Electron Energy Loss Spectra from Silica Glass Optical Fibers

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Abstract

To investigate the possible structural differences between silica glass fibers and bulk silica glasses, electron energy loss spectroscopy (EELS) has been used to study the short-range and medium-range structures of both forms of silica glasses. The short-range structure of silica glass, such as the coordination and symmetry, was investigated by the energy loss near edge structure (ELNES) of Si $L_{2,3}$-edges. The ordering structure in the medium-range was analyzed by the exponential optical absorption edge also known as the Urbach edge of the glasses. The optical absorption data were obtained

from the low energy loss spectrum of EELS through Kramers-Kronig analysis. The results show that silica fiber has the same short-range structure as the bulk specimen, but is significantly more disordered than the bulk glasses.

1. Introduction

Glass in the form of fibers is known to have physical properties that differ substantially from those of more massive specimens of glass. It is characteristic of fiber to yield very high values of strength and much less brittle than bulk glass specimens. Strength values higher than 10 GPa on some silica fibers were reported.[1,2] Besides silica fiber, other types of fibers, such as E-glass fiber with extremely high tensile strength were also reported.[3] In contrast, for all bulk vitreous silica specimens, the measured strength is in the range from 15 to 150 MPa, which is several orders of magnitude lower than that of fibers.[4] The high strength of glass fiber is generally explained by Griffith's paper.[5] Griffith assumed the presence of tiny cracks or other flaws in the glasses. The true fracture stress is actually reached in a very small

volume of the specimen while the mean stress may remain very low. Griffith also explained that the dangerous cracks of glasses are at the surface. Therefore, the strength begins to rise rapidly when the diameters of the fibers are reduced because of the reducing surface area of thin fibers.

Although many researchers have attempted to prove the difference of strength between the bulk glass and fibers in terms of Griffith's concept, evidences contradicting Griffith's concept have been reported. For example, experimental works of Otto and Thomas showed when fibers with different diameters are formed under controlled nearly identical conditions, the tensile breaking strength of glass fibers is identical, and there is no significant effect of the diameter of fibers.[6,7] Otto's experiments also showed that the strength of the fibers is associated with the forming conditions of fibers. For fibers formed at different temperatures, but with a constant diameter, the tensile strength of the fibers increases with the forming temperature. Since the internal structures of materials are dependent on the thermal forming processes, these results imply that the strength difference between bulk glasses and fibers might be caused by the difference in their internal structures. For crystalline materials, the structural differences caused by

temperature can be conveniently studied by X-ray or electron diffraction techniques. However, to study the structure of glasses, conventional diffraction techniques are not very useful. This is because the long-range structure of glasses is entirely random, and the diffraction patterns of the silica glasses have no sharp peak and contain only a broad band. More than 60 years after the works of Otto and Thomas, the difference of the internal structures of fibers from that of bulk glasses remains unrevealed.

The purpose of this work is to investigate the possible structural differences between the optical fibers and the bulk silica specimens, using Electron Energy Loss Spectroscopy (EELS). EELS is one important analytical tool of modern transmission electron microscopy (TEM). EELS can be used for quantitative chemical microanalysis, also for studying the local atomic, chemical, and electronic structures.[8,9] By comparing EELS data obtained from silica fibers with that from bulk silica, the internal structure character of the fiber may be identified. The result is expected to improve the current understanding of the mechanical properties of glasses and the processes of producing glasses with better mechanical properties.

2. Fiber and bulk silica glass specimens

The silica glass fibers used in this study were purchased from Beyondtech®. They are single-mode optical fibers with a 125 μm diameter. The outer layer of the fibers is pure silica glass, and the 10 μm in diameter core is doped with Ge. Figure 1 shows a silica fiber bent as a circlet with a diameter of 2 cm. The coating layers of the silica fiber in Fig. 1 have been removed except at the left end of the fiber. The ability to form such a circle without breaking is evidence that the glass fiber is more flexible than a bulk glass. For comparison, the bulk glass used for this study is a high purity silica glass containing less 1 ppm OH and 1000 ppb other impurities.[10]

The bulk glass specimens for EELS study were prepared by the ion mill method for TEM observation. The samples were polished to about 10 μm in thickness by mechanical polishing and dimpling. Final thinning to electron transparency was carried out using a Gatan PIPS2 ion mill. The acceleration voltage of the ion beam was 6 kV with final thinning at 3 kV at 7° incident angle. The specimens were coated with a thin carbon layer in a vacuum chamber to minimize charging during EELS study. However, to prepare fiber specimens, additional procedures had to be employed. The optical fiber was

cut to 2 mm long after removing all coating materials outside the fiber. Several pieces of the short fibers were parallelly glued on a slot TEM grid by M-bond before mechanical polishing. Figure 2 is an image of a prepared fiber specimen used in this study.

3. EELS measurements

The EELS measurements were carried out using a 200 kV field emission TEM (FEI Tecnai F20) equipped with a Gatan imaging filter (GIF). The energy resolution, measured by the FWHM of the zero-loss peak, was about 0.6 eV. Prior to the EELS measurement, the samples were examined on a CM200 microscope equipped with an ultra-thin window X-ray detector for microchemical analysis. The EDS data show that the outer layer of the optical fiber and the bulk specimens are formed from Si and O without other detectable elements. It has been reported that the structure on the surface layer as well as in the subsurface layer might be different from the internal structure of the glasses.[11,12] In this study, data were taken from the specimens, which are at least a few μm away from the surface of the sample. Both energy loss near edge spectrum (ELNES) and the low energy loss spectrum were

analyzed. ELNES is the intensity fluctuation on the core loss absorption edge above the onset and is sensitive to the local atomic environment in the specimens. ELNES analysis has been successfully used to study the coordination and valence states of elements in glasses.[13-15] This study compares the ELNES profiles of fibers with that of bulk specimens. For improving the signal to background ratio of the energy loss edges, the EELS data were acquired with the microscope in the diffraction mode. The background of the near edge spectra was removed from each energy loss edge by fitted a power law to the pre-edge region in the form of AE^{-r}.[8] The core loss spectra were not deconvoluted to remove contributions of multiple energy losses, because the multiple scattering does not have a considerable influence on the ELNES in the region of interest, i.e. 0-15 eV, above the threshold energy.[15]

For the low energy loss measurements, the intensities of signals are orders of magnitude higher than that of the core loss, and the microscope was in the image mode. Previous studies show that the optical absorption coefficient α in the energy range 0-40 eV can be obtained from low loss EELS data by Kramers-Kronig (K-K) analysis.[10] Silica glass has a wide bandgap near 10 eV.

In the energy range from 8 to 10 eV, the relation of the optical absorption to the energy is exponential. Such an exponential absorption edge was given the name of the Urbach edge after the scientist who first observed it in the transmission spectra of silver and alkali halides.[16] The parameter of the Urbach edge is the logarithmic slope of the absorption coefficient in the Urbach region and is influenced by the average structural disorder of the specimen.[17,18] Thus, the investigation of the slopes of Urbach edges of fibers and bulk glass can reveal the difference in their ordering structure. The details of the theory of the measurements can be found in references.[10,19] The procedures of finding the slope of Urbach edge from the EELS are outlined in the following figures. Figure 3(a) is a raw EELS spectrum over the range 0-40 eV, taken from a bulk specimen. Fourier-log deconvolution is then used to remove the multiple scattering contributions from the raw EELS spectrum. The result is the single scattering profile of the spectrum, as shown in Fig. 3(b). Next, the surface contribution is removed from the spectrum and K-K analysis is applied to yield the optical absorption coefficient, α, as a function of energy, shown in Fig. 3(c). From Fig. 3(c), $\ln(\alpha)$ as a function of energy

can be easily calculated and should be a straight line. The slope of the straight line is the slope of the Urbach edge by definition.

4. Results

(1) ELNES study

Figure 4(a) shows Si $L_{2,3}$-edges taken from fiber specimens after removing the background. In the near edge region of the Si $L_{2,3}$-edges, two major peaks located at about 108 eV and 115 eV are clearly observed. On the left side of the peak of 108 eV, there is a recognizable shoulder at 106 eV. All features, shown in Fig. 4(a), including the intensities and the energy distances of the peaks, are similar to those of bulk specimens. For comparing, Fig. 4(b) shows the Si $L_{2,3}$-edges obtained from the bulk silica specimen. Both profiles shown in Figs. 4(a) and 4(b) are the same as the published data for silica.[20] In addition, the ELNES of the O K-edge and the Si K-edge obtained from fiber specimens were also recorded and are shown in Fig. 4(c) and Fig. 4(d), respectively. Again, the profiles shown in Figs. 4(c) and 4(d) are identical with corresponding spectra obtained from bulk specimens.[20]

(2) Low energy loss study

Following the procedures described in section 3 and as demonstrated by Figs. 3(a), 3(b) and 3(c), the optical absorption coefficient as a function of energy were obtained for both fiber and bulk specimens. As shown in Fig. 3(c), the bandgap energy of silica glass is located around 10 eV, at which the slope changes abruptly.[10] To determine the slope of the Urbach absorption edge, the relation of ln(α) versus E in the energy range of 8-10 eV was calculated from obtained data of α versus E. The relationship between ln(α) and E is expected to be linear.[10] Figures. 5(a) and 5(b) are those results for the fibers and the bulk samples, respectively. For convenience to compare, Fig. 5(c) places both natural logarithm of the Urbach absorption edges of the bulk and the fiber in the same graph. In Fig. 5(c), the slope of the low line for fibers is not as high as that of the above line for the bulk specimen. Simple calculations of the slopes in the energy range from 8.5 eV to 9.5 eV reveal a slope of 1.05±0.05/eV for the fiber and a slope of 1.30±0.05/eV for the bulk specimen.

5. Discussion and conclusion

The results of the ELNES study show that the fibers and bulk glasses have the same short-range structure, described by the Zachariasen's continuous random

network theory (CRN).[21,22] According to CRN theory, Si and O atoms of the silica glass form a nearly perfect SiO_4 tetrahedron that serves as the basic building block for the silica network.

Although there is no short-range structure difference identified between the fibers and bulk specimens, the difference in the medium-range structure is evidenced by the results of the low energy loss study. The slope of the Urbach edge is known to be inversely related to the structural disorder in the medium-range.[17,18] The measured slope of the Urbach edge for fiber being 1.05±0.05/eV is significantly lower than that for the bulk sample in this study. This result means the degree of structural disorder of the fiber is much higher than that of the compared bulk specimen. From the published data, the slopes of the Urbach edge of bulk silica glasses vary in the range from 1.15±0.05/eV to 1.40±0.05/eV depending on the fictive temperature of the specimens.[10] The sample with the highest fictive temperature of 1500 °C has the lowest Urbach edge slope of 1.15±0.05/eV. Since the slope of the Urbach edge of fiber is even lower than 1.15±0.05/eV, the fictive temperature of the fiber is expected to be higher than 1500 °C. Due to the small diameter of the fiber and extremely fast cooling from its surface to the inside, the fibers have a very

high fictive temperature, which, in turn, avoid the formation of a large amount of ordering structures.

The question of whether surface defects or internal structure play a significant role in the high strength of fibers has been debated for a long time. This study provides experimental evidence supporting the idea that the internal medium-range structure is the key to the high fiber strength rather than the lack of surface defects. To fully understand the question, a reliable model of the medium-range structure of silica glass is needed. In the past, several models of the medium-range structure of silica glass have been proposed; however, none of the models has been yet widely accepted by the glass science community.[23,24] Finding the exact medium-range structure in the silica glass and explaining the different properties between fibers and bulk glass from their structural differences remains a major challenge.

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Captions:

Figure 1. Silica fiber bent as a circlet with a diameter of 2 cm. The coating layers of the silica fiber have been removed except at the left end of the fiber.

Figure 2. A prepared fiber specimen used in EELS study. The fibers, M-bond and the TEM grid are indicated by arrows.

Figure 3. The procedures of finding the slope of the Urbach edge from EELS data. 3(a) The raw EELS spectrum over the range 0-40 eV. 3(b) The single scattering profile of the spectrum after applying the Fourier-log deconvolution to remove the multiple scattering contributions from the raw EELS spectrum. 3(c) The optical absorption coefficient, α, as a function of energy, yielded by the K-K analysis.

Figure 4. ELNES results. 4(a) The Si $L_{2,3}$-edges taken from the fiber specimen after removing the background. 4(b) The Si $L_{2,3}$-edges obtained from the bulk silica specimen. 4(c) The O K-edge from the fiber specimen. 4(d) The Si K-edge from the fiber specimen.

Figure 5. $\ln(\alpha)$ versus energy (a) for fiber sample, (b) for bulk sample. (c) Data of both bulk and fiber samples in the same figure. The slope for the fiber is 1.05/eV, and for the bulk specimen is 1.30/eV.