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Report:

The phenomena of supercooling and glass formation in viscous liquids have been the subject of considerable study in recent years. The approach of supercooled "fragile" liquids to a glass transition at *Tg* is especially interesting because of a rapid change in dynamical properties like viscosity at about 1.2*Tg* (*Tc*) where their temperature dependence becomes super-Arrhenius. Melts in the CaO-Al_2O_3 system are extremely fragile, with viscosities of less than 1 poise at 2*Tg* [1] (compared with, e.g., 10^4 poise in SiO_2), which have to rise to the conventional value of 10^{13} poise at *Tg*. Thus, in order to correlate structural and dynamic changes in the supercooled region and vicinity of the glass transition in a fragile liquid, we have studied the microscopic dynamics of liquid $CaAl_2O_4$ by inelastic x-ray scattering (IXS).

Measurements have been perfomed above the melting point at 1920 K and in the supercooled state, above and below *Tc* (at 1700 and 1420 K). In order to avoid any problem with containers and access to a deep supercooling, we used a containerless environment specially designed for the ID16 beamline. This setup has been used recently for studying the dynamics in molten magnesium aluminates at 2423 K [2].

The IXS experiments were carried out using the horizontal high energy-resolution spectrometer with an incident energy of 21.747keV giving an overall resolution of 1.5meV. Data were collected simultaneously by five analyzers over an energy transfer range of -30 to 30 meV at three positions of the first analyzer (1, 2, and 3 nm^{-1}) covering the Q range 1-16 nm^{-1}. The counting time was about 6 hours at each Q position.

During this experiments, it has been possible to collect data in the supercooled state at the approach of the glass transition. Calculations are still in progress but first results are very interesting . Fig 1 shows the dynamic structure factors $S(Q, \omega)$ at Q ~1 nm^{-1} for the temperatures (1700 and 1420 K) and at Q ~1.5 nm^{-1} for the temperatures (1920 and 1700 K). All curves exhibit a well defined triplet - central Rayleigh peak and two lateral Brillouin peaks - showing a clear evolution with the temperature. In particular, one can observe a shift of the Brillouin peaks to higher energies when the temperature is decreased. This corresponds to higher sound velocities in the supercooled state as observed with liquid alumina [3]. We can see also a sharpning of the Brillouin peak when we lower the temperature. This means that changes are occuring with the viscosity.

Fig 2. shows the dependence of the frequency of the Brillouin peaks ωs on wave vector Q. A linear fit is shown for T=1700 K, giving a sound velocity of 6000 m/s. In the high Q region, one can observe different evolutions of the dispersion. This is characteristic of structural changes and should be connected to the evolution of the short and medium range order observed previously [4]. The inset shows the evolution of the sound velocity calculated from the linear fits for the three temperatures.

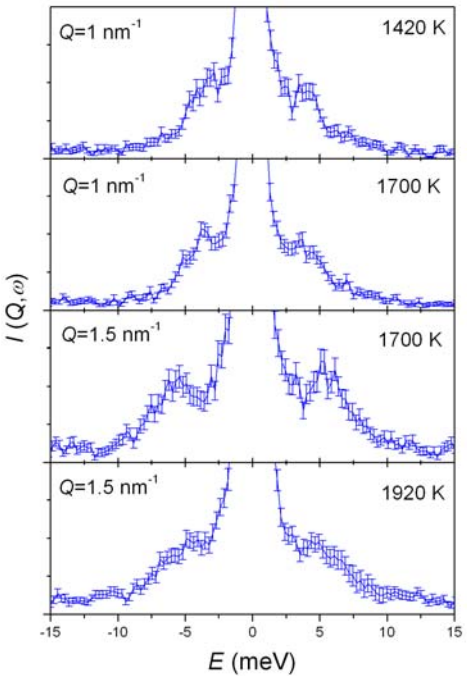

Fig 1. IXS spectra of $CaAl_2O_4$ at Q=1 nm^{-1} for the three temperatures

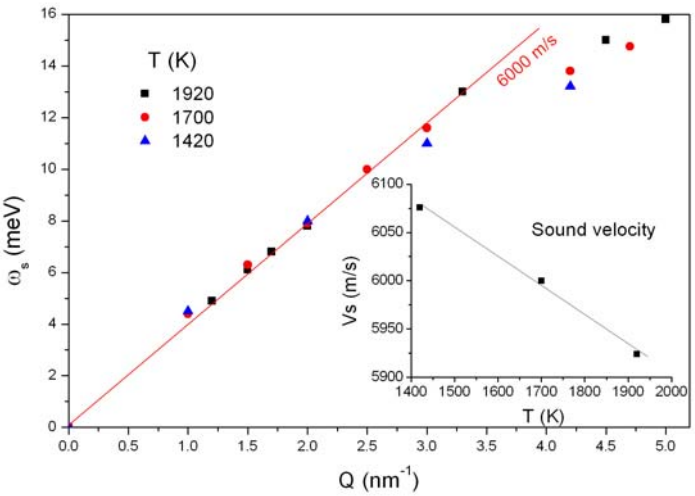

Fig 2. Dependence on wave vector Q of the frequency ωs. The solid line represents ωs= Vs/Q with Vs = 6000 m/s.
The inset shows the evolution of Vs as a function of the temperature

The determination of the viscosities is not perfomed yet. As in our previous study [2], we will use a model derived from the generalized hydrodynamics and describe by the memory function:

$$M(Q,t) = \Delta_\alpha^2(Q)e^{-t/\tau_\alpha(Q)} + 2\Gamma_S(Q)\delta(t)$$

where τ_α- the structural relaxation time, Δ_α- the structural relaxation strength, and Γ_s -the Brillouin linewidth. This model includes a slow component described by a single relaxation time and an effectively instantaneous fast component. The longitudinal viscosity will be determined using the formla:

$$\eta_l(Q) = \frac{\rho\left[\Delta_\alpha^2\tau_\alpha + \Gamma_S(Q)\right]}{Q^2}$$

In summary, our first results show an increase of the the sound velocity when we lower the temperature and shows different dispersion behaviors at large Q. The structural evolution during supercooling from the stable liquid phase is characterized by an increase in the degree of both intermediate-range and short-range orders [4]. These structural transformations could be responsible for changes with the dispersion at large Q. Our finding reflects the complexity of fragile glass-formers, calling for further investigations. Molecular Dynamics simulations are in progress and will be compared to the experimental data. This will well for the interpretation.

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