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Cerium redox state in silicate glasses and melts: implications for properties change and structural roles

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The detection and the quantification of redox species dissolved in glasses have a strong impact in many fields. In this study we want to enhance the understanding of the factors influencing Ce redox ratio, and provide a method to detect and quantify the $Ce^{3+}/\Sigma Ce$ ratio in silicate glasses/melts, and to relate it to changes in glass structure and properties.

Optical, structural properties and redox were studied for Ce-bearing silicate and aluminosilicate glasses, by X-ray Absorption, Raman and Photoluminescence Spectroscopy, whereas Ce redox kinetics for different temperatures and imposed oxygen fugacities were studied by “in-situ” Dispersive-XAS spectroscopy.

The presence of Ce ions affects the glass network, and induces modifications both in the short and medium range order. Glass polymerization, or introduction of Al_2O_3 in Ce-bearing silicate glasses strongly influence the redox, and additionally induces modifications in the Ce^{3+} surrounding.

The theoretical optical basicity values for the glasses here investigated can be used satisfactorily to predict the Ce redox states, however, Ce^{3+} optical properties cannot be easily correlated to the optical basicity since the chemical control is largely the primary factor influencing Ce structural role.

Keywords: silicate glasses, silicate melts, glass structure, Raman spectroscopy, XANES, redox kinetic, photoluminescence