_S(y) = (2S+1)/2S \; cth[(2S + 1)y/2S] - 1/2S cth\, y/2S, \text{ with } y = g\mu_B SH / k_B T_{eff} \quad (2)$$

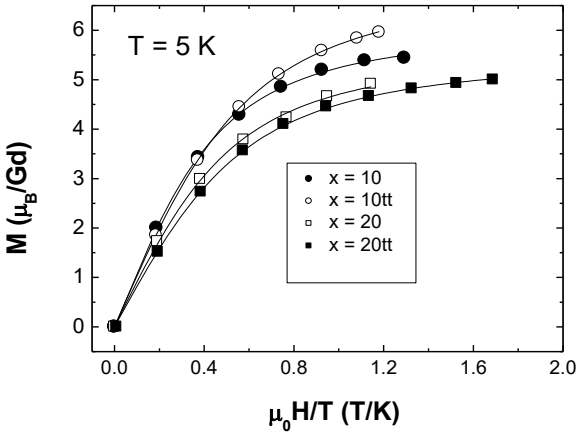

Fig. 2. Magnetization versus the variable μ0H/T at temperature T = 5 K for (100 – x)[4Bi2O3 · PbO] xGd2O3 thermal untreated and treated glasses with x = 10 and 20 mol%. The lines are the best fit to Eq. (1).

The experimental data at T = 5 K and T = 15 K (temperatures at which the saturation magnetization may be observed at relatively not so high magnetic fields), for both thermal untreated and treated samples with x = 10 and 20 mol%, are found to be in good agreement with equation (1), as one can see in Fig. 2 and Fig. 3, M_S and T_0 being treated as adjustable parameters.

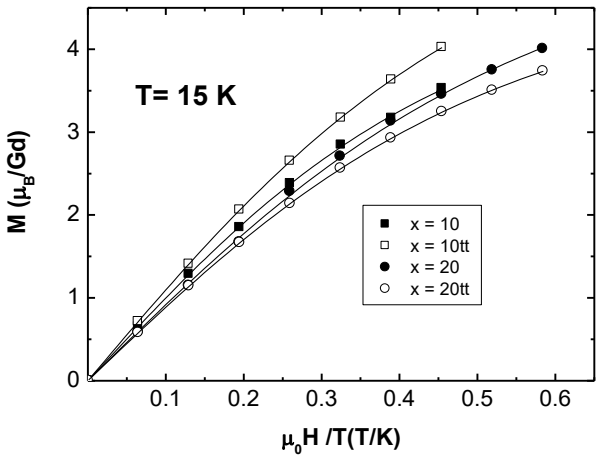

Fig. 3. Magnetization versus the variable μ0H/T at temperature T = 15 K for (100 – x)[4Bi2O3 · PbO] xGd2O3 thermal untreated and treated glasses with x = 10 and 20 mol%. The lines are the best fit to Eq. (1).

The effective temperature T_{eff} is higher than the actual temperature, i.e., $T_0 < 0$, and the parameter M_S turns out to be smaller than the full value for the Gd^{3+} spin, S = 7/2. The values for M_S and T_0 obtained from the fits to Eq. (1) for samples with x = 10 and 20 mol% are listed in Table 1. Also in this table are given the values for an effective Gd concentration $x_S = xM_S/M_0$, which contributes to the saturation magnetization, where $M_0 = 7\ \mu_B$/Gd is the theoretical saturation magnetization.

Table 1. Parameters obtained from fits to Eq. (1).

T(K)	x(mol%)	$M_S(\mu_B/Gd)$	T_0(K)	x_S(mol%)
5	10	5.90	- 0.3	8.43
5	10 tt	6.80	- 1.6	9.71
15	10	5.40	- 1.0	
15	10 tt	6.60	- 2.9	
5	20	5.45	- 1.0	15.57
5	20 tt	5.34	- 1.5	15.26
15	20	5.94	- 4.4	
15	20 tt	5.27	- 2.8	

In Fig. 4 are shown the room temperature derivative Gd^{3+} - EPR spectra of (100 – x)[$4Bi_2O_3$ · PbO] xGd_2O_3 thermal untreated glasses. These spectra are the superposition of the well known U type spectrum [3], containing prominent features with $g_{eff} \approx 5.9$, 2.85 and 2.0 and of a resonance line at $g_{eff} \approx 4.8$ with unusual intensity in X band for a vitreous sample. The U type Gd^{3+} - EPR spectrum is characteristic for Gd^{3+} ions in structurally

disordered systems. From this spectrum we have chosen the well-established isolated ion peak at $g_{eff} \approx 5.9$ and observed the variation of the width of this peak with increasing concentration of Gd ions. In Fig. 5 is shown the width of this peak as a function of Gd_2O_3 concentration in the investigated glasses. At low concentration the width increases almost linearly with concentration, then the curve presents a concavity to the x – axis with a maximum al about x = 10 mol% and finally the width decreases abruptly when approaching the concentration x = 20 mol%.

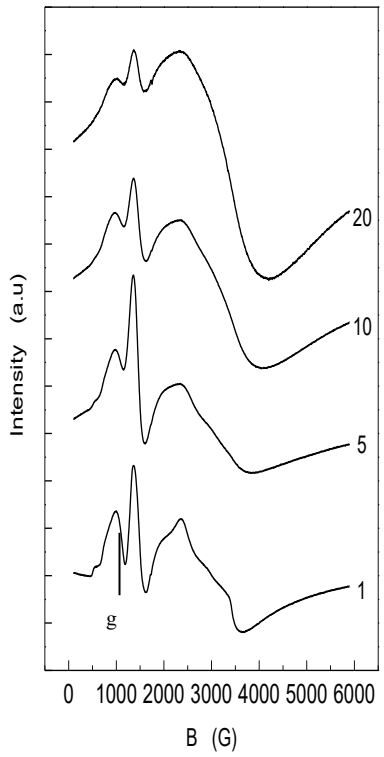

Fig. 4. Room temperature EPR derivative spectra for (100 – x)[4Bi2O3 · PbO] xGd2O3 thermal untreated glasses.

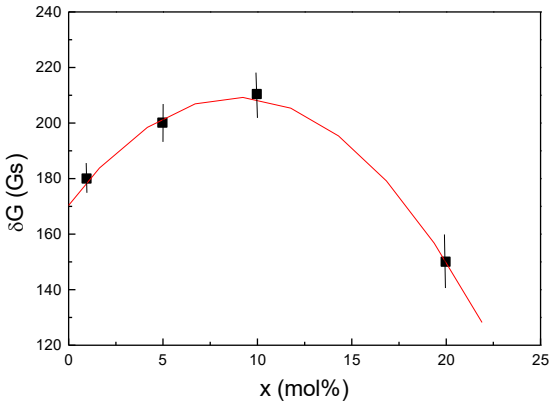

Fig. 5. The Gd^{3+} - EPR line width of the absorption at $g_{eff} \approx 5.9$ in (100 – x)[4Bi2O3 · PbO] xGd2O3 glasses against the Gd2O3 concentration. The continuos line is a guide for the eyes.

4. Discussion

The negative value of T_0 (see Table 1) indicates that the magnetic interactions between the Gd ions in (100 – x)[4Bi2O3 · PbO] xGd2O3 glasses are antiferromagnetic of short range as superexchange via oxygen ions. The antiferromagnetic temperatures T_0 increases with increasing Gd_2O_3 concentration but depend also on the thermal treatment of the glasses. This is expected since the average antiferromagnetic interaction between the magnetic ions increases as the average distance between them decreases.

The saturation magnetization parameters M_S for all investigated samples are smaller than the expected value for Gd^{3+} ions, namely 7 μ_B/Gd. The values of the magnetic moments, determined from the magnetization curves at T = 5 K, decrease with increasing Gd_2O_3 concentration, the lowering of the magnetic moments being more pronounced for the thermal treated samples. On the other hand, the magnetic moments, determined from the magnetization curves at T = 15 K, increase for untreated samples, but decreases for thermal treated samples. The smaller values of the saturation parameter in (100 – x)[4Bi2O3 · PbO] xGd2O3 and also the results obtained from magnetic susceptibility measurements [1] may be explained if one consider that the majority of Gd ions behave as free Gd ions, while the others as antiferromagnetically coupled pairs Gd^{3+} - O - Gd^{3+} in the form of magnetic clusters whose sizes depend on the Gd_2O_3 concentration in the glasses. The fraction of magnetically active ions x_S/x decreases with increasing the Gd_2O_3 concentration for both untreated and thermal treated glasses. By thermal treatment takes place a structural relaxation of the glasses, more Gd ions behave as free Gd^{3+}, that could explain the difference in the magnetic moments for untreated and thermal treated samples at relatively low Gd_2O_3 concentration. At high Gd_2O_3 concentration, bigger than 10mol%, the co-operative antiferromagnetic interactions are relatively strong, so that the thermal treatment has a small influence on the number of coupled pairs Gd^{3+} - O - Gd^{3+}.

The presence of the magnetic clusters in (100 – x)[4Bi2O3 · PbO] xGd2O3 glasses is also confirmed by the dependence of the Gd^{3+}- EPR line width on the Gd_2O_3 concentration (Fig. 5). The broadening of the analysed peak in the low-concentration region is due to the dipole interaction between individual ions. With increasing Gd_2O_3 concentration the exchange coupling between the ions inside the clusters becomes competitive with the dipolar broadening, but of opposite sign, what explains the abruptly decrease of the line width at higher Gd_2O_3 concentration approaching 20 mol%.

Similar results obtained from magnetic and EPR measurements have been reported on various classes of glasses containing TE or RE elements [1-4]. Furthermore, in a series of sodium-aluminoborosilicate glasses with Gd_2O_3, the Raman bands near 300 and 910 cm^{-1} indicated formation of Gd -O –Gd clusters at high Gd_2O_3 concentrations [13]. The co-operative nature of clusters development at high Gd_2O_3 concentration, based on the

strong magnetic interactions between the Gd ions, agrees with the molecular simulations of a model liquid showing the glass transition when it becomes very dense, and/or very cold. As predicted by simulations of several model glass-formers, a wide range of cluster sizes in colloids was observed, and the typical size grew rapidly as glass transition approached [11].

5. Conclusions

Both EPR and magnetic measurements in high magnetic field confirmed the development of magnetic clusters in $(100 - x)[4Bi_2O_3 \cdot PbO]\ xGd_2O_3$ glasses at high Gd_2O_3 concentration. These results are in good agreement with other findings on glasses containing TM or RE ions and with the molecular simulations of a model liquid showing the glass transition.

It seems that the magnetic clusters development in glasses containing TM or RE ions at high concentration is a general property, which is based on the local structure leading to the existence of M-O-M (M=TM or RE) dimmers and on the co-operative nature of the strong magnetic interactions between the magnetic ions.

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