Supplementary information

Details on EELS microanalysis

Spectra used to perform EELS microanalysis were acquired in image mode (convergence and collection angle of 0.1 and 20 mrad, respectively) and the obtained information were relative to the zone defined by the superposition of the circular spectrometer aperture (2 mm of diameter) and the image. Using this configuration, the size of the analyzed zone depends on the magnification and can be easily varied.

The edge detection was defined by the minimum permissible signal/noise (S/N) ratio as 3, corresponding to 98% certainty for detection of the element. [1]

Spectral processing for the estimation of the atomic ratios was performed according to the Egerton procedure. [2] In order to calculate the atomic ratio, the following relation was used:

$$\frac{N_x}{N_y} = \frac{S_x(\alpha, \Delta)\, \sigma_y(\alpha, \Delta)}{S_y(\alpha, \Delta)\, \sigma_x(\alpha, \Delta)} \qquad (2)$$

where S_X is the integrated core edge intensity for element x in an energy window Δ, with a collecting angle α and σ_X, σ_Y are the ionization cross-sections calculated from the hydrogenic model [3,4] using the same energy and angle values. In general, a power law [1,5] describes the background under the edge:

$$B(E) = A\, E^{-r} \qquad (3)$$

the two parameters A and r are obtained by the least-square minimization in a limited energy region λ before the edge and extrapolated above the edge region to be integrated. The correlation coefficient between the experimental points in the energy window λ and the points relative to the chosen background was used as test of fit.

To optimize both fitting parameters and energy windows used, the EELS microanalysis was carried out on a standard SiO_2 sample of α-quartz (NIST standard 1878A). For both the Si-L edge and the

O-K edge the widths of the fitting ranges (λ) were 10 eV and 190 eV respectively and the width of energy window used to calculate the element relative quantification (Δ) was 25 eV for both elements.

Error sources in EELS microanalysis have been extensively discussed. [1,6] Statistical limitation, approximate calculation of the appropriate cross-sections and, mainly, uncertainty in the background subtraction are the principal sources. The error bar relative to EELS measurements was estimated to be about 20% when particular problems in the background interpolation are absent, that is when correlation coefficients between experimental points and background are higher than 0.9 (corresponding to a probability that the two curves are not correlated less than 0.001).

Elemental composition was analyzed by means of Digital Micrograph software (version 3.9.5, Gatan Inc, Pleasanton, Ca, USA).

References:

[1] R. F. Egerton, *Electron Energy Loss Spectroscopy in the Electron Microscope*, Plenum Press, New York and London, 1986.

[2] R. F. Egerton, *Ultramicroscopy*, 1978, **3**, 243.

[3] R. F. Egerton, *Ultramicroscopy*, 1979, **4**, 169.

[4] R. D. Leapmann, P. Rez and D. F. Mayers, *J. Chem. Phys.*, 1980, **72**, 1232.

[5] D. R. Liu and L. M. Brown, *J. Microscopy*, 1987, **147**, 37.

[6] C. Colliex, in *Electron Energy Loss in the Electron Microscope. Advances in Optical and Electron Microscopy*, Vol. 9, (Eds: R. Barer, V. E. Cosslet), Academic Press, London and New York, 1984.