REPORT ON EVALUATION OF PARAMAGNETIC CHARACTERISTICS OF MN^{2+} IONS IN GLASSES CONTAINING ZNO AS A MODIFIER

Abstract

Zeeman splitting of electron energy spin states of Mn^{2+} ion (hyperfine splitting) has been discussed. Paramagnetic nature of the Mn^{2+} ions in various ZnO- mixed host glasses has been reported. Various magnetic properties viz., magnetic moment (μ), volume paramagnetic susceptibility (χ_v), mass paramagnetic susceptibility (χ_g), molar paramagnetic susceptibility (χ_m) and Curie constant (C) of the glass samples have been determined with the help of the experimental g-value reported in the literature. It has been noticed that the magnetic properties of manganese ions depend on chemical composition of the glasses. The Mn^{2+} ions-doped oxide glasses containing heavy metal oxides viz., PbO, Sb_2O_3 and SrO have exhibited the significant magnetic behavior; whereas, oxy-fluoride glasses (CaF_2 and LiF mixed glasses) have shown less paramagnetic nature relatively.

Keywords: Glasses; Manganese ions; EPR spectroscopy, Magnetic moment, Magnetic susceptibility.

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I. INTRODUCTION

Glasses are transparent non-crystalline solids in the wide range of UV-Visible-NIR regions; and they are also good electric insulators. The glasses are more resistant to corrosion than polycrystalline metals [1, 2]. Recently, there is a huge demand for a kind of amorphous materials known as glass coatings and glass hosts. The glass coatings are used to enhance oxidation resistance of various metal substrates effectively. Often certain metal substrates like ferrites, magnetic metal-alloy, carbon-steel, super-alloy, titanium-alloy and stainless-steel substrates have been coated with the amorphous materials for manufacturing applications [3]. The paramagnetic ions- doped glass hosts are also important for corrosion free technologies and they are familiar as glass magnets and soft-core magnets [4].

Zinc oxide (ZnO) is well known as a very wide bandgap (≈2.5-3.3 eV) semiconductor [5, 6]. ZnO is a fabulous chemical compound for its gifted characteristics such as good biocompatibility, good transparency in UV-Visible region, prominent electron mobility and robust quantum efficiency of luminescence [5, 6]. ZnO mixed- oxide glasses have been examined for many years because of their exceptional technical aspects that include high refractive index, low viscosity, high density, high hardness and good chemical stability. ZnO plays dual role as a former as well as a modifier in the glass structure. ZnO is an intermediate glass former in terms of tetrahedral ZnO_4 units; whereas it modifies the glass network by means of octahedral ZnO_6 units [7].

Magnetic properties of ZnO mixed- glasses incorporated with small content of various magnetic ions have been explored in literature [8-14]. Manganese ions are interesting transition metal ions, which affect the magnetic characteristics of the glasses. MnO doped-glasses contain two paramagnetic ions Mn^{2+} and Mn^{3+} ions in the glass matrix. Both divalent (Mn^{2+}) and trivalent (Mn^{3+}) manganese ions have been investigated as paramagnetic in nature. Mn^{2+} ions are active centres for luminescent glass host materials. And, MnO can form the glass network as MnO_4 tetrahedral units [13, 14].

Generally, the paramagnetic Mn^{2+} ions exhibit electron spin magnetic resonance lines confining to g≈2.0, 3.3 and 4.3 in the EPR spectrum of the glass hosts. Thus, these glasses may act as magnetic materials used in magnetic detectors, microphones, flux meters, damping devices, magnetic separators etc [13-22]. Thus, the study of magnetic nature of manganese ions in ZnO mixed- glasses is quite interesting. In this chapter, we would like to showcase the procedure to evaluate various paramagnetic characteristics of Mn^{2+} ions in different ZnO modifier- glass hosts, which is helpful to the researchers as well as academicians in this field. Also, this chapter will be useful as a ready reference to under-graduate students, post-graduate students, and research scholars to understand the magnetic behavior of manganese ions in various zinc oxide mixed glasses.

II. METHODOLOGY

The electron configuration of divalent manganese ion (Mn^{2+} ion) can be expressed as $[Ar]3d^5$ with electron spin (S_Z=±½), nuclear spin (I_Z=5/2) and angular momentum (L=0). The hyperfine splitting of Mn^{2+} ions produces the characteristic electron spin paramagnetic resonance in presence of applied weak magnetic field. Eigen energy state of each $3d^5$-electron spin states (S_Z=±½) will be splitting into six substrates attributed to the hyperfine interactions among electron spin levels (S_Z) and nuclear spin (I_Z) revealing six transitions as shown in Figure 1. Thus, the glasses containing Mn^{2+} ions may act as magnetic sensors in science and technological applications [13-22].

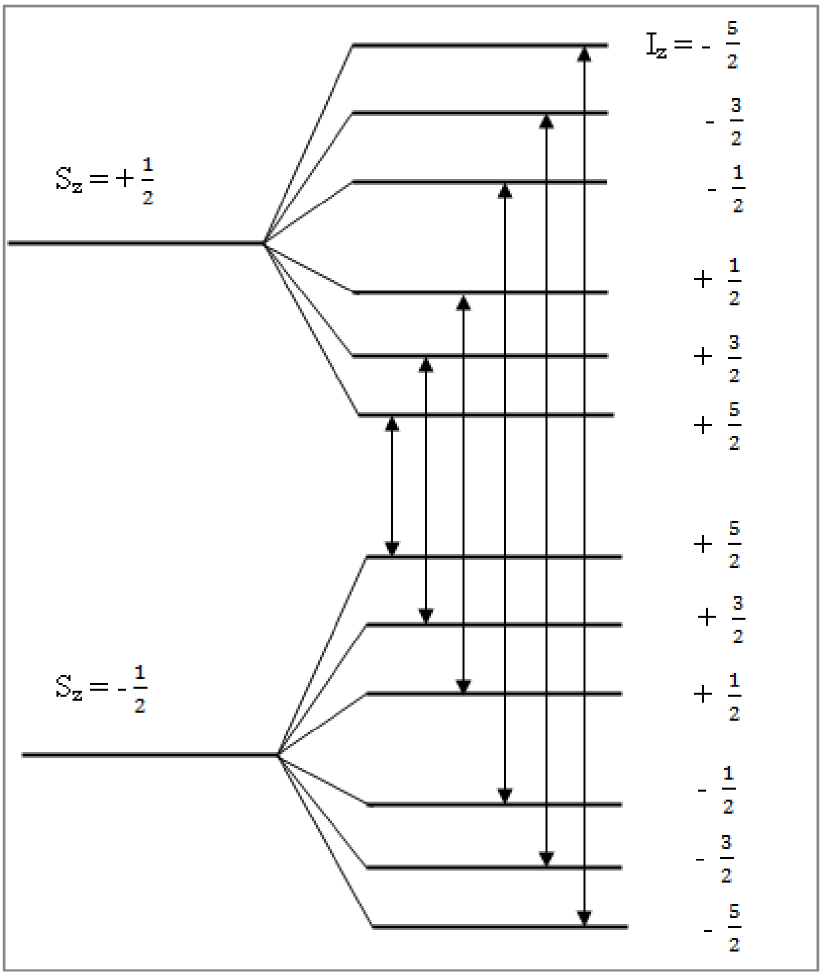

Figure 1: Zeeman splitting of electron energy spin states of Mn^{2+} ion (hyperfine splitting).

A typical EPR spectrum of Mn^{2+} ions in amorphous medium (glass host) is shown in Figure 2. The resonance signals are obtained at g≈2.0 and 4.3 by means of electronic transition between energy levels of the Kramer's doublets |±3/2> and |±½> respectively [14]. The signal at low field (g≈4.3) is attributed to the tetrahedral (rhombic) surroundings of Mn^{2+} ions in high crystal field. On the other hand, the second signal at g≈2.0 is attributed to Mn^{2+} ions in an octahedral symmetry. Usually, one can clearly realize a sextet of resonance lines, which are well resolved by hyperfine interactions at high field among the spin states of $3d^5$-electron (S=±½) and the ^{55}Mn nucleus (I=5/2) [23].

The magnetic properties of Mn^{2+} ions- doped glasses (such as P_2O_5, B_2O_3, and SiO_2 glasses) containing intermediate glass formers/modifiers (like ZnO, SrO, PbO, Sb_2O_3 etc.), and ZnO crystals have been reported in literature [14-22]. All these glass samples were synthesized by means of melt-quenching method [1]. Here, ZnO is the common chemical component in the composition of the glasses as shown in Table 1. Landé g- factor (g) of the

Mn^{2+} ions in the glasses is reported by using the X- band (8-10 GHz) EPR spectra. The magnetic properties are evaluated by the well-known relations in the literature [23, 24].

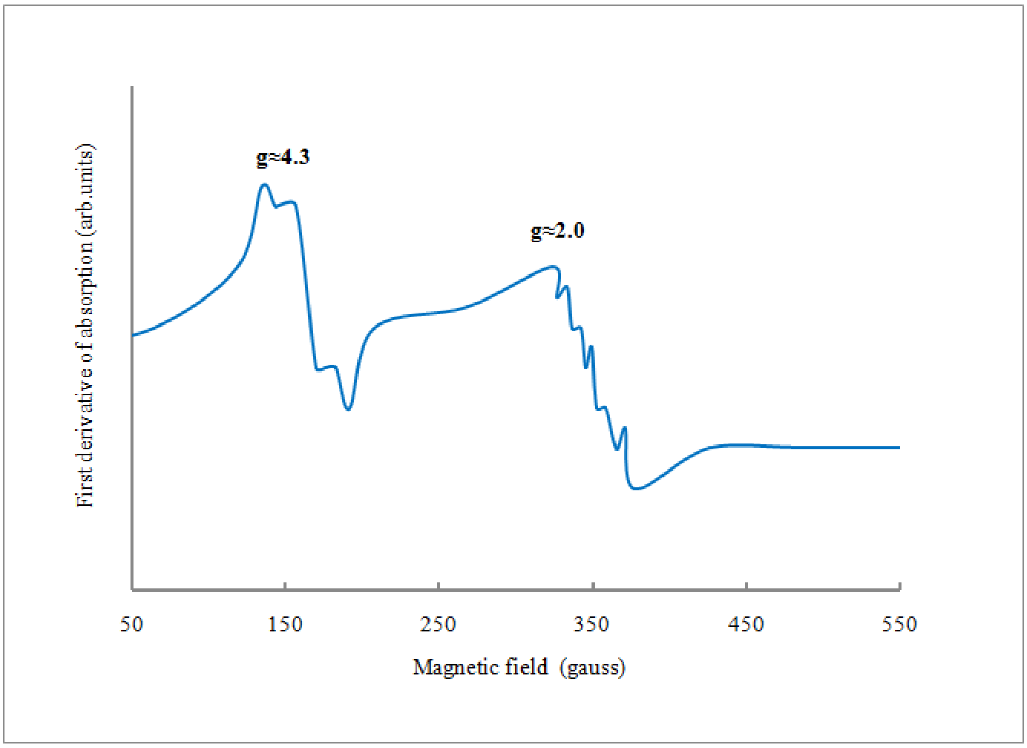

Figure 2: Typical EPR spectrum of Mn^{2+} ion in amorphous medium

The magnetic moment (μ) of the Mn^{2+} ions is calculated with the g-value obtained from EPR spectra by using the relation:

$$\mu = g\sqrt{S(S+1)} \text{ -------- (1)}$$

where, S is the spin of Mn^{2+} ions (S=5/2) in glass system.

But, theoretically the magnetic moment is given by the relation:

$$\mu = \sqrt{[n(n+2)} \approx 5.9161 \text{ B.M. -------- (2)}$$

where, n is number of unpaired electrons of Mn^{2+} ions (here n= 5, high spin is assumed).

The volume paramagnetic susceptibility (χ_v) is evaluated by using the relation:

$$\chi_v = \frac{\mu^2}{7.997\,T} \text{ -------- (3)}$$

where, T is the temperature of the sample in kelvin (the room temperature ≈ 303 kelvin).

The mass paramagnetic susceptibility (χ_g) is evaluated by using the relation:

$$\chi_g = \frac{\chi_v}{\rho} \text{ -------- (4)}$$

where, ρ is density of glass sample.

The molar paramagnetic susceptibility (χ_m) is evaluated by using the relation:

$$\chi_m = \frac{M\chi_g}{Z} \text{ -------- (5)}$$

where, M is molecular weight of the sample and Z is number of moles of Mn^{2+} ions in the sample.

The inverse relationship of the paramagnetic susceptibility (χ_v) and temperature (T) of a paramagnetic material is given by the Curie's law:

$$\chi_v = \frac{C}{T} \text{ -------- (6)}$$

where C is the Curie constant in kelvin.

Table 1: Magnetic characteristics of Mn^{2+} ions in various ZnO- modifier glasses

S. No.	Glass composition	Ref.	g-factor	μ B.M.	χ_v ($x10^{-3}$) emu-cm^{-3}	χ_g ($x10^{-3}$) emu-g^{-1}	χ_m ($x10^{-3}$) emu-mol^{-1}	C (kelvin)
1	$19.4ZnO–40Sb_2O_3–40B_2O_3:0.6MnO$	[14]	2.02	5.9752	14.7347	3.9345	10.541	4.4646
2	$60ZnO–39P_2O_5:1MnO$	[15]	2.01	5.9457	14.5892	3.3524	1.8796	4.4205
3	$10SrO–29.1ZnO–60B_2O_3:0.9MnO$	[16]	2.023	5.9841	14.7785	3.6384	3.0910	4.4779
4	$40PbO–10ZnO–49B_2O_3:1MnO$	[17]	2.015	5.9605	14.6618	2.9620	3.9171	4.4425
5	$Zn_3(PO_4)_2:MnO$	[18]	2	5.9161	14.4446	4.0257	7.7079	4.3766
6	$24.5CaF_2–10Y_2O_3–5ZnO–20B_2O_3–40SiO_2:0.5MnO$	[19]	2.0026	5.9238	14.4819	4.9469	8.3196	4.3880
7	$24.50LiF–10Sb_2O_3–05ZnO–20B_2O_3–40SiO_2:0.5MnO$	[20]	2.0049	5.9306	14.5152	5.1518	8.0254	4.3981
8	$40P_2O_5–55ZnO:5MnO$	[21]	2.025	5.9900	14.8077	3.4357	0.7221	4.4867
9	99ZnO:1MnO nanocrystals	[22]	1.957	5.7889	13.8299	2.4665	6.7246	4.1905

III. RESULTS & DISCUSSION

When MnO is added into the glass composition, some amount of Mn^{2+} ions may be transformed as Mn^{3+} ions during the synthesis of the glasses as per the following redox equations [25]:

$Mn^{2+} \leftrightarrow Mn^{3+} + e^{-}$ -------- (7)

$Mn^{2+} + ½O_2 \leftrightarrow Mn^{3+} + O_2^{-}$ -------- (8)

Thus, the Mn^{3+} ions coexist with Mn^{2+} ions in the glasses. The model structure of B_2O_3-ZnO-Sb_2O_3: MnO glass system is built using free molecular editor software, Avogadro [26] and shown in Figure 3.

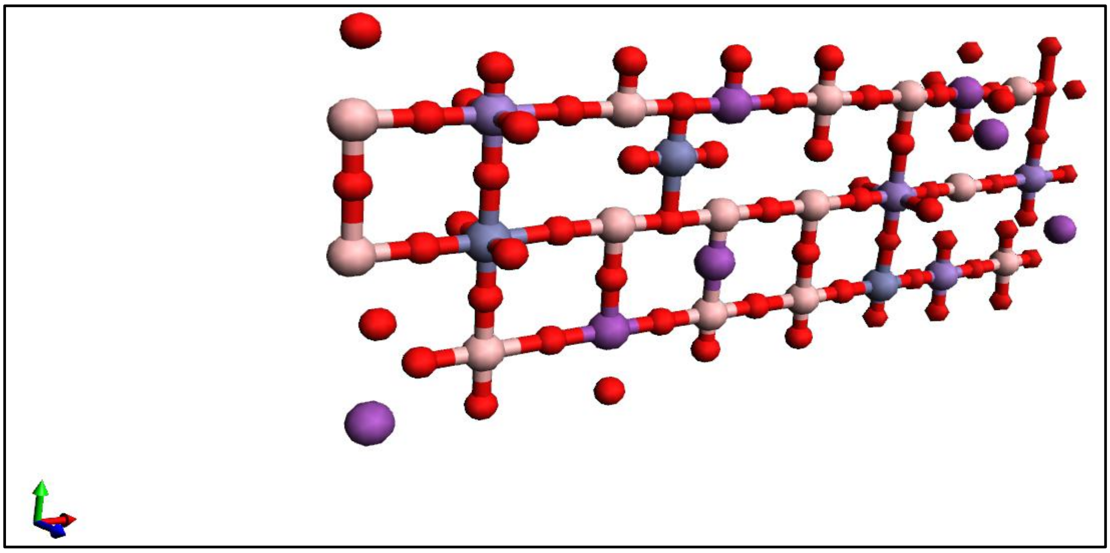

Figure 3: Schematic of B_2O_3–ZnO–Bi_2O_3: MnO glass structure
(Color code for representation of atoms is as follows: Red- Oxygen, Pink- Boron, Violet- Bismuth, Blue- Zinc, Bluish and violet- Manganese**)**.

Figure 3 shows the co-occurrence of manganese ions in two ionic states (Mn^{2+} and Mn^{3+}) as per the redox equations (7) and (8). The manganese ions subsist mainly in two valence states: First one is Mn^{2+} with both tetrahedral MnO_4 and octahedral MnO_6 environment; whereas second one is Mn^{3+} state with octahedral MnO_6 coordination. However, here we have considered the viability of the Mn^{2+} ions corresponding to the g-factor≈2 in the EPR spectra [14, 25]. With the help of the experimental g-value reported in the literature, we have evaluated magnetic moment (μ) and hence, volume paramagnetic susceptibility (χ_v), mass paramagnetic susceptibility (χ_g), molar paramagnetic susceptibility (χ_m) and Curie constant (C) of the same samples and showcased in Table 1. The magnetic moment (μ) determined by the equation (1) in terms of the obtained g-factor (from EPR spectra) are slightly greater than that of the theoretical value evaluated by using equation (2). This shows that there is a clear effect of local structure of the host glasses on the magnetic nature of the Mn^{2+} ions.

With the help of the values of susceptibility (χ_v) and Curie constant (C), we can understand the thermal motion of the Mn^{2+} ions make them move in random directions and oppose the alignment of the magnetic dipoles of the paramagnetic Mn^{2+} ions under the external magnetic field. Hence the observed paramagnetic susceptibility (χ_m) of the samples changes with change of temperature (T) due the impact of thermal motion of Mn^{2+} ions [23, 24]. It has been noticed that the glass composition 40P_2O_5-55ZnO: 5MnO has shown highest values of μ, χ_v and C. This may be attributed to the high concentration of MnO and moderate mixture of ZnO into the glass composition [21]. On the other hand, 60ZnO-39P_2O_5:1MnO glass has shown the poor values of μ, χ_v and C. This may be due to the rich addition of ZnO and small concentration of MnO into the glass composition [15].

The glasses containing PbO, Sb_2O_3 and SrO have exhibited the significant values of the magnetic parameters of Mn^{2+} ions [14, 16, 17]; while CaF_2 and LiF mixed glasses have displayed slightly less values relatively [19, 20]. We could understand that the heavy metal oxide glasses (like glasses containing PbO, Sb_2O_3 and SrO) doped with Mn^{2+} ions yield the paramagnetic nature, because of their high polarization and refractive index. But, the fluoride glasses have limitation because of their poor glass forming ability and low softening temperature [19, 20]. It is also observed that the ZnO-MnO nanocrystals have revealed less magnetic moment (μ) and susceptibility (χ) than that of the glasses comparatively [22]. Thus, the magnetic glasses can determine potential applications over the magnetic nano-crystals [27, 28]. Thus, these magnetic glasses will have the potential applications in magnetometers, magnetic sensors, and magneto-optical devices [29-31].

IV. CONCLUSION

Zeeman splitting (hyperfine splitting) of electron spin states of Mn^{2+} ion has been discussed. We have reported the magnetic characteristics of Mn^{2+} ions in various glasses containing ZnO as a modifier oxide. Co-occurrence of Mn^{2+} and Mn^{3+} ions in the glass host has been illustrated by redox equations. Free molecular editor software, Avogadro has been employed to illustrate the structure of glass network by MnO_4 and MnO_6 units. It is observed that the glasses containing heavy metal oxides have significant magnetic moment (μ) and susceptibility (χ_v) relatively.

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