Study of GeO₂ addition in silica-germania glasses by XAS

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Introduction

Silica-germania (SiO₂-GeO₂) glasses have been widely used in photonics, such as optical fibers, waveguides, sensors, and second-order optical nonlinearity devices. Structural inhomogeneities and Gerelated defects, that play a key role in silica-germania properties, strongly depend on the synthesis method and process conditions [1]. In the present study the local structure of the silica-germania preform samples with GeO2 content in the range 7.9 to 25.8 wt% were investigated by XANES and EXAFS methods.

Method

Silica-germania preforms were prepared by vaporphase axial deposition (VAD) technique at the Laboratory of Photonic Materials & Devices, UNICAMP. Nanoparticles synthesis was performed by oxidation and hydrolysis of silicon and germanium tetrachlorides for deposition of nanoporous soot preforms. Completely clear and bubble-free preforms are obtained after thermo-chemical treatments [2].

 GeO_2 concentration was in the range 7.9 to 25.8 wt. %. For the standard sample, the germanium dioxide powder (quartz-like GeO₂, Aldrich, 99.999%) was used.

The XAS spectra at the Ge K-edge were recorded in transmission mode at Photon Factory, BL-12C beamline equipped with a Si(111) double-crystal monochromator. The data analysis was performed with the Athena and Artemis software, based on FEFF programs.

Results and discussion

In Figure 1, the oscillation shapes and energy positions of XANES spectra of silica-germania samples containing 7.9, 10.9, 18.3, and 25.8 wt. % GeO₂ present a good similarity with the standard sample. This result suggests the occurrence of tetrahedral geometry around Ge (IV), that means a quartz-like GeO₂ structure. The A, B and C peaks correspond to the multiple scattering of the photoelectron within the tetrahedron of the standard sample [3].

The results of silica-germania samples show something smeared out A peaks, represented by the A' peaks, while the C peaks are just smoothed, represented by C' peaks, indicating that their structures are tetrahedral at short range distance despite of the amount of GeO_2 .



Figure 1. Ge Kedge Xanes spectra of SiO_2 -GeO₂: (SS) standard sample; (S1) sample with 7.9; (S2) 10.9; (S3) 18.3; (S4) 25.8 wt. % GeO₂.



Figure 2. Back Fourier transform magnitude EXAFS spectra for (dashed line) fitting, and (solid line) sample with 25.8 wt. % GeO₂.

By using EXAFS oscillations, the estimated Ge-O distance for standard sample was 1.73 Å, with coordination number 4.07 \pm 0.32. For other samples, the Ge-O distance was 1.72 Å with coordination number between 4.44 to 4.55 \pm 0.25. The Ge tetrahedral coordination did not change even for samples with high concentration of GeO₂, according to XANES results.

References

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