

Synthesis of Iron Group Metal Sulfides from the Elements under Hydrothermal Condition

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Iron group metal sulfides were synthesized from the elements under hydrothermal condition. For nickel sulfides, two kinds of nickel metal powder, coarse powder passed through 63 μm mesh and fine powder passed through 3 μm mesh, were used as the starting materials. The reaction with the coarse Ni powder gave NiS with appreciable amount of Ni, Ni_3S_2 , and Ni_9S_8 . Pure NiS was obtained by the reaction with the fine Ni powder at 240°C for 10 h. The lowest nickel sulfide Ni_3S_2 was obtained as a single phase product of the reaction if the coarse Ni powder was used. From these results, the fine and coarse powders were found to be suitable for the syntheses of NiS and Ni_3S_2 , respectively. The lowest cobalt sulfide Co_9S_8 was obtained almost as a single phase though the XRD pattern of the product showed some unidentified peaks. Pure Co_9S_8 was obtained by washing the reaction product with HNO_3 . In the Fe–S system, FeS was obtained with a small amount of Fe_3O_4 .

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1. Introduction

Metal sulfides are traditionally prepared by the reaction of hydrogen sulfide gas with the aqueous solution of the metal salt or by the thermal reaction of the elements in an evacuated silica tube at high temperature. In recent years, low temperature syntheses of metal sulfides have been pursued especially for the preparation of nano-sized particles.

Sea-urchinlike nanocrystalines of NiS and Co_9S_8 were synthesized via a hydrothermal route from the thiourea and hydrated metal chloride in hydrazine hydrate solution.¹⁾ Uniform NiS nanowhiskers were prepared via hydrothermal reaction between $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of surfactant $\text{C}_{17}\text{H}_{33}\text{COOK}$.²⁾ Nanocrystalline Co_9S_8 was prepared by hydrothermal treatment of $\text{Co}(\text{Ac})_2$ and thiourea in hydrazine solution at 170°C.³⁾

In these reactions, complex compounds were used as starting materials. If metal sulfides can be prepared from the elements, the possibility of the formation of complex impurities can be avoided. Two reports were known for the hydrothermal synthesis from the elements. One was the reaction of copper and sulfur to form CuS. The reaction proceeds well at 60°C in the presence of water.⁴⁾ The other report was about the hydrothermal synthesis of MnS at 260°C.⁵⁾

In this study, we tried to synthesize the lowest sulfides of the iron group elements, FeS, Co_9S_8 , Ni_3S_2 , and NiS from the elements under hydrothermal condition.

2. Experimental

The powders of the metal and sulfur were weighed, ground, and introduced along with 10 mL of distilled water into 25 mL a Teflon-lined pressure vessel, which was then heated at 150–240°C for 10 or 60 h. Two kinds of nickel metal powder, coarse powder passed through 63 μm mesh and fine powder passed through 3 μm mesh, were used as the starting material. For cobalt system, cobalt powders passed through 5 μm mesh and 1–2 μm mesh were used. Two kinds of iron powders passed through 150 μm mesh and 3–5 μm mesh were used.

After heating, the pressure vessel was allowed to cool to room temperature. The precipitates were filtered and washed with distilled water several times. After drying in a desiccator for 12 h, the powder was collected for characterization.

Powder X-ray diffraction (XRD) patterns were measured

with $\text{Cu K}\alpha$ radiation on a RINT2000 diffractometer (Rigaku) equipped with a graphite monochromator. The morphology and particle size of the products were observed by FE-SEM images, taken with S-4500 system (Hitachi).

3. Results and discussion

3.1 NiS

Ni and S were weighed in the stoichiometric ratio of Ni : S = 1 : 1. Two kinds of nickel metal powder, coarse powder passed through 63 μm mesh and fine powder passed through 3 μm mesh, were used as the starting materials.

The XRD patterns of the product obtained from the coarse powder were shown in Fig. 1. The hydrothermal reaction at 180°C for 10 h yielded trigonal Ni_3S_2 (ICSD 73839) as the

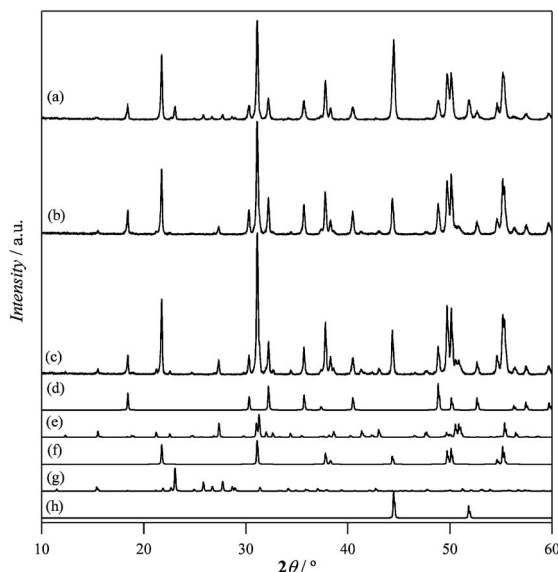


Fig. 1. XRD patterns of the products obtained from the coarse nickel powder and sulfur in the ratio of Ni : S = 1 : 1 at (a) 180°C for 10 h, (b) 240°C for 10 h, and (c) 240°C for 60 h. Reported patterns of (d) NiS (ICSD No. 40054), (e) Ni_9S_8 (ICSD No. 63080), (f) Ni_3S_2 (ICSD No. 73839), (g) S (ICSD No. 200453), and (h) Ni (ICSD No. 44767).

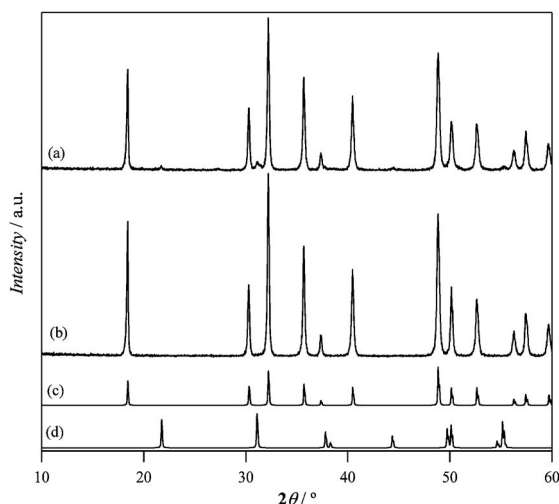


Fig. 2. XRD patterns of the products obtained from the fine nickel powder and sulfur in the ratio of Ni : S = 1 : 1 at (a) 180°C for 10 h, and (b) 240°C for 10 h. Reported patterns of (c) NiS (ICSD No. 40054), and (d) Ni₃S₂ (ICSD No. 73839).

main product, although some trigonal NiS (ICSD 40054) and unreacted Ni (ICSD 44767) and S (ICSD 200453) were observed. When the reaction temperature was raised up to 240°C, a small amount of orthorhombic Ni₉S₈ (ICSD 63080) in addition to NiS and Ni₃S₂ was formed, and single phase NiS were not obtained though unreacted Ni and S were disappeared. Prolonged reaction time (60 h) did not change significantly the composition of the products. Any metastable phase was not detected in this system, as these trigonal NiS, trigonal Ni₃S₂, and orthorhombic Ni₉S₈ are stable at room temperature.⁶⁾

Next, the reaction products were investigated by using the fine nickel powder as the starting materials. **Figure 2** shows the XRD patterns of the product. While a small amount of Ni₃S₂ was formed by the reaction at 180°C for 10 h, single phase NiS was obtained by the reaction at 240°C.

In the hydrothermal synthesis of NiS from the elements, the particle size of the nickel was found to influence the product strongly. The fine nickel powder, which has a large surface area, was easier to react with sulfur to form NiS.

The SEM image of NiS synthesized at 240°C for 10 h by using the fine nickel powder is shown in **Fig. 3**. As for the synthesized NiS particle, the tendency to grow up to one direction was observed.

3.2 Ni₃S₂

Since a considerable amount of Ni₃S₂ was formed in the synthesis of NiS, the hydrothermal synthesis of Ni₃S₂ was tried by using the starting materials mixed in the stoichiometric ratio of Ni : S = 3 : 2.

The products were dependent on the particle size of nickel. **Figure 4** shows the XRD pattern of the products obtained by the reactions at 180°C and 240°C. At both temperatures, the fine nickel powder gave more NiS than the coarse powder. Thus, the coarse powder was more suitable for the hydrothermal synthesis of Ni₃S₂ to avoid the formation of NiS. Generally, for the synthesis of a metallic sulfide with a lower oxidation state, the metal powder with smaller surface area may be suitable since the excess sulfuration of the metal is prevented. Some XRD peaks of Ni were observed especially in the samples obtained at 240°C for 10 h using the coarse powder (see Fig. 4 (d)). Hence, the synthesis of a pure Ni₃S₂ using the coarse

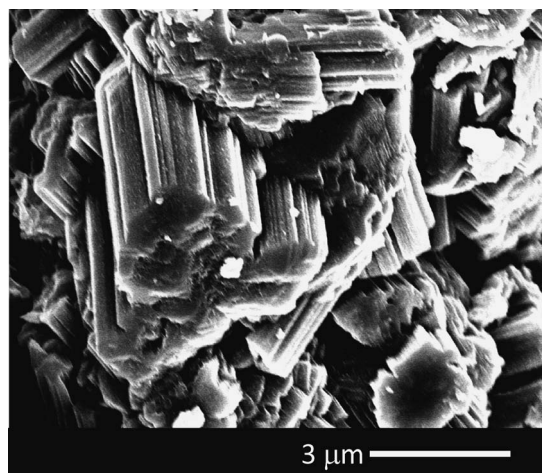


Fig. 3. FE-SEM image of the product, NiS, using fine nickel powder in the case of the heat condition at 240°C for 10 h.

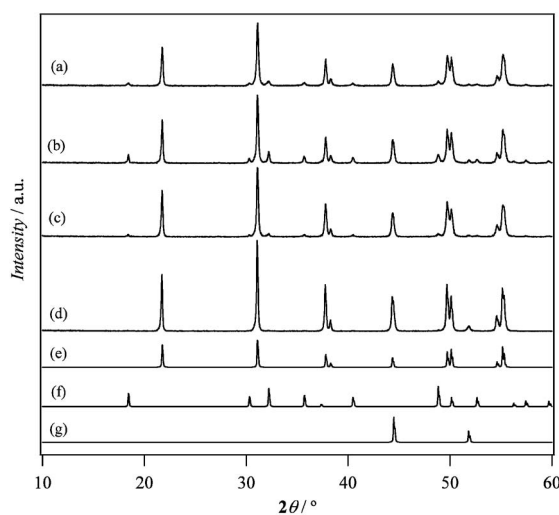


Fig. 4. XRD patterns of the products obtained from the nickel powder and sulfur in the ratio of Ni : S = 3 : 2. The heating conditions are at (a) 180°C for 10 h, and (b) 240°C for 10 h using the fine nickel powder, and at (c) 180°C for 10 h, and (d) 240°C for 10 h using the coarse nickel powder. Reported patterns of (e) Ni₃S₂ (ICSD No. 73839), (f) NiS (ICSD No. 40054), and (g) Ni (ICSD No. 44767).

nickel powder was attempted by increasing the ratio of sulfur. 0.01–0.03 g excess of sulfur from the stoichiometric value, 0.005 mol Ni (0.29347 g) and 0.0033 mol S (0.10689 g), was added and the syntheses were performed at 240°C for 10 h. The XRD pattern of the products is shown in **Fig. 5**. The amount of unreacted Ni decreased with the increase of sulfur up to 0.02 g. The reaction with 0.03 g excess sulfur gave considerable amounts of NiS and Ni₉S₈, the best excess amount of Ni was ca. 0.02 g in this study. However, a small amount of Ni remained in the condition at 240°C for 10 h. When reaction time was extended to 60 h, single phase Ni₃S₂ was obtained as shown in **Fig. 6**.

The shapes of the Ni₃S₂ particles synthesized at 240°C for 60 h was investigated by SEM (see **Fig. 7**). Most of the particles were globular: some of them have a hole as shown in Fig. 7 and some others were observed resembling collapsed balls. The sizes of the particles were about 60 μm, which were

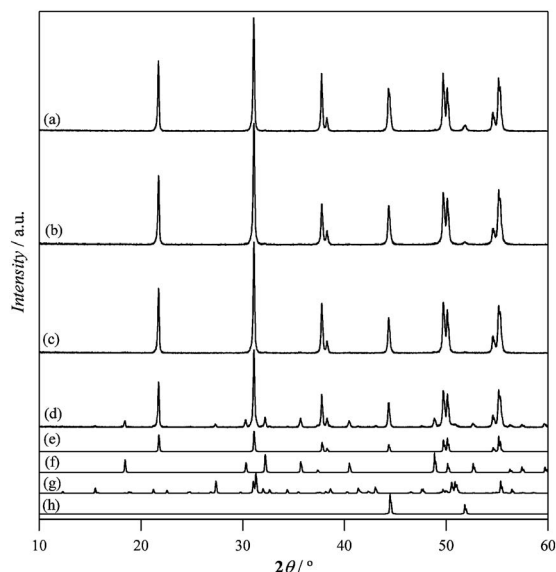


Fig. 5. XRD patterns of the products obtained by increasing the ratio of sulfur. (a) 0.00 g, (b) 0.01 g, (c) 0.02 g, and (d) 0.03 g excess of sulfur from the stoichiometric value. Reported patterns of (e) Ni_3S_2 (ICSD No. 73839), (f) NiS (ICSD No. 40054), (g) Ni_9S_8 (ICSD No. 63080), and (h) Ni (ICSD No. 44767).

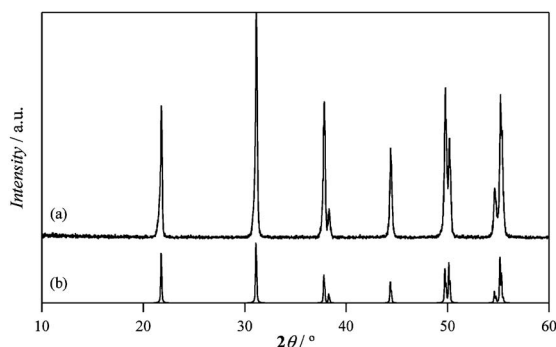


Fig. 6. XRD patterns of the products obtained by adding (a) 0.02 g excess of sulfur from the stoichiometric value. Reported patterns of (b) Ni_3S_2 (ICSD No. 73839).

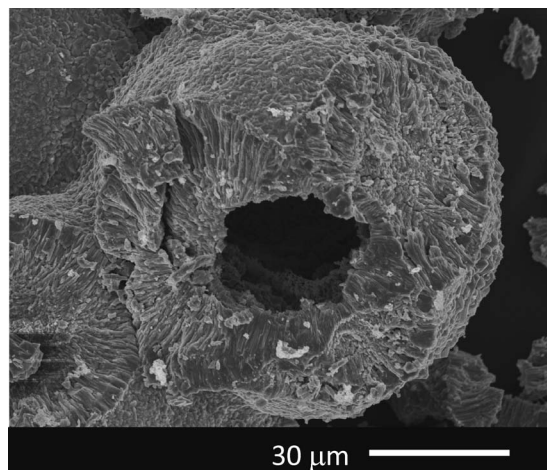


Fig. 7. FE-SEM image of the product, Ni_3S_2 , using coarse nickel powder in the case of the heat condition at 240°C for 60 h.

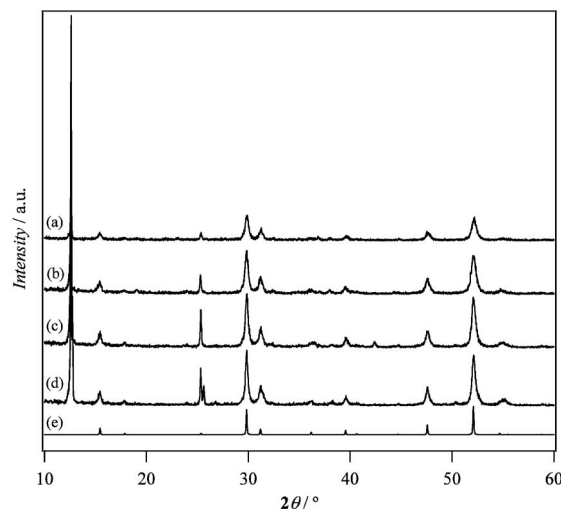


Fig. 8. XRD patterns of the products obtained from the fine cobalt powder and sulfur in the ratio of $\text{Co} : \text{S} = 9 : 8$ at (a) 180°C for 10 h, (b) 180°C for 60 h, (c) 240°C for 10 h, and (d) 240°C for 60 h. Reported patterns of (e) Co_9S_8 (ICSD No. 40046).

similar to those of the starting nickel particles. These observations suggest that the shapes of the starting metal particle remain to some degree through the sulfuration reaction. This aspect of the sulfuration reaction is inherent to the syntheses where metal particles are used as the metal source. If a metal salt is used as the metal source, it is usually dissolved well in water.

3.3 Co_9S_8

Though three stable phases, Co_9S_8 , Co_3S_4 , and CoS_2 were reported at room temperature,⁷⁾ we investigated the lowest sulfide, Co_9S_8 . Thus, the starting materials were mixed in a ratio of $\text{Co} : \text{S} = 9 : 8$. We used two kinds of cobalt powders: ca. $2\ \mu\text{m}$ and ca. $5\ \mu\text{m}$ in the particle size.

First, the synthesis was tried by using the powder of the Co particle size of $1\text{--}2\ \mu\text{m}$. **Figure 8** shows the XRD patterns of the products synthesized by changing the reaction condition. Cubic Co_9S_8 (ICSD 40046) was obtained as the main product under any reaction conditions. Some unidentified peaks were observed at 12.6° and 25.3° in 2θ , which corresponded to the d values $0.702\ \text{nm}$ and $0.351\ \text{nm}$, respectively. Because $0.351\ \text{nm}$ is a half value of $0.702\ \text{nm}$, these two peaks are due to the reflections of the same crystal planes. Because no known cobalt sulfides or oxides have such d values, these peaks indicate that a new compound has formed in the hydrothermal reaction. Two additional peaks were observed at 12.7° and 25.6° in 2θ , which were also due to the reflections of the same planes, as shown in Fig. 8(d). Because the intensities of these unknown peaks increase with increasing temperature, we investigated the product at the temperature as low as 150°C . The results are shown in **Fig. 9**. While the intensities of unknown peaks were decreased, the intensities of the peaks for Co_9S_8 were also decreased. $\text{Co}(\text{OH})_2$ (ICSD 88940), which was not formed in the reactions at higher temperature, was observed.

The reactions with the Co powder of the coarser particle size ($5\ \mu\text{m}$) yielded the products whose XRD patterns are shown in **Fig. 10**. In the products, the unknown peaks at the same angles as observed in the reactions with finer powder were again observed. $\text{Co}(\text{OH})_2$ was also observed in the products at 150°C and 180°C for 10 h. The intensities of the unknown XRD peaks were the smallest for the sample prepared at 180°C

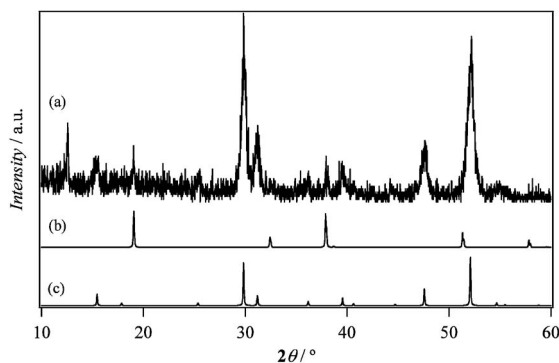


Fig. 9. XRD patterns of the products obtained from the fine cobalt powder and sulfur in the ratio of Co : S = 9 : 8 at (a) 150°C for 10 h. Reported patterns of (b) $\text{Co}(\text{OH})_2$ (ICSD No. 88940) and (c) Co_9S_8 (ICSD No. 40046).

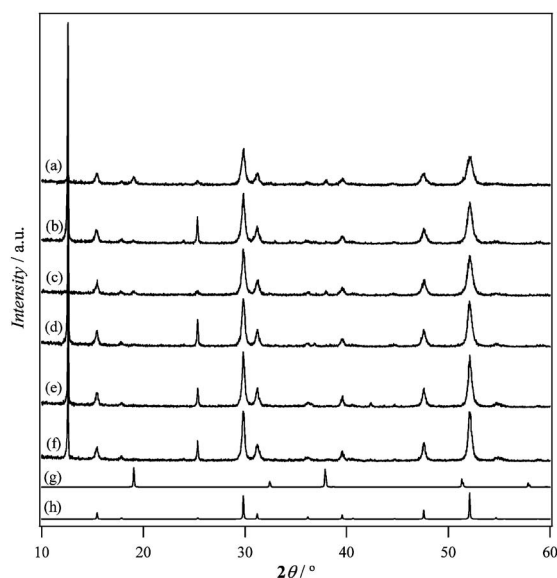


Fig. 10. XRD patterns of the products obtained from the coarse cobalt powder and sulfur in the ratio of Co : S = 9 : 8 at (a) 150°C for 10 h, (b) 150°C for 60 h, (c) 180°C for 10 h, (d) 180°C for 60 h, (e) 240°C for 10 h, and (f) 240°C for 60 h. Reported patterns of (g) $\text{Co}(\text{OH})_2$ (ICSD No. 88940) and (h) Co_9S_8 (ICSD No. 40046).

for 10 h using coarse cobalt powder in this study. We tried to remove the impurities from the product by washing with HNO_3 . The product was suspended in 1 mol/dm³ HNO_3 aqueous solution and the precipitation was filtered. Pure Co_9S_8 was obtained as shown in Fig. 11(a). It was found that not only $\text{Co}(\text{OH})_2$ but also the unknown phase were dissolved in 1 mol/dm³ HNO_3 aqueous solution and could be removed from the product. By the same method, pure Co_9S_8 was obtained also from the products that had larger XRD peaks of the unknown phase (see Fig. 11(b)).

3.4 FeS

The hydrothermal synthesis of the FeS single phase was tried by using the starting materials mixed in the stoichiometric ratio of Fe : S = 1 : 1.

First, the hydrothermal synthesis of FeS was studied by using the coarse Fe powder. The XRD profiles of the products are shown in Fig. 12. The hydroxides of $\text{FeO}(\text{OH})$ (ICSD 93948) and $\text{Fe}(\text{OH})_3$ (JCPDS 38-0032) were observed in the

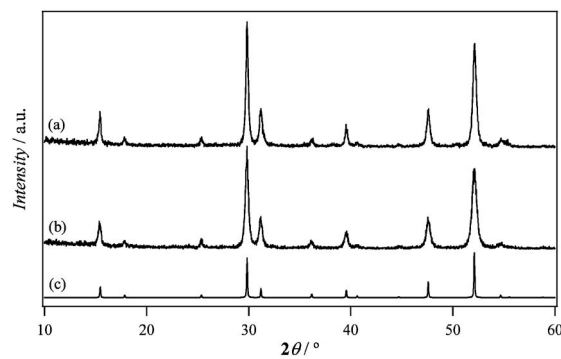


Fig. 11. XRD patterns of the samples, showing the effect of washing. The products at (a) 180°C for 10 h and (b) 240°C for 60 h were washed with 1 mol/dm³ HNO_3 . Reported pattern of (c) Co_9S_8 (ICSD No. 40046).

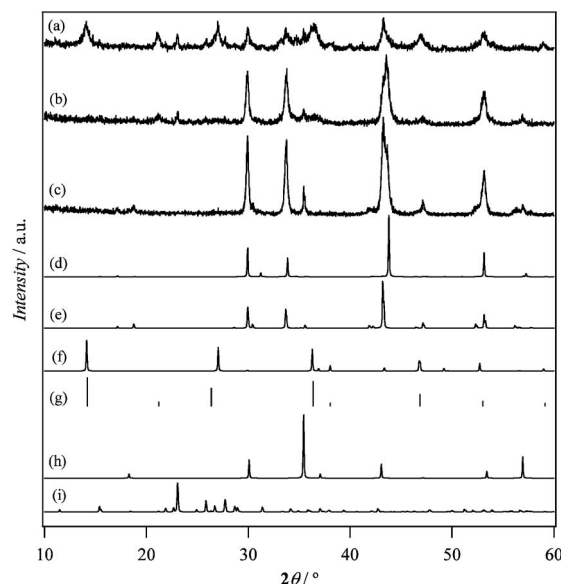


Fig. 12. XRD patterns of the products obtained from the coarse iron powder and sulfur in the ratio of Fe : S = 1 : 1 at (a) 180°C for 10 h, (b) 180°C for 60 h, and (c) 240°C for 10 h. Reported patterns of (d) FeS (ICSD No. 51002), (e) $\text{Fe}_{0.985}\text{S}$ (ICSD No. 68849), (f) $\text{FeO}(\text{OH})$ (ICSD No. 93948), (g) $\text{Fe}(\text{OH})_3$ (JCPDS No. 38-0032), (h) Fe_3O_4 (ICSD No. 50567), and (i) S (ICSD No. 200453).

products of the reactions at a lower temperature (180°C) for 10 h. In the products of these reactions, unreacted sulfur (ICSD 200453) was observed while no iron was detected. When reaction time was extended to 60 h, the XRD pattern of the product became simple and the peaks were mostly attributed to FeS. However, S and Fe_3O_4 remained. Then, the reaction temperature was raised up to 240°C. The XRD pattern is shown in Fig. 12(c). FeS was obtained as a main product and the impurity was Fe_3O_4 (ICSD 50567). However, the strongest peak of the product shifted to a lower angle than the position expected for the peak of hexagonal FeS (ICSD 51002). In a Fe-S system, Fe-deficient compound, Fe_xS , is also stable in addition to stoichiometric FeS and FeS_2 .⁶⁾ Therefore, this compound is considered to be Fe-deficient FeS like $\text{Fe}_{0.985}\text{S}$ (ICSD 68849). From the results, this reaction using the coarse powder is not suitable for the synthesis of stoichiometric FeS because the reactivity is low.

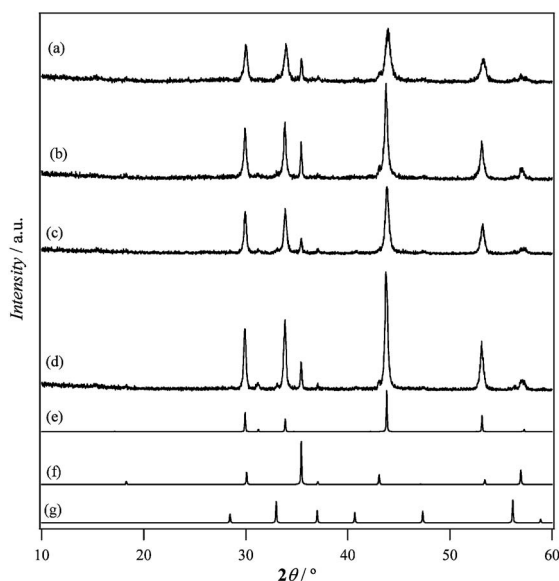


Fig. 13. XRD patterns of the products obtained from the fine iron powder and sulfur in the ratio of Fe : S = 1 : 1 at (a) 180°C for 10 h, (b) 180°C for 60 h, (c) 240°C for 10 h, and (d) 240°C for 60 h. Reported patterns of (e) FeS (ICSD No. 51002), (f) Fe₃O₄ (ICSD No. 50567), and (g) FeS₂ (ICSD No. 316).

The reaction with a fine iron powder (3–5 μm) gave the products whose XRD patterns were shown in Fig. 13. In these

products, hexagonal FeS was the main product even at the low temperature of 180°C. The hydroxides, which were formed in the reactions with coarse Fe powder, were not observed, though Fe₃O₄ was observed in the XRD pattern. The peak intensities of FeS became stronger with the increasing reaction temperature and/or reaction time. The positions of the peaks were the same as those of stoichiometric FeS. In contrast to the reactions with the coarse Fe powder, a small amount of cubic FeS₂ (ICSD 316) was detected in the products. In summary, hydrothermal reactions of the elements is a versatile method for the syntheses of late transition sulfides. In this method, appropriate selection of metal particle size is critical. The sulfides obtained as a single phase by this method are NiS, Ni₃S₂, Co₉S₈, and FeS (with small amount of Fe₃O₄).

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