Inhomogeneities and dynamics in glasses collapsed from zeolites

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Introduction

Zeolites collapse close to the glass transition temperature, T_g, of the corresponding alumino-silicate glass and well below the melting points of feldspar minerals [1]. From the dynamics of zeolite amorphisation, a low density amorphous phase (LDA) has been identified, in addition to the final high density glass (HDA) - the viscosities of the two differing substantially at T_g, the LDA having the characteristics of a superstrong liquid [2]. Two level system (TLS) modes have been discovered in zeolites and glasses in the sub THz range [2] below the Boson Peak (BP). There is strong evidence that zeolite collapse is driven by TLS vibrations which in silicates originate from librational dynamics associated with corner-sharing tetrahedral linkages [2]. We report new inelastic neutron (INS) and inelastic X-ray (IXS) scattering data for zeolite Y, identifying changes in the density of TLS modes during collapse and in glass homogeneity.

Methods and Materials

Ex situ INS experiments at 10K were performed on the MARI spectrometer at ISIS using 8meV neutrons with a resolution of 0.2 meV (Fig. 1). IXS data was obtained on ID16 at ESRF with a resolution of 1.6 meV for a range wavevectors down to 2 nm^{-1} (Fig. 2). Amorphisation was conducted *in situ* at 1073K with IXS measurements being made at 873K, well below T_g.

Results

The increasing density during amorphisation was interpolated between the zeolite and the HDA glass from the size of the BP (Fig. 1). The fractions of LDA and HDA during amorphisation were obtained from the density and from the SAXS invariant [3] at different stages of collapse (Fig. 2). These reveal that the intermediate LDA phase rises to a maximum at ~80% amorphisation and the the HDA is not prominent until 95% of the zeolite has collapsed. During this transformation the INS TLS band at 1.8meV drops dramatically in intensity (Fig. 1), signifying a huge reduction in the density of librational modes. At the same time the Brillouin peak in IXS around 6.6meV can only be identified once 95% of the zeolite has collapsed (Fig. 2), at which point the fraction of HDA becomes larger than LDA

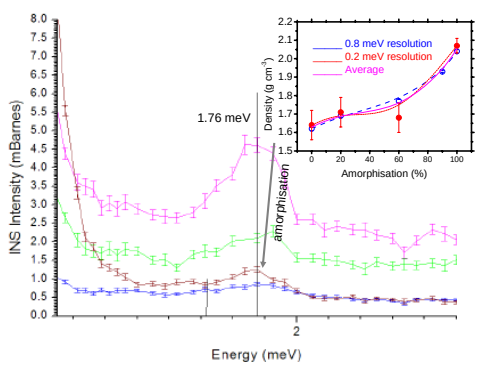

Fig 1. INS TLS modes at 1.76meV (0.43 THz) in zeolite Y during collapse. Inset: densities over whole amporphisation process.

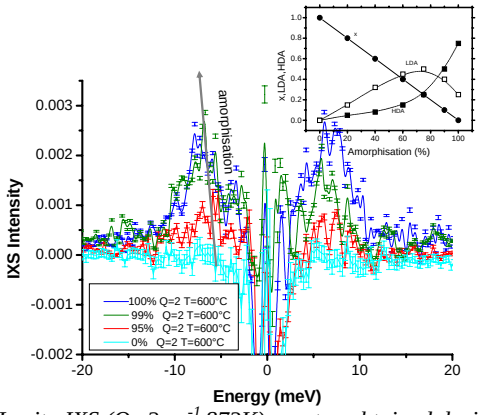

Fig 2. In situ IXS (Q=2nm^{-1} 873K) spectra obtained during the collapse of zeolite Y . Inset: zeolite, LDA and HDA fractions.

Discussion

The Brillouin peak for the HDA glass (Fig. 2, 100% amorphisation) yields a longitudinal speed of sound (ω/Q) of 5400ms^{-1}, slower than in silica (6180ms^{-1}) but comparable to zeolite Y (5181ms^{-1}) [2]. Clearly microporosity does not affect propagation through the network. Preliminary analysis points to a value of 0.18 for the non-ergodicity factor, $f(Q\rightarrow 0,T)$, in the low Q limit at 873K. Scopignio [4] has identified f_0 with the dimensionless temperature-independent factor, $\alpha = T_g(1-f_0)/f_0T$, which he finds scales for many glass formers with melt fragility and hence with complexity in the energy landscape [4]. For the HDA phase α_{HDA}=0.26, which is close to that of silica – nephelite and silica melts having similar fragilities (m=0.27). For the mixed LDA-HDA phases at 95% amorphisation (Fig. 2), we estimate α_{LDA} ~0.1 which matches the very low fragility of m=12, found from *in situ* XRD amorphisation studies [1]. As greater non-ergodicity reflects more inhomogeneity, the LDA phase (and the starting zeolite) is far less homogeneous than the HDA phase and the melt far stronger. The LDA phase also has far more TLS modes (Fig. 1) – the density being similar to the zeolite [2] – and is also structurally more ordered [3] – suggestive of the Kauzmann limit [1]. It may also have greater rigidity, with a Poisson's ratio less than quartz or diamond [5].

References

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