Experimental report

20/10/2017

Proposal: **INTER-332**

Council: 4/2016

Title: Internal time on D11

Research area:

This proposal is a new proposal

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Samples: SiO_2,B_2O_3,Na_2O,Al_2O_3,ZnO,K_2O,CaO

Instrument	Requested days	Allocated days	From	To
D11	2	2	07/06/2016	08/06/2016

Abstract:

D11 experimental report – INTER 332

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1 Introduction

The borosilicate glasses studied here have shown remarkable differences in term of macroscopic behaviour. Borofloat and N-ZK7 are known to shrink under irradiation [1] up to 2 % and 1 %, respectively. This trend has been correlated to a compaction of their silica network [2] which is known to be unstable to irradiation [3] and compact up to 3 %. On the contrary, N-BK7 and S-BSL7 are more stable and have a very similar behaviour. They swell under irradiation but at rate which is, on the absolute, 10 and 5 times smaller that Borofloat and N-ZK7, respectively. This was correlated to the homogeneous internal structure of these glasses that show a mixing of the boron atoms with silicon and form reedmergnerite like structures [2, 4, 5].

2 Materials and methods

The four borosilicate glasses studied are industry-grade alkali-borosilicate standards, namely Borofloat, N-ZK7, N-BK7 and S-BSL7. The first three are commonly used for neutron guide manufacturing. In all cases the glass samples were provided by different neutron guide manufacturers. As far as sample sizes are concerned, they were measuring $10 \times 10 \times 0.3$ mm^3. The chemical composition of those glasses is reported in [2]. In that table, are also reported the proportion four-fold coordinated boron atoms (written N4) and, among them, their speciation between (4 Si, 0 B) and (3 Si, 1B) sites. Such values are extracted from the MAS-NMR signals, published in a previous study [2], acquired on a 18.8 T machine.

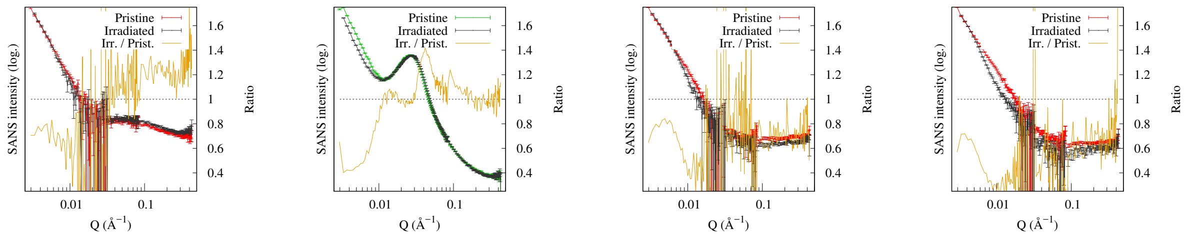
The thermal neutron irradiations have been carried out in the T4 tube at ILL that provides an unperturbed flux of 2×10^{13} n/cm^2/s. Maximum sample temperature has been calculated to be about 65 °C. More details on the irradiation conditions are given in [1]. The maximum temperature of the samples has been estimated considering the worst case scenario of an irradiation shuttle fully loaded with 1.1 mm thick samples, without flux perturbation due to ^{10}B(n,α) reactions, and cooling with solely conduction to surrounding water. It yielded a maximum temperature around 65 °C [1], which low enough to avoid thermal effects on the vitreous structure. The fluence of irradiated samples was 7.9×10^{17} n/cm^2.

SANS measurements were done at the ILL D11 instrument [6, 7]. Beam wavelength was set to 6 Å and its diameter to 7 mm. The data shown in the result section comes from measurements acquired with the detector located at 1.5 m, 8 m and 20 m from the sample.

3 Results

The effects of thermal neutron irradiation on scattering intensity are reported in Fig. 1a, 1b, 1c, and 1d. One can observe that N-BK7 and S-BSL7 have similar trends while Borofloat and N-ZK7 exhibit noticeable features such as a broad intensity band around 0.08 Å^{-1} and a peak around 0.03 Å^{-1}, respectively. All materials, at low momentum transfer, show an intensity ramp that increases with decreasing Q.

On each plot, one can see the pristine and irradiated state intensities, and the ratio of them. For Borofloat, one can see a shift of the band toward higher momentum transfer. Concerning N-ZK7, the peak is also shifted to higher Q while the intensity of the low Q ramp is decreased. N-BK7 and S-BSL7



(a) Borofloat (b) N-ZK7 (c) N-BK7 (d) S-BSL7

Figure 1: SANS intensities.

	Borofloat	N-ZK7	N-BK7	S-BSL7
Pristine	3.54 ± 0.05	3.13 ± 0.02	3.67 ± 0.02	3.60 ± 0.02
Irradiated	3.95 ± 0.08	3.31 ± 0.03	4.25 ± 0.05	4.69 ± 0.02

Table 1: Exponential slopes derived at low-Q ($< 10^{-2}$ Å).

curves show a similar behavior: their intensity is decreased on the whole study range and appears to be more marked between 0.006 Å^{-1} and 0.1 Å^{-1}.

For Q-value below around 10^{-2} Å, the intensity curves of the different glasses in both states have been fitted with a power law function, $I(Q) = a \cdot Q^{-p} + b$. Where a stands for a scaling factor, p for the power law exponent, and b the background. The derived p parameters are gathered in Table 1. The SANS curve analysis mentioned in this work was done with the SASview software [8].

A Guinier fit was done for Borofloat on the broad intensity band around 0.08 Å^{-1} with a function $I(Q) = a \cdot \exp(\frac{-r_g^2 Q^2}{3}) + b$, where r_g is the gyration radius [9]. The analysis was done for $Q \in [3 \cdot 10^{-2}\ ;\ 30 \cdot 10^{-2}]$ Å^{-1}. It yielded a gyration radius of 13.5 ± 0.4 Å for the pristine state that decreases to 11.8 ± 0.3 Å after irradiation.

The peak position of N-ZK7 and its shift under irradiation was obtained by fitting the SANS signal with a Gaussian function between $16 \cdot 10^{-3}$ and $43 \cdot 10^{-3}$ Å^{-1}. It gave a peak around 0.0264 Å^{-1} before irradiation that drifts to 0.0272 Å^{-1} after, with associated uncertainties below $2 \cdot 10^{-5}$ Å^{-1}

4 Discussion

All glasses show a noticeable increase of the slope at low-Q. It indicates the conversion of surface-fractal interfaces into mass fractal. Considering measurements made on the same samples but in powder, the intensity in that region has considerably been reduces using solid samples [2]. Also, the fact that it is affected by irradiation means that it carries information on the vitreous "network" itself and not solely the surface. In a further study, using mirror polished sample should allow to diminish even more the signal coming from samples' surface.

N-BK7 and S-BSL7 SANS curves have a similar evolution under neutron flux. On the whole Q-range, the intensity decreases which could be related to an attenuation of the background. As noted in Table 1, the slope appears to increase of at least 15 % for both glasses when it is fitted by one function. However, one can remark an inflexion point around 0.008 Å^{-1}. From that one could support the use of two power laws to fit the curve. As an example, for irradiated N-BK7, it is possible to fit the data with a set of p parameters equal to 3.7 and 5.2 with a crossover location found around 0.007 Å^{-1}. Such an analysis would suggest that (n,$alpha$) reaction induce a coexistence of surface-fractal and mass-fractal interfaces. This type of feature may be hinted for Borofloat, from the slight curve infliction in the same Q-region, but is not at all seen for N-ZK7.

The SANS signal of Borofloat shows two remarkable features : the low-Q ramp, that corresponds to Porod's law, and the broad intensity band at higher Q, that corresponds to a Guinier regime. Due to its relatively low content in alkali, Borofloat's vitreous network is characterized by alkali-borate-rich areas intermingled with a silica-rich phase. The noticeable decrease under irradiation of the gyration radius from 13.5 ± 0.4 Å to 11.8 ± 0.3 Å could be related to the compaction of the silica-rich phase. Such a trend is usually detected through Raman spectroscopy [2] or diffraction technique [ref sur des mesures de D4]. It corresponds to an increase of three-members silicon rings at the expense of bigger structures.

A fit with a power law for $Q \geqslant 0.1$ Å yields a p parameter around 1.3. This corresponds to elongated structures [REF] which is what has been observed for glass of similar composition [10]. A fit using a cylindrical model was intended but without success to extract significant informations. However, it has to be noted that compared to a preceding study on Borofloat, the use of thin solid samples allowed to detect the existence of a Guinier regime. A deeper analysis could require even thinner samples, if technically possible, and different level of fluence. The later parameter should allow to validate, or not, if the variation of the gyration radius is related to the compaction of the silica-rich phase. Finally, one can notice that there is no significant decrease of intensity due to irradiation. This means that the phases detected before irradiation are not noticeably blended because of irradiation.

The remarkable feature for N-ZK7 is the structure peak located around 0.026 $Å^{-1}$ that shifts to a higher value due to irradiation. This signs the existence of aggregates and the peak position can be related to the distance between them. TEM imaging on that glass demonstrated the existence zinc-alkali-rich areas with spherical shape, typical diameter between 10 and 20 nm, and centre-to-centre distance between 20 and 30 nm. Application of Bragg's law on the structure peaks yields a distance between the aggregates of 23.8 nm and 23.0 nm before and after irradiation, respectively. Such dimensions are comparable with what has been obtained by TEM imaging.

One can notice a peak in the ratio curve around 0.09 $Å^{-1}$. However, since it corresponds to the junction between two detectors positions (1.5 and 8 m), as one can see from the change in binning density, that peak probably does not contain significant informations.

Considering the composition of N-ZK7, the silicon-boron phase separation should also feature a Guinier regime as it has been detected for Borofloat. However, considering the intensity and width of the broad structure peak, one can estimate that the Guinier regime could be hidden in the "high-Q tail" of the peak.

This study calls for the production of glasses with fixed boron-oxide content and variable alkali / silica ratio. There analysis by SANS could possibly show the disappearance of the Guinier feature that reveal the existence of phase segregation.

References

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