Simple synthesis of zinc sulfide and cadmium sulfide under hydrothermal conditions

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Pure ZnS and CdS were synthesized under hydrothermal conditions. The reactions of Zn or ZnO with S at 240°C yielded pure ZnS. Similar reactions at lower temperatures gave plate crystals of an unknown phase along with ZnS and ZnO. Pure CdS was obtained by the reaction between CdO and S at 240°C while the reaction of metal Cd and S gave a mixture. The as-prepared CdS crystals had rod shapes.

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Key-words : Hydrothermal synthesis, Zinc, Cadmium, Sulfide

[Received September 10, 2010; Accepted November 5, 2010]

1. Introduction

Metal sulfides are traditionally prepared by thermal reactions of the elements in an evacuated silica tube at high temperature or by the reaction of hydrogen sulfide gas with the aqueous solution of the metal salt. Both of the two methods have advantages and disadvantages. Reactions between elements in a sealed tube are simple but needs high temperature^{1,2)} or long time milling³⁾ in order to get pure metal sulfide. For example, copper is very reactive with sulfur and their reaction starts even at room temperature. However, the reaction occurs only on surface, and much stronger conditions are required to complete the reaction.¹⁾ On the other hand, reaction in aqueous solution proceeds completely at room temperature. However, complex compounds such as CuSO₄ and Na₂S must be used as starting materials because simple oxide or metal does not dissolve in water.

As the third method for sulfide syntheses, we have been interested in reactions between metal and sulfur under hydrothermal conditions. We have found that pure CuS is obtained easily at low temperature, 60°C.^{4,5)} Silver sulfide (Ag₂S),⁵⁾ iron sulfide (FeS),⁶⁾ cobalt sulfide (Co₉S₈),⁶⁾ nickel sulfides (NiS, Ni₃S₂),⁶⁾ and complex sulfides AgCuS⁷⁾ and Ag₃CuS₂⁷⁾ can also be prepared under similar conditions.

In this study, we have aimed at simple preparations of ZnS and CdS under hydrothermal conditions using elemental metal or metal oxide as starting materials. ZnS is well known as an electroluminescent (EL) material⁸⁾ and is a promising material for a photocatalyst.⁹⁾ CdS is also known as photo sensor in addition to the same applications as ZnS.¹⁰⁻¹²⁾

2. Experimental

Zn (2N, Kojundo chemical laboratory), ZnO (3N5, Kanto chemical), Cd (3N, Wako pure chemical industries), CdO (4N, Kojundo chemical laboratory) and S (4N, Kojundo chemical laboratory) were used as starting materials. Metallic source (5 mmol) and sulfur powder (5 mmol) were weighed and ground in an agate mortar. The mixtures were added into 10 mL distilled

water in a Teflon-lined pressure vessel with the capacity of 25 mL. Then, the pressure vessel was sealed and heated at 180–240°C (at 30°C interval) for 1, 10, 40, or 60 h. 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 Cu-K α radiation on a RINT2200 diffractometer (Rigaku) equipped with a graphite monochromator. The morphology and particle size of the products were observed by scanning electronic microscopy (SEM) images, taken with JSM5610 system (JEOL). EMAX-5770 (Horiba) Energy dispersive X-ray fluorescence spectrometer (EDX) was used for evaluation of the compositions of the products.

3. Results and discussion

3.1 ZnS

For reactions between zinc and sulfur, the XRD patterns of the reaction products are shown in **Fig. 1**. Pure ZnS was obtained at 240°C for 40 and 60 h. Although ZnS phases were observed even in the product at a lower temperature, 180°C, unreacted sulfur, zinc oxide, and unknown phase were also observed. In order to investigate the effect of water, reaction without water was performed at 240°C for 60 h. The XRD pattern of the product is shown in **Fig. 2**. The main peaks correspond to those of Zn, S, and ZnO, and ZnS was hardly formed. This result indicates that hydrothermal condition is essential and very efficient for synthesis of ZnS from zinc metal and sulfur at 240°C. As mentioned previously, the reaction between Cu and S is restricted to the surface of particles although the reaction occurs even at room temperature. Thus, the complete reaction between Cu and S needs higher temperature and/or long time milling. Because under hydrothermal condition even at low temperature, 60°C, with low vapor pressure, the reaction is completed,⁴⁾ the most important role of water is to enhance the diffusion of starting materials. For the reaction between Zn and S under hydrothermal condition, the effect of the diffusion by water is essential, although high vapor pressure at 240°C may also progress the reaction. The yield of ZnS was ~80% based on Zn.

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Fig. 1. The XRD patterns of the precipitates of hydrothermal reactions between Zn and S at (a) 240°C for 60 h, (b) 240°C for 40 h, (c) 240°C for 10 h, (d) 240°C for 3 h, and (e) 180°C for 10 h. Reported patterns of (f) ZnS (JCPDS Card No. 05-0566), (g) ZnO (JCPDS Card No. 36-1451), and (h) S (JCPDS Card No. 08-0247). Filled inverted triangles show the main peaks of the unknown phase with the d spacing of 0.702 nm.

Fig. 2. (a) The XRD pattern of the precipitates of reaction between Zn and S without water at 240°C for 60 h. Reported patterns of (b) ZnS (JCPDS Card No. 05-0566), (c) Zn (JCPDS Card No. 04-0831), (d) ZnO (JCPDS Card No. 36-1451), and (e) S (JCPDS Card No. 08-0247).

The SEM image of ZnS particles obtained at 240°C for 60 h is shown in **Fig. 3(a)**. The sizes of the particles are about 0.1 μm .

When the reaction temperature was lowered to 180°C, the powder pattern of the precipitates showed an unknown phase. Three strong unidentified peaks by the unknown phase in the XRD profile were observed at 12.6, 25.3 and 50.6° in 2θ , which corresponded to the d spacings 0.702, 0.351 and 0.17 nm, respectively. The ratio of these spacings are 1:1/2:1/4, and it is very probable that these three peaks are due to the same set of crystal planes. Because no known zinc sulfides nor sulfates has such a d spacing, the peaks indicate that a new compound is formed in the hydrothermal condition. The powder pattern in which all of the strong diffractions are due to a set of planes, which means very strong preferred orientation, indicates that the sample consists of plate crystals stacked along the base plane. This inference was confirmed by the observation of crystal

Fig. 3. The SEM images of the products from Zn and S. (a) ZnS particles obtained at 240°C for 60 h and (b) unknown crystal obtained at 240°C for 10 h.

Fig. 4. The XRD patterns of the precipitates of hydrothermal reactions between ZnO and S at (a) 240°C for 60 h, (b) 240°C for 10 h, (c) 180°C for 60 h, and (d) 180°C for 10 h. Reported patterns of (e) ZnO (JCPDS Card No. 36-1451), and (f) ZnS (JCPDS Card No. 05-0566). Filled inverted triangle show the main peaks of the unknown phase.

shapes by SEM as shown in **Fig. 3(b)**. EDX analysis of the crystal showed the existence of sulfur and oxygen in addition to zinc. However, oxygen composition could not be determined precisely because of the limit of EDX analysis for lighter elements.

The reaction of ZnO, instead of Zn metal, with S at 240°C for 10 h yielded ZnS as a single phase (**Fig. 4**). The reaction time was much shorter than 40 h required for the reaction between Zn and S. This result indicates that the reactivity of ZnO with S is

Fig. 5. (a) The XRD pattern of the residue after evaporation of the filtrate obtained by hydrothermal reactions between ZnO and S at 240°C for 10 h. (b) Reported pattern of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (JCPDS Card No. 33-1476).

Fig. 6. The SEM images of the products obtained at 240°C for 10 h from ZnO and S. (a) ZnS particles and (b) plate crystals.

better than that of zinc metal. The yield of ZnS was 76% based on zinc. We estimate the reaction as follows.

If the reaction proceeds completely, the yield of ZnS is calculated to be 75%. The calculated yield is very close to 76%. If the reaction of equation (1) occurs, the filtrate after the reaction includes ZnSO_4 . Thus, we evaporated the filtrate to dryness to obtain white powder. Its XRD pattern agreed well with that of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ (PDF No. 33-1476, see Fig. 5) and the reaction (1) was confirmed. The shape of the particle was similar to the particle synthesized from Zn and S [see Fig. 6(a)]. The importance of water was confirmed also in the reaction between ZnO and S. The reaction without water at 240°C for 10 h gave the products shown in Fig. 7. Although the reaction proceeded more than the reaction between the elements without water, ill-crystallized ZnS was formed with unreacted ZnO and

Fig. 7. (a) The XRD pattern of the products obtained by the reaction between ZnO and S without water at 240°C for 10 h. Reported patterns of (b) ZnO (JCPDS Card No. 36-1451), (c) ZnS (JCPDS Card No. 05-0566), and (d) $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (JCPDS Card No. 33-1476).

Fig. 8. The XRD patterns of the precipitates of hydrothermal reactions between Cd and S at (a) 240°C for 60 h, (b) 240°C for 10 h, and (c) 180°C for 10 h. Reported patterns of (d) CdS (JCPDS Card No. 41-1049), (e) $\text{Cd}(\text{OH})_2$ (JCPDS Card No. 31-0228), (f) Cd (JCPDS Card No. 05-0674), and (g) S (JCPDS Card No. 08-0247).

$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$. From the result, hydrothermal condition was found to be useful to promote the reaction efficiently. In the reaction between ZnO and S, the role of water may be similar to that for the reaction between the elements, although the starting materials are different.

If the reaction temperature was below 240°C and/or the reaction time was shorter than 10 h, the powder pattern of the products showed that they included the same unknown compound as observed in the products of the reactions between the elements (see Fig. 4). In SEM images, we confirmed plate crystals again [see Fig. 6(b)].

3.2 CdS

The reaction between the elements (Cd and S) gave impurities such as CdO, $\text{Cd}(\text{OH})_2$, Cd, and S besides CdS. We could not obtain the single phase of CdS even at 240°C for 60 h (Fig. 8).

Fig. 9. The XRD patterns of the products of hydrothermal reactions between CdO and S at (a) 240°C for 10 h, (b) 180°C for 60 h, (c) 180°C for 10 h, and (d) 180°C for 1 h. Reported patterns of (e) CdS (JCPDS Card No. 41-1049), (f) Cd(OH)₂ (JCPDS Card No. 31-0558), and (g) S (JCPDS Card No. 08-0247).

Fig. 10. The XRD patterns of the residue after evaporation of the filtrate obtained by hydrothermal reactions between CdO and S at (a) 240°C for 10 h. Reported pattern of (b) CdSO₄·H₂O (JCPDS Card No. 20-1411).

The cause of the unsuccessful synthesis is not only the low reactivity between cadmium metal and sulfur but also the low purity of cadmium metal powder, whose surface is easily oxidized in a humid air.

When CdO and S were used as starting materials, CdS was obtained almost as a single phase even at low temperature, 180°C (see Fig. 9). In this reaction condition, unreacted CdO was changed to cadmium hydroxide Cd(OH)₂. The single phase of CdS was obtained at 240°C for 10 h. The yield of CdS was 77% based on cadmium. We guess the reaction as follows with the reference to the reaction between ZnO and S.

In this reaction, the theoretical yield is calculated to be 75%, which is very close to the experimental value, 77%. The XRD pattern of the residue obtained by evaporation of the reaction solution was consistent with CdSO₄·H₂O (PDF No. 20-1411, see Fig. 10), supporting the reaction (2). The reaction without water

Fig. 11. The XRD pattern of the products obtained at (a) 240°C for 10 h from CdO and S without water. Reported pattern of (b) CdS (JCPDS Card No. 41-1049) and (c) CdSO₄·H₂O (JCPDS Card No. 20-1411).

Fig. 12. The SEM image of the products obtained at 240°C for 10 h from CdO and S.

was investigated at 240°C for 10 h. The XRD pattern of the products is shown in Fig. 11. Because CdS is formed as a mixture with CdSO₄·H₂O, the hydrothermal condition is useful to promote the reaction efficiently. The reaction mechanism also seems the same as that between ZnO and S as mentioned above.

Hexagonal rod-like crystals with ~200 nm in diameter were observed in the SEM image of as-prepared CdS samples as shown in Fig. 12. Because CdS has the wurtzite structure with hexagonal system, the crystals grow to [001] direction.

4. Summary

Pure ZnS were synthesized by hydrothermal reactions between simple starting materials, zinc/zinc oxide and sulfur, at 240°C. A new compound with the d spacing 0.702 nm was observed in the reaction products in weaker conditions.

CdS was also prepared by similar reactions between CdO and S at 240°C, while the reaction between Cd and S gave a mixture. The particles of obtained CdS were rod-like with ~200 nm in diameter.

These hydrothermal methods using simple starting materials were found to be very efficient to prepare ZnS and CdS.

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