ESRF

Experiment title: The role of Zr in the formation of glass ceramics in the CaO-SiO_2-ZrO_2 system: an anomalous scattering experiment for the calculation of the differential RDF.	Experiment number: CH-389
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Report:

This experimet has been performed with the aim to reveal the local structure of Zr in CaO-SiO_2-ZrO_2 ceramics and to investigate the role of Zr in the devitrification process.
Anomalous Wide Angle X-Ray Scattering (AWAXS) and EXAFS (Extended X-Ray Absorption Fine Structure) experiments were performed on three CaO-SiO_2-ZrO_2: one as prepared and the other two annealed for 1 h at 800 C and 1000 C. EXAS, XRD and AWAXS results were compared in order to have a complete description of the sample structure as a function of the thermal treatment.
The figure 1 reports the total pair correlation functions g(r) (a), the differential pair correlation functions $\Delta_{Zr}g(r)$ measured at the Zr K edge. The figure 2 shows the modulus of the Fourier transform of the EXAFS signal at the Zr K edge with the best fit data obtained using the GnXAS package.
The growth of diffraction peaks in the raw XRS data clearly demonstrates the progress of the recrystallization process as a function of T.
The first three principal peaks in the g(r) can be interpreted in terms of SiO_2, CaO and/or $CaSiO_3$ (Wollastonite) contributions that becomes more ordered increasing the annealing temperature.
The first two peaks in the $\Delta_{Zr}g(r)$ and $FT(\chi(k)$ represent the first and second coordination shell of Zr. The first one can be fitted in both EXAFS and AWXAS data, with about 7 O neighbors at around 2.1 Å. Combining EXAFS and AWAXS data it is possible to demonstrate that the second coordination shell is principally due to Zr-Ca and Zr-Si correlations, while Zr-Zr correlations are expected to be small.
The most interesting result is that while the Zr-O first coordination shell is only weakly influenced by the temperature treatment, the second one (Zr-Ca+Zr-Si) growth as a function of the annealing temperature.

The weak effect observed on the first coordination shell is not surprising since Zr-O bond distribution presents a wide sub-shell distribution ranging between 2.05 and 2.3 Åalso in the crystalline ZrO_2. On the contrary the large effect observed in the second shell demonstrates that i) a phase in which Zr is coordinated to Ca and/or Si already exists in the precursor glass and ii) the Zr environment is ordered during the thermal annealing at temperatures well below the T=1100 °C that is the critical crystallization temperature of the $2CaO{\cdot}4SiO_2{\cdot}ZrO_2$ phase observed in samples treated at high temperatures.

[1] P. Li et. Al. Phys. Rev. B 48, 10063 (1993).

Fig. 1: XRS and AWAXS results: a) Total Pair correlation function, b) differential pair correlation function. Experimental data are reported as dots and best fit function with full lines.

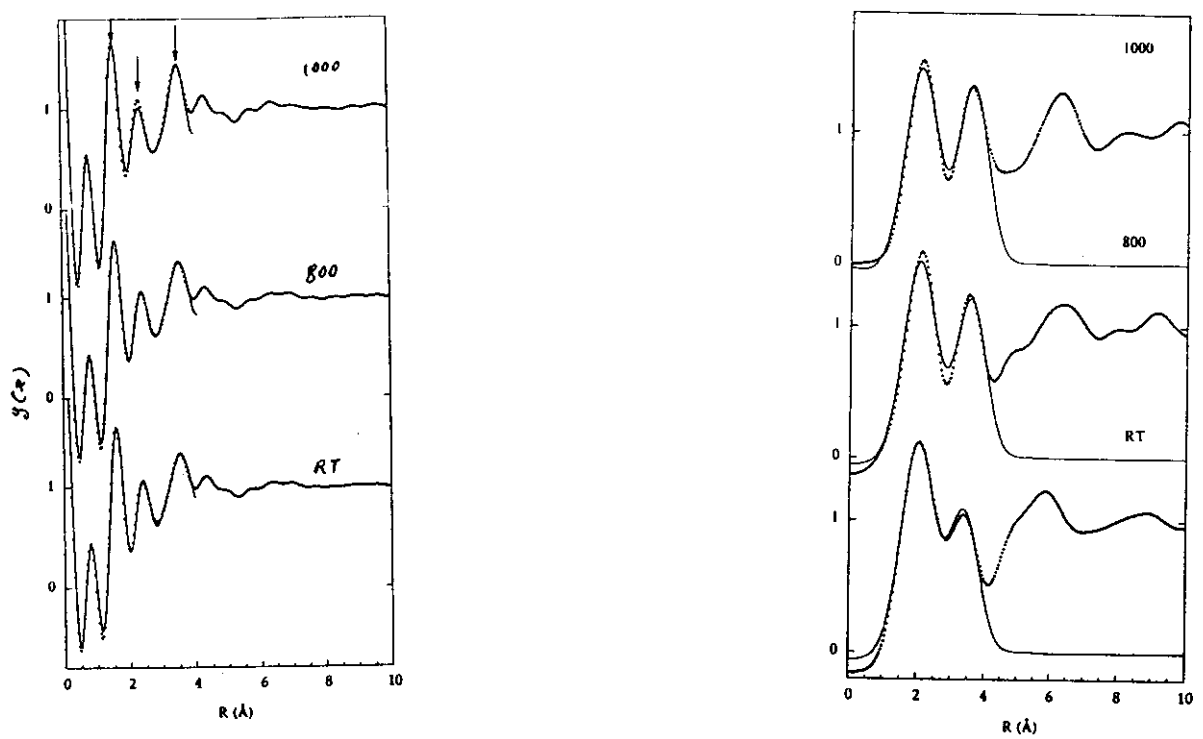

fig.2: K^3 weighted FT of the experimental and best fit data at the Zr K edge.