XAFS Investigations of Light Rare-Earth Elements in Hydrothermal Solutions Using a Modified Hydrothermal Diamond Anvil Cell

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Introduction

Determination of the structure of aqueous ions from near-ambient conditions up to high-grade metamorphic temperatures and pressures is of considerable interest to geochemists studying fluid-related processes in the Earth's crust. A number of high-temperature cells have recently been constructed for the purpose of conducting x-ray absorption spectroscopy of ions in hydrothermal solutions.[1-5] An important feature in the design of these cells is the x-ray window, which must be strong enough to withstand high internal pressures, yet thin enough to effectively transmit the x-ray photons of interest. Attenuation by relatively thick (> 1 mm) silica glass or diamond windows precludes the analysis of light elements having characteristic x-ray absorption energies less than ~ 6000 eV. Modified hydrothermal diamond anvil cells are able to overcome these problems.[6] In this study the hydration structure of low concentrations (1000 ppm) of La^{3+} in aqueous nitrate solutions, under conditions ranging from ambient to 300°C 1600 bars, is investigated in a hydrothermal diamond anvil cell designed specifically for XAFS analysis in the fluorescence mode.

Methods and Materials

The new hydrothermal diamond anvil cell has a 300-µm-diameter cup-shaped cavity and grooves cut into the face of one of the diamond anvils. The grooves extend from the edge of the diamond to within 0.08 mm of the sample chamber, which is a cup-shaped cavity in the center of the upper diamond anvil face. Figure 1 shows the percentage of transmission of x-rays through windows of different thickness of silica glass and diamond. The new cell has the advantage of extending analytical capabilities to elements having x-ray absorption edge energies as low as 2900 eV up to temperatures of 700°C and several kilobars of pressure. A 1000 ppm La standard aqueous solution was loaded in the sample chamber of a hydrothermal diamond anvil cell. The solution was sealed in the chamber by compressing the two diamond anvil faces onto a Re gasket (3 mm OD and 0.3 mm ID). La L_{III}-edge (5483 eV) XAFS spectra were collected on the undulator PNC-CAT 20-ID beamline at the APS.

Results and Discussion

Figure 2 shows the magnitude of the Fourier transforms (FT's) generated from the XAFS($k^2\chi$) data. The data are shown as solid lines, and the best fits of these data are shown as dashed lines. The FTs of the 25°C & 100°C data were calculated in the 2.0 to 8.2 Å k-range and those of the 255°C data in the 2.0–8.6 Å k-range. Analysis indicates that each La^{3+} ion has a hydration number of 9. Using results from available literature,[7] we infer that the hydration waters surround the ion in a tricapped trigonal prismatic arrangement. At 255°C, the bond distance between the equatorial plane oxygens and the La^{3+} ions increases from 2.59 ± 0.02 to 2.71 ± 0.04 Å. Conversely, the bond distance of the non-equatorial oxygens reduces from 2.59 ± 0.02 to 2.46 ± 0.04 Å. This study also demonstrates the capability of the modified hydrothermal diamond anvil cell for in situ x-ray spectroscopic analysis of a wide range of elements in dilute solutions at elevated temperatures and pressures. The results provide a basis for future studies of lanthanide complexing with ligands such as Cl^-, F^-, OH^-, CO_3^{-2}, SO_4^{-2} and PO_4^{-3}.

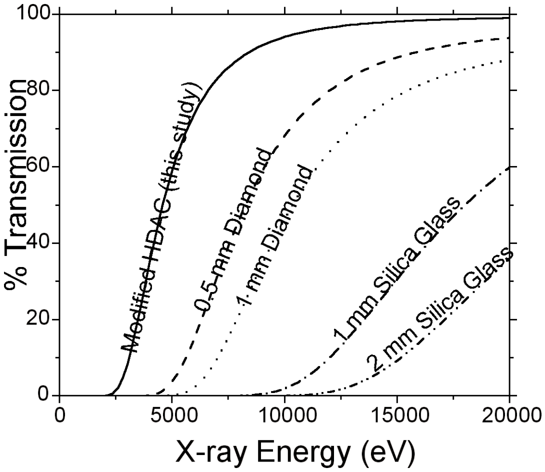

FIG. 1. A comparison of x-ray transmission through diamond and glass windows in various high-temperature cells used for XAFS investigations of hydrothermal solutions.

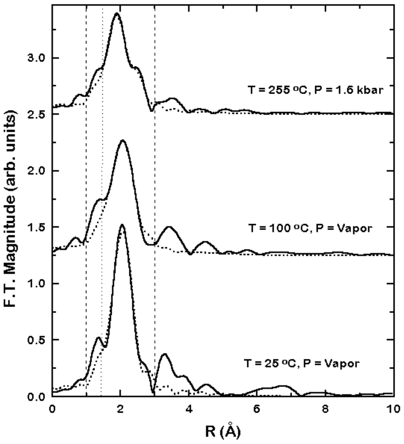

FIG. 2. The magnitude of the Fourier transforms (FT) generated from the XAFS data (line) and the best-fit model (dashed lines).

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