MAGNETIC SUSCEPTIBILITY STUDY OF B_2O_3BaO GLASS MATRIX DOPPED WITH IRON IONS

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Abstract

EPR and magnetic susceptibility measurements have been performed on $xFe_2O_3(1-x)[3B_2O_3BaO]$ glasses with $0 < x \leq 50$ mol%. The influence of a gradual increase in Fe_2O_3 content on the glass matrix (B_2O_3BaO) structure and magnetic interactions involved iron ions have been discussed. By EPR data, the Fe^{3+} ions in sites of distorted octahedral symmetry were evidenced. EPR and magnetic susceptibility results indicate that in studied glasses the iron ions participate at the dipolar or/and superexchange magnetic interactions. From magnetic data it was evidenced that the iron ions are in Fe^{3+} and Fe^{2+} valence state and are antiferomagnetic coupled, these are depending on the iron content of the glasses.

Key words: Barium-borate glasses, manganese ions, EPR and magnetic susceptibility

INTRODUCTION

Glasses are noncrystaline solids materials having a disorder structureand a local order. Glasses present a large variety of properties due to the variety of the compounds. Because of these the glasses have wide technological applications.

The study of the properties of borate glasses with iron ions represented an attraction point for the researchers due to the possibility of those existing in the valence states Fe^{3+} and Fe^{2+}

B_2O_3 is one of the most important former oxides glasses and has been incorporated into various kinds of glass system in order to obtain the desired physical and chemical properties for both scientific and industrial applications. The properties of the glasses are due to the fact that the boron atoms can assume trigonal and tetrahedral coordination and also to the way that borate buildings units can be link together.

Magnetic susceptibility measurements revealed as very useful to determine the structural distribution in the glass matrix, the valence states of transition metal ions and the type of interactions involving them over various composition range.

An antiferromagnetic coupling between iron ions was reported in borate (Burzo, Ardelean, 1970, Ardelean et al., 1989, 1999), phosphate (Wilson et. al., 1975, Kumar, Chen, 1994), tellurite (Ardelean, et al., 1979, 1997, 1998) and lead-bismuthate (Ardelean et. al. 1994) oxide glasses. The concentration range over which antiferromagnetic interactions occur depends on the glass matrix structure, the conditions of sample preparation and the Fe^{3+}/Fe^{2+} ratio (Burzo et al., 1980, Kumar et. al., 1992)

MATERIALS AND METHODS

Glasses of the system $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot BaO]$ were prepared using reagent grade purity H_3BO_3, $BaCO_3$ and Fe_2O_3 in suitable proportion over the range $0 \leq x \leq 50$ mol %. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 1250°C, in an electrical furnace. After 30 minutes, the molten material was quenched at room temperature by pouring onto a stainless – steel plate. The samples were analyzed by means of X-ray diffraction and did not shown any crystalline phase.

The magnetic susceptibility measurements were performed using a Faraday-type balance, in the 80-300 K temperature range.

RESULTS AND DISCUSSIONS

The temperature dependence of the reciprocal magnetic susceptibility shows a Curie-type behaviour for glasses with $x \leq 10$ mol % and Curie-Weiss type one, with negative paramagnetic Curie temperature (θ_p) for glasses with a higher Fe_2O_3 content (Figs. 1 and 2). This suggests that for $x \leq 10$ mol %. are predominant the isolated iron ions and those which participate to the dipole-dipole interactions. For higher concentrations of Fe_2O_3 the high temperature susceptibility data indicate that the iron ions in the glasses experience negative exchange interactions and are coupled antiferromagnetically. In this case, the antiferromagnetic order takes place only at short-range and the magnetic behaviour of the glasses can be described by the so–called mictomagnetic type order (Beck, 1971)

The absolute magnitude of the values of θ_p increased for $x > 10$ mol % (Table 1). In general the exchange increases as the concentration of the magnetic ions is increased in the glass (Friebele et al., 1971) As a result the magnitude of the paramagnetic Curie temperature increases

To determine accurately the values of the Curie constants, corrections due to the diamagnetism of the glass matrix and Fe_2O_3 were taken into account.

The composition dependence of the molar Curie constant (C_M) is presented in Table 1. For the glasses with x > 10 mol %, the experimental values obtained for molar Curie constant and consequently for effective magnetic moments are lower than those which correspond to Fe_2O_3 content, considering that all iron ions are in Fe^{3+} valence state. In this way we consider that in these glasses are present both, Fe^{3+} and Fe^{2+} ions. In this case, having in view the atomic magnetic moment values $\mu_{Fe^{3+}} = 5.92\,\mu_B$ and $\mu_{Fe^{2+}} = 4.90\,\mu_B$ (Mulay, 1973) we can estimate in first approximation the molar fraction of these ions in the investigated glasses using the relations:

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

and

$$x = x_1 + x_2 ,$$

where $\mu_{eff} = 2.827\,[C_M/2x]^{1/2}$

the experimental effective magnetic moment, x_1 and x_2 the molar fraction of iron in Fe^{3+} and Fe^{2+} valence states. The results are presented in Table 1.

Table 1.

The molar Curie constant (C_M), paramagnetic Curie temperature (θ_p), Fe^{3+} and Fe^{2+} ions concentration

x [mol %]	C_M [emu/mol]	μ_{eff} [μ_B]	θ_p [K]	x_1 [mol % $Fe_2^{3+}O_3$]	x_1 [mol % $Fe_2^{2+}O_3$]
1	0.08763	5.92	0	1	0
3	0.26185	5.91	0	3	0
5	0.43757	5.92	0	5	0
10	0.87677	5.93	0	10	0
20	1.63832	5.73	-18,5	16	4
35	2.70194	5.56	-28,5	22	13
50	3.66798	5.42	-41,0	24	26

According to the obtained data (Table 1) the glasses with x ≤ 10 mol % contain only the Fe^{3+} species while for glasses containing x > 10 mol % the Fe^{3+} and Fe^{2+} ionic species coexist. It was observed the progressive increasing for both Fe^{3+} and Fe^{2+} ions concentration with the increasing of the Fe_2O_3 content, the proportions of Fe^{2+} ions being prevalent for x > 35 mol %, as can be seen in fig.1.

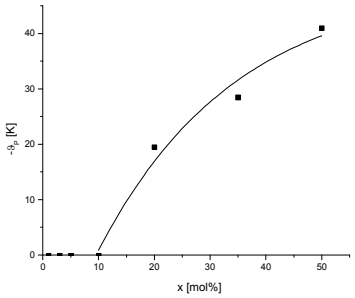

Fig.1. The dependence of paramagnetic Curie temperature (θ_p) by Fe^{3+} and Fe^{2+} ions concentration

CONCLUSIONS

Glasses of the system $xFe_2O_3 \cdot (100-x)[3B_2O_3 \cdot BaO]$ were obtained over the $0 \leq x \leq 50$ mol % concentration range.

From magnetic susceptibility data we have established that the iron ions are isolated or participate to the dipole-dipole interactions for $x \leq 10$ mol % and to the antiferromagnetic interactions for higher concentrations.

Fe^{2+} ionic species were detected in glasses with $x > 10$ mol %, together with the Fe^{3+} ions.

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