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Studies of the effect of paramagnetic impurity in the structure of sodium disilicate glass

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Magic angle spinning nuclear magnetic resonance (MAS NMR) is used to measure the ^{29}Si chemical shift and full width at half maximum in $Na_2O{\cdot}2SiO_2{\cdot}x$MnO for $0.0 \leq x \leq 0.8$ glasses. The large space varying magnetic field of the paramagnetic centers increases the line width and moves the chemical shift to a lower frequency, i.e. more shielded, with the increase of Mn^{++}. The T_1 relaxation time falls rapidly and the relaxation rate is shown to be proportional with the concentration of MnO. The differential thermal analysis (DTA) results show that the glass transition temperature, T_g, crystallization temperature, T_x, and liquidus temperature T_L do not change due to addition of MnO. This suggests that Mn^{++} does not form chemical bond with the network. However, the Mn^{++} acts as nucleating agent and enhances the crystallization and the rate of crystallization can be tailored by judicious choice of the amount of MnO.

1. Introduction

The sodium silicate glass structure has been investigated by several techniques, e.g. infrared [1], radial distribution function obtained from X-ray diffraction, X-ray photoemission spectroscopy and Raman spectroscopy [2–4], and nuclear magnetic resonance (NMR) [5–10]. The later technique is sensitive to the local order of network former silicon nuclei in silicate glasses and information can be obtained about nearest and next nearest neighbor in an efficient way. However the ^{29}Si spinlattice relaxation time T_1, which is a characteristic of the rate of transfer of energy from the nuclear spin system to its surroundings following a perturbation, is typically 10–60 minutes [11] in an undoped sample and prolongs the NMR experimentation. Thus the reasonable signal-to-noise ratio for the ^{29}Si nuclei is difficult to achieve and several attempts [6, 8, 9] have been made to facilitate the NMR experiments by incorporating the paramagnetic centers into the glass systems that reduces the ^{29}Si T_1 relaxation time.

The presence of paramagnetic impurities induces line shifts and nuclear spin relaxation because of the space varying magnetic field produced by the impurity moment [12–17]. The paramagnetic centers change the chemical shift and reduce spin-lattice relaxation time of quadrupolar nuclei [16, 17]. The impurity moment has also a significant effect on the line shape. The change of ^{29}Si relaxation time due to incorporation of paramagnetic impurities has been reported qualitatively by several authors [6, 7, 9] but the change of full width at half maximum (FWHM) and chemical shift (CS) in glasses has not been reported. Moreover the presence of any paramagnetic centers may influence nucleation [18] and hence enhance phase separation, crystallization etc. This may also affects the structural and chemical properties of glasses.

Considering all the facts we have chosen sodium disilicate glass with varying amounts of MnO to perform a quantitative measurement of the ^{29}Si nuclear properties using MAS NMR. A systematic study of the relative crystallization in the system as a function of impurity concentration is also reported to observe the Mn lattice site with the help of differential thermal analysis (DTA).

2. Experimental

2.1. Glass preparation

Glasses of nominal composition $Na_2O{\cdot}2SiO_2$ with varying amounts of MnO were prepared from reagent grade Limoges quartz, sodium carbonate and manganese carbonate. The $MnCO_3$ was added, in amounts of 0.0, 0.05, 0.1, 0.2, 0.4 and 0.8 mol%, henceforth referred to as N2S0, N2S05, N2S1, N2S2, N2S4 and N2S8 respectively depending on the concentration of Mn, to observe its effect in nuclear and structural properties. Glasses were melted in platinum crucibles at 1100 °C and then quenched to room temperature by pressing between two carbon coated steel plates.

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2.2. NMR measurements and DTA

The NMR measurements were carried out using a Bruker MSL 360 spectrometer. Samples for ^{29}Si MAS NMR were spun at 3–4 kHz and a $\pi/6$ pulse, followed by a sufficient relaxation delay to unsaturate the signal, was employed to collect the spectra. Tetramethyl silane was used as a reference to set the chemical shift, $\delta = 0$. The T_1 relaxation time of the ^{29}Si resonance was measured using a saturation recovery method [19] where a train of ten $\pi/2$ pulses followed by an observatory pulse with sufficient relaxation delay was employed. The time T_1 is measured from the slope of the straight line. An exponential line broadening of 50 Hz, i.e. effective increases in line width of about 0.2 ppm was applied during the processing of the ^{29}Si MAS NMR spectra. All the glasses were examined by DTA, using a Stanton Redcroft DTA 1500, to determine the glass transition temperature, T_g, the crystallization temperature, T_x, and the liquidus temperature, T_L.

3. Results

3.1. ^{29}Si NMR and relaxation time

The changes in the ^{29}Si MAS NMR spectra of $Na_2O{\cdot}2SiO_2{\cdot}x$MnO for $0.0 \leq x \leq 0.8$ are shown in Fig. 1. Semilogarithmic plots of recovered magnetization versus relaxation delay of the samples N2S0, N2S1–N2S8 are shown in Fig. 2 and the effect of paramagnetic centers on the relaxation rate is shown in Fig. 3. The relaxation rate is roughly linear, i.e. a steep drop in T_1 for low concentration of Mn^{2+}. The gradient ($\Delta T^{-1}/\Delta C$), where C is the concentration of MnO, gives 0.66 s^{-1}/%. The spectral parameters and the T_1 relaxation times are summarized in Table I. The

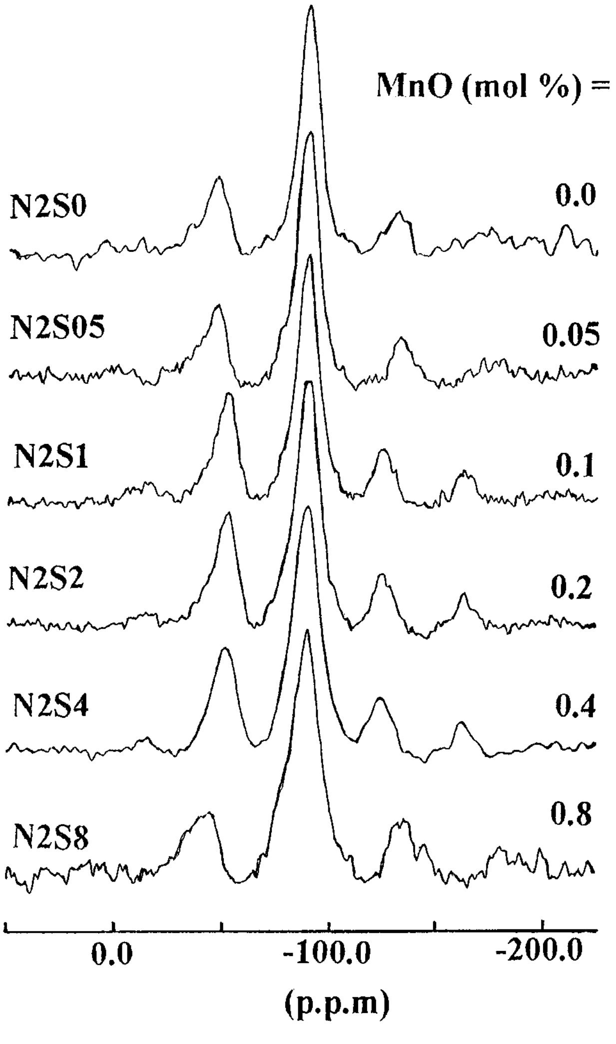

Figure 1 ^{29}Si spectra of $Na_2O{\cdot}2SiO_2$ glasses with varying amounts of MnO.

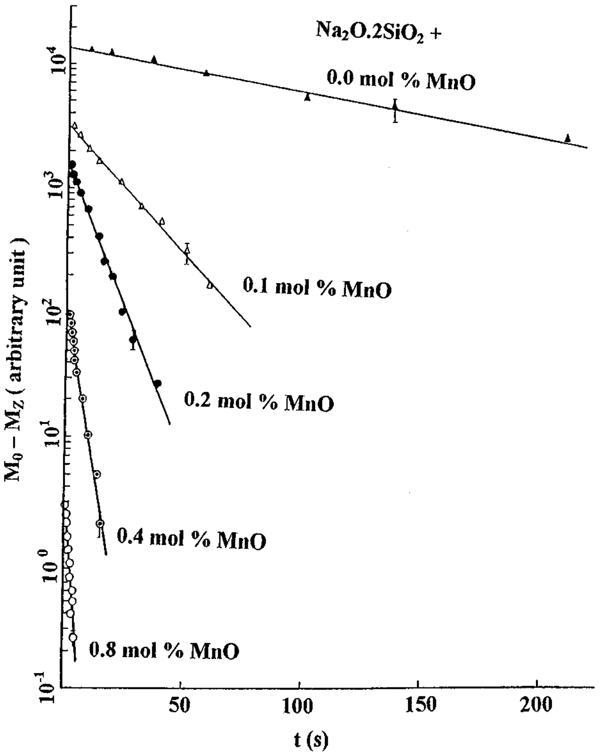

Figure 2 ^{29}Si relaxation of sodium disilicates with different amounts of MnO. In order to prevent overlapping ($M_o - M_Z$) of each plot is shifted.

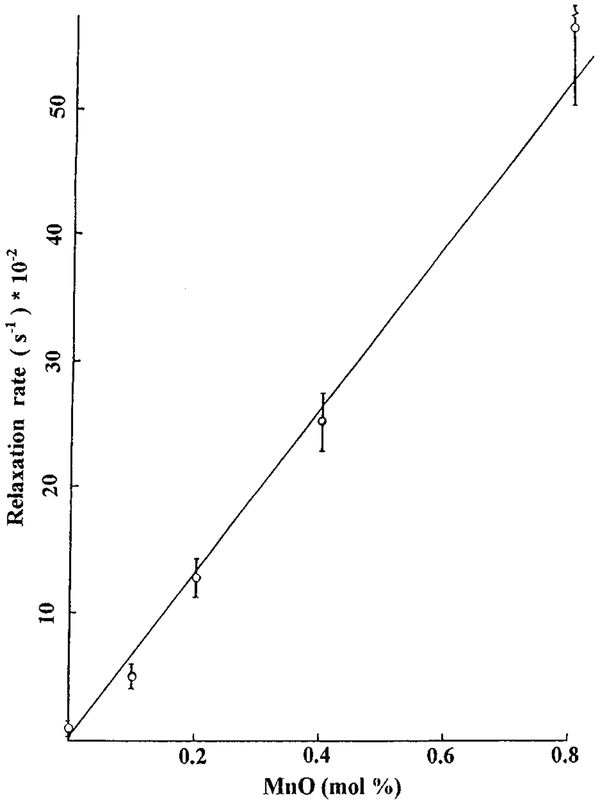

Figure 3 ^{29}Si relaxation rate as a function of MnO content in sodium disilicate base glasses.

TABLE I Spectral parameters, relaxation times, T_g, T_x and T_L of $Na_2O{\cdot}2SiO_2{\cdot}x$MnO glasses

Sample	Level of MnO (mol %)	Chemical shift (ppm) ±0.5	FWHM (ppm) ±0.5	T_1 relaxation time (s)	Relaxation rate (s^{-1}) × 10^{-2}	Glass transition temperature, T_g (°C) ±5	Crystallization temperature, T_x (°C) ±2	Liquidus temperature, T_L (°C) ±2
N2S0	0.0	−88.8	10.5	112.0 ± 9.8	0.90 ± 0.08	457	643	890
N2S05	0.05	−88.8	10.6	—	—	—	—	—
N2S1	0.1	−89.0	11.5	21.0 ± 2.2	4.81 ± 0.5	453	639	887
N2S2	0.2	−89.2	12.5	8.0 ± 1.0	12.7 ± 1.6	459	643	888
N2S4	0.4	−89.4	14.0	4.0 ± 0.3	25.1 ± 1.9	451	638	884
N2S8	0.8	−89.9	15.0	1.8 ± 0.2	56.8 ± 6.3	456	640	889

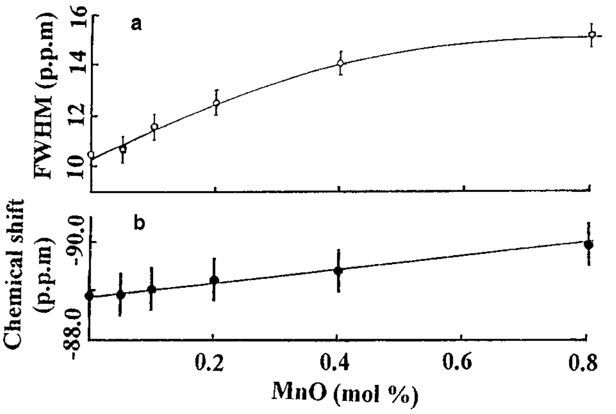

Figure 4 Variation of (a) full width at half maximum (FWHM) and (b) chemical shift (CS) with MnO content in $Na_2O{\cdot}2SiO_2$ glasses.

variation of FWHM and chemical shift as a function of MnO content is shown in Fig. 4.

3.2. DTA

In order to observe the relative rate of crystallization due to varying amounts of MnO in $Na_2O{\cdot}2SiO_2$ DTA experiments were carried out. The glass transition temperature, T_g, the crystallization temperature, T_x and the liquidus temperature, T_L, of the glasses are recorded in Table I. The T_g, T_x and T_L do not change due to addition of paramagnetic impurity, MnO, in the system but the rate of crystallization increases with the impurity concentration. An example of this is shown in Fig. 5. Exactly the same pair of crucibles and the same amounts of samples were taken for the measurements. Therefore the relatively large area under the exothermic peak must represent the higher crystallization rate.

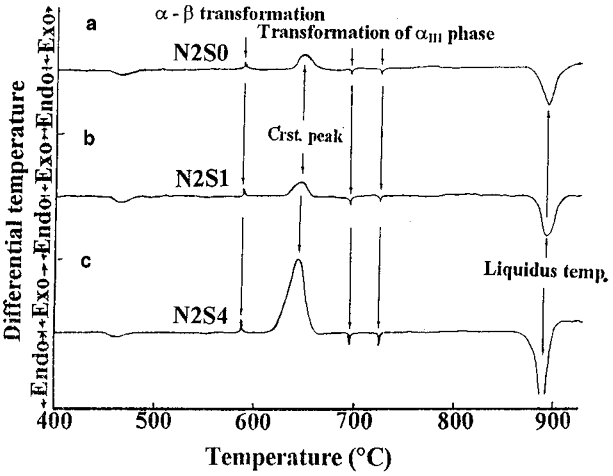

Figure 5 DTA traces of sodium disilicate glasses with (a) 0.0 MnO (b) 0.1 mol% MnO and (c) 0.4 mol% MnO. Peak heights are normalized.

4. Discussion

4.1. NMR results

Impurities are unavoidable constituents in the glass system. The presence of paramagnetic impurities in the diamagnetic solids changes the magnetic properties of the constituent elements. The large impurity moment may have an influence on the line width and on the chemical shift.

The alkali to silicon ratio is constant for all the samples and it would be expected that the amounts (%) of Q_4 and Q_2, where Q_m ($0 \leq m \leq 4$) represents the number of bridging oxygen of the network former silicon, might be the same in all the materials. Therefore the Q_3 chemical shift is relatively unaffected by the connections $Q_3 \leftrightarrow Q_4$ and $Q_2 \leftrightarrow Q_3$. The apparent change in the ^{29}Si line widths and chemical shifts (Fig. 4; Table I) with the increase of paramagnetic centers is due to modification of the local field in the vicinity of silicon nuclei [20]. The chemical shift moves towards a lower frequency, i.e. more shielded and a similar effect is observed for alkali ions [16, 17].

The magnetization M due to the presence of paramagnetic centers is given by [21]

$$M \cong N \frac{g^2 \mu^2}{3} \frac{S(S+1)}{kT} B_0 \qquad (1)$$

Where N is the number of impurity ions per unit volume, g is the Lande g-factor, μ is the Bohr magneton, S is the spin of manganese, k is the Boltzmann constant and T is the temperature. All the terms in the right hand side of Equation 1, except N, are constant. The value of N for 0.1 mol% MnO in $Na_2O{\cdot}2SiO_2$ is 7.87×10^{26} m^{-3} and that for 0.8 mol% MnO is 6.3×10^{27} m^{-3}, i.e. M increases linearly with N. Moreover the field varies as $1/r^3$, i.e. the silicons at different distances see different fields. Thus the ^{29}Si in the neighborhood of paramagnetic centers sees a large field in comparison to its average local field. Therefore the nearby silicons do not contribute to the NMR signal, i.e. within a radius 'b' there will be no spin diffusion [13]. Thus the large space varying magnetic field is the cause of relatively wider line width and more shielded chemical shift. Increased addition of MnO will ultimately wipe out the ^{29}Si signal.

4.2. T_1 relaxation time

The overall process involves the rate at which diffuse energy to the paramagnetic centers and the rate at which the magnetic centers equilibrate spins in their neighborhood [14, 15]. For both fast and slow diffusion limits several authors [12–17] have shown that the relaxation rate is proportional to the concentration of the impurity ion. Fig. 2 and Table I shows the marked change of relaxation time and Fig. 3 clearly shows that the ^{29}Si relaxation rate in $Na_2O{\cdot}2SiO_2{\cdot}x$MnO is proportional, within the experimental error, to the impurity concentration as expected. Although the sample N2S0 does not contain MnO but it does contain some impurities, e.g. $Fe_2O_3 \cong 11$ ppm, $Al_2O_3 \cong 162$ ppm, which could reduce the relaxation time. Thus the straight line of Fig. 3 is not expected to be passed through the origin.

4.3. Thermal analysis

Impurities enhance nucleation, phase separation, crystallization etc. and hence change the glass property [22]. Paramagnetic impurities may also have a profound effect in this respect. Addition of paramagnetic impurity up to 0.8 mol% is not reflected in any appreciable change of T_g, T_x and T_L (Table I). This suggests that MnO is not chemically bonded to the network.

The area under the crystallization peak for the samples N2S0 (0.0 mol% MnO) and N2S1 (0.1 mol% MnO) are almost the same but that for N2S4 (0.4 mol% MnO) is larger. This indicates that up to 0.1 mol% MnO the rate of crystallization does not change appreciably. Therefore it can be concluded that up to 0.1 mol% MnO can be added to facilitate the NMR experiments for structural investigation in silicate glasses. The impurity MnO acts as nucleating agent, i.e. higher the impurity concentration higher the nucleation centers and hence the comparatively large crystallization peak in Fig. 5. Therefore by adding a precise amount of MnO the crystallization property of the silicate matrix can be tailored to the desired level.

5. Conclusion

Incorporation of paramagnetic impurity, MnO, in sodium disilicate system broadens the ^{29}Si resonance and shifts the chemical shift towards lower frequency region. For a certain amount of Mn^{++} the signal will be wiped out due to large space varying magnetic field of the impurity. The Mn^{++} reduces the T_1 relaxation time significantly without occupying any lattice sites. The MnO enhances crystallization, which is confirmed by DTA. Much further work with other paramagnetic impurities, e.g. Cd^{++}, Gd^{++} etc. is also possible and the work is in progress to present the results.

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