Structure of Arsenic on Iron-Montmorillonite from 50 – 200 ppb Solution by XAFS Utilizing Fluorescence Spectrometry

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The regulation of arsenic (As) concentration in the environmental water is becoming to be 10 ppb. In *User Experiment Report* 2002B0738, XANES study of As on Fe-montmorillonite, developed as new adsorbent, was reported adsorbed from 16 ppm of As^{3+}/As^{5+} solution. In this study, 50 – 200 ppb of As^{3+} solution was adsorbed. As K-edge EXAFS was also measured in addition to the speciation based on XANES.

As K-edge XAFS spectra for 0.13 – 0.20 wt% of As adsorbed on Fe-montmorillonite were measured in fluorescence mode utilizing secondary fluorescence spectrometer. The fluorescence spectrometer was tuned to As $K\alpha_1$ peak of each sample and XAFS spectrum was measured. A few measurements in transmission mode were also carried out for adsorbed As to evaluate the energy resolution of each mode.

As K-edge XANES spectra are summarized in Figure 1. The inflection point energy of As adsorbed from 50 – 200 ppb arsenite (f, g) was 11871.5 – 11872.0 eV, similar to that for $KH_2As^{V}O_4$ (c). A shoulder feature appeared at 11868.8 – 11869.8 eV due to the minor contribution of adsorbed As^{III} for **e** and **f**. It was difficult to evaluate the minor contribution in the case of **g**. The inflection peak taken in transmission mode was broader compared to those of **d** – **f** measured in fluorescence mode utilizing secondary spectrometer.

As K-edge EXAFS was measured for the samples of Figure 1e – g. The As-O distance was 1.68Å with *N* of 3 – 4. The As•••Fe distance was 3.17 – 3.22Å with *N* of 2. The formation of tetrahedral species $[As^{V}(OH)_2(\mu\text{-}OFe)_2]$ was demonstrated via the surface oxidation upon adsorption from As^{3+}.

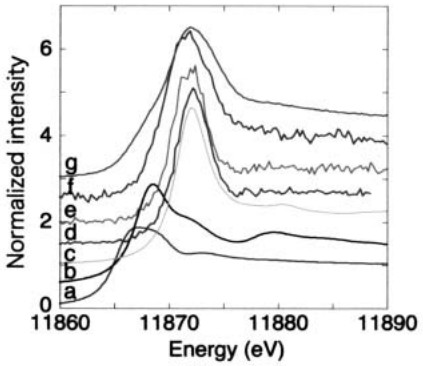

Figure 1. As K-edge XANES spectra measured at 290 K for As metal (a), $As^{III}_2O_3$ (b), $KH_2As^{V}O_4$ (c), and the As adsorbed on Fe-montmorillonite (Fe 15.3 wt%) from the test solution of 16 ppm of KH_2AsO_4 (d), 16 ppm of As_2O_3 (e), 200 ppb of As_2O_3 (f), and 50 ppb of As_2O_3 (g). Spectra of (a) – (c) and (g) were measured in the transmission mode and those of (d) – (f) were measured in fluorescence mode utilizing secondary fluorescence spectrometer.

Phase transformation of Al_2O_3 under high pressure and temperature

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Corundum (α-Al_2O_3) is an important material in geophysics, high-pressure physics, and ceramic science. The pressure-induced shift of the Cr^{3+} fluorescence wavelength of ruby (Cr^{3+} doped α-Al_2O_3) is widely used as a pressure calibrant in diamond anvil cell experiments (Xu et al., 1986). The ruby fluorescence shift was observed up to 550 GPa, using the extrapolated ruby pressure scale calibrated with Au up to180 GPa (Xu et al., 1986). Corundum is commonly used as a window in shock wave experiments. Therefore, the stability of corundum under high pressure and high temperature is important in understanding the ruby pressure scale, the results of shock-wave experiments, and the geophysical properties of the Earth.

Theoretical calculations predict that the corundum (space group: $R\bar{3}c$) transforms to the Rh_2O_3(II) structure (space group: Pbcn) at approximately 78 ($\pm$4) GPa and then to the Pbnm-perovskite structure at 223 ($\pm$10) GPa (Thomson et al., 1996). The phase transformation from the corundum structure to an orthorhombic structure was observed to occur at ~100 GPa in the high-pressure X-ray diffraction experiments after high-temperature laser heating at ~1000 K (Funamori and Jeanloz, 1997), but other high-pressure X-ray diffraction experiments to 175 GPa at 300 K did not observe such a phase transformation. The predicted X-ray spectrum of the Rh_2O_3(II) structure is similar to that of the corundum structure, suggesting that the Rh_2O_3(II) structure could go undetected.

We have studied the phase stability of Al_2O_3 to 136 GPa and high temperatures with in situ X-ray diffraction in a laser heated diamond anvil cell at BL10XU, Spring-8. Our results show that α-Al_2O_3 transforms to an orthorhombic structure at approximately 120 GPa. The volume change across the phase transformation is about 4%. Tentatively, the high-pressure phase is indexed as the Rh2O3 (II) structure, but the possibility of the perovskite structure can not be ruled out from present study. We are conducting more experiments in order to get higher quality diffraction patterns and to refine the structure of the high-pressure phase.

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