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High thermal neutron flux effects on structural and macroscopic properties of alkali-borosilicate glasses used as neutron guide substrate

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ABSTRACT

The behaviour of four alkali-borosilicate glasses under homogeneous thermal neutron irradiation has been studied. These materials are used for the manufacturing of neutron guides which are installed in most facilities as devices to transport neutrons from intense sources such as nuclear reactors or spallation sources up to scientific instruments. Several experimental techniques such as Raman, NMR, SANS and STEM have been employed in order to understand the rather different macroscopic behaviour under irradiation of materials that belong to a same glass family. The results have shown that the remarkable glass shrinking observed for neutron doses below $0.5 \cdot 10^{18}$ n/cm^2 critically depends upon the presence of domains where silicate and borate network do not mix.

1. Introduction

Neutron guides are optical components widely employed in large neutron facilities running either static sources such as a nuclear reactor or at accelerator-driven centres. The surge of such now widespread devices was motivated by two technical reasons, namely to allow the installation of more scientific instruments on a single source and to lower the background noise on instrument detectors. They are used to transport thermal or cold neutrons to experimental stations that can be positioned several tens of metres away from the neutron production point. They have enabled the technique to significantly widen its scope, allowing the development of a suite of instruments able to tackle problems pertaining to a wide spectrum of disciplines such as condensed matter, neutron and nuclear physics, chemistry, materials science and engineering, bio- and geosciences.

The guides are usually made of polished flat borosilicate glass coated with metallic nickel or some supermirror multilayer. The use of a boron-rich glass substrate fulfils two different purposes, first assuring the desired surface quality for the neutron reflecting material and also to absorb the neutrons that are not reflected by the mirror through (n, α) reactions on ^{10}B.

The motivation behind our efforts comes from episodes of neutron guide failures reported from different facilities [1–4]. Such failures usually result in breakup of the guide structure leading to an implosion due to loss of vacuum and the generation of a pressure wave which may transport relatively large guide debris at speeds of a few tens of metres per second, thus able to cause some significant damage. The issue is known since decades. In fact, the ILL had faced troubles with in-pile thermal-guide elements[1] as early as 1978, that is less than five years after their installation. At that time, Pyrex glass had been identified as the cause of failure and was then replaced by A8866 from Corning. Later, efforts have been focused onto the understanding of the irradiation ageing of neutron supermirrors [5,6]. Finally, the ILL restarted its investigations on this topic following guide early damages that took place on several of its beam lines (H113, H17 and H25).

The origin of these failure episodes was promptly ascribed to radiation damage effects on the glass substrate. Within those, radiation resulting from the capture reaction $^{10}B + n \rightarrow {}^{7}Li + \alpha$ was assumed to be the most deleterious [7]. For some 6% of the capture reactions, the decay proceeds to the ground state of ^{7}Li whereas the remaining 94% events decay via the excited state of ^{7}Li and are accompanied by emission of a 478 keV gamma ray. Conservation of energy and momentum gives values of 1.16 MeV for ^{7}Li and 1.78 MeV for the α particle for the ground state reaction and 0.84 MeV for ^{7}Li and 1.47 MeV for α particle generated by the gamma-ray accompanied reaction.

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[1] H1 and H2 systems.

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Both charged particles have high linear energy transfer and short range, hence deposit their kinetic energy locally within few tens of micrometers away from the point of capture. The macroscopic behaviour of this glasses under thermal neutron irradiation has been reported in a previous article [8]. Here, our aim is to describe the glass network evolution under thermal neutron flux and how it translates into changes of the macroscopic properties of the material.

2. Materials and methods

The four studied materials concern industry-grade alkali borosilicate glass 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 have been provided by different neutron guide manufacturers. As far as sample sizes are concerned, we have examined samples with typical dimensions $10 \times 10 \times 1.1$ mm. Chemical composition and density of those glasses have been gathered in Table 1.

The thermal neutron irradiations have been carried out in the T4 tube at ILL that provides an unperturbed flux of $2 \cdot 10^{13}$ n/s/cm^{-2}. Maximum sample temperature has been calculated to be about 65 °C. More details on the irradiation conditions are given in [8]. Table 2 summarises the irradiation characteristics and damages induced by the ^{10}B(n,α)^{7}Li reactions. Table 3 reports the five different neutron doses that the samples were exposed to and the associated damages estimated by SRIM [9].

A LabRAM HR800 spectrometer from Horiba with green laser (532 nm) was used for the Raman analysis at CEA-Marcoule. Specifically, the irradiated samples were analysed through an optical microscope (100× objective) in a hot cell of the ATALANTE facility which was coupled to the spectrometer through an optical fibre.

Table 1
Chemical composition and density of the studied glasses.

mol.%	Borofloat	N-ZK7	N-BK7	S-BSL7
SiO_2	82	66	73	73.5
B_2O_3	12	11.5	10	9.5
ZnO		10		
Al_2O_3	1.5	4	0.25	
MgO			1.25	
Na_2O	4	7.5	10	10
K_2O	0.5		5	5.5
CaO		1	0.25	
BaO			0.25	0.5
Density (g/cm^2)	2.20	2.47	2.491	2.50

Small Angle Neutron Scattering experiments were carried out at the D11 instrument of the ILL suite. In that case, pristine and irradiated samples were crushed into powder and used to fill 0.5 mm thick cells. This was done to increase the SANS intensity as 1.1 mm thick samples were too absorbent. Finally, single pulse MAS-NMR experiments were done on the pristine glasses with 400 MHz and 800 MHz Bruker spectrometer for ^{29}Si and ^{11}B respectively. The 800 MHz measurements were made possible thanks to the TGIR-RMN-THC program. Details concerning the experimental parameters are reported in Table 4.

3. Results

3.1. Pristine glasses

The Raman signals of the four pristine glasses are plotted in Fig. 1a. From the Fig. 1a one can see that the materials are split into two well differentiated groups. On one hand, Borofloat and N-ZK7 show Raman spectra with features characteristic of silica and borate glasses [10] [11]. Specifically, the Si–O–Si rocking and bending vibration band (named R band) position is very close to the one of silica glass [12]. Moreover the spectral region of Si–O stretching vibration between 850 and 1200 cm^{-1} is also very similar to silica spectra with mainly two bands at 1060 and 1200 cm^{-1}. Moreover a large band is observed in the region between 750 and 810 cm^{-1}, with mainly two contributions at around 770 and 810 cm^{-1} which is characteristic of borate glasses. The first contribution is generally assigned to diborate units, a borate ring with boron in three and four fold coordination. The second contribution is generally assigned to boroxol rings, boron only in trigonal configuration [10] [13]. On the other hand, N-BK7 and S-BSL7 show Raman spectra features characteristic of borosilicate glass with a good mixing of borate and silicate units. R-band is located at higher Raman shift (around 506 cm^{-1}) and the borate bands are less intense. In addition, one can notice the existence of a strong peak around 630 cm^{-1} that has been associated [14–16] to structures close to reedmergnerite or danburite crystals composed of ring of boron and silicon tetrahedra.

The ^{11}B and ^{29}Si MAS-NMR spectra are reported in Fig. 2a and b respectively. The measurement of ^{11}B MAS-NMR signal with an intense magnetic field (18.8 T) gives a clear splitting of the BO_3 triangles and BO_4 tetrahedra contribution around 12 ppm and −2 ppm respectively. The number of fourfold coordinated boron atoms (N4) can be directly calculated by the integration and ratio of the two peaks [17]. The value for the N4 parameter has been calculated for the different glasses and is reported in Table 5. Looking at the low chemical shift, one can see in the Borofloat ^{11}B spectra

Table 2
Informations on thermal neutron irradiation in T4 tube (ILL) and damages induced by ^{10}B(n, α)^{7}Li. Perturbed flux measured by in situ zirconium foil activation.

$\phi_{unperturbed}$ (n/cm^2/s)	$\phi_{perturbed}$ (n/cm^2/s)	Maximum temperature °C	α Particle		Li ion recoil nuclei	
			Displaced atoms (ion^{-1})	Range (μm)	Displaced atoms (ion^{-1})	Range (μm)
$2 \cdot 10^{13}$	$7 \cdot 10^{12}$	65	160	4.5–5	400	2.4–2.6

Table 3
Thermal neutron irradiation doses and corresponding deposited energy by ionisation and nuclear interactions.

Dose number	F1	F2	F3	F4	F5
Fluence (n/cm^2)	$1.3 \cdot 10^{17}$	$2.9 \cdot 10^{17}$	$3.9 \cdot 10^{17}$	$7.6 \cdot 10^{17}$	$2.2 \cdot 10^{18}$
(n, α) reactions (/cm^3)	$5.1 \cdot 10^{17}$	$1.1 \cdot 10^{18}$	$1.5 \cdot 10^{18}$	$3.0 \cdot 10^{18}$	$8.7 \cdot 10^{18}$
$E_{ioniz.}$ (keV/cm^3)	$1.2 \cdot 10^{21}$	$2.6 \cdot 10^{21}$	$3.5 \cdot 10^{21}$	$6.9 \cdot 10^{21}$	$2.0 \cdot 10^{22}$
$E_{nucl.}$ (keV/cm^3)	$1.7 \cdot 10^{19}$	$3.8 \cdot 10^{19}$	$5.1 \cdot 10^{19}$	$1.0 \cdot 10^{20}$	$2.9 \cdot 10^{20}$
dpa	0.0041	0.0091	0.012	0.024	0.070