Asian Journal of Chemistry Vol. 21, No. 7 (2009), 5167-5170

Synthesis and Structure - Property Relations in xFe_2O_3 $(1\text{-}x)Bi_2O_3$ $(0.1 \le x \le 0.5)$ (A1-A5: x = 0.1, 0.2, 0.3, 0.4, 0.5) Glasses

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Synthesis of the xFe_2O_3 $(1\text{-}x)Bi_2O_3$ $(0.1 \le x \le 0.5)$ (A1-A5: x = 0.1, 0.2, 0.3, 0.4, 0.5) glasses was done *via* nitrate-citrate gel route. Glassy phase is ascertained by XRD studies. Magnetic susceptibility results in the range 4.2-400 K show ferromagnetic nature with exchange integrals ~60 μ eV in the glasses. The electron paramagnetic resonance in the range 4.2-363 K shows g = 2.0 and g = 4.3 which are due to octahedral symmetry with tetragonal distortion and tetrahedral $[FeO_{4/2}]^{2-}$ symmetry with rhombic distortion, respectively of Fe^{3+} $(3d^5)$ ions.

Key Words: Synthesis, Structural property, Glasses.

INTRODUCTION

Fe_2O_3-containing glasses exhibit interesting electrical conductivity[1] where electrical conductivity is due to hopping of small polaron[2] from the Fe^{2+} $(3d^6)$ to Fe^{3+} $(3d^5)$ state. Bi_2O_3-containing glasses also exhibit interesting change in coordination number of bismuth in the glasses[3]. In this paper, the structural-property relations in xFe_2O_3-$(1\text{-}x)Bi_2O_3$ $(0.1 \le x \le 0.5)$ glasses are reported mainly by EPR spectroscopy and magnetic susceptibility measurements.

EXPERIMENTAL

Reagent grade ferric nitrate and bismuth nitrate solutions of 0.01 M each and 2 M citric acid solutions were used to prepare the sol which was air dried *ca.* 60 ºC to get the gel. The gel was then decomposed into fine powder at 120 ºC and then melted in silica crucibles *ca.* 1073-1133 K and air quenched to prepare the glass. The powder XRD of the samples was recorded on a RIKAGU MINIFLEX X-ray diffractometer using CuKα radiation in the range 5º to 80º in 2θ. The differential scanning calorimetric (DSC) traces were recorded on a universal V2.6D TA instruments in the range 30-550 ºC. The concentrations of the Fe^{2+} and Fe^{3+} ions were determined by wet chemistry method and the density by liquid displacement method. The IR spectra were recorded at 300 K in the range 4000-400 cm^{-1} by an FTIR-8700 spectrometer using KBr pellet technique. Magnetic Susceptibility data in the range 4.2-300 K were recorded with a SQUID magnetometer in a magnetic field of 3 kG. X-band EPR data at 300 and 77 k were recorded with a Jeol JES-TE 100 ESR spectrometer with 100 KHz field modulation. The magnetic field calibration was done with DPPH (g_{DPPH} = 2.00354), which is used as a field ‘marker’. The EPR data at 4.2 K were recorded at X-band on a varian EPR spectrometer using an Air products Helitran cryostat. The magnetic field was calibrated using a Varian NMR Gauss meter.

RESULTS AND DISCUSSION

The powder XRD patterns of A1-A5 show broad peak around 30º in 2θ, which vanishes at higher diffraction angles[4] typical of glassy phase. However, in the case of samples A1 and A2 a few diffraction peaks are observed with weak intensities and characterized due to the polycrystalline Bi_2O_3 dispersed in the glassy phase. Using the Scherer relation[5] the average crystallite sizes in A1 and A2 are determined which are found to be in the range 142.28-430.54 Å and 43.14-430.54 Å, respectively. The DSC traces in the range 27-600 ºC show that the glass transition temperature, T_g, increases from *ca.* 440-480 ºC with increasing Fe_2O_3 content. The densities of the glasses A1-A5 are found to be 2.188, 2.620. 2.415, 2.154 and 2.289 g/cm^3 while the concentrations of Fe^{2+} and Fe^{3+} ions are found to be in the range 6.38×10^{20}–1.45×10^{21} ions/g and 5.0×10^{19}–7.93×10^{19} ions/g, respectively. The values of the small polaron radius, r_p and the average transition-metal ion separation, R, are calculated using the relations reported earlier[6] and are shown in the Table-1. The values of r_p are found to be consistently less than that of R in each case. The IR spectra at 300 K show the presence of pyramidal $[BiO_{2/2}O]^-$ (symmetric bending[7]: 471-481 cm^{-1}; symmetric strech[7]: 530 cm^{-1}; asymmetric stretch[8]: 830 cm^{-1}) unit and Fe-O 9880 cm^{-1} bonds[9] in the glasses.

TABLE-1
CALCULATED SMALL POLARON RADIUS, r_p, av. TRANSITION METAL SEPARATION, R, IN THE GLASSES A1-A5 of xFe_2O_3-$(1-x)Bi_2O_3$ ($0.1 \leq x \leq 0.5$) SYSTEM

Glass No.	r_p (Å)	R (Å)	Curie constant C (emu K/g)	Weiss constant θ (K)	TIP (emu/g)	Exchange integral j (μeV)
A1	4.44	5.65	13.459	-4.09	0.5	60
A2	3.22	4.08	13.395	-4.08	0.5	60
A3	3.33	4.74	13.543	-4.10	0.5	60
A4	3.42	4.31	13.559	-4.11	0.5	60
A5	3.88	4.23	13.390	-4.07	0.5	60

Fig. 1 shows the plots of inverse magnetic susceptibility, χ^{-1}, *versus* absolute temperature, T (K) of the glasses A1-A5 in the range 4.2-473 K. The plots show Curie-Weiss behaviour of the samples in the above range. The plots are fitted to the relation, C = C/(T+θ) + TIP, where C = Curie constant, θ = Weiss constant and TIP = temperature independent paramagnetism and the fitted values are shown in Table-1. The negative values of the Weiss constants show the ferromagnetic nature of the glasses. The calculated values of the exchange integrals[10], j of the polarons are found to be *ca.* 60 μeV(*ca.* 10^{11} Hz).The TIP term is found to be 0.5 emu/g.

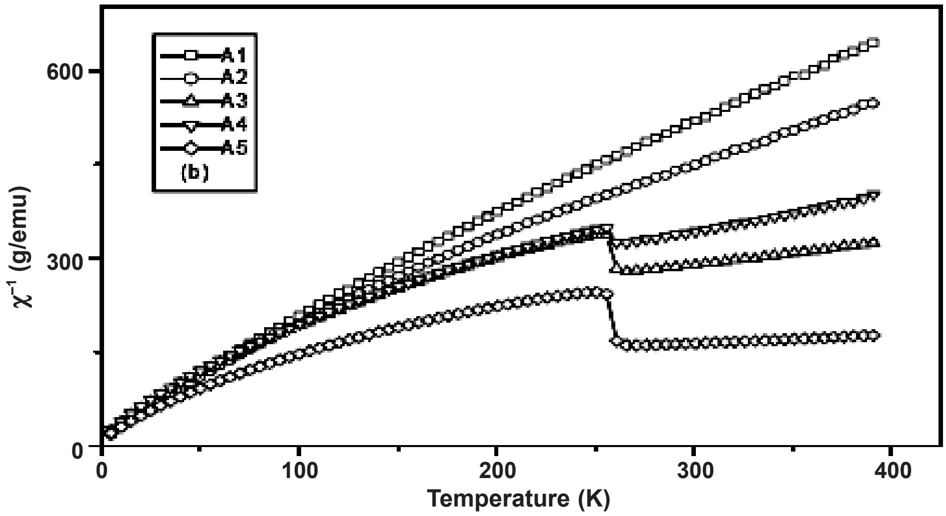

Fig. 1. Inverse magnetic susceptibility, χ^{-1}, *versus* absolute temperature, T (K) of the glasses A1-A5 in the range 4.2-473 K

Fig. 2 shows representative EPR line shapes of the glasses A1-A5 at 4.2 K. The resolutions of the line shapes are found to decrease gradually from 4.2 to 463 K and also at a particular temperature with increase in the Fe_2O_3 content. The calculated g-values are shown in Table-2. The free Fe^{3+} ($3d^5$) ion has ^6S ground state. Table-2 shows two g-values around g = 2.0 and 4.3 in the glasses. Thus it is plausible to assume that the paramagnetic sites Fe^{3+} ($3d^5$) ions have octahedral $[FeO_{6/2}]$ (g = 2.0) as well as tetrahedral $[FeO_{4/2}]^{2-}$ (g = 4.3) symmetries[10]. The isotropic g-values of A1 and A2 at g = 2.0 at 4.2 K shifts to a higher value of g = 2.13 and finally smears out in A4 and A5. However, the resonance at g = 4.3 is found to persist in the samples A1-A5 over the range $0.1 \leq x \leq 0.5$ at 4.2 K. This result shows that tetragonal distortion of the octahedral $[FeO_{6/2}]^{2-}$ unit is more rapid as compared with the rhombic distortion of the tetrahedral $[FeO_{4/2}]^{2-}$ unit with increasing Fe_2O_3 content in the matrix. The similar result is observed in the glasses at higher temperatures also.

TABLE-2
OBSERVED g-VALUES OF THE GLASSES A1-A5 of
xFe_2O_3-(1-x) Bi_2O_3 ($0.1 \leq x \leq 0.5$) at 4.2, 77, 300 and 363 K

Glass No.	4.2 K		77 K		300 K		363 K	
	g-values		g-values		g-values		g-values	
A1	2.00	4.30	1.99	4.05	2.03	4.23	2.04	–
A2	2.00	4.30	2.01	4.21	2.02	4.23	2.02	–
A3	2.13	3.50	2.06	4.21	2.02	–	1.99	–
A4	–	3.70	2.00	4.20	2.02	–	2.08	–
A5	–	3.50	2.00	4.30	2.02	–	–	–

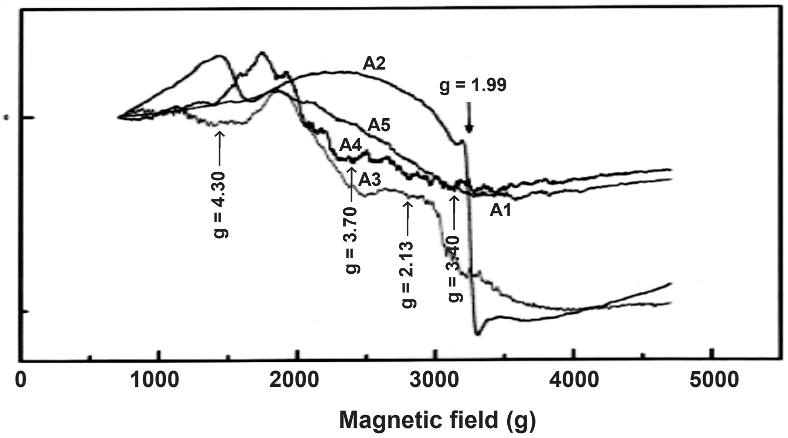

Fig. 2. EPR line shapes of glasses of glasses A1-A5 at 4.2 K

Conclusion

Powder XRD results ensured glass formation in the samples. IR-spectral results at 300 K show the presence of pyramidal $[BiO_{3/2}O]^-$ units in the glasses. The magnetic susceptibility studies in the range 4.2-400 K shows the ferromagnetic nature of the glasses. The calculated value of the j is found to be 60 µ eV. Observed EPR g = 2.0 and g = 4.3 are ascribed to octahedral symmetry with tetragonal distortion and tetrahedral $[FeO_{4/2}]^{2-}$ symmetry with rhombic distortion, respectively of the Fe^{3+} ions.

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(*Received*: 13 May 2008; *Accepted*: 29 April 2009) AJC-7450