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Synthesis of tetragonal mackinawite-type FeS nanosheets by solvothermal crystallization

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ABSTRACT

Mackinawite, a metastable 1:1 compound of iron and sulfur that adopts an anti-PbO-type structure, is of interest because of its relationship to known iron chalcogenide superconductors, as well as its biogeochemical relevance. Colloidal nanosheets of mackinawite-type FeS were synthesized by first generating an amorphous Fe–S precursor *via* the aqueous room-temperature co-precipitation of Fe^{2+} and S^{2-}, then solvothermally crystallizing it in ethylene glycol at 200 °C in an autoclave. The product is highly crystalline, with lattice constants of $a=3.674(3)$ Å and $c=5.0354(3)$ Å. The nanosheets, with their surface normal oriented along the [0 0 1] direction, are irregularly faceted with edge lengths that range from 100 nm to over 1 μm and average thicknesses of approx. 30 nm. The samples showed a ferromagnetic background signal with no evidence of superconductivity.

1. Introduction

Mackinawite, a metastable 1:1 compound of iron and sulfur, adopts an anti-PbO-type structure with layers of edge-sharing Fe–S tetrahedra that are held together through van der Waals interactions [1–4]. This FeS compound is of growing interest among the large family of iron sulfide phases that span a diverse range of electronic, magnetic, and optical properties with applications that include solar cells [5–7] and lithium ion batteries [8]. Mackinawite has been explored as a material for microbial fuel cells [9] and as a substrate for the removal of toxic trace metals from water [10]. Also, mackinawite FeS is isostructural to superconducting FeSe and $FeSe_{1-x}Te_x$, and while superconductivity has not yet been reported in this tetragonal FeS phase, it is attracting significant attention because of its structural, compositional, and electronic similarities to the known iron chalcogenide superconductors [11–13]. Mackinawite-type FeS is also of interest because of its biogeochemical relevance: it is produced by sulfate-reducing bacteria [14], it occurs in sedimentary mineral deposits [1], it is a precursor to pyrite [15], and it is implicated in origin of life theories [16].

Mackinawite is generally considered to be the first Fe–S phase that forms from the aqueous reaction of Fe^{2+} with S^{2-} solutions under ambient conditions [4,13], and it has also been observed as a product of iron and steel corrosion in aqueous H_2S [1]. Most reports of synthetic mackinawite mimic the natural processes under which it is known to form, including biological precipitation [17] and aqueous co-precipitation of Fe^{2+} and S^{2-} at ambient (or near-ambient) temperature and pressure [18]. As a result, generating highly crystalline pure samples can be challenging, in part because of the competing iron oxides and sulfides that form under similar conditions and the tendency of mackinawite to serve as a reactive precursor to other iron sulfide phases that are more stable [4]. Synthetic mackinawite is often described in the literature as either amorphous or nanocrystalline [19], and in general it is observed as morphologically irregular nanostructures with significant aggregation [14,18,19].

Here, we describe a two-step route to crystalline nanostructures of mackinawite with well-defined nanosheet morphologies. An amorphous Fe–S precursor is first synthesized by co-precipitation of Fe^{2+} and S^{2-} in water, which is a standard route for this system. This amorphous precursor is then solvothermally annealed in a non-aqueous solvent, ethylene glycol, at temperatures and pressures that mimic those of hydrothermal vents. The product consists of highly crystalline colloidal nanosheets of tetragonal mackinawite-type FeS. This synthetic pathway provides a straightforward and reproducible route to isolatable quantities of this interesting metastable phase, for which only a small number of reports exist relative to other iron

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sulfide compounds. Also, it produces nanostructures of mackinawite that are among the most well-defined and crystalline reported to date. This is important, given the biogeochemical interest in mackinawite as well as its potential applications in superconductivity, environmental remediation, lithium ion batteries, and solar cells.

2. Experimental section

2.1. Chemicals

$FeCl_2 \cdot xH_2O$ (reagent grade, 99%) and $Na_2S \cdot 9H_2O$ (ACS, 98% min.) were purchased from Alfa Aesar. Ethylene glycol (99.0%) was purchased from BDH. Sodium hydroxide pellets were purchased from EMD. All chemicals were used as received.

2.2. Synthesis of mackinawite

A stock solution of Na_2S was prepared by combining 750 mg (3.12 mmol) of $Na_2S \cdot 9H_2O$ with 1.148 g (28.7 mmol) of NaOH in a 40-mL glass reaction vial. NANOpure water (10 mL, from a NANOpure Diamond ultrapure water system) was added and the vial was capped and sonicated (1510 Branson sonicator at room temperature) until the solid was completely dissolved. In a separate 20-mL reaction vial, a solution of $FeCl_2$ was prepared by sonicating 108 mg (0.5 mmol) of $FeCl_2 \cdot xH_2O$ in 10 mL of NANOpure water until the solid was completely dissolved. Then, 1.0 mL of the Na_2S stock solution was rapidly injected into the $FeCl_2$ solution. A black precipitate formed immediately. The reaction was capped, stirred for 10 min, then centrifuged at 10,000 rpm for 5 min. The supernatant was discarded, the precipitate was dispersed in 20 mL of ethanol by sonication, and then it was centrifuged again at 10,000 rpm for 5 min. This ethanol cleaning procedure was repeated one time.

The precipitate was dispersed into 11 mL of ethylene glycol by sonication for 30–60 min, and this dispersion was loaded into a 23-mL Teflon-lined autoclave and sealed. The autoclave was heated to 200 °C over 1 h and held at this temperature for 4 h before cooling naturally. When fully cooled to room temperature, the product was removed from the autoclave and centrifuged at 10,000 rpm for 5 min. The supernatant was discarded and the precipitate was dispersed in 20 mL of a 1:1 mixture of ethanol and hexanes followed by centrifuging at 10,000 rpm for 5 min. This washing procedure was repeated until the supernatant was clear and colorless, often requiring ten or more washes. The powder was then dried under vacuum and stored as a dry powder.

2.3. Characterization

Powder X-ray diffraction (XRD) data were collected on a Bruker Advance D8 X-ray diffractometer using Cu K_α radiation. Lattice constants were refined using ChekCell. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained from a JEOL 1200 EX II operating at 80 kV. Energy dispersive X-ray (EDX) spectra were acquired using a FEI Quanta 200 environmental scanning electron microscope operating in high vacuum mode. Atomic force microscope (AFM) images were collected using a Bruker Dimension Icon AFM equipped with Scanasyst-Air peak force tapping mode AFM tips from Bruker. Magnetic characterization was performed using a Quantum Design SQUID magnetometer.

3. Results and discussion

Crystalline mackinawite is synthesized by first generating an amorphous precipitate, formed by the aqueous co-precipitation of Fe^{2+} and S^{2-}, then solvothermally crystallizing it in ethylene glycol. Fig. 1 shows the powder XRD pattern for this precursor, which appears largely amorphous with a few low-intensity reflections that cannot be unambiguously identified. Energy dispersive X-ray (EDX) spectra indicate that the amorphous precursor has an average Fe:S ratio of 87:13, which is consistent with the excess iron used in the co-precipitation step. After solvothermal treatment in ethylene glycol, the crystalline FeS product must be washed multiple times in order to isolate it from dissolved Fe^{2+} species. This suggests that the amount of sulfur in the amorphous precursor is the limiting reagent during the crystallization step, with a large part of the remaining Fe being dissolved and washed away.

The powder XRD pattern for a typical product isolated after solvothermal treatment of the amorphous precursor is shown in Fig. 2. This XRD pattern matches well with the simulated XRD pattern for mackinawite, which is shown for comparison, as well as the experimental patterns in the PDF database (e.g., 86-0389). The refined lattice parameters are $a=3.674(3)$ Å and $c=5.0354(3)$ Å, and these values compare favorably with literature reports, which are generally close to $a=3.67$ Å and $c=5.03$ Å [20]. The peaks of solvothermally-crystallized mackinawite are fairly narrow, with good resolution of closely spaced reflections (110 *vs.* 002 and 200 *vs.* 112). This indicates unusually large grain sizes and long-range crystalline order relative to typical samples of as-made

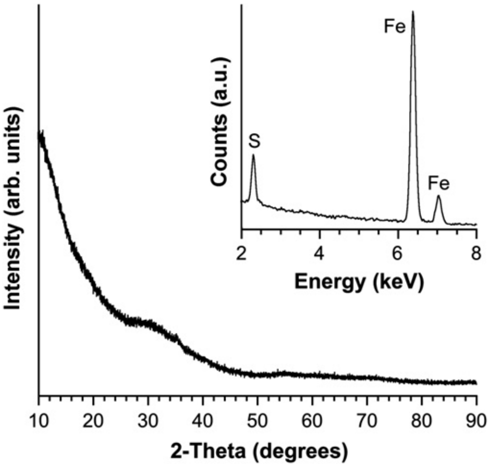

Fig. 1. Powder XRD pattern (main panel) and EDX spectrum (inset) for the amorphous Fe–S precursor.

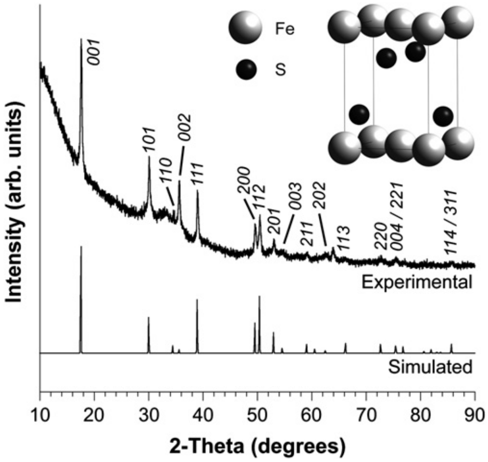

Fig. 2. Experimental (top) and simulated (bottom) powder XRD patterns for mackinawite-type FeS. The crystal structure of mackinawite is shown in the inset.