Experimental Report

Proposal: **6-05-922** **Council:** 10/2012

Title: Structure of Intermediate Phase Glasses

This proposal is a new proposal

Researh Area: Materials

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Samples: GeSe3 or GeSe4 with 70Ge, 73Ge and 76Se isotopes

Instrument	Req. Days	All. Days	From	To
D4	8	8	02/05/2013	07/05/2013
			13/07/2013	17/07/2013

Abstract:

The objective of this proposal is to measure the full set of partial structure factors for two glasses, GeSe3 and GeSe4, that mark the boundaries of the so-called intermediate phase in the Ge-Se glass-forming system. The intermediate phase is common to a wide variety of network glass-forming systems and represents a range of compositions for which the network is deemed to self-organize on glass formation to give a rigid system that is optimally constrained to avoid stress. The results will provide the maximum information on the structure of these glasses that can be made available by using diffraction experiments, and will therefore give unprecedented insight into the structural signatures of the intermediate phase. In particular, they will provide the information that is required (e.g. on homopolar bond distances and coordination numbers) to distinguish between the various structural models that have been proposed. The new diffraction results will inform and be complemented by on-going first principles simulations. Additional information will be provided by new 73Ge and 77Se MAS NMR experiments.

Structure of intermediate phase glasses

The aim of this proposal was to measure the full set of partial structure factors for glassy $GeSe_4$ and $GeSe_3$ using the method of neutron diffraction with isotope substitution. These materials are part of a family of network-forming glasses Ge_xSe_{1-x} ($0 \le x \le 1$) that have a transition in their physical properties around a finite interval of compositions near $x = 0.2$ [1]. This interval is associated with a so-called intermediate phase where the network self-organises on formation to give a rigid system that is optimally constrained to avoid stress [2]. $GeSe_4$ and $GeSe_3$ are two compositions that bracket the intermediate phase window for the Ge_xSe_{1-x} system.

For the experiment on $GeSe_4$ glass, samples of $^{N}Ge^{N}Se_4$, $^{70}Ge^{N}Se_4$, $^{N}Ge^{Mix}Se_4$ and $^{73}Ge^{76}Se_4$ were prepared in Bath using an identical procedure from germanium of natural isotopic abundance ^{N}Ge (99.999%, Alfa Aesar), ^{70}Ge (95.30 % enrichment, Isoflex USA), ^{73}Ge (95.60 % enrichment, Isoflex USA), selenium of natural isotopic abundance ^{N}Se (99.999+%, Sigma Aldrich), ^{76}Se (99.8% enrichment, Isoflex USA) or a 50:50 mixture of ^{N}Se and ^{76}Se (99.8% enrichment, Isoflex USA) which will be referred to as ^{Mix}Se. Oxygen impurities in the germanium isotopes were removed by reduction under a hydrogen gas flow at 600 ^{o}C. After the first diffraction experiment on $GeSe_4$ glass had been completed, additional germanium was added to make samples of glassy $^{N}Ge^{N}Se_3$, $^{70}Ge^{N}Se_3$, $^{N}Ge^{Mix}Se_3$ and $^{73}Ge^{76}Se_3$ for the second diffraction experiment.

The measured total structure factors $F(q)$ for $GeSe_4$ and $GeSe_3$ glass are shown in figures 1 and 2, respectively. The results will be used to calculate the full set of partial structure factors for both materials, thereby giving the maximum information available from diffraction on the structure of this family of intermediate phase glasses. All of this will provide the structural information required to test and refine the various structural models that have been proposed [3, 4].

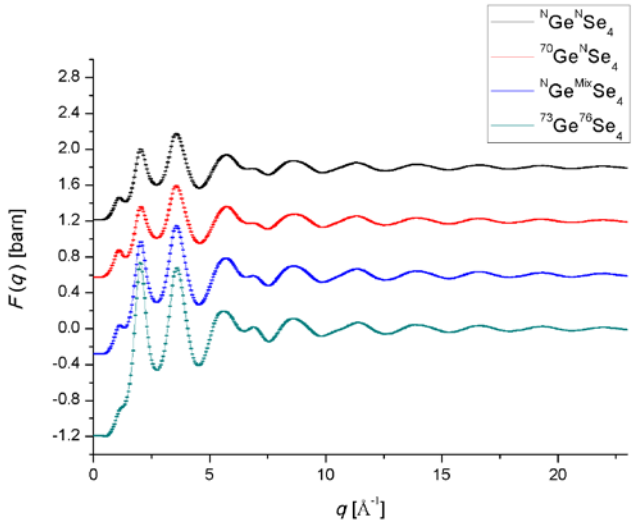

Figure 1: The total structure factors $F(q)$ measured for $GeSe_4$ glass using D4c. Vertical bars give the statistical errors on each data point and are smaller than the line thickness at all q-values. The data sets for $^{N}Ge^{N}Se_4$, $^{70}Ge^{N}Se_4$ and $^{N}Ge^{Mix}Se_4$ have been shifted vertically for clarity of presentation.

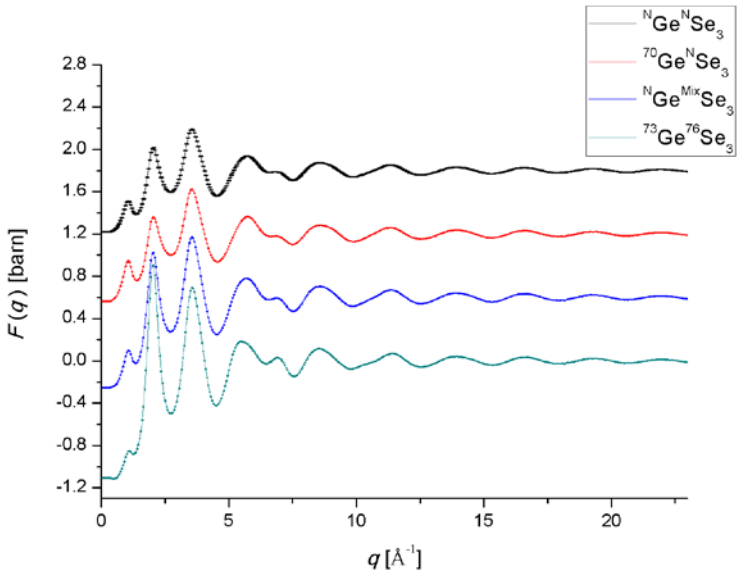

Figure 2: The total structure factors $F(q)$ measured for $GeSe_3$ glass using D4c. Vertical bars give the statistical errors on each data point and are smaller than the line thickness at all q-values. The data sets for $^{N}Ge^{N}Se_3$, $^{70}Ge^{N}Se_3$, $^{N}Ge^{Mix}Se_3$ have been shifted vertically for clarity of presentation.

[1] P. Boolchand *et al.* 1986 *Phys. Rev. Lett.* **56** 2493

[2] M. F. Thorpe *et al.* 2000 *J. Non-Cryst. Solids* **266-269** 859

[3] K. Sykina *et al.* 2012 *Chem. Phys. Lett.* **547** 30

[4] M. Micoulaut *et al.* 2013 *Phys. Rev. B* **88** 054203