

Solvothermal Route to Prepare the Metastable Phase 3c-Fe₇S₈ with Hexagonal Platelet Morphology

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Abstract: The metastable phase 3c-Fe₇S₈ with the hexagonal platelet morphology has been prepared by using solvothermal route. The product was characterized by means of X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) and X-ray photoelectron spectra (XPS). The experiment results show that the as-prepared Fe₇S₈ is a metastable phase with the hexagonal platelet morphology.

Keywords: 3c-Fe₇S₈, solvothermal route, hexagonal platelet.

Studies of vacancy and magnetic spin orderings have been of special importance in solid state research because they lead directly to an understanding of crystallographic and magnetic structures. Nonetheless, two complications make such studies difficult: First, there is no method to directly probe the individual vacancies and magnetic spins. The macroscopic observations are averages over correlations among the vacancies and spins. Second, the temperature, cooling rate, and other factors usually influence the resultant ordering, it is difficult to achieve nearly perfect ordering in a crystal.

Pyrrhotites, which are iron sulfides with the general composition Fe_{1-x}S ($x = 0\sim 0.125$), are typical defect compounds. Among the defect iron sulfides that can be described as ordered vacancies in the NiAs-type structure, Fe₇S₈ is an extreme¹. Only two sequences in Fe₇S₈ have been identified by X-ray diffraction studies (monoclinic symmetry with $C = 4c$ and trigonal structure with $C = 3c$, respectively). The 4c monoclinic structure has been found in natural pyrrhotite minerals² and laboratory-grown samples³, but the 3c trigonal structure was only found in the quenched samples⁴⁻⁵.

The relationship of these two structures has little been studied, so it has remained unclear whether the 3c-Fe₇S₈ is an intermediate superstructure phase stable at certain temperatures or forms as a metastable phase. As for the laboratory-grown samples at high temperature⁶, the mixed phase of both 3c trigonal structure and 4c monoclinic structure is most often encountered. These complications have hindered the understanding of phase relations for the high temperature samples.

Herein we report a novel solvothermal route for synthesizing the pure Fe₇S₈ with 3c

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triagonal structure.

Experimental

Analytically pure $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mol), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.05 mol) and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.1 mol) were put into a 200 mL Teflon liner autoclave, the ethylene glycol was used to fill the tank to 80% of the total volume. The autoclave was maintained at 240°C for 120 h and then allowed to cool to room temperature naturally. The product was filtered and washed with distilled water and absolute ethanol several times. After drying in a vacuum at 80°C for 2 h, a final dark product was obtained.

XRD analysis were conducted on a Japan Rigaku D / max- γ B X-ray diffraction with Cu $\text{K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The composition of the products was obtained by X-ray photoelectron spectra (XPS), which was collected on a VGESCALAB MKII X-ray photoelectron spectrometer. To examine the morphology and phase structure of the samples, the transmission electron microscope (TEM) images and electron diffraction (ED) were taken on a Hitachi model H-800.

Results and Discussion

Figure 1 shows the XRD patterns of the as-prepared sample. All peaks could be indexed to the hexagonal 3c- Fe_7S_8 (JCPDS card, 24-220), which is consistent with the metastable form of pyrrhotite Fe_7S_8 reported by A. Nakano, *et al.*⁴. Whether is it an intermediate superstructure phase? We tried to research it by TEM analysis.

Figure 2a shows that Fe_7S_8 crystallites are mainly in the uniform shape of hexagonal platelets. The image of electron diffraction (ED) for the as-prepared Fe_7S_8 shows that single crystallite character with hexagonal symmetry (**Figure 2b**). It does not be found that the diffraction image with satellite shape occurs in the as-prepared Fe_7S_8 , which is described in the literature⁶, thus it is not an intermediate superstructure phase.

Figure 1 The X-ray diffraction patterns of the as-prepared sample

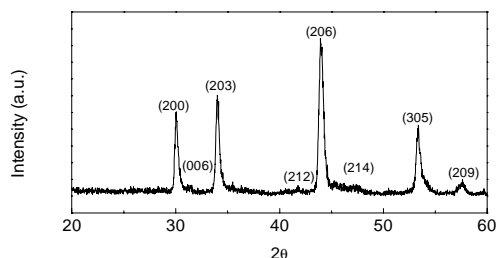


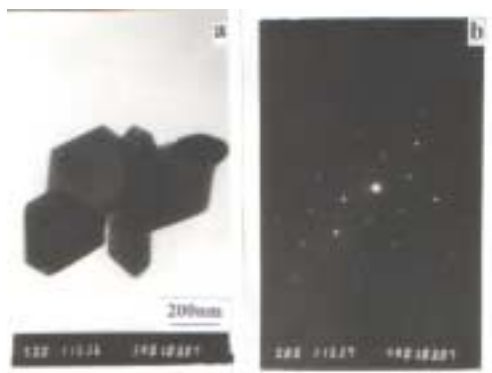
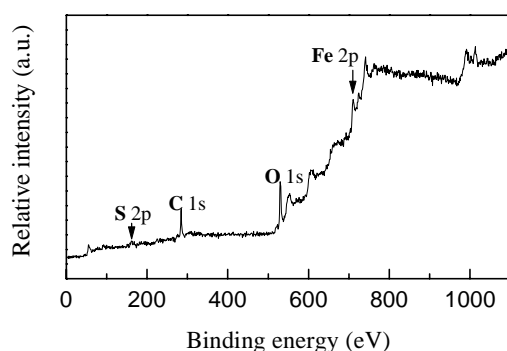
Figure 2 The TEM and ED images of the as-prepared 3c-Fe₇S₈**Figure 3** XPS spectra of the as-prepared 3c-Fe₇S₈.

Figure 3 shows the X-ray photoelectron spectra (XPS) of the as-prepared 3c-Fe₇S₈. No obvious impurities (*e.g.* chloride ion) could be detected in the samples. The binding energy of Fe 2p 3/2 for the as-prepared sample is 710 eV and the binding energy of S 2p 3/2 is 161.5 eV, all of that is close to ones of FeS. The quantification of the XPS peaks gives the ratio of S / Fe is 1.12, which is almost consistent with the stoichiometry of Fe₇S₈.

It is well known that solvents can influence the reaction pathway. In this system, Ethylene glycol, a bidentate solvent, was selected due to its strong O-chelation ability. It can act as a bidentate ligand to form a relatively stable Fe²⁺ complex, which can incorporate dissolved S²⁻. As temperature increases, the tri-valence iron sulfide causes disproportionation reaction to produce FeS₂ and solvation FeS. The formation of 3c-Fe₇S₈ with hexagonal platelet morphology may be through a solid-solution diffusion process.

Conclusion

In summary, we have succeeded in the synthesis of the hexagonal platelet 3c-Fe₇S₈ by the solvothermal route. The structure and property of the solvent can strongly influence the reaction process. It opens a new way to further research property of vacancy and magnetic spin orderings.

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