Infrared Band-Shape Studies of Sulphate Glasses *

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IR band-shape analysis has been carried out on the 620 cm^{-1} deformation band of the sulphate ion in several Na_2SO_4-K_2SO_4-$ZnSO_4$ glasses. Variations of correlation times and second moments suggest that reorientational motions of sulphate ions begin to evolve prior to the glass-transition temperature. The correlation times may support a cluster model for the glass-transition.

Introduction

Several vibrational band-shape studies which have used either Raman or infra-red (IR) spectroscopy have been reported in the literature [1–3]. With very few exceptions [4, 5], however, the studies have generally been performed on symmetrical molecules in non-viscous fluids. In such situations molecular motions may be characterized with little ambiguity [6].

Translational and rotational motions of groups generally lead to a broadening of the vibrational bands. It is in fact possible to show that the band-shape ($I(\omega)$) is the Fourier transform of the correlation function, $\varphi(t)$, of the transition dipole moment at times 0 and t.

$I(\omega)$ can be expressed as

$$I(\omega) = \int_{-\infty}^{+\infty} \exp(-i\omega t)\langle \boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\rangle \,\mathrm{d}t, \qquad (1)$$

where $\boldsymbol{u}(0)$ and $\boldsymbol{u}(t)$ are the transition dipole moment vectors at times 0 and t, respectively. $\langle \boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\rangle$ represents the correlation function $\varphi(t)$ and can be obtained [7] by Fourier inversion of (1):

$$\varphi(t) = \langle \boldsymbol{u}(0)\cdot\boldsymbol{u}(t)\rangle = \int_{\text{band}} \hat{I}(\omega)\exp(i\omega t)\,\mathrm{d}\omega,$$

where

$$\hat{I}(\omega) = I(\omega)/\int_{\text{band}} I(\omega)\,\mathrm{d}\omega.$$

$\varphi(t)$ is a measure of the average variation of the angle between $\boldsymbol{u}(0)$ and $\boldsymbol{u}(t)$ between times 0 and t; such a variation could be caused by molecular reorientation. However, relaxation through vibrational excited states can also affect $\varphi(t)$. Therefore the total dipole correlation function can be written [8, 9] as

$$\varphi(t) = C_{\varphi}^{\mathrm{R}}(t)\, C_{\varphi}^{\mathrm{V}}(t), \qquad (2)$$

where $C_{\varphi}^{\mathrm{R}}(t)$ and $C_{\varphi}^{\mathrm{V}}(t)$ are the rotational and vibrational correlation functions, respectively. $C_{\varphi}^{\mathrm{R}}(t)$ in (2) includes the effects of both rotational and roto-diffusive motions. Separation of $C_{\varphi}^{\mathrm{R}}(t)$ and $C_{\varphi}^{\mathrm{V}}(t)$ is accomplished through Raman spectroscopy [3]. IR band-shape analyses cannot unambiguously separate $C_{\varphi}^{\mathrm{R}}(t)$ and $C_{\varphi}^{\mathrm{V}}(t)$.

In a situation like the glass transition, which corresponds to the onset of diffusive motion manifested by viscous flow, we should expect that band-broadening arises from rotational and roto-diffusional motion rather than from vibrational relaxation. Therefore, we thought that it would be instructive to analyse IR band-shapes assuming that vibrational band-broadening is not significant as compared to the effect of particle reorientation.

In this laboratory we have investigated sulphate glasses in considerable detail [10, 11]. These glasses are ionic and contain discrete SO_4^{2-} ions. Therefore the vibrational bands of these ions may be used for such investigation in the light of the foregoing remarks.

Experimental

Preparation of these glasses has been described in detail elsewhere [10]. For IR studies, a sample — KBr mixture was ball-milled for ~ 15 mins and pelletised under 7 kb pressure. The resultant pellets were transparent at ambient temperature but tended to opacify at higher temperatures. IR spectra were recorded on a Perkin-Elmer 580 spectrometer using a SPECAC variable-temperature

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cell and temperature controller. Temperature stability was good to ± 1 K.

The sulphate deformation mode (ν_4) [12] at 620 cm^{-1} was chosen for band-shape analysis as it was relatively free of side-bands. Care was taken to record intensities in the wings of the band. The baseline was drawn by visual inspection. Errors using this approach did not seem to be serious, as repeated transforms using different likely baselines yielded correlation functions little different from one another. Fourier transformation was carried out on a DEC-1090 system using only that half of the band which was free of side-band. Intensities were measured at 2 cm^{-1} intervals in order to perform numerical integration.

The full-width at half-maximum (FWHM) was measured both for the complete band and also by doubling the width of the side-band-free half of the band. There was no significant difference between the two values so obtained since the side-band reaches maximum intensity only in the wing of the ν_4 band. The FWHM values that we have measured agree well with Raman and IR results on other crystalline and molten sulphate systems [13, 14]. Second moments, M_2, were calculated using the formula

$$M_2 = \int_{\text{band}} (\omega - \omega_c)^2 I(\omega)\, d\omega .$$

Results and Discussion

The 620 cm^{-1} band used is shown for a typical glass in Figure 1. Figure 2 shows typical $\varphi(t)$ vs t plots of a single glass for a few temperatures. Curvature of $\varphi(t)$ at small t, indicative of relatively free rotation at short times, is clearly seen in Figure 2. τ_c values are also shown on the $\varphi(t)$ plots. Figure 3 shows the variation of these τ_c values as a function of T/T_g (where T_g is the calorimetric glass transi-

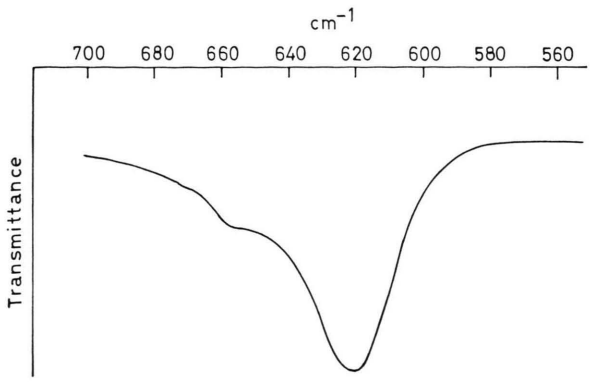

Fig. 1. A typical 620 cm^{-1} band that was used in the Fourier transformation.

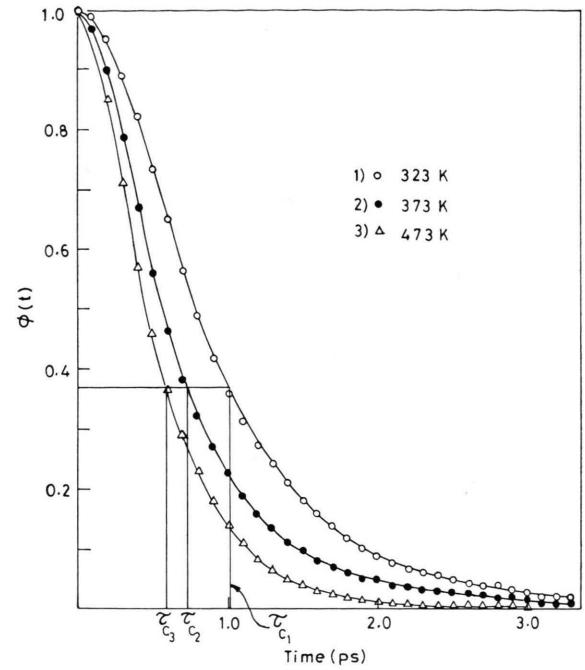

Fig. 2. Correlation function $\varphi(t)$ as a function of time (t) for the $50ZnSO_4{\cdot}40K_2SO_4{\cdot}10K_2SO_4$ glass for three temperatures. τ_c is indicated for each temperature.

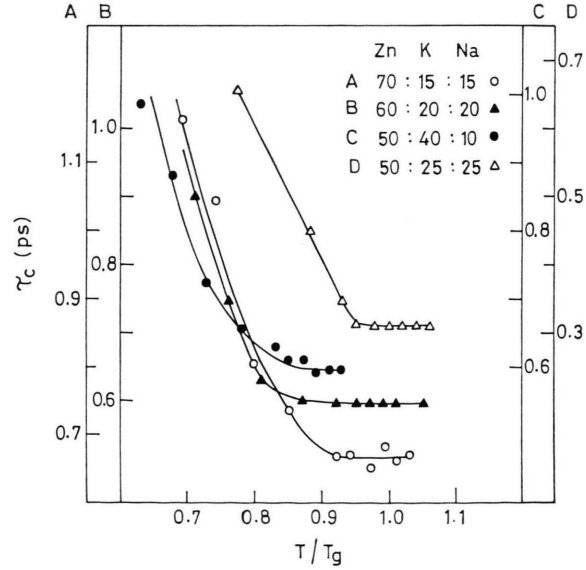

Fig. 3. Correlation time τ_c as a function of T/T_g for glasses of the indicated compositions.

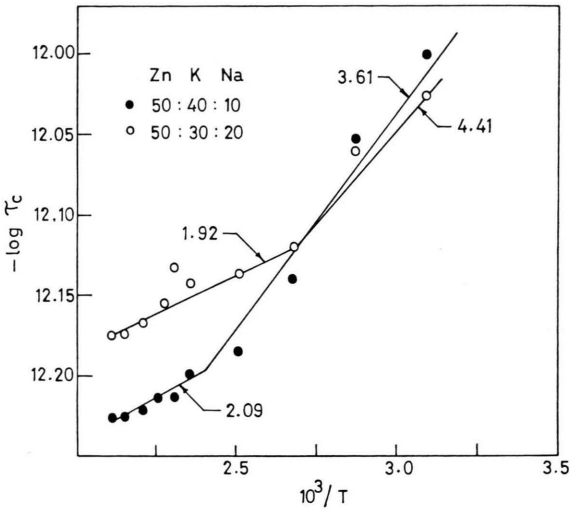

Fig. 4. Log τ_c against $10^3/T$ for two glass compositions. The figures indicate activation energies in kJ mol^{-1}.

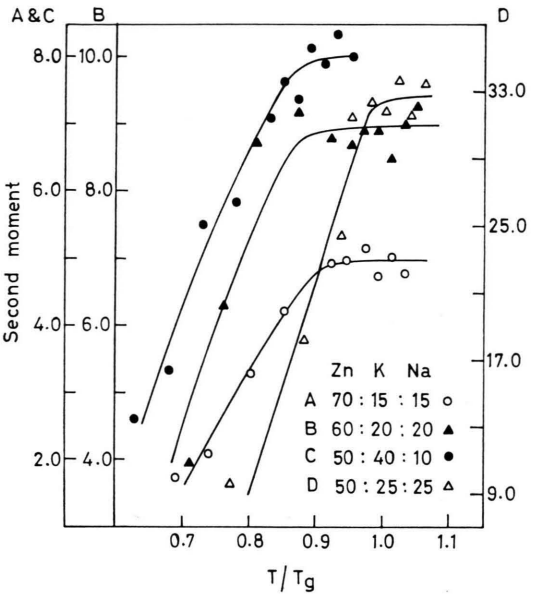

Fig. 5. The second moment as a function of T/T_g for four glass compositions: The Y-scales are for the indicated compositions.

tion temperature) for various glass compositions. τ_c decreases smoothly and levels off around $T/T_g \sim 0.9$. τ_c was fitted to an Arrhenius-type equation. Typical log τ_c against $10^3/T$ plots are shown in Figure 4. A sharp bend is observable in the glassy region ($T/T_g < 1$). The activation energy (E_a) in this region is high. Above the glass transition ($T/T_g > 1$) a lower activation energy is observed. The E_a's in both regions are indicated in Figure 4. E_a is of the order of 5—10 kJ mol^{-1} in the glass, which is quite reasonable [7], and decreases by 40% near T_g. Second moments in a few glasses were evaluated and plotted as a function of T/T_g in Figure 5. There is an initial rise after which the second moments level off at $T/T_g \sim 0.9$.

The decrease in τ_c and the increase in second moment as a function of temperature may be considered as indications of the onset of reorientational motion around T_g. Since we have assumed that vibrational relaxation is relatively unaffected by temperature, we prefer to attribute the decrease in τ_c to reorientational motions.

We suggest that the rapid decrease in τ_c (uncorrelation) may arise from hindered rotation coupled with translational motion. It is possible that the anions acquire a state of large amplitude libration or possibly free rotation (roto-diffusion) as suggested by the behaviour of second moments in Figure 5. For $T/T_g > 1$ it is likely that saturation values of rotation energies are reached. We cannot however rule out the likelihood of motional narrowing of the band caused by such diffusional motion, but this is possibly more than compensated for by heterogeneous band broadening [5], leaving τ_c effectively constant for $T/T_g \geqq 1$ (see Figure 3).

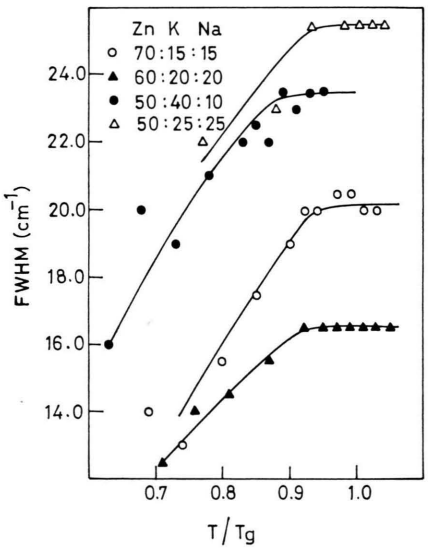

Fig. 6. FWHM of the 620 cm^{-1} band as a function of T/T_g for glasses of the indicated compositions.

This would accord well with the behaviour of FWHM itself as a function of temperature (Figure 6). FWHM increases as temperature increases and levels off around $T/T_g \sim 0.9$. The behaviour is similar to that of the second moments. It may be noted that an approximate correlation time τ_c' is often defined as $\tau_c' = 1/(2\pi x \text{FWHM})$. We find that τ_c' so determined is generally almost equal to τ_c. We have thus tentatively attributed the levelling-off of τ_c ($T \geqq T_g$) in Fig. 3 to two competing factors which become important at $T/T_g > 1$.

It is evident from Fig. 3 that τ_c decreases by $\sim 50\%$ around $T/T_g \cong 1$. It is interesting to note that τ_c for the symmetrical SO_4^{2-} ion studied here is of the order of 1×10^{-12} s as compared to about 2.5×10^{-12} s for the unsymmetrical NO_3^- ion [5].

It is natural to expect that the process of reorientational motion is sensitively affected by the potential field of the cations present at the SO_4^{2-} site. Figure 7 (a) shows variations of τ_c and E_a as a function of $ZnSO_4$ concentration. The observed increase in τ_c and decrease in E_a with increasing $ZnSO_4$ content is to be expected on account of the local coulombic fields. However, the density also increases as the $ZnSO_4$ content in glass increases. This may also contribute to the observed increase in τ_c. In Fig. 7 (b) τ_c and E_a are plotted as a functions of K_2SO_4 content in $50\,ZnSO_4 \cdot x\,K_2SO_4 \cdot (50 - x)\,Na_2SO_4$ glasses. An increase of τ_c may again be expected since K^+ ions are likely to produce steric hindrance to SO_4^{2-} motion.

There is increasing evidence for the presence of clusters in glasses. In an earlier work using ESR spectra of an organic spin-probe in organic glasses [15—17], we observed that clustering begins to occur on the high-temperature side of T_g and is reflected in a sharp increase of spin-spin correlation times. In the present investigation the observed decrease in τ_c as T_g is approached from the liquid could possibly originate from (a) melting of intercluster SO_4^{2-} ions or (b) from surfacial melting of clusters which causes loosening of SO_4^{2-} ions. In either event the present findings attribute the origin of τ_c variations to intercluster material. Thus the observations are consistent with the cluster model for the glass-transition. Further, the "knee" temperature of Fig. 3 and the cluster formation "knee" temperature [18] in our earlier study help to understand, at least tentatively, the origin of the upper and lower temperature bounds of the glass transition region.

IR band shape studies of sulphate glasses therefore yield valuable information with respect to ionic motion. Though IR studies alone cannot quantitatively characterize all features of band broadening, temperature and chemical composition effects have been used in the present study in order to extract meaningful information on such particle motion particularly near T_g.

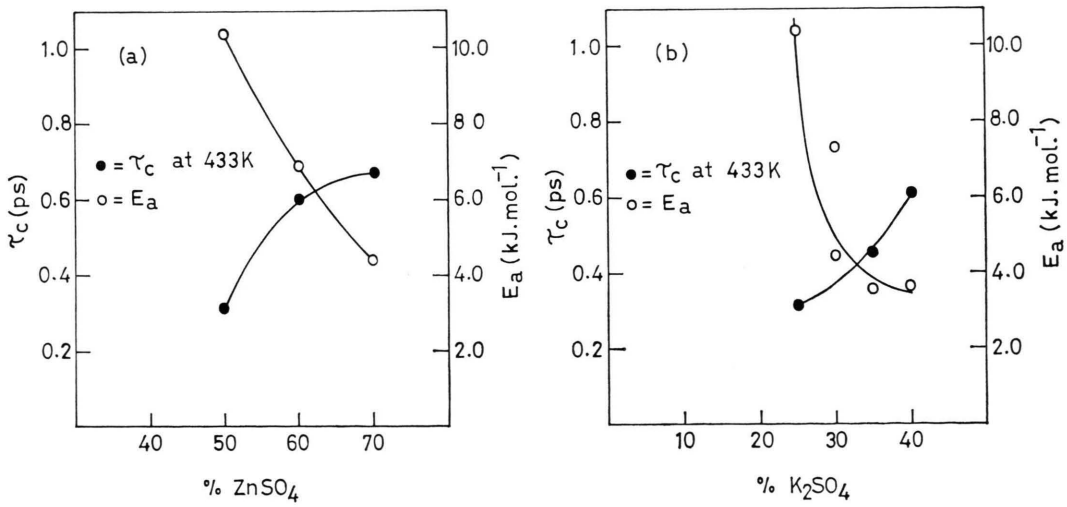

Fig. 7. (a) τ_c and E_a as a function of $ZnSO_4$ concentration, the remaining alkali being $Na_2SO_4 : K_2SO_4 : 1:1$. — (b) τ_c and E_a as a function of K_2SO_4 concentration for $50\,ZnSO_4 \cdot x\,K_2SO_4 \cdot (50 - x)\,Na_2SO_4$ glasses.

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