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EPR and magnetic behaviour of some borate glasses containing Dy_2O_3 ♣

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Glasses of the $x Dy_2O_3(1-x)Na_2B_4O_7$ system with $0.01 \leqslant x \leqslant 0.15$ were studied using density and magnetic susceptibility and electron paramagnetic resonance measurements. The density data show that the dysprosium ions play a network modifier role in the studied glasses. Magnetic susceptibility data show a mictomagnetic type behavior due to the presence of both isolated and exchange coupled Dy^{3+} ions. The electron paramagnetic resonance (EPR) spectra consist of single broad absorption lines located at g ≈ 2.15.

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1. Introduction

Glasses and crystals containing rare-earth ions are the subject of a great deal of interest due to their important optical, mechanical and magnetic properties (Erbium [1], Gd in Bi_2O_3 – GeO_2[2-4], Sc, Lu in calcium borate glasses [5], Pr in As_2S_3 [6], Eu and Sn in silica glasses [7] . Recently, magnetic behavior of some borate glasses containing gadolinium ions was reported [1-4]. Electron paramagnetic resonance (EPR) and magnetic susceptibility investigations of these glasses shown that their magnetic behavior is due to the Gd^{3+} ions. EPR data evidentiated three types of micro vicinities available for the Gd^{3+} ions. The magnetic ions were found to be randomly distributed in the glass matrix having no preference for a certain type of micro vicinity.

In order to extend the available information on magnetic behavior of glasses containing rare-earth ions we investigated the $(1-x)Na_2B_4O_7$ x Dy_2O_3 vitreous system using magnetic susceptibility and EPR measurements. Our aim was to characterize the magnetic behavior of the studied glasses witch respect the distribution of dysprosium ions in the host glass.

2. Experimental

Samples of the $(1-x)Na_2B_4O_7$ x Dy_2O_3 glass system (noted x NBD) with x = 0,01; 0,02;0,03; 0,05; 0,07 and 0,1 were preparated starting from reagent grade Dy_2O_3 and $Na_2B_4O_7$. First the base borate glass of $Na_2B_4O_7$ composition was obtained by melting dehydrated borax at 1000°C for 1 hour in alumina crucibles. The melt was quenched by pouring on stainless steel block.

This base glass were mixed and milled in an agate ball mill1 hour. Than, the mixtures were melted at 1100 °C for 1 hour. The melts were quenched by pouring on stainless steel block. Magnetic susceptibility measurements were performed on a Faraday type balance in the temperature range from 77 to 300 K. EPR measurements were performed on a standard JEOL equipment in the X-band, at room temperature. X-ray diffraction investigation indicated that all the samples were amorphous.

3. Results and discussions

The EPR spectra of the xNBD glasses, with $0.01 \leq x \leq 0.10$consist of a single broad absorption line located at g ≈ 2,15. A tipical EPR spectrum characteristic of the studied xNBD glasses is presented in figure 1. The spectra due to Dy^{3+} ions located at sites with low symmetry[11]. In principle, the sites occupied by the Dy^{3+} ions in the host glass matrix may be of network forming or of network modifying type.

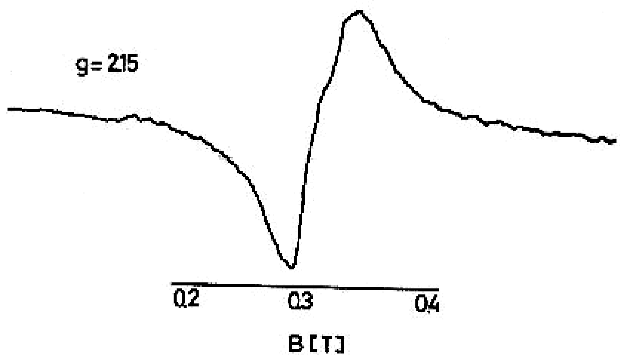

Fig.1. The EPR spectrum for the sample with x=0.02.

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Simple ionic radius consideration suggests that dysprosium ions cannot substitute the much smaller boron ions and thus, only the network modifier sites is acceptable. The large values for the EPR line width(see fig. 1.) is due to the fluctuations of local environment of Dy^{3+} ions.

The $Na_2B_4O_7$ host glass is well studied heterogeneous glass consisting of a sodium-rich and a boron-rich vitreous phase[5]. Its heterogeneous nature offers the possibility of more than one type of micro vicinities available to the Dy^{3+} ions. However, the EPR data suggest that the Dy^{3+} ions are located at sites having only one type of micro vicinity available in the host glass. This may suggest that the Dy^{3+} ions exhibit a tendency toward a preferred type of micro vicinity available in the host glass. This behavior is quite different from that of Gd^{3+} ions, that were found to occupy three different sites in the $Na_2B_4O_7$ host glass.

The temperature dependence of inverse magnetic susceptibility of xNBD glasses, shown in Fig. 2, displays a Curie type magnetic behavior. The composition dependence of the Curie constants C is presented in Fig. 3. Using the C values, derived from the experimental data, we calculated the effective magnetic moment per dysprosium ions (μ_{eff}). The obtained μ_{eff} values, shown in Fig. 3, range from 10.08 μ_B to 10.27 μ_B and are not composition dependent. The linear dependence of the Curie constant on the dysprosium oxide content of xNBD glasses suggests that the magnetic Dy^{3+} ions act isolated species and are randomly distributed in the host glass matrix. This is also supported by the μ_{eff} values that are close to the free dysprosium ion magnetic moment, 10.2 μ_B [13]. This behavior is due to the 4f magnetic electrons that are well screened by the outer 5s and 5p electrons. The magnetic data obtained for the xNBD glasses re in agreement with those recently reported for the $Re_xY_{2-x}O_3$ crystalline system with low re content, where Re = Dy and Ho [14,15].

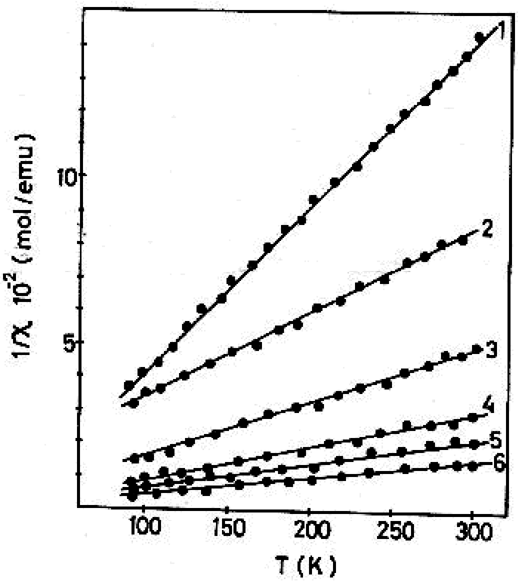

Fig. 2. The thermal variation of the reciprocal magnetic susceptibility of glasses with x=0,01; 0,03; 0,05; 0,07 and 0,10.

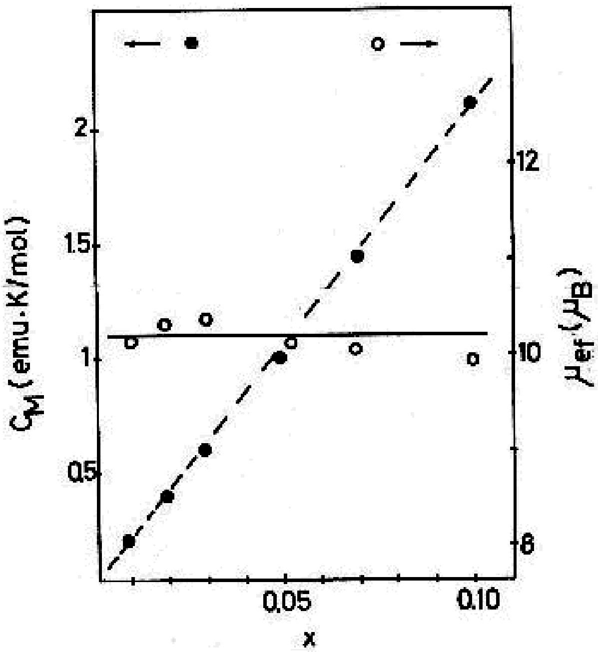

Fig. 3. The composition dependence of Curie constant C and the effective magnetic moment μ_{eff} for the xNBD glasses.

4. Conclusion

EPR data for $(1-x)Na_2B_4O_7$. xDy_2O_3 glasses evidentiate the presence of Dy^{3+} ions localized at sites of one type of micro vicinity in the host glass. Magnetic susceptibility data evidentiate a Curie type paramagnetic behavior. The magnetic parameters calculated from the experimental data, namely C and μ_{eff}, suggest that the magnetic Dy^{3+} ions appear in the host glass matrix as isolated species randomly distributed in the host glass matrix.

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