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2002 J. Phys.: Condens. Matter 14 11297

(http://iopscience.iop.org/0953-8984/14/44/470)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 11297–11300 PII: S0953-8984(02)39357-3

# Pressure-induced phase transition of nanocrystalline iron sulphide coated by polyvinyl alcohol

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Received 1 June 2002
Published 25 October 2002

**Abstract**

Nanocrystalline iron sulphide (FeS) coated with polyvinyl alcohol, with particle size ranging from several to several tens of nanometres, has been prepared by the chemical precipitation synthesis method. The phase transition of FeS has been investigated by using *in situ* high-pressure diffraction with synchrotron radiation at pressures up to 42.5 GPa. Most of the diffraction lines are broadened and weakened. At the pressure of 11.8 GPa, a new phase transition was observed. However, only eleven x-ray reflections were recorded under high pressure; the crystal structure is unknown.

## 1. Introduction

Nanomaterials attract considerable attention in modern-day technology. Nanomaterials are very different from their bulk counterparts because the particle diameter is less than the Bohr excitation radius. Previously, phase transitions in iron sulphide (FeS) have been investigated at high pressure and room temperature [1–5], at high temperature and ambient pressure [6, 7] and at high pressure and high temperature [8]. Stoichiometric FeS has a NiAs-type hexagonal structure with a $(\sqrt{3}a, 2c)$ unit cell at ambient conditions, called troilite (FeS I). At 3.4 GPa [5], troilite transforms to a MnP-type structure (FeS II). Then a high-pressure phase (FeS III) forms at pressures above 6.7 GPa [1, 3], although some investigations have indicated that its structure is uncertain [9]. At 15.0 GPa, Fei *et al* [8] found a stable phase, FeS IV, with a NiAs-type structure. A high-pressure phase transition study of nanocrystalline FeS will help clarify the mechanism of formation of the Earth and Mars. There has been no work reported on the properties of nanoscale FeS under high pressure up to now. In this paper, we report the experimental results of a high-pressure x-ray diffraction study of nanocrystalline FeS at pressures up to 42.5 GPa, and compare the results with those for bulk samples.

0953-8984/02/4411297+04$30.00

## 2. Experimental details

Nanometre-sized FeS was prepared by the chemical precipitation synthesis method. The method enabled size-selective preparation of FeS nanoparticles that are very narrowly dispersed in diameter. The experimental procedure was as follows: first, nitrogen gas ($N_2$) was made to flow into the $FeCl_2$ aqueous solution which was diluted with a predetermined amount of deionized water ($\rho > 18$ M$\Omega$ cm$^{-1}$) with low speed of the mixer; then $Na_2S$ aqueous solution was quickly poured over the $FeCl_2$ aqueous solution purged of $N_2$ before combination. At once, we saw black sediment. Next, the aqueous solution of polyvinyl alcohol (PVA) was added to the FeS suspension. The volume ratio of the PVA solution to the FeS suspension was 1:1. The advantage of using PVA is that the samples are protected against oxidation during drying. Finally, we adjusted the mixer to the speed of 1500 revolutions min$^{-1}$ and maintained a constant $N_2$ flow for 15 min. The suspension obtained was put into a semipermeable membrane bag and dialysed against deionized water. The water was changed once a day until no ions could be detected in the dialysate. We obtained three kinds of sample, FeS/PVA-1–FeS/PVA-3, whose grain sizes are 5, 12 and 20 nm, respectively, by changing the concentration of the reactant.

Powder x-ray diffraction (XRD) investigation was carried out in a Rigaku D/max-rA diffractometer using Cu K$\alpha$ radiation.

The high-pressure energy-dispersive XRD experiment was carried out at High Pressure Experiment Station beamline 3W1A of the Beijing Synchrotron Radiation Facility (BSRF). A Mao–Bell-type diamond anvil cell (DAC) driven by gear-worm-level system was used to generate high pressure. The flats of the diamonds are 500 $\mu$m in diameter. Black FeS powder was loaded with the pressure-transmitting medium in a hole with a diameter of 240 $\mu$m in an L605 stainless steel gasket which was precompressed to 10 GPa before being used. The size of the x-ray spots was 144 × 144 $\mu$m. A Si(Li) solid detector was used to collect the diffraction data under various pressures, and each spectrum was collected for 600–900 s. Pt was used as an internal pressure standard as its equation of state (EOS) is known. The $d$-spacing of the sample $d_{hkl}$ was calculated by using the following relation:

$$E_{hkl}d_{hkl} = 0.619\,927/\sin\theta \text{ (keV nm}^{-1}\text{)}.$$

The experimental diffraction angle $\theta$ is 6.3698°.

## 3. Results and discussion

Figure 1 shows the XRD patterns. Comparing FeS/PVA-1–FeS/PVA-3, it is obvious that the diffraction line is gradually broadened and weakened with decreasing nanocrystalline size. They have the same structure. From XRD results, we see that pure nanocrystalline FeS was obtained by controlling the molar ratio of the chemicals and the cell volume of the FeS ultrafine particles while increasing the grain size. Pure FeS nanoparticles are available over a wide range of $Na_2S$ and $FeCl_2$ concentrations, and the particle size can be changed arbitrarily over an appropriate range.

At ambient pressure, the structure of bulk FeS is similar to the hexagonal structure of NiAs type. Taylor and Mao [1] revealed a new high-pressure phase at 120 ± 40 kbar and 22 °C for bulk samples. From table 1, and comparing with the subsequent XRD findings, we found that the structure of nanocrystalline FeS at atmospheric pressure is probably related to the high-pressure structure of Taylor and Mao's [1] bulk FeS. We think that with decrease of the sample size, the surface stress increases at the same time. And when the sample size has decreased to a certain extent—to a special value—the surface stress of nanometre phase materials can be comparable to the phase-transition-induced stress of bulk materials [10–12]. Eventually this will result in nanometre phase materials presenting a high-pressure phase at ambient pressure.

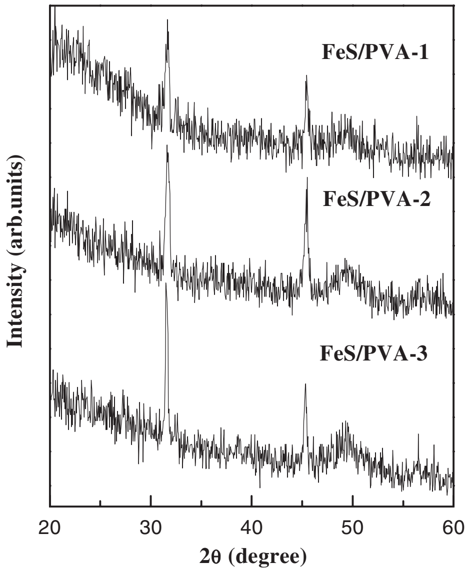

**Figure 1.** XRD patterns of FeS/PVA-1–FeS/PVA-3 (the sample grain sizes are respectively 5, 12, 20 nm at room temperature and ambient pressure).

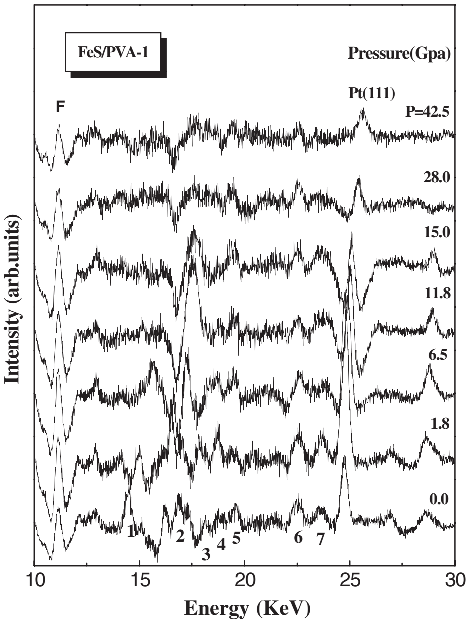

**Figure 2.** Energy dispersive XRD patterns of FeS/PVA-1 under various pressures: F: fluorescence; P: increasing pressure.

**Table 1.** The XRD data for atmospheric pressure and high-pressure FeS.

| FeS/PVA-1, atmospheric pressure | | Taylor and Mao's sample | | | |
|---|---|---|---|---|---|
| | | 120 ± 40 kbar 22 °C | | 50 ± 20 kbar 120 ± 30 °C | |
| *d* | Intensity | *d* | Intensity | *d* | Intensity |
| | | 3.645 | 10 | | |
| 3.408 | 68 | | | 3.366 | 10 |
| 3.226 | 90 | 3.236 | 10 | | |
| 2.840 | 100 | 2.843 | 100 | 2.869 | 100 |
| 2.560 | 35 | 2.582 | 60 | 2.617 | 40 |
| 2.436 | 54 | 2.444 | 60 | 2.475 | 40 |
| 2.254 | 58 | 2.250 | 20 | 2.278 | 20 |
| 2.103 | 50 | 2.113 | 60 | 2.155 | 30 |
| 2.000 | 69 | 1.979 | 100 | 2.015 | 50 |
| | | 1.881 | 40 | 1.909 | 10 |
| 1.841 | 57 | | | 1.845 | 10 |
| 1.745 | 48 | 1.754 | 50 | 1.770 | 50 |
| 1.638 | 43 | 1.632 | 60 | 1.644 | 90 |
| | | 1.502 | 30 | | |
| | | 1.412 | 20 | 1.425 | 30 |

This provides us with a way to use the properties and phenomena of nanometre phase material at atmospheric pressure to understand some unique interesting potential properties and new effects of bulk materials at high pressure.

The energy-dispersive XRD spectra of FeS/PVA-1 at various pressures are shown in figure 2. Most of the diffraction lines shift to higher energy with increasing pressure. At atmospheric pressure, the stronger diffraction peaks of FeS/PVA-1 such as 1–7, although not the diffraction line of Pt, can be seen clearly. The diffraction line with $d = 0.3863$ nm (peak 1) shifts to the high-energy side with increasing pressure and disappears at 11.8 GPa; and a new diffraction line appears. We can infer that FeS particles undergo a structural phase transition at 11.8 GPa. The diffraction lines of FeS cannot be indexed and the structure is unknown.

## 4. Conclusions

Nanocrystalline FeS coated with PVA can be prepared by the chemical precipitation synthesis method. The structure of nanocrystalline FeS at atmospheric pressure is the same as the high-pressure structure of Taylor and Mao's [1] bulk FeS III. At 11.8 GPa, a new phase was observed and the structure is unknown.

## Acknowledgments

The authors would like to thank Dr Liu Jing and her colleagues of the High Pressure Experiment Station of the Beijing Synchrotron Radiation Facility (BSRF) of the Institute of High Energy Physics for their suggestions and support regarding synchrotron radiation techniques.

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