Can electron energy-loss spectroscopy measure the local structure of germanate glasses?

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Ge is four-fold coordinated in pure GeO_2 glass. Unlike silica SiO_2, the addition of cations, e.g. alkali, converts some four-fold Ge to six-fold coordination, rather than creating non-bridging oxygen (NBO). Only beyond a certain amount are NBOs formed. Various techniques have been used to study the coordination number of Ge in germanate glasses, including x-ray near-edge structure (XANES). Can its electron counterpart, electron energy-loss near-edge structure (ELNES) also be applied to the germanate glasses? As we known, germanate glasses are extremely susceptible to electron irradiation. Several seconds of irradiation under normal operating conditions in a transmission electron microscope (TEM) can precipitate Ge nano-particles in GeO_2 glass [1]. Therefore, the use of O K edge ELNES or higher-energy edges is prohibited for damage-free spectra. We have therefore used the lower-energy Ge M_{45} edge at ~30eV, whose acquisition time can be milliseconds, rather than seconds. However, the interpretation of low-energy core-edge-loss spectrum is more complicated than the O K edge, due to the dispersion of the initial electronic states.

To test this idea, we compare the Ge M_{45} ELNES of the crystalline and glassy forms of GeO_2. It is known that GeO_2 is polymorphic. At room temperature, crystalline GeO_2 has the stable rutile structure, in which Ge is six-fold coordinated. In the melt, Ge is four-fold coordinated. When the melt is quenched to glass, the four-fold local structure is retained. Figure 1 shows a comparison. The most significant difference is the shape of peak B at ~38.1eV. In the $[GeO_6]$ form, this peak, relative to peaks C (~41.2eV) and D (~44.3eV), is much higher than that in the $[GeO_4]$ form. Time-resolved EELS also reveals that peak B gradually decreases along with the gradual transition from rutile GeO_2 to the amorphous form by electron irradiation. Another notable difference is the shape and position of peak A. In the $[GeO_6]$ form, it is only step-like at ~34.8eV, while it becomes a clear small peak, peaking at ~34.2eV in the $[GeO_4]$ form. (Energy-resolution of spectrometer is 0.9eV.) Can these differences be used as "fingerprints" for four- and six-fold Ge, and what is the reason for the differences?

To answer these questions, we carried out simulations of the Ge M_5 edge in three GeO_2 polymorphs: rutile $[GeO_6]$, α- and β-quartz $[GeO_4]$. The latter two give very similar results and thus only the results of α-quartz are compared with rutile GeO_2 in figure 2. The most striking difference is that peak B is much higher in the rutile-GeO_2 than that in the quartz-GeO_2. Compared with experimental data, the simulation for quartz-GeO2 fits experimental data for glassy GeO_2 very well; both peak positions and their relative intensities have been reproduced. However, peaks C and D in the rutile-GeO_2 are not reproduced in the calculation. One reason may be that the experimental spectrum may not be "purely" from the rutile-GeO_2. An amount of amorphous GeO_2 may already be induced by irradiation even though the irradiation time was only a fraction of a second. Thus, peaks C and D in the rutile-GeO_2 could be from amorphous-GeO_2. Nevertheless, the shape and intensity of peak B can be used as a "fingerprint" to identify the coordination of Ge in the germanate glasses.

The experiments used a 200kV JOEL 2010 TEM, equipped with field emission gun and Gatan EELS system. All spectra were deconvoluted using the Fourier-log method to eliminate plural scattering. The backgrounds were fitted using a power-law function, and subtracted from the original data. The calculations were carried out using FEFF8, based on multiple scattering theory using self-consistent muffin-tin potentials. The core hole effect was included using the "frozen" core hoe approximation. Supported by NSF DMR 0245702

References:

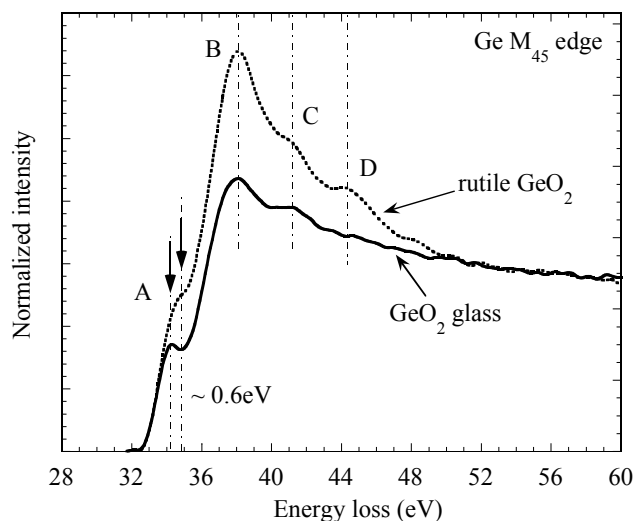[1] N. Jiang, J. Qiu, and J. C. H. Spence, Appl. Phys. Lett. 86, 143112 (2005).

Figure 1 Comparison of experimental Ge M_{45} edge ELNES between rutile- and glassy GeO_2. Two spectra were normalized to the intensities between 50 and 60eV. The vertical chained lines are guide for eyes, indicating peak positions.
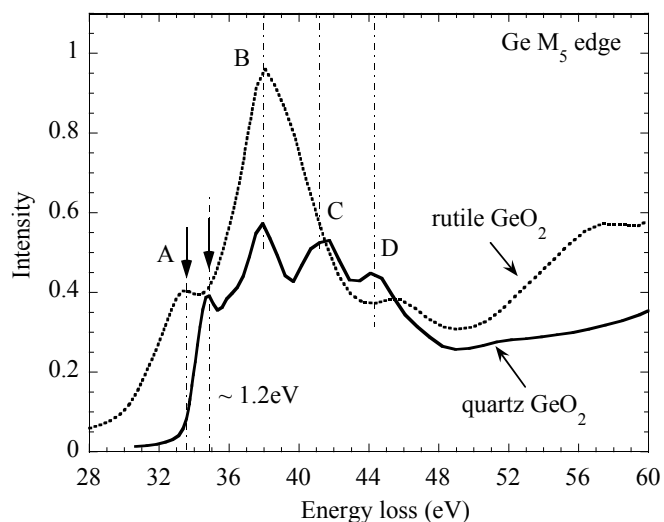

Figure 2 Comparison of calculated Ge M_5 edge ELNES between rutile- and glassy GeO_2. The calculated spectra are aligned to the position of peak B. The vertical chained lines are guide for eyes, indicating peak positions.