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Quantitative Raman spectroscopy: Challenges, shortfalls, and solutions—Application to calcium silicate glasses

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Abstract

This paper focuses on the determination of the speciation in calcium-silicate glasses from Raman spectra and describes in detail the statistical method to determine quantitatively the speciation from collected spectra. We developed a novel statistical method employing optimization technique to determine the number of active species and partial spectral contributions for overlapped spectra. This method allows deconvoluting overlapping spectra from spectral data such as UV-vis, Raman, X-ray, photoelectron spectroscopy (XPS), or other. We treat spectral methods that have absolute and relative information. By viewing the data as noisy or uncertain, we put all steps to deconvolute spectral data on a unified statistical approach, which allows to model spectral data with more realism. The suggested method enables us to calculate from overlapping spectra directly the individual contributions of each active component (species) present in the system without making any assumptions on the shape or peak positions of the components in individual spectra.

To determine quantitatively the speciation in calcium silicate glasses, we have collected Raman spectra of the glasses in the range of 45 to 52 mol% SiO_2. The spectra are strongly overlapped, and therefore, cannot be directly deconvoluted. Therefore, spectra were deconvoluted using our statistical approach. This lead to the discovery of partial spectra, which can be attributed to contributions of three different species. In addition, we have determined the equilibrium constant for the reaction

$$2Q^2 \leftrightarrow Q^1 + Q^3 \quad (1)$$

where $\log K_2$ is found to be 1.15 ± 0.1, being in good agreement with available NMR study.

Keywords: Quantification of spectral data, optimization, spectroscopy, silicate glasses