



Experiment title: EXAFS study of glass formation : Effect of metal ions on glass forming ability.	Experiment number: CH-780
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Report:

In this experiment, we set out to investigate the glassforming processes that occurred in a number of aqueous metal nitrate systems. The systems investigated were all fragile glassformers of the type $X^{a+}(\text{NO}_3)_a \cdot \text{NH}_4\text{NO}_3 \cdot 4/6 \text{H}_2\text{O}$ where a denotes the charge on the metal ion of type X (either 1+ or 2+). Furthermore, those that have been tested exhibit β relaxations below T_g in the glassy system and similar nitrate systems like $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ have been shown to show reorientational motion of the NO_3^- ion well below the glass transition temperature [1]. This motion can in part explain the β -relaxational process observed in $X^{a+}(\text{NO}_3)_a \cdot \text{NH}_4\text{NO}_3 \cdot 4/6 \text{H}_2\text{O}$ glasses. However, the mode-coupling theory demands that density fluctuations are not single particle like [2] and within these system, the metal ion hydration sphere is the most likely candidate to contain these effects should they exist. Indirectly, it has been shown in the case of X=Ca system that the Ca^{2+} ion has a significant change in local environment between the liquid and the glassy state [3].

We wished to determine both the local structure for the metal ions going from the glass to the liquid and the extent over which temperature region that changes take place. Additionally, since the X^+ are more mobile than the X^{2+} ions, we were able to investigate the effect of the ions mobility in defining the local structure, which gives insight into whether the relaxation processes that define the local structure are cooperative or isolated, and hence whether changes to the short range local structure contribute to the glassification dynamics.

The results of the experiment are extremely interesting. In the case of Ni^{2+} and Zn^{2+} , we did not observe an apparent change between the liquid and any undercooled or glassy phase, outside the expected temperature damping of the EXAFS signal. It is clear from the glass that the arresting of motion significantly enhances the EXAFS signal but that structural changes do not take place. [This does not mean that the structure is unchanged just that the local structure of the ion is unperturbed.] The water structure of Ni^{2+} is extremely stable ($>10^6$ seconds) [4] and thus is consistent with the results. At the moment it is less apparent as to why Zn^{2+} is so unchanged within this system.

In the figure below, are the EXAFS signals for the Sr^{2+} case, this shows the crystalline form as a reference. There is clearly a change in structure between the low T, and as the system approaches T_g . These results were repeatable if the system is re-cool at anytime before crystallisation.

The results for Ag^+ also show considerable change, firstly is that the electronic environment of the Ag^+ changes significantly in the just below the glass transition temperature, (signified by a strong increase in the white line) which disappears upon either crystallisation or melting and secondly there is a small structural change between the undercooled liquid and the glass.

The results are currently being analysed further using EXAFS fitting procedures, based of possible clusters from simulation.

References

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