In situ synchrotron X-ray scattering study of thermal transformation of modified Si-doped ferrihydrite

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Here we report the results of a detailed structural investigation using *in situ* synchrotron-based X-ray scattering diffraction (HR-XRD) and pair distribution function analysis (PDF) on a series of Si-bearing synthetic analogues of ferrihydrite in an attempt to elucidate thermal transformation mechanisms. Si-ferrihydrites are more stable and closer analogues of natural minerals than pure phase. These minerals with fine structure are also partly "x-ray amorphous" and very difficult for structural analysis. Application of this methodologie was enabled us to follow structural changes in all phases involved in the reaction - pristine materials, intermediate metastable phases and end-products of the reaction - as well as to evaluate the degree of the influence of Si on the decomposition pathways for these mineral analogues. Silicon content representing a range of Si/Fe a.f.u. ratio between 0.0 and 1.5 was used which is relevant to geological environments. Ferrihydrites were synthesized by precipitation from aqueous solutions of $Fe_2(SO_4)_3$ with NaOH in the presence of Na_2SiO_3 at pH 8.2. The *in situ* synchrotron-based HR-XRD and PDF measurements were conducted using a flow-cell/furnace for in-situ real-time phase analysis. The actual sample temperature was determined from room temperature to 860°C, at 20°C min^{-1} in flowing air by a variety of phase and by the placement of thermocouple in the samples position. The temperature was varied with controller and monitored with thermocouple. The synchrotron measurements of this experiment were conducted using an amorphous Si detector system manufactured by Perkin-Elmer. Total scattering data were obtained at X-ray wavelength of 0.2113 Å and 0.1430 Å, using variable sample-to-detector distances. A CeO_2 standard was used to calibrate experiment geometry. Samples for PDF analysis were ground to the micrometer scale and were packed into polyimide capillaries 1 mm in diameter. Synchrotron X-ray total scattering data were used to obtain PDFs, which were subsequently, analyzed using GSASII and Fourier transformed to get G(r). Structure models were refined against the PDF data within PDFgui.

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