

## Structural incorporation of arsenic(V) into hematite

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Arsenic belongs to the world's most widespread contaminants and represents a considerable risk for human health [1]. The adsorption of As<sup>5+</sup> to iron oxides is well studied [2,3,4], the possibility of structural incorporation, however, is still neglected. In our work, we present data which indicate the structural incorporation of As<sup>5+</sup> into the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) structure, using angelellite (Fe<sub>4</sub>As<sub>2</sub>O<sub>11</sub>) as a starting model. Hematite is built by a hexagonal close packing (hcp) array of oxygen atoms, with the Fe<sup>3+</sup> ions residing in the octahedral interstitial cavities [5]. Tetrahedral interstitial sites are empty in the hcp array in hematite. Just like hematite, the structure of angelellite is based on a hcp oxygen array. In contrast to hematite, both octahedral and tetrahedral cavities are occupied by Fe<sup>3+</sup> and As<sup>5+</sup> in angelellite, respectively. The two crystal structures are closely related and can be epitaxially intergrown. Therefore we propose that As<sup>5+</sup> can be incorporated into the hematite structure in the form of angelellite-like local clusters.

For the synthesis of As<sup>5+</sup>-doped hematite, two-line ferrihydrite was prepared after [6]. The ferrihydrite suspension was immediately adjusted to pH 4 by adding nitric acid (65 %), and then doped with pre-selected volumes of a 15 mM solution of arsenic pentoxide. Afterwards the samples were stored at 70 °C for 16 days. The combination of powder X-ray diffraction (PXRD) and inductively-coupled-plasma optical-emission-spectroscopy (ICP-OES) show hematite as the only transformation product with molar As:Fe ratios of 0.002, 0.006, and 0.02. Single crystals of As<sup>5+</sup>-doped hematite were analyzed by transmission electron microscopy (TEM) in energy dispersive mode (EDX). Arsenic K-edge extended X-ray absorption fine structure (EXAFS) spectra were collected at the SUL-X beamline at the Angströmquelle Karlsruhe, Germany. The spectra show that the local structure of As-doped hematite is consistent with the local structure of angelellite, indicating As<sup>5+</sup> on tetrahedral sites embedded within the hematite structure, not merely adsorbed on its surface. This process of structural incorporation of As in an iron oxide has to be considered in environments where hematite is not pre-existent but may form during the presence of dissolved As.

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