Structure of glasses for $^3$He neutron spin filter cells

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Abstract. In spin-exchange optical pumping, there is unknown excess relaxation, called the $X$-factor, that limits attainable $^3$He polarization. It is known that the $X$-factor depends on the glass containers. Hence, it is expected that there are cell-to-cell variations in microscopic structure among the cells and that these variations affect the attainable $^3$He polarization. However, microscopic structure of the glasses for $^3$He neutron spin filters has not been clarified yet. In this paper, we have performed precise X-ray diffraction measurements for the glasses at SPring-8 using synchrotron radiation. The structural differences are observed between several types of glasses, and also, between the GE180 glass pieces with different thermal treatment. Based on the results, the structural influence on the performance of $^3$He neutron spin filters is discussed.

1. Introduction

Polarized $^3$He neutron spin filters have attracted much attention as polarizing neutron devices for polarized neutron scattering experiments because of their wide coverage in neutron energy range and large acceptance in solid-angles. Due to the recent progress in the high $^3$He polarization technique, they are now used as one of the options at neutron instruments in several neutron scattering facilities [1]. Spin-exchange optical pumping (SEOP) is one of the methods to polarize $^3$He gas and its polarization can now reach about 80% [2-4]. From an application point of view, it is desired to obtain much higher $^3$He polarization. However, the attainable polarization seems to be saturated at about 80%. In recent studies on the SEOP, it is reported that there is an unknown excess relaxation, called the X factor, that scales linear with alkali-metal density limiting the attainable $^3$He polarization to $P_{^3\text{He}}<1/(1+X)$ [2, 5]. According to a number of measurements, the X factor
has surface to volume dependence that varies greatly from cell to cell [2]. Considering this fact, the microstructure of the glass cell could be an important parameter to help understand the nature of the X factor, although there could be other factors influencing the X factor such as purity of rubidium and cleanliness of the cell. In addition, it is empirically pointed that reblown glass has typically yielded the longest relaxation times [5, 6]. This can also support that the micro-structural difference affects the $^3$He polarization. Probably, subtle differences in the glass fabrication process leads to a structural difference in the glass cells. However, as far as we know, there has been no prior study to show such differences from a microscopic point of view. Recently, we have performed X-ray diffraction measurements of glasses used for $^3$He neutron spin filters, including GE180 [7]. GE180 is an aluminosilicate glass that is regarded as the most suitable material for SEOP cells. In this work we found that there could be a structural differences between GE180 pieces with different thermal treatments [8], but we could not make definite conclusions because of the accuracy of the measurements. In this paper, we have measured X-ray diffraction for several glasses for $^3$He neutron spin filters using synchrotron radiation at SPring-8. Based on the results, the structural difference in the glasses is discussed.

2. Experimental
The high-energy X-ray diffraction experiments were carried out at the bending magnet beamline, BL04B2 [9] of SPring-8 with a two-axis diffractometer for disordered materials [10]. The incident photon energy of 61.7 keV, which was obtained from a bent Si (220) crystal, was used for the experiment. The measurements were performed in transmission geometry.

The samples that we measured are as follows; (1) vitreous silica, (2) BOROFLOAT [11], which is borosilicate glass and corresponds to Pyrex produced by Corning (3) GE180 and (4) PS-94 [12]. PS-94 is a lead-free glass and does not contain boron. Therefore, we thought that PS-94 could be a possible substitution for GE180. For the GE180 glass samples, we prepared four pieces with different thermal treatments; (1) a glass piece obtained from a glass tube after purchasing with no treatment (tube) (2) a blown GE180 glass piece, which was prepared for $^3$He neutron spin filters and annealed at 780 °C for 30 min (blown) (3) a GE180 plate, which was molten and solidified in a mould and annealed at 750 °C for 20 min (plate, annealed). (4) a GE180 plate, which was molten and solidified in a mould, but without annealing (plate, not annealed).

3. Results and discussion
3.1. Structure factor
Fig. 1 shows the structure factor, $S(Q)$, for several types of glasses. We could obtain the structure factor in the $Q$-range from 0.16 Å$^{-1}$ to 25.3 Å$^{-1}$ with good accuracy; in previous measurements using an in-house X-ray diffractometer, the covered $Q$-range was from 0.4 Å$^{-1}$ to 7.0 Å$^{-1}$ and we could only observe the first peak and the other peaks could not be recognized. Comparing the data of GE180 with other three glasses, the features at 2.9 Å$^{-1}$ and 6.5 Å$^{-1}$ are clearly different. This could be a sign of the appearance of a new local structural order produced by the addition of other elements such as aluminium to the original SiO$_2$ matrix. As seen in Fig. 1(b), a difference in the position of the first sharp diffraction peak (FSDP) is also observed. This is consistent with our previous result [8]. The FSDP indicates the presence of a medium-range order with about 4.2 Å (for $Q$=1.5 Å$^{-1}$) and it is interpreted as an indicative peak of either the cages formed by the topological connection of tetrahedral Si(O$_{1.5}$)$_4$ units [13] or voids [14]. Assuming the void model, the peak position indicates the size of the microscopic holes. Such holes are responsible for helium permeation that can cause $^3$He depolarization [15]. Since the FSDP position of GE180 is higher ($Q$=1.87 Å$^{-1}$) than that of vitreous silica ($Q$=1.53 Å$^{-1}$), the helium permeation constant of GE180 is expected to be less than that of vitreous silica. Also, the FSDP position of PS-94 ($Q$=1.96 Å$^{-1}$) is higher than that of vitreous silica. As far as the size of microscopic holes is concerned, PS-94 seems to be suitable for $^3$He neutron spin filter cells.
In Fig. 2, the correlation between the position of FSDP and helium permeation velocity constant, $K$, at 100 °C [16] is shown. To plot the point of borosilicate, the FSDP position of BOROFLOAT and the helium permeation velocity constant of Pyrex are used. To plot the point of aluminosilicate, the FSDP position of GE180 and the helium permeation velocity constant of Corning 1720 are used [17]. This good correlation confirms our expectation that the position of the FSDP indicates the size of the microscopic holes in the glass network.

**Figure 1.** Structure factor, $S(Q)$, for several types of glasses. (a) $S(Q)$ measured over the whole $Q$-range (b) $S(Q)$ in the range from $Q=0.5-3.0$ Å$^{-1}$.

**Figure 2.** Correlation between the position of the FSDP and helium permeation velocity constant at 100 °C [16].
Fig. 3 shows the structure factor for several GE180 pieces with different thermal treatment. The curves almost overlap each other. However, the feature of blown GE180 is a little bit different from the others; a decrease in intensity from 5 to 17 Å\(^{-1}\) and a difference in symmetry of the peak at 20 Å\(^{-1}\). Such change would be related to the changes in the short-range order, rather than the medium range. In the previous measurement, we have pointed out that the position of the FSDP can be different among those GE180 pieces. However, we could not find a clear difference in the position in the present work as shown in the inset.

![Structure factor, S(Q), for several GE180 pieces with different thermal treatment.](image)

**Figure 3.** Structure factor, \(S(Q)\), for several GE180 pieces with different thermal treatment.

![Pair distribution functions, g(r), of several types of glasses.](image)

**Figure 4.** Pair distribution functions, \(g(r)\), of several types of glasses.
3.2. **Pair distribution functions**

Fig. 4 shows the pair distribution functions, \( g(r) \), for several types of glasses. The peaks from the first to the fifth for vitreous silica are related to the first Si-O bond, the first O-O bond, the first Si-Si bond, the second Si-O bond and the second O-O bond, respectively. The peak positions are consistent with previously measured results for vitreous silica [18]. For BOROFLOAT and PS-94, the positions of the first, the second and the third peaks are basically the same as that for vitreous silica. This means that the network structure composed of Si-O bonds is preserved and the constitutional unit of Si(O\(_4\))\(_{1/2}\) tetrahedron is also preserved in the glasses. For GE180, the first peak is a little bit asymmetrical and it is considered that a new peak appeared at the longer-\( r \) side, which is attributed to Al-O bonds [19]. From double-Gaussian fitting, the position was estimated to be 1.74 Å. Although the positions of the second and the third peaks are not exactly the same as those for vitreous silica, the structure of Si(O\(_4\))\(_{1/2}\) tetrahedral unit is supposed to be preserved in GE180. The difference in this region would arise from appearance of new local order due to the addition of other element like aluminium.

![Figure 4. Pair distribution functions, \( g(r) \), for several types of glasses.](image)

**Figure 5.** Pair distribution functions, \( g(r) \), of several GE180 glass pieces.

Fig. 5 shows the pair distribution functions, \( g(r) \), for several GE180 pieces with different thermal treatment. The position and the height of the first peak are almost the same among the four GE180 glass pieces. However, there is a clear difference in the second and the third peaks between the blown GE180 glass piece and the others; the second and the third peaks for the blown GE180 piece are more broadened. This indicates that the bond angles of Si-O-Si and O-Si-O in the blown glass are more widely distributed than the others, in other words, the tetrahedral units are more distorted from perfect tetrahedron in the blown GE180 glass. The increase of such structural randomness by the blowing process is plausible because external force was applied in molten condition (mobile for atoms) and the more disordered status was quenched. As the FSDP result in Fig. 3 indicates, the average size of the microscopic holes is considered to be almost the same. Interestingly, these situations are very similar to those in high temperature vitreous SiO\(_2\) [20]. In the real space, the first peak does not change and the second peak decreases. In \( Q \)-space, the FSDP does not change. From the similarities, the structure of blown GE180 glass can be
Regarded as a quenched state with more disordered structure in the molten state. Considering the cages, which are frameworks of microscopic holes, two different cages are orthogonally linked and centred at the Si atom in one tetrahedral Si(O₁/₂)₄ unit. When the bond angles become flexible the angles between the two cages also become flexible. This will lead to more complicated three-dimensional arrangement of the cages in the glass. Hence, it is expected that helium atoms do not pass through the microscopic holes as easily, and that the local helium permeation near the glass surface is suppressed.

3.3. Structural consideration on ³He neutron spin filter cells

In order to find what the unknown excess relaxation process is, it would be helpful to perform a study on the worst scenario because the changes due to the process would be maximized there. Among the glasses used for ³He spin filters, vitreous silica is known as a glass with high X factor [2], in which the excess relaxation is greatly affected. For such vitreous silica cells, Ino et al. have obtained long relaxation time close to the dipole-dipole limit [21] using the blown cells [22]. We infer that similar situation occurs in vitreous silica to that in GE180; helium permeation is decreased by blowing the glass and the situation must have minimized the influence of magnetic impurities in the glass. During optical pumping, there should be a different process. Because of the size of the microscopic holes, helium atoms can permeate the glass while rubidium atoms cannot. In this situation, unpolarized helium atoms in the glass do not have a chance to polarize by colliding with polarized rubidium atoms. Presence of such unpolarized helium atoms would limit the attainable ³He polarization. Actually, the vitreous silica cells, which have large microscopic holes, have lower attainable ³He polarization [22-24].

In the present study, it was found that blown GE180 glass has more disordered structure. From the result, we inferred that the local helium permeation near the glass surface is suppressed. This could work to reduce the content of helium atoms which do not have a chance to collide with polarized rubidium atoms, and hence to get higher attainable ³He polarization. Such possibilities have to be examined by further analysis on the structure of the glasses used for ³He spin filters.

4. Summary

We have performed precise X-ray diffraction measurement of several glasses for ³He neutron spin filter cells using synchrotron radiation in SPring-8. From the measurement, it was found that the FSDP can be a good measure to estimate the size of microscopic holes through which helium atoms can pass. More disordered structure has been observed in blown GE180 glass. This structural change would give rise to the decrease in the local helium permeation near the glass surface, and thus, lead to higher ³He polarization and longer relaxation times. The empirical finding that blown GE180 glass had typically yielded the longest relaxation times is considered to be related to such microscopic structural changes.

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