Report on evaluation of paramagnetic characteristics of Mn2+ ions in glasses containing ZnO as a modifier

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ABSTRACT

Zeeman splitting of electron energy spin states of Mn2+ ion (hyperfine splitting) has been discussed. Paramagnetic nature of the Mn2+ ions in various ZnO- mixed host glasses has been reported. Various magnetic properties viz., magnetic moment (μ), volume paramagnetic susceptibility (χv), mass paramagnetic susceptibility (χg), molar paramagnetic susceptibility (χm) 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 Mn2+ ions- doped oxide glasses containing heavy metal oxides viz., PbO, Sb2O3 and SrO have exhibited the significant magnetic behavior; whereas, oxy-fluoride glasses (CaF2 and LiF mixed glasses) have shown less paramagnetic nature relatively.

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

#  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 ZnO4 units; whereas it modifies the glass network by means of octahedral ZnO6 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 Mn2+ and Mn3+ ions in the glass matrix. Both divalent (Mn2+) and trivalent (Mn3+) manganese ions have been investigated as paramagnetic in nature. Mn2+ ions are active centres for luminescent glass host materials. And, MnO can form the glass network as MnO4 tetrahedral units [13, 14].

 Generally, the paramagnetic Mn2+ 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 Mn2+ 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.

# METHODOLOGY

 The electron configuration of divalent manganese ion (Mn2+ ion) can be expressed as [Ar]3d5 with electron spin (SZ=±½), nuclear spin (IZ=5/2) and angular momentum (L=0). The hyperfine splitting of Mn2+ ions produces the characteristic electron spin paramagnetic resonance in presence of applied weak magnetic field. Eigen energy state of each 3d5- electron spin states (SZ=±½) will be splitting into six substrates attributed to the hyperfine interactions among electron spin levels (SZ) and nuclear spin (IZ) revealing six transitions as shown in Figure 1. Thus, the glasses containing Mn2+ ions may act as magnetic sensors in science and technological applications [13-22].

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**Figure: 1 Zeeman splitting of electron energy spin states of Mn2+ ion (hyperfine splitting).**

A typical EPR spectrum of Mn2+ 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 Mn2+ ions in high crystal field. On the other hand, the second signal at g≈2.0 is attributed to Mn2+ 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 3d5- electron (S=±½) and the 55Mn nucleus (I=5/2) [23].

The magnetic properties of Mn2+ ions- doped glasses (such as P2O5, B2O3, and SiO2 glasses) containing intermediate glass formers/modifiers (like ZnO, SrO, PbO, Sb2O3 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 Mn2+ 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 Mn2+ ion in amorphous medium**

The magnetic moment (µ) of the Mn2+ ions is calculated with the g-value obtained from EPR spectra by using the relation:

$μ=g\sqrt{S(S+1)} $-------- (1)

where, S is the spin of Mn2+ ions (S=5/2) in glass system.

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

$μ=\sqrt{[n\left(n+2\right) }$≈ 5.9161 B.M. -------- (2)

where, n is number of unpaired electrons of Mn2+ ions (here n= 5, high spin is assumed).

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

 $χ\_{v}=\frac{μ^{2}}{7.997 T}$ -------- (3)

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

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

$χ\_{g}=\frac{χ\_{v}}{ρ}$ -------- (4)

where, ρ is density of glass sample.

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

$χ\_{m}=\frac{Mχ\_{g}}{Z}$ -------- (5)

where, M is molecular weight of the sample and Z is number of moles of Mn2+ ions in the sample.

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

$χ\_{v}=\frac{c}{T}$ -------- (6)

where C is the Curie constant in kelvin.

### **Table 1: Magnetic characteristics of Mn2+ ions in various ZnO- modifier glasses**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| S. No. | Glass composition | Ref. | g-factor | μ B.M. | χv(x10-3) emu-cm-3  | χg (x10-3) emu-g-1  | χm (x10-3) emu-mol-1  | C (kelvin) |
| 1 | 19.4ZnO–40Sb2O3–40B2O3:0.6MnO | [14] | 2.02 | 5.9752 | 14.7347 | 3.9345 | 10.541 | 4.4646 |
| 2 | 60ZnO–39P2O5:1MnO | [15] | 2.01 | 5.9457 | 14.5892 | 3.3524 | 1.8796 | 4.4205 |
| 3 | 10SrO–29.1ZnO–60B2O3:0.9MnO | [16] | 2.023 | 5.9841 | 14.7785 | 3.6384 | 3.0910 | 4.4779 |
| 4 | 40PbO–10ZnO–49B2O3:1MnO | [17] | 2.015 | 5.9605 | 14.6618 | 2.9620 | 3.9171 | 4.4425 |
| 5 | Zn3(PO4)2:MnO | [18] | 2 | 5.9161 | 14.4446 | 4.0257 | 7.7079 | 4.3766 |
| 6 | 24.5CaF2–10Y2O3–5ZnO–20B2O3–40SiO2:0.5MnO | [19] | 2.0026 | 5.9238 | 14.4819 | 4.9469 | 8.3196 | 4.3880 |
| 7 | 24.50LiF–10Sb2O3–05ZnO–20B2O3–40SiO2:0.5MnO | [20] | 2.0049 | 5.9306 | 14.5152 | 5.1518 | 8.0254 | 4.3981 |
| 8 | 40P2O5–55ZnO: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 |

# RESULTS & DISCUSSION

 When MnO is added into the glass composition, some amount of Mn2+ ions may be transformed as Mn3+ ions during the synthesis of the glasses as per the following redox equations [25]:

Mn2+ ↔ Mn3+ + e− -------- (7)

Mn2+ + ½O2 ↔ Mn3+ + O2− -------- (8)

Thus, the Mn3+ ions coexist with Mn2+ ions in the glasses. The model structure of B2O3-ZnO-Sb2O3: MnO glass system is built using free molecular editor software, Avogadro [26] and shown in Figure 3.



**Figure 3: Schematic of B2O3–ZnO–Bi2O3: 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 (Mn2+ and Mn3+) as per the redox equations (7) and (8). The manganese ions subsist mainly in two valence states: First one is Mn2+ with both tetrahedral MnO4 and octahedral MnO6 environment; whereas second one is Mn3+ state with octahedral MnO6 coordination. However, here we have considered the viability of the Mn2+ 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 (χv), mass paramagnetic susceptibility (χg), molar paramagnetic susceptibility (χm) 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 Mn2+ ions.

 With the help of the values of susceptibility (χv) and Curie constant (C), we can understand the thermal motion of the Mn2+ ions make them move in random directions and oppose the alignment of the magnetic dipoles of the paramagnetic Mn2+ ions under the external magnetic field. Hence the observed paramagnetic susceptibility (χm) of the samples changes with change of temperature (T) due the impact of thermal motion of Mn2+ ions [23, 24]. It has been noticed that the glass composition 40P2O5-55ZnO: 5MnO has shown highest values of μ, χv 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-39P2O5:1MnO glass has shown the poor values of μ, χv 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, Sb2O3 and SrO have exhibited the significant values of the magnetic parameters of Mn2+ ions [14, 16, 17]; while CaF2 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, Sb2O3 and SrO) doped with Mn2+ 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].

# CONCLUSION

 Zeeman splitting (hyperfine splitting) of electron spin states of Mn2+ ion has been discussed. We have reported the magnetic characteristics of Mn2+ ions in various glasses containing ZnO as a modifier oxide. Co-occurrence of Mn2+ and Mn3+ 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 MnO4 and MnO6 units. It is observed that the glasses containing heavy metal oxides have significant magnetic moment (μ) and susceptibility (χv) relatively.

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