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Effect of Ultrasound Irradiation on Size and Morphology of Scorodite Particles Synthesized under Different Acidic Conditions

異なる酸性条件で合成したスコロダイト粒子のサイズや形態に与える超音波の影響

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1. Introduction

Arsenic is toxic for the human body. Therefore, waste materials and factory effluents containing arsenic must be treated and stored using the appropriate methods. In mining field, arsenic is commonly found in the form of enargite (Cu_3AsS_4) and tennantite ($Cu_{10}Fe_2AsS_{13}$) sulfide minerals that are present in the copper ore deposits.[1] Recently, disposal of the highly-concentrated arsenic accrued by the repeated processing of flue cinder in copper smelting has become difficult because of the increased arsenic concentration in the copper mineral. Because of the use of sulfuric acid to leach copper in the flue cinder, arsenic removal and storage materials must be stable under acidic conditions. Scorodite ($FeAsO_4{\cdot}2H_2O$) has been studied as a promising storage material of arsenic.[2,3] Scorodite releases little arsenic when the pH value of the solution is changed in acidic reageon. Scorodite is synthesized by oxidation in an acidic solution containing divalent iron [Fe(II)] and pentavalent arsenic [As(V)]. A larger particle size is preferred because a low surface-to-volume ratio makes it difficult to dissolve scorodite in an acidic solution. Large scorodite particles(>10 μm) are synthesized in a strong acdic solution of pH 1.0 using stirrer at high temperature (>90°C).[2] Therefore, the reaction temperature and the pH condition are important factors to synthesize large scorodite using stirring method. We have been studied reaction temperature during ultrasound irradiation on the size and morphorogy of the syntheiszed scorodite particles.[4,5] In this study, we investigated the effect of pH conditions on the size and morphorogy of the scorodite particles synthesized using ultrasound irradiation.

2. Experimental

The acidic solutions containing various concentration of As(V) were prepared using $Na_2HAsO_4{\cdot}7H_2O$, H_2SO_4, and ion-exchange water. Then, Fe(II) solution was added to the As(V) solution. Finally Fe(II)-As(V) solution (50 mL) was adjusted to a Fe/As molar ratio of 1.5. As(V) concentration of the solution was 20 g/L. pH of the solution was adjusted at pH 1.0, 1.5, 2.0, 2.5, and 3.0. Sonication was performed with an ultrasonic generators (TA-4021; KAIJO) and submersible transducers (KAIJO). The Output and the frequency of the transducer were set to 200 W and 200 kHz. **Fig. 1** shows the experimental apparatus of ultrasound irradiation. A submersible transducer was placed at the bottom of a tank filled with water, and a flat-bottom flask containing the solution was placed directly above the transducer. The temperature of the irradiated solution was controlled at 70°C using hot water circulation around the flat-bottom flask. Before the sonication of the solution, oxygen gas (100 mL/min) was flowed into the solution for 20 min to replace the air with oxygen gas in the flask. With or without sonication for the solution was conducted at 70°C for 3 h under oxygen gas flow. The precipitates from the above process were filtered using a 0.45 μm pore diameter membrane filter. After drying, the precipitates were analyzed using X-ray diffraction (XRD) measurement, scanning electron microscope (SEM) observation.

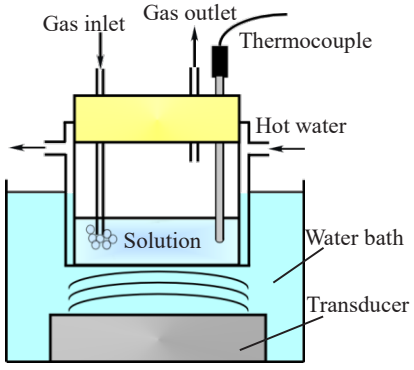

Fig. 1 Schematic of the experimental apparatus.

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3. Results and Discussion

Fig. 2 shows the XRD patterns of precipitated samples synthesized using with and without ultrasound irradiation under different pH conditions. The intensity of XRD peaks of scorodite synthesized at pH 1.0, 2.5, and 3.0 differs between two conditions (with or without ultrasound irradiation). Using ultrasound irradiation, scorodite peaks (PDF No. 00-037-0468) were shown at all pH conditions. The intensity of XRD peaks of scorodite became lower when the pH became higher value of 2.5. Crystallinity values of scorodite synthesized at different pH were >90% (pH 1.0~2.0), 84% (pH 2.5), 56% (pH 3.0). On the other hand, without ultrasound irradiation, scorodite peak was disappeared at pH 3.0. The intensity of XRD peaks of scorodite showed lower intensity at pH 1.0 and 2.5 than that at pH 1.5 and pH 2.0. Crystallinity values of scorodite synthesized at different pH were 77% (pH 1.0), >90% (pH 1.5~2.0), 53% (pH 2.5), 3% (pH 3.0). When scorodite is synthesized at high pH conditions (pH 2.5 and 3.0), large amount of gel like precursor was generated after start of experiment. Thus, low crystallinity scorodite were obtained because the luck of oxygen gas to oxidize precursor enough. Therefore, we consider that these different results gained from two conditions should come from the effect of physical action with/without ultrasound irradiation. (**Fig. 3**). On the other hand, at the lowest pH of 1.0, oxidation of the precursor (crystallization) is difficult because the precursor is easily dissolute into the solution. The intensity of XRD peaks of scorodite synthesized without ultrasound was lower than that synthesized by ultrasound irradiation. The reason of above results would come from oxidation effect of OH radicals generated and oxygen gas miniaturized under ultrasound irradiation.

4. Conclusion

To investigate the effect of pH conditions on the size and morphology of scorodite synthesized using ultrasound irradiation, we performed the synthesis of scorodite particles at different pH conditions (pH 1.0, 1.5, 2.0, 2.5, and 3.0) for 3 h with the oxygen gas flow. The intensity of XRD peaks of scorodite synthesized at pH 1.0, 2.5, and 3.0 was different between two conditions (using or without using ultrasound irradiation). When scorodite is synthesized at pH 2.5 and 3.0, scorodite with low crystallinity was synthesized. This is because supplied amount of oxygen gas was not enough to oxidize the large amount of gel like precursor generated by ultrasound irradiation. The crystallinity value of scorodite synthesized using with and without ultrasound irradiation at pH 1.0 was >90% and 77%, respectively. The different results of two conditions (with or without ultrasound) should come from the oxidation amount by radicals generated by ultrasound irradiation.

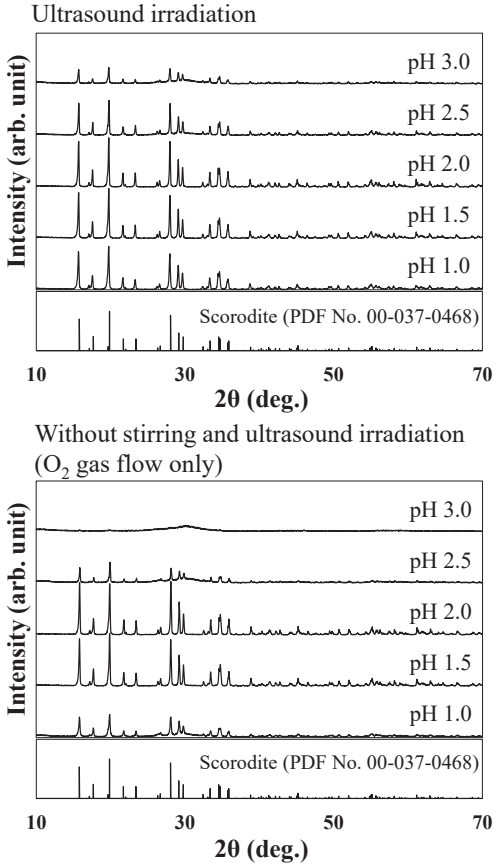

Fig. 2 XRD patterns of precipitated samples synthesized using with and without ultrasound irradiation under different pH conditions.

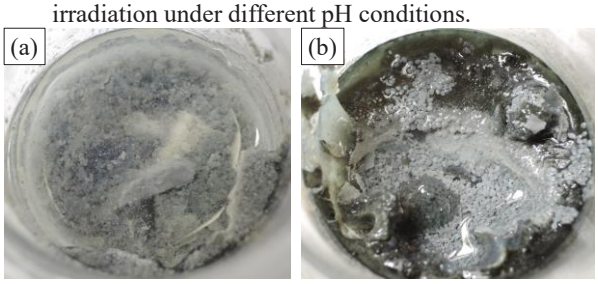

Fig. 3 Solutions after each reaction at pH 2.5 ((a)ultrasound, (b)without ultrasound).

Acknowledgment

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