Experimental report

16/02/2020

Proposal: 6-05-1009 **Council:** 4/2019

Title: Structural change in phosphate-based glassy precursors to superionic conducting glass-ceramic electrolytes

Research area: Materials

This proposal is a resubmission of 6-05-1003

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Samples: Na_(1+x)Ge_(2-x)Al_x(PO_4)_3
Na_(1+y)Ti2Si yP3-yO12

Instrument	Requested days	Allocated days	From	To
D4	4	4	14/09/2019	18/09/2019

Abstract:

The onset of homogeneous nucleation in the Na_(1+x)Ge_(2-x)Al_x(PO4)_3 family of phosphate materials will be investigated using neutron diffraction. The crystalline phases of these materials are superionic conductors, and are best prepared via the glass-ceramic route to create a uniform distribution of crystallites of controllable size and shape throughout the bulk material. The objectives are to (1) measure the coordination environment of Ge, (2) understand the structural relationship between an ion-conducting glass ceramic and its precursor glass, and (3) monitor the structural rearrangements that occur during the early stages of crystallization. The latter is of general scientific interest for any glass undergoing homogeneous nucleation, but has not been explored in non-siliceous systems.

Structural change in phosphate-based glassy precursors to superionic conducting glass-ceramic electrolytes

The onset of crystallisation in the $Na_{(1+x)}Ge_{(2-x)}Al_x(PO_4)_3$ family of phosphate glasses with x = 0, 0.4 or 0.8 was investigated by using neutron diffraction. The as-prepared glass was annealed near the glass transition temperature T_g for different amounts of time in order to realise structural change. Several of the measured total structure factors $F(q)$ for the x = 0 glass are shown in Fig. 1, where q is the magnitude of the scattering vector. As shown in Fig. 2, there is a small but measurable change to the structure of the x = 0 glass in the onset to nucleation, i.e., before Bragg peaks start to appear. The results are being combined with those from ^{31}P and ^{27}Al magic angle spinning nuclear magnetic resonance spectroscopy in order to build a complete picture of the structure that includes the Ge-O coordination environment, and to establish how this structure changes as the glass crystallises.

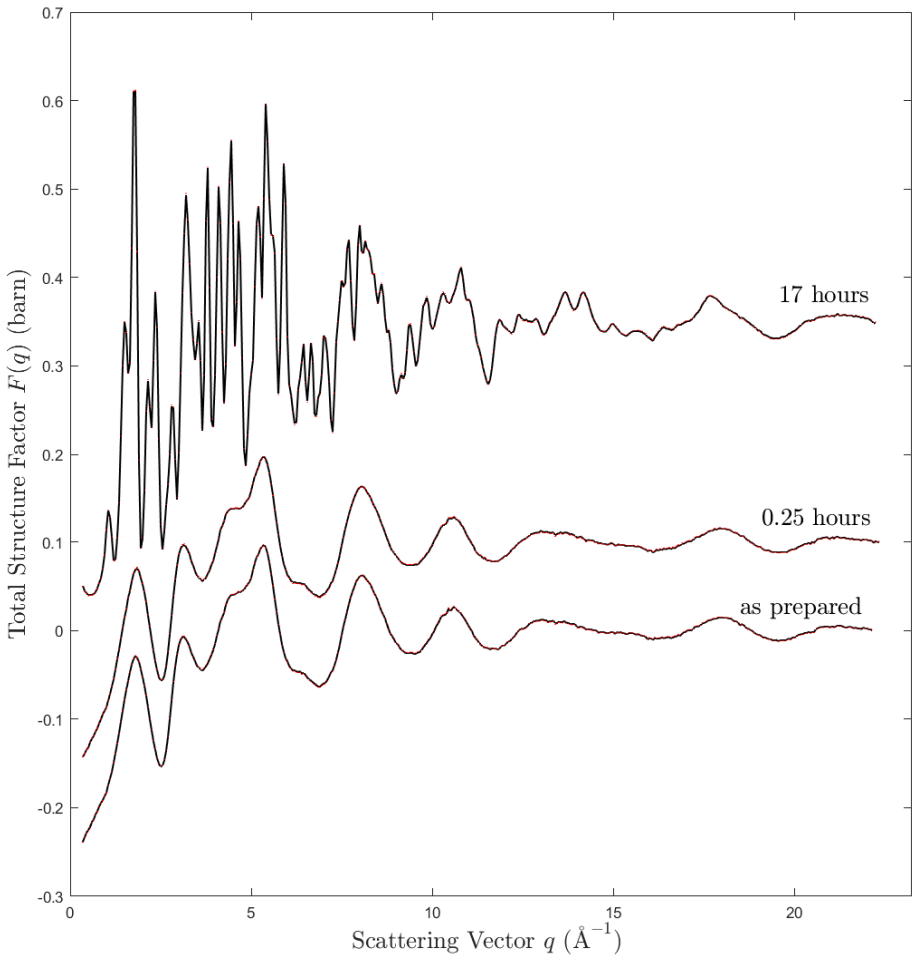

Fig. 1. The neutron total structure factors $F(q)$ for $NaGe_2(PO_4)_3$ measured for the as-prepared glass, the glass after annealing near T_g for 0.25 h, and the crystal formed by annealing the as-prepared glass near T_g for 17 h.

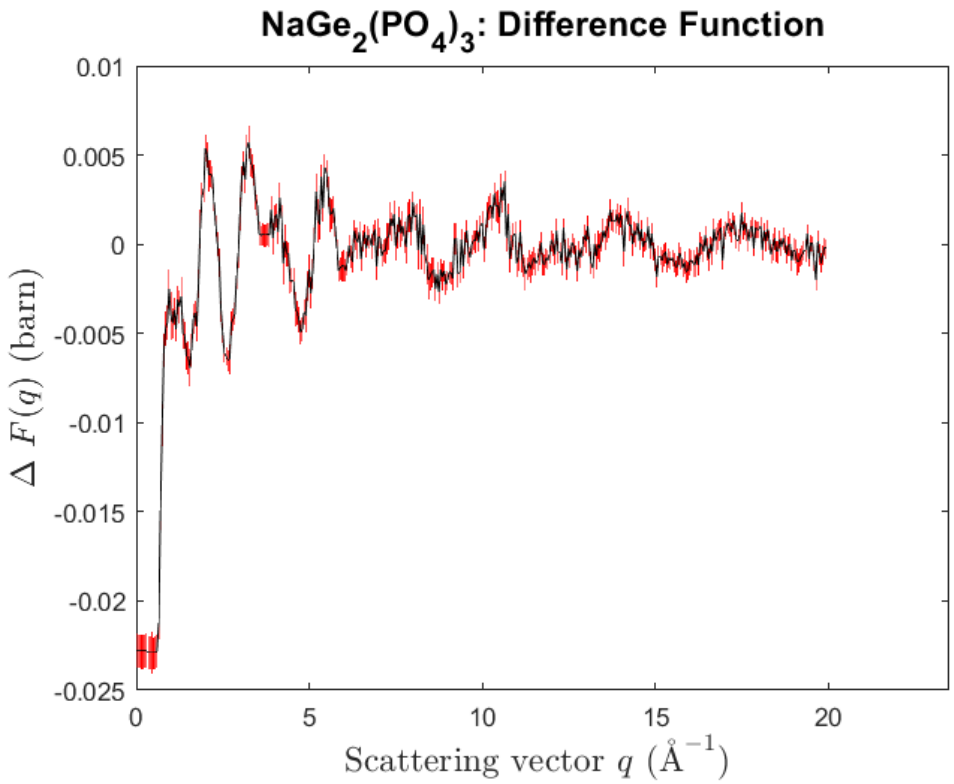

Fig. 2. Difference between the neutron total structure factors $F(q)$ measured for the as-prepared glass and the glass after annealing near T_g for 0.25 h.