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Spectroscopic properties of Mn^{2+} in new bismuth and lead contained fluorophosphate glasses

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ABSTRACT Luminescence, absorption and electron spin resonance (ESR) spectroscopic measurements are performed for two new Mn^{2+} doped fluorophosphate glass systems containing bismuth and lead, respectively, i.e., $45Ba(PO_3)_2$-$55BiF_3$ and $45Ba(PO_3)_2$-$55PbF_2$, to elucidate the nature of dopant–ligand bonding in terms of the covalence degree of dopant–ligand bond and ligand field strength. It is found from luminescence measurements that an octahedral coordination of dopant is formed, which is the same as that in fluoroberyllate and phosphate glasses. The optical absorption measurements indicate that the position of the absorption band, $^4T_{1g}(G)$, is red shifted, and the Racah coefficient B is 625 and 627 cm^{-1}, respectively, as ligand field strength increases in the order of fluoroberyllate, fluorophosphate, phosphate and silicate glasses. The hfs constant A determined from the ESR measurements is 94.33 and 92.12 Oe for two glass systems, respectively. The hfs constant A is also found to be 89.98 Oe and 94.33 Oe in the respective crystalline and glasses $45P_2O_5$-$55BiF_3$. In addition, the resonance observed at $g \simeq 2$ in both glass systems is mainly attributed to Mn^{2+} ions in an environment close to octahedral symmetry distorted by agglomeration of resonant centers. It, thus, can be concluded from the ESR measurements that the degree of covalency of dopant–ligand bond in both fluoroberyllate and phosphate glasses is similar, and the crystallization of the glass leads to an increase in the degree of covalency of the ligand–Mn^{2+} bond.

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1 Introduction

Glass host materials for active elements are essential for the laser and amplifier application [1–3]. Among many potential laser host materials, fluorophosphate glasses are of importance because of their potential for hosting a relatively large amount of rare earth dopants without clustering, their relatively low phonon energy, relatively low nonlinear refractive index, and relatively high transmission range up to mid IR [4–6]. In addition to laser application, fluorophosphate glasses show great potential in communication and monitoring applications in spaceborne systems and nuclear environments. It has been well known that electronic or photonic components may suffer from exposure to various radiation fields. Fluorophosphate glasses have received great attention for radiation resistant candidates owing to their high electronegativity of fluorine and reverse change of valency of d^n and f^n elements [7]. Moreover, fluorophosphate glasses containing lead or bismuth show extremely high radioactive resistance because of the high density and atomic number. Thus, fluorophosphate glasses containing heavy metals, which are able to absorb radioactive irradiation, can be used to host radioactive waste as well as to produce radiation resistant optical devices.

For all possible technical applications of fluorophosphate glasses doped with rare earth dopants, an understanding of dopant–ligand bonding must be achieved. Spectroscopic probe ions, including Mn^{2+} ion [8–13], are frequently used to evaluate the degree of covalence of dopant–ligand bond, the strength of ligand field, the coordination state of dopants, and regularity of glass micro structure surrounding Mn^{2+} ion. ESR spectroscopy can be used for detecting Mn^{2+} ions and for investigating the microstructural environment surrounding those ions because $3d$ ions are more influenced by their environment than $4f$ ions.

The purpose of this paper is to report for the first time the nature of dopant–ligand bonding in $45Ba(PO_3)_2$-$55BiF_3$ and $45Ba(PO_3)_2$-$55PbF_2$ glass systems. The heavy metal fluorophosphate glasses containing high concentrations of bismuth and lead up to 55 mol% are synthesized. Spectroscopic properties, including luminescence, absorption and the ESR spectra of Mn^{2+} ions, are obtained in the lead- and bismuth-fluorophosphate glasses. The spectroscopic results are compared with those obtained from other host glasses. In addition, the crystallization effect on the bond of covalency between ligand and Mn^{2+} ions is also investigated by comparing the ESR spectra of Mn^{2+} in both crystalline $45P_2O_5$-$55BiF_3$ and glassy $45P_2O_5$-$55BiF_3$ systems.

2 Experimental procedure

The starting materials used in this work were $Ba(PO_3)_2$, BiF_3, and PbF_2 with 99.5% purity. All batch materials were weighed according to batch composition of $45Ba(PO_3)_2$-$55BiF_3$ and $45Ba(PO_3)_2$-$55PbF_2$ (mol %) and

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prepared by the standard method. The dopant was introduced into the batch compositions in the form of MnF_2. The amount of Mn^{2+} ion in the batch compositions ranged from 0.5 to 15 weight percent. The mixed batch materials were loaded in vitreous carbon crucibles and melted under an Ar atmosphere at 1300–1350 °C for 6 h. The resulting glasses were cut and annealed at 300–350 °C for 10–15 h to remove internal stress.

The luminescence spectra of glasses, doped with MnF_2, were recorded up to 900 nm. The wavelength of pumping source for the luminescence measurement was 436 nm. The source of excitation was mercury lamp. Absorption and luminescence spectra were recorded at 295 K using a spectrophotometer (Specord), operating in the regions of 250 to 700 nm and 550 to 800 nm, respectively. The ESR spectra of the glasses, at 295 K, were recorded on a radiospectrometer (Karl Zeiss ER-9), which had a working frequency of 9370 MHz.

3 Results and discussions

3.1 *Luminescence properties*

The color of luminescence changes from yellow to dark red as MnF_2 concentration increases in both the $45Ba(PO_3)_2$-$55BiF_3$ and the $45Ba(PO_3)_2$-$55PbF_2$ glass systems. Figure 1 shows the luminescence spectra of Mn^{2+} ions in $45Ba(PO_3)_2$-$55BiF_3$ glasses as Mn^{2+} ion concentration increases. The peak position is approximately 610 nm when the MnF_2 concentration is 0.5 wt. % and 720 nm when MnF_2 concentration is 15 wt. %. The luminescence spectra of Mn^{2+} ion in $45Ba(PO_3)_2$-$55PbF_2$ glasses are recorded at Fig. 2. The luminescence peak moves from 650 nm to 720 nm, respectively when MnF_2 concentration increased 0.5 and to 15 wt. %.

Changes in dopant–ligand bonds are a main factor affecting the luminescence. Luminescence spectra of the bismuth and lead contained fluorophosphate glasses show similarities in comparison with the spectra of fluoroberyllate [14] and phosphate [3] glasses. Phosphorus in fluorophosphate and phosphate glasses has a relatively stronger bonding to the oxygen or fluorine than the silicon in silicate glasses. Phosphorus has a relatively larger nuclear charge and it forms five covalent bonds as compared to four covalent bonds in silicon. Fluorophosphate glasses, in which F–Mn–F, –O–Mn–O– or F–Mn–O– bonds may occur, have the degree of covalence between phosphate and fluoroberyllate glasses. When concentration of Mn^{2+} ion increases, the covalency between ligand and Mn^{2+} decreases and takes place change of ligands coordination around manganese ions, which cause spectral shifts.

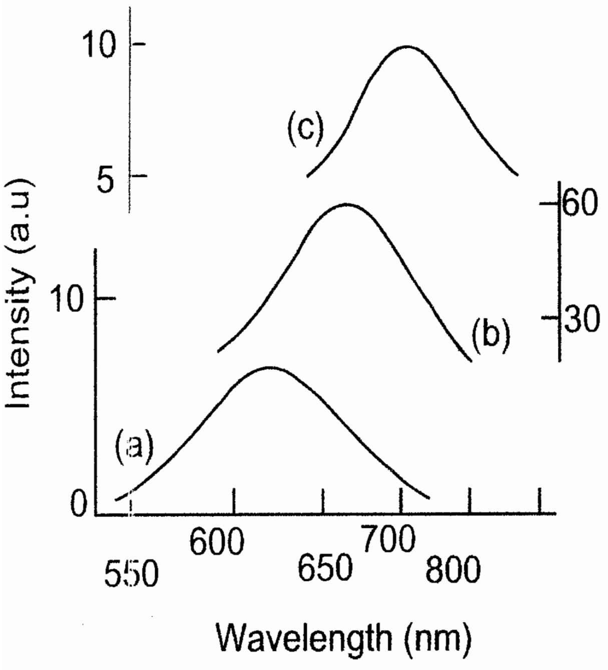

FIGURE 1 Luminescence spectra of Mn^{2+} in $45Ba(PO_3)_2$-$55BiF_3$ glasses: (a) 0.5 wt. %, (b) 8 wt. % and (c) 15 wt. % MnF_2

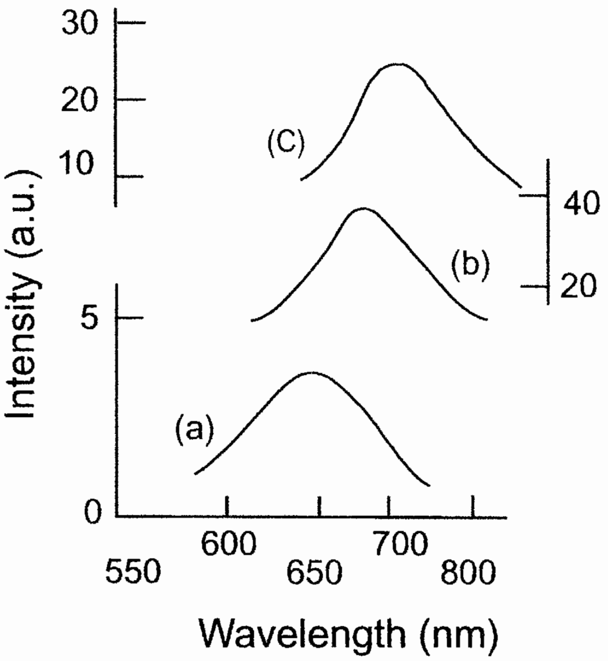

FIGURE 2 Luminescence spectra of Mn^{2+} in $45Ba(PO_3)_2$-$55PbF_2$ glasses: (a) 0.5 wt. %, (b) 8 wt. % and (c) 15 wt. % MnF_2

3.2 *Absorption properties*

Absorption spectra of the $45Ba(PO_3)_2$-$55BiF_3$ and the $45Ba(PO_3)_2$-$55PbF_2$ glass systems are shown in Figs. 3 and 4. The absorption band corresponding to the $^6A_{1g}(S) \rightarrow {}^4E_g(G)$ transition is the most intense. The absorption position with the maximum intensity for the investigated glasses is 24 320 cm^{-1}. In fluoroberyllate, phosphate and silicate glasses, the maximum intensity of absorption spectra occurs at approximately 25 200, 24 450–24 580 and 23 500–23 800 cm^{-1}, respectively [2, 7]. The second absorption band we are interested in is at 28 700 cm^{-1} in fluorophosphate glasses, as shown in Fig. 3. The position of the absorption band is due to the $^6A_{1g}(S) \rightarrow {}^4E_g(D)$ transition and does not depend on the strength of the ligand field. In fluoroberyllate glasses, the position of the maximum is at 30 050 cm^{-1}, and in phosphate and silicate glasses they are at 28 850 and 28 000 cm^{-1}, respectively [2, 7]. The absorption bands, $^4T_{1g}(G)$, of Mn^{2+} in glasses are shifted towards the longer wavelength of the spectrum with an increase in the degree of covalence of dopant–ligand bond [15].

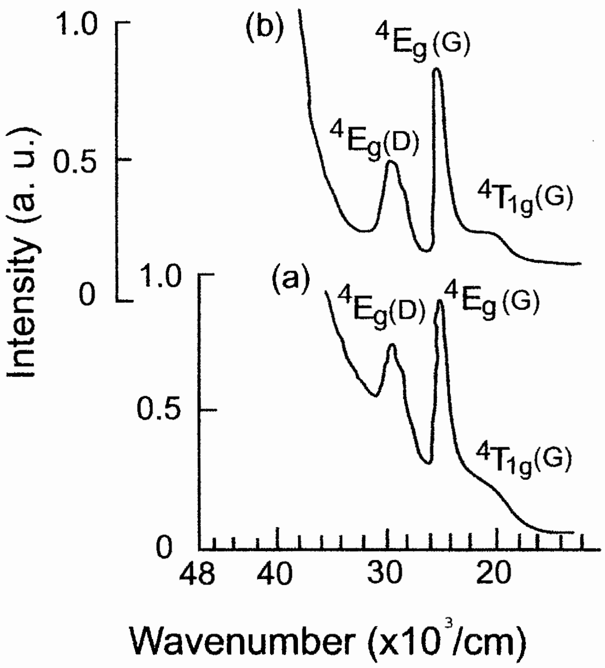

FIGURE 3 Absorption spectra in $45Ba(PO_3)_2$-$55BiF_3$ system with respect to MnF_2 concentration: (a) 15 wt. %, (b) 8 wt. %

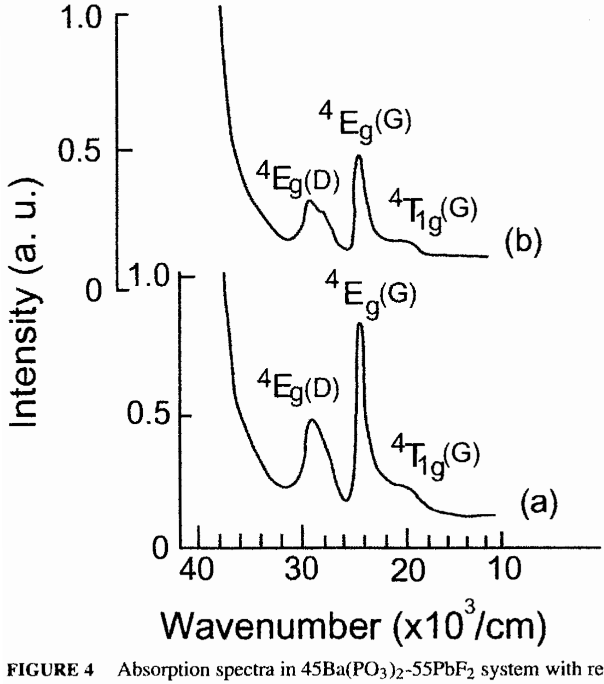

FIGURE 4 Absorption spectra in $45Ba(PO_3)_2$-$55PbF_2$ system with respect to MnF_2 concentration: (a) 15 wt. %, (b) 8 wt. %

The absorption bands, $^4T_{1g}(G)$, of Mn^{2+} for the 45Ba $(PO_3)_2$-$55BiF_3$ and the $45Ba(PO_3)_2$- $55PbF_2$ glass systems are approximately 20 000 cm^{-1}. The maximum of absorption bands for the transition $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$ are 21 150 cm^{-1} for fluoroberyllate and 19 750–19 880 cm^{-1} for phosphate and 15 250–15 550 cm^{-1} for silicate glasses. Thus, it is reasonable to assume that the fluorophosphate glasses are close to the phosphate glasses in the degree of covalence of dopant–ligand bond. This is also confirmed by comparison with the Racah coefficient B for these glasses. The Racah coefficient B is an electrostatic parameter which is a measure of the interelectronic repulsion. The appearance of electrons in the $4s$ and $4p$ shells also produces lowering of the Racah coefficient B [16, 17]. A decrease in the Racah coefficient B can be used to infer an increase in the degree of covalency of manganese (dopant) with the surrounding ligands [18]. The coefficient B can be calculated from the Tanabe–Sugano equation [19]:

$$^6A_{1g}(S) \rightarrow ^4E_g(G) = 10B + 5C \tag{1}$$

$$^6A_{1g}(S) \rightarrow ^4E_g(D) = 17B + 5C\,. \tag{2}$$

Where Racah parameter C was estimated to be 3614–3615 cm^{-1} for current fluorophosphate glasses based on the Tanabe–Sugano equation [19]. In bismuth and lead contained fluorophosphate glasses $B = 625$ and 627 cm^{-1}, respectively. For fluoroberyllate, phosphate and silicate glasses, the parameter B is approximately 700, 620 and 600 cm^{-1}, respectively [7]. In the spectrum, there is a $^4T_{1g}(G)$ band, whose position depends on the strength of the ligand field. This makes it possible to compare the strength of the ligand fields in glasses with various compositions for dopant ions with d^n electrons [20]. According to our data, the energy differences between the terms $^4E_g(G)$ and $^4T_{1g}(G)$ for the fluorophosphate glasses are approximately 4320 cm^{-1} for the $45Ba(PO_3)_2$-$55BiF_3$ and the $45Ba(PO_3)_2$-$55PbF_2$ glass systems as shown in Figs. 3 and 4. For fluoroberyllate, phosphate and silicate glasses, the values are 4070, 4700 and 8250 cm^{-1}, respectively [14, 20]. The strength of the ligand field increases in the order of fluoroberyllate, fluorophosphate, phosphate and silicate glasses. Table 1 listed all the energies and parameters for the different types of glasses.

3.3 *Electron spin resonance (ESR) spectra*

The concentration dependence of ESR spectra was analyzed for Mn^{2+} ions in the $45Ba(PO_3)_2$-$55BiF_3$ and $45Ba(PO_3)_2$-$55PbF_2$ glass system. The character of the bond which exists between the ligand-glass forming agent and ligand–dopant ions plays an important role. The hyperfine splitting (hfs) constant A for Mn^{2+} ions is directly proportional to the number of ionic bonds in the ligand–dopant series [21–23]. In other words, the hyperfine splitting (hfs) constant A indicates the qualitative measure of the ionic degrades of probe ion–ligand bonding and is mainly affected by the electronegativity of the anion neighbor. Generally, the covalency between ligand and dopant (ligand–Mn^{2+}) decreases, when the magnitude of the hfs (A) increases. The hyperfine splitting (hfs) constant A for Mn^{2+} ions in $45Ba(PO_3)_2$-$55BiF_3$ and $45Ba(PO_3)_2$-$55PbF_2$ glass system was found to be 94.33 and 92.12 Oe, respectively. The resonance observed at $g \simeq 2$ in both systems is mainly attributed to Mn^{2+} ions in an environment close to octahedral symmetry distorted by agglomeration of resonant centers [7, 24]. The hyperfine resonance absorption line is obtained only in case that Mn^{2+} ion concentration is below 0.1 wt. %. It indicates that the manganese ions are far away enough to avoid strong dipole interactions and lead to hyperfine structure. As the concentration of Mn^{2+} ions increases, the width of the hfs lines increases in $45Ba(PO_3)_2$-$55BiF_3$ glass system giving single broad band as shown in Fig. 5. It is mainly due to spin–spin coupling

TABLE 1 Relative comparisons of energy bands and nephelauxetic effects in fluoroberyllate, phosphate, silicate and fluorophosphate glass

	Fluoroberyllate	Phosphate	Silicate	Fluorophosphate
$E[^4E_g(G)]\,(\mathrm{cm}^{-1})$	25200	24450–24580	23500–23800	24320
$E[^4E_g(D)]\,(\mathrm{cm}^{-1})$	30050	28850	28000	28700
$E[^4T_{1g}(G)]\,(\mathrm{cm}^{-1})$	21150	19750–19880	15250–15550	20000
B	700	620	600	625–627
$\beta = B/B_\times 100(\%)$ (nephelauxetic relation)	81	72	69	72–73
References	[14]	[7]	[7]	Current work

between adjacent manganese ions [25]. Above 0.5 wt. % in Mn^{2+} ion, the hfs lines do not provide the resolved hyperfine structure in $45Ba(PO_3)_2$-$55BiF_3$ glass system. Similar results can be achieved by comparing the hyperfine splitting (hfs) constant A of the investigated fluorophosphate ($A = 94.33$ and 92.12 Oe), with those of fluoroberyllate ($A = 96$ Oe) [20], phosphate ($A = 95$ Oe) [7], and silicate ($A = 89$ Oe) [7] glasses. Consequent upon the compared hyperfine splitting (hfs) constant A, the investigated fluorophosphate systems is similar to the phosphate and fluoroberyllate glasses.

Figure 6 illustrates ESR spectra of Mn^{2+} in both glassy (curves a and b) and crystalline (curves c and d) bismuth fluorophosphates. Some significant differences can evidently be observed in ESR spectra and the hfs constant A between the glassy and crystalline forms. The hyperfine splitting (hfs) constant A for the bismuth fluorophosphate glass is 94.33 Oe, but for its crystalline counterpart of the same composition, it is 89.98 Oe. Figure 6 shows the strength of the ligand field on Mn^{2+} in crystalline samples is significantly higher than in glass. The hyperfine splitting (hfs) constant A in glass and crystalline states shows the different covalency between ligand and Mn^{2+} ions. During the crystallization of the glass, the covalency between ligand and Mn^{2+} ions (or any dopants) is increased ($A = 89.98$ Oe). The results also indicate that the local structure in the vicinity of Mn^{2+} ion in $45Ba(PO_3)_2$-$55BiF_3$ glass is similar to that of $45P_2O_5$-$55BiF_3$ glass as shown in Figs. 5 and 6(a) and (b). It is, thus, concluded that the similarity of dopant–ligand bonding in different glasses (fluoroberyllate, fluorophosphates, phosphate, silicate, germanate borax and other) lead to analogous spectrochemical and spectroscopic parameters.

4 Conclusions

Spectroscopic measurements have been performed for two new fluorophosphate glass systems containing bismuth and lead, i.e., $45Ba(PO_3)_2$-$55BiF_3$ and $45Ba(PO_3)_2$-

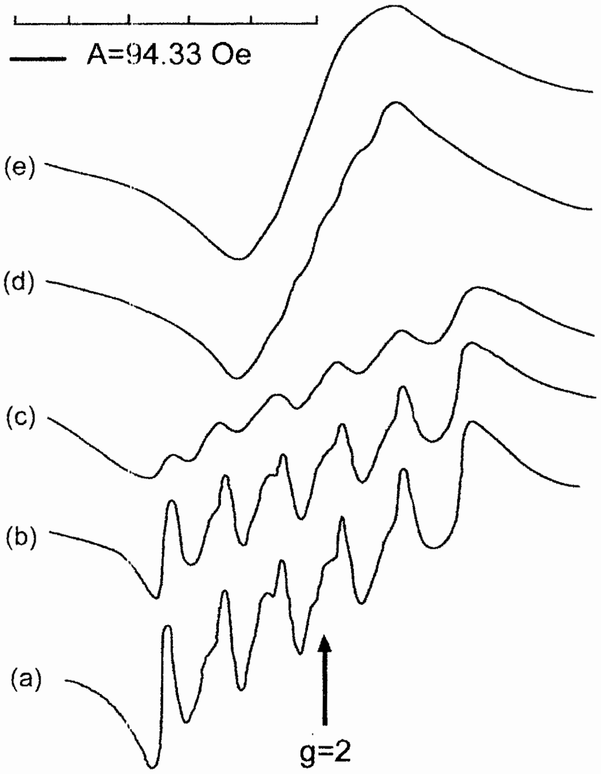

FIGURE 5 ESR spectra of Mn^{2+} in $45Ba(PO_3)_2$-$55BiF_3$ glass system: (a) 0.05 wt. %, (b) 0.1 wt. %, (c) 0.5 wt. %, (d) 1.0 wt. %, and (e) 2.0 wt. % MnF_2 [7]

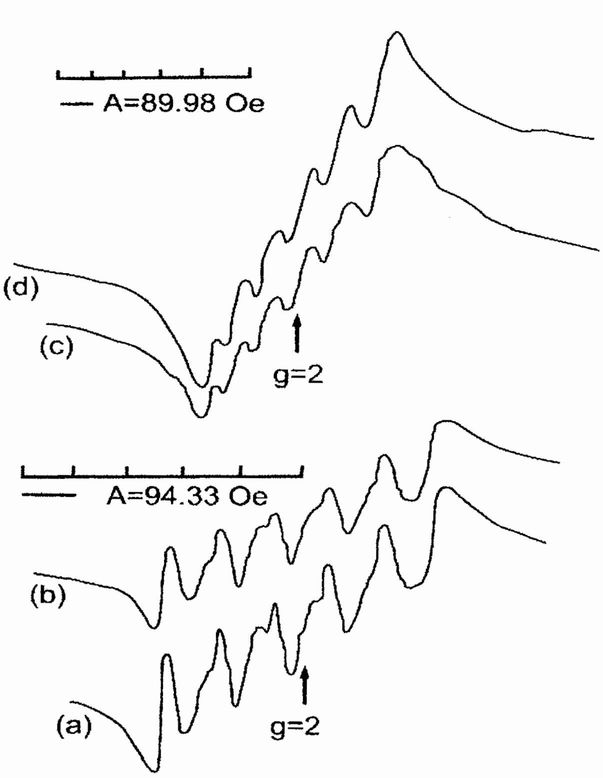

FIGURE 6 ESR spectra of Mn^{2+} in 45P2O5-55BiF3 system: (a) 0.05 wt. % (b) 0.1 wt. % MnF_2 in glass system and (c) 0.05 wt. %, (d) 0.1 wt. % MnF_2 in crystalline system

$55PbF_2$. It has been found that an increase in the concentration of MnF_2 leads to a shift in the broadband emission spectrum towards a longer wavelength region. For both glasses, Racah coefficients B have been determined to be 625 and 627 cm^{-1} and the hyperfine splitting (hfs) constants A for Mn^{2+} ions have been found to be 94.33 and 92.12 Oe, respectively. The strength of the ligand field increases in the order of fluoroberyllate, fluorophosphate, phosphate and silicate glasses. It is assumed that the fluorophosphate glasses are close to the phosphate glasses in the degree of covalence of the dopant–ligand bond based on Racah coefficients B and the position of $^4T_{1g}(G)$ band. The ligand field in the glassy and crystalline $45P_2O_5$-$55BiF_3$ has been investigated through ESR spectra of Mn^{2+}. The hyperfine splitting (hfs) constant A is found to be 89.98 Oe in the crystalline $45P_2O_5$-$55BiF_3$ and 94.33 Oe in glassy $45P_2O_5$-$55BiF_3$. It is found that the crystallization of the glass leads to an increase in the bond of covalency between ligand and Mn^{2+} ions.

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