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Electron Spin Resonance (ESR) and Optical Absorption Spectra of a Manganese Doped Soda-Lime-Silicate Glass System

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ABSTRACT

A (65-x)SiO_2:10CaO:25Na_2O:xMnO_2 glass system with $0 \leq x \leq 0.5$ mol% was prepared and investigated by X-ray diffraction, optical absorption and ESR spectroscopies. The XRD pattern of undoped glass confirmed the formation of an amorphous vitreous structure. The optical absorption spectra exhibited a predominant broad band around 500 nm and its increase was clearly observed from 0.1 mol% of MnO_2. This band corresponded to an allowed transition from $^5E_g \rightarrow {}^5T_{2g}$, of Mn^{3+} ions. When the MnO_2 concentration was increased, the absorption band due to Mn^{3+} ions dominated. The ESR spectra results exhibited resonance signals at $g \approx 2.0$ with a sextet of hyperfine lines and less intensity at $g \approx 4.3$. The group of hyperfine lines at $g \approx 2.0$ represented Mn^{2+} ions in octahedral symmetry. However, these lines were broader and disappeared for higher MnO_2 concentrations. This behavior indicated the reduction of Mn^{2+} ions in the glass system as the concentration of MnO_2 was increased by increasing the Mn^{3+} ions.
Key words: soda-lime-silicate glass, manganese ion, transition metal ion, ESR

INTRODUCTION

Glass systems containing transition metal ions have attracted a great interest for their use as photo-conducting devices, magnetic materials, etc. (Hirashima *et al*.,1987; Nakamura and Ichinose, 1987; Glebov *et al*., 2000). It is known that glass containing transition metal ions has many colors depending on the chemical composition of the glass system, the type of transition metal ion or the characteristics of the transition metal ions in the structure. In this work, all samples were soda-lime-silicate glass systems containing manganese ions used to probe the glass structure and study any favorable solarization reaction of the glass (Masaru *et al*., 2004).

Manganese (^{55}Mn) ions have been frequently used as paramagnetic probes to explore the structure and properties of vitreous systems, as their ions have a strong bearing on the optical and magnetic properties of the glass. A large number of interesting studies are available on the environment of manganese ion in various inorganic glass systems (Vaidhyanathan *et al*., 1998; Chakradhar *et al*., 2003 and 2005; Reddy *et al*., 2006).

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There are various techniques to investigate the characteristic structure of glass systems, such as Fourier transform-infrared (IR), Raman, ultraviolet-visible (UV-Vis) or electron spin resonance (ESR). The ESR and optical absorption studies are recognized as powerful tools for probing the local environment of a paramagnetic impurity and mapping the crystal field (Chakradhar *et al*., 2000, 2003 and 2005; Reddy *et al*., 2006). In the present study, the behavior of manganese ions was investigated in soda-lime-silicate using optical absorption and ESR techniques. The effects on ESR signals of the concentration of manganese ions and the content of manganese from different valency-state coordinations existing in the glass were studied.

MATERIALS AND METHODS

The glass samples used consisted of high purity composite; (65 x)SiO_2:10CaO:25Na_2O:xMnO_2. MnO_2 was doped into prepared glass bulk at five different doping concentrations: 0.02, 0.05, 0.1, 0.3 and 0.5 %mol. Each batch weighing about 50 g was melted under atmospheric conditions in porcelain crucibles in an electrical furnace at 1,100°C for 1 h. The melts were quenched in air at room temperature by pouring the melt onto a stainless steel mold, with dimensions of 3 × 6 × 1 cm^3, and pressing using another stainless-steel slab. The quenched glass samples were annealed at 500°C for about 3 h, to reduce thermal stress and cooled down to room temperature. All glass samples were cut and polished to proper sample shape for further studies. The formations of a vitreous structure were observed by X-ray diffraction (XRD).

The optical absorption spectra were also recorded on a Shimadzu, spectrophotometer in the UV-Vis-NIR region in the range 200 to 900 nm. The spectra of the glass samples were recorded for different concentrations of xMnO_2 (x = 0.02, 0.05, 0.1, 0.3 and 0.5 mol%).

The glass samples prepared for ESR studies were ground into fine powder in a mortar. All ESR measurements were performed at room temperature on a Bruker E 500 CW ESR spectrometer operated in the X-band microwave frequency. A standard rectangular cavity operating in TE_{102} mode was used. The spectrometer operating conditions adopted during the experiment were: 350.0 mT central magnetic field; 0-650 mT scan ranges; 9.859 GHz microwave frequency; 0.64 mW microwave power; 100 kHz field modulation frequency; 0.3 mT field modulation amplitude and 0.02 s time constant. 1, 1-diphenyl-2-picrylhydra-2l (DPPH) with a g factor of 2.0036 was used as an internal standard for g factor calculations. Approximately 0.36 g of each sample was inserted into a fused quartz tube of 3 mm internal diameter. Then, the sample tube was positioned in such a way that the sample was situated symmetrically with respect to the cavity center.

RESULTS AND DISCUSSION

XRD pattern

The XRD patterns for two of the representative glass samples from the (65 x)SiO_2:10CaO:25Na_2O:xMnO_2 system are presented in Figure 1. The two XRD patterns presented a broad diffuse scattering at low angle, which indicated a long-range structural disorder characteristic of vitreous solids.

Optical absorption

Figure 2 shows the optical absorption spectra of the (65 x)SiO_2:10CaO:25Na_2O:xMnO_2 glass samples at different manganese concentrations in the wavelength region of 200-900 nm. The absorption edge occurred at a wavelength of about 355 nm for all MnO_2 concentrations. It can be observed that the absorption edge was slightly shifted to a higher wavelength with increasing MnO_2 concentration.

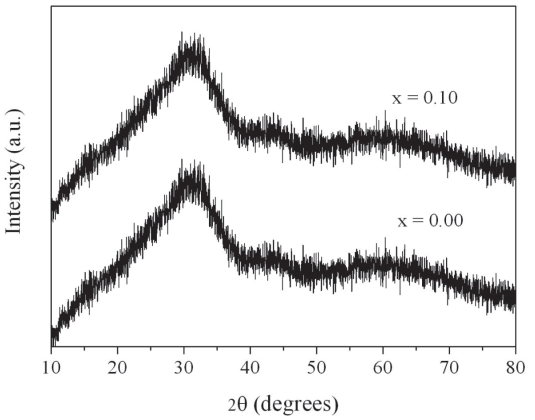

Figure 1 XRD patterns of (65-x)SiO_2 : 10CaO : 25Na_2O : xMnO_2 glass system with 0 ≤ x ≤ 0.5 mol% at room temperature.

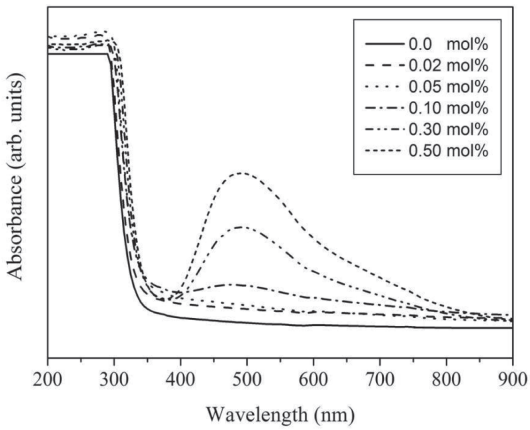

Figure 2 Optical absorption spectra of Mn-doped glass.

The spectra at a concentration of MnO_2; 0.1, 0.3 and 0.5 mol% exhibited a predominant broad band around 500 nm. This absorption band is assigned to a single allowed transition $^5E_g \rightarrow {}^5T_{2g}$, due to Mn^{3+} ions being in octahedral symmetry (Vaidhyanathan *et al*., 1998; Chakradhar *et al*., 2005; Reddy *et al*., 2006). Furthermore, this band was asymmetric, indicating that the octahedral ligand field had suffered a tetrahedral deformation by the Jahn-Teller effect. The most common manganese ions found in oxide glass are Mn^{2+} and Mn^{3+}ions. However, the Mn^{2+}ions could not be observed as they had a lower intensity than the Mn^{3+} ions and in addition, the Mn^{2+}ion had a $3d^5$ configuration and all transitions are spin-forbidden.

ESR measurement

All ESR measurements for the different MnO_2 concentrations glass samples were normalized by weight and the obtained intensities were subtracted from those of undoped glasses.

Figure 3 shows a typical ESR spectra of glass samples with MnO_2 concentrations of 0.02 mol%. All the glass samples doped with manganese ions exhibited two resonance signals at $g \approx 2.0$ and $g \approx 4.3$. The resonance signals at $g \approx 2.0$ displayed a predominant broad resonance, which consisted of a sextet of hyperfine lines. The total peak width for this signal was about 51 mT. The sextet of hyperfine lines produced from the Mn^{2+} ions ($3d^5$) are generated from the interaction between the electron spin and nuclear spin in manganese. The energy level of the electron spin under an external magnetic field is further split by the magnetic field produced by the nuclear spin states. The nuclear spin, I = 5/2, interacts with

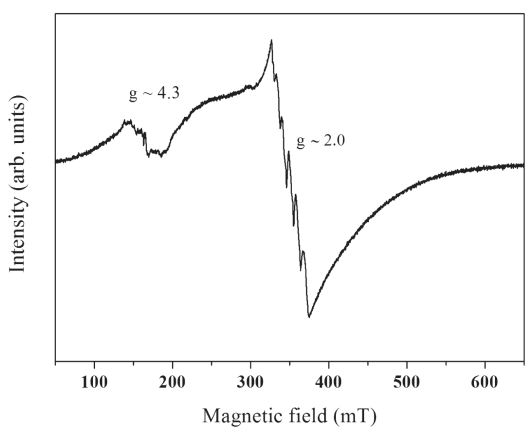

Figure 3 ESR spectra of manganese in (65-x)SiO_2:10CaO:25Na_2O:xMnO_2 glass system at room temperature when x = 0.02 mol%.

electron spin, $S = {}^1/_2$, and usually gives rise to six lines in the X-band range (Ikeya, 1993). The position of the group of hyperfine lines at g ≈ 2.0 occurred due to the effect of the site of the Mn^{2+} ion, which was expected to replace the Si^{2+} ion in an environment that is close to octahedral symmetry. It is known that it arises from the transition between the energy levels of the lower doublet, $|\pm 1/2\rangle$, while the resonance at $g \approx 4.3$ is attributed to the rhombic surroundings of the Mn^{2+} ions and arises from the transitions between the energy levels of the middle Kramer's doublet, $|\pm 3/2\rangle$ (Chakradhar *et al.*, 2005).

Figure 4 shows the ESR spectra for the different concentrations of soda-lime-silicate where the manganese was at 0.02, 005, 0.1, 0.3, and 0.5 mol%. The sextet of hyperfine lines slowly disappeared at higher MnO_2 concentration. On the other hand, the intensity of broad resonance at $g \approx 2.0$ increased as a linear function of the MnO_2 concentration (Figure 5). The way the sextet of lines disappeared indicated that there was a decrease in Mn^{2+} ions with higher MnO_2 concentration.

The intensity of the broad resonance at g ≈ 4.3 also increased with an increase in MnO_2 concentration.

CONCLUSIONS

Optical absorption and ESR spectra were studied in a soda-lime-silicate glass system which had a chemical composition; $(65\text{-}x)SiO_2$:10CaO: $25Na_2O$:$xMnO_2$, where x is 0.00, 0.02, 0.05, 0.10, 0.30 and 0.50 mol%. The optical absorption of samples which contained a MnO_2 concentration

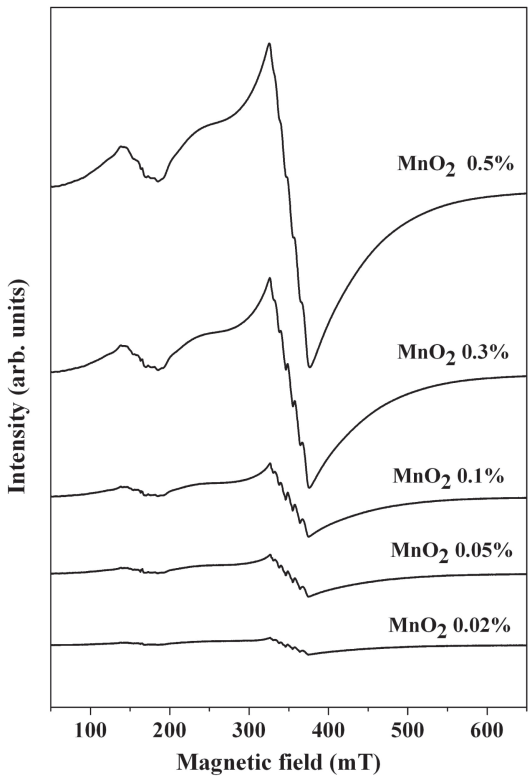

Figure 4 Comparison ESR spectra of various MnO_2 doped in $(65\text{-}x)SiO_2$: 10CaO : $25Na_2O$: $xMnO_2$ glass system at room temperature.

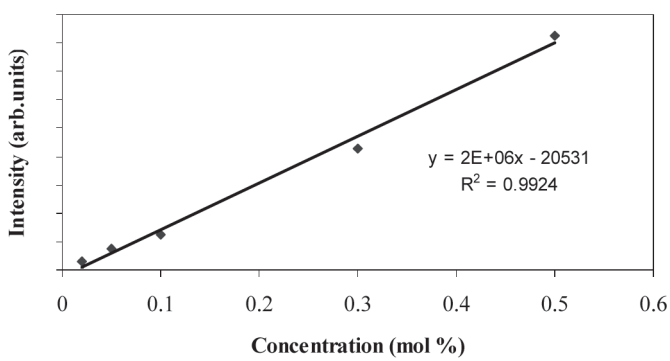

Figure 5 A Pplot ofbetween concentration of manganese and intensity of the ESR spectra.

up to 0.1 mol% showed a dominant broad band around 500 nm corresponding to the $^5E_g \rightarrow ^5T_{2g}$ transition, due to the Mn^{3+} ions being in octahedral symmetry and this band was asymmetric indicating structural disorders.

All the glass samples investigated using ESR showed two resonance signals from the Mn^{2+} ions at $g \approx 2.0$ and $g \approx 4.3$. A sextet of hyperfine lines at $g \approx 2.0$ slowly disappeared as their resonance broad line intensity increased as the MnO_2 concentration increased. From the results of the optical absorption and ESR spectra, it may be concluded that the Mn^{2+} ions decreased, unlike the Mn^{3+} ions that increased at higher MnO_2 concentrations.

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