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Sonochemical Synthesis of Copper and Silver Chalcogenides

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$Cu_{1.96}S$, Cu_3Se_2, αCu_2Se, and Ag_2Se were prepared by irradiating mixturs of the elements in methanol with ultrasound at 28 kHz, using a commercial ultrasonic cleaner. Scanning electron microscopy and electron probe microanalyis investigations on Cu_3Se_2 showed that the compositions of both Cu and Se particles changed continuously to Cu_3Se_2 as the irradiation time increased. © 1998 Academic Press

The mechanical alloying (MA) method has been widely applied for the preparation of many intermetallics and compounds and is now a useful technique for synthesizing unique microstructures (1). Recently, we prepared many chalcogenides of Cu, Ag, and Sm by milling mixtures of the elements using a planetary ball mill (2, 3). The notable results are that the metastable high-pressure phases of tetragonal $Cu_{2-x}S$ and pyrite-type $CuSe_2$ were prepared by MA (2). These are the first preparations of high-pressure phases by MA.

Suslick *et al.* have extensively investigated the mechanochemical effects of high-intensity ultrasound which result from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in liquids (4–9). They found a variety of sonochemical reactions in liquid–solid mixture systems, i.e., intercalation into layered inorganic solids (7), syntheses of amorphous metal powders (8), and metal semicarbides (9). In the present work, we have prepared copper and silver chalcogenides by irradiating the elemental mixtures immersed in methanol with ultrasound.

$Cu_{1.96}S$, Cu_3Se_2, αCu_2Se, and Ag_2Se were prepared as follows. The mixture of the elements in the desired ratio (0.5 g in weight) was immersed in 0.3 cc of hydrocarbon liquid (methanol, ethanol, hexane, benzene, or liquid paraffin), which was contained in a silica tube with an inner diameter of 8.0 mm and a wall thickness of 1.0 mm. The silica tube was partly submerged in 1.5 dm^3 of water in a common ultrasonic cleaner (Shimadzu, SUS-103; 110 V, 100 W). The water in the bath was kept at room temperature. The bottom of the silica tube was situated at 15 mm above the base of the bath. The organic liquid slurries were irradiated with ultrasound at 28, 45, or 100 kHz or 4–8 h at room temperature. The starting elements were Cu (Katayama Chemical Ind., 99.9%, 300 mesh), Ag (Wako Pure Chemical Ind., 99%, 200 mesh), S (Nakalai Tesque, 99.999%, ingot), and Se (Wako Pure Chemical Ind., 99.999%, ingot). The S and Se ingots were crushed into 100–200 mesh powders in an agate mortar. The temperature of the reaction mixtures was measured by a radiation thermometer. Obtained samples were identified by XRD (X-ray diffraction) measurements using Cu$K\alpha$ radiation (Rigaku, RAD-B). Scanning electron microscopy (SEM) observations were performed on Cu_3Se_2 samples obtained for a different irradiation time (Hitachi, X-650).

The reactions were found to be most favorable under the irradiation of methanol slurries at 28 kHz for all the compounds. The temperature was observed to be near room temperature in the course of the reactions. Figure 1 shows the XRD pattern of $Cu_{1.96}S$, which was obtained by irradiating the mixture of the desired ratio of Cu and S powders in methanol with ultrasound at 28 kHz for 4 h. The pattern shows a two-phase mixing state of a stable phase of djurleite and a metastable tetragonal phase. The pattern was not changed by further irradiation. The tetragonal phase of $Cu_{2-x}S$ is stable at pressures higher than 0.8 kbar (10). The two-phase mixing state implies that the effective pressure generated by the present experiments is not high enough to produce a single high-pressure phase. Figure 2 shows the XRD pattern of Cu_3Se_2, which was obtained by irradiating the mixture of 3Cu and 2Se in methanol with ultrasound at 28 kHz for 8 h. The pattern is identical with the published data of the tetragonal structure (11). Cu_2Se was obtained by irradiating a mixture of 2Cu and Se in methanol with ultrasound at 28 kHz for 8 h. The pattern is identical with the monoclinic αCu_2Se phase (12). Ag_2Se was prepared by irradiating a mixture of 2Ag and Se in methanol with ultrasound at 28 kHz for 4 h. The pattern is identical with the literature data of an orthorhombic structure (13).

Figure 3a shows a SEM image of the starting mixture of Cu (spherical in shape) and Se powders (angular or irregular in shape). Figure 3b shows the image of the Cu particle

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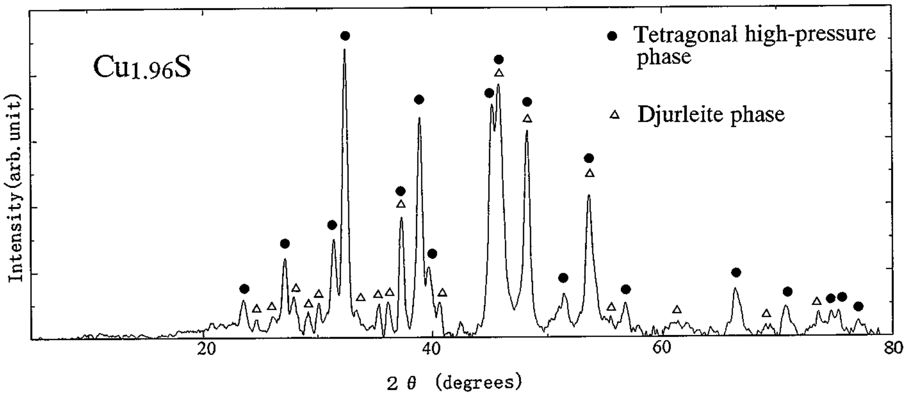

FIG. 1. X-ray diffraction pattern of $Cu_{1.96}S$, which was obtained by irradiating the mixture of the desired ratio of Cu and S in methanol with ultrasound at 28 kHz for 4 h. Closed circles and open triangles indicate the tetragonal high-pressure and djurleite phases, respectively.

obtained after irradiation for 0.5 h. The surface is covered with many granules. Electron probe microanalysis (EPMA) showed that the surface is rather homogeneous and has a composition near Cu_7Se. The inner part of the particle is considered to remain unreacted, because the XRD pattern showed the existence of a large amount of elemental copper. The composition was observed to increase continuously to Cu_3Se_2 as the irradiation time increased. The image of the Se particle after the irradiation for 0.5 h is shown in Fig. 3c. EPMA showed that the small particles attached to the surface have the composition of $CuSe_{2\sim7}$ and that the basal surface is elemental Se. The averaged surface composition was observed to change continuously to Cu_3Se_2 as the irradiation time increases. Figure 3d shows the image of the final product of Cu_3Se_2 obtained by irradiation for 8 h. Suslick *et al.* observed that the interparticle collisions induced by ultrasonic irradiation in hydrocarbon liquids generated effective transient temperature as high as 3000°C, and resulted in fusion at the impact points using an apparatus with a 50 W/cm^2 direct immersion ultrasonic horn (4–6). Figure 3d shows that the particles do not appear to be fused together and that many Cu and Se particles seem to retain their initial shapes, although Cu_3Se_2 melts at 523°C (14), suggesting that this reaction proceeded under rather mild conditions, as compared with those of Suslick *et al.*

As in the above experiments, the elemental mixtures immersed in methanol were kept at room temperature without ultrasound irradiation. XRD measurements showed that the elements gradually reacted with each other to form the compounds. The reaction rates were quite slow compared to those under the ultrasonic irradiation. The rates were observed to increase as the temperature increased. For example, the mixture of 3Cu + 2Se reacted almost entirely to Cu_3Se_2 when kept at 40°C for 3 days, while only a part of the mixture reacted when kept at room temperature for 3 days. These observations suggest that the ultrasonic irradiation is not necessarily fully responsible for the reactions. But, it is surely concluded that ultrasonic irradiation plays an important role in the acceleration of the reactions. More detailed observations will be reported elsewhere.

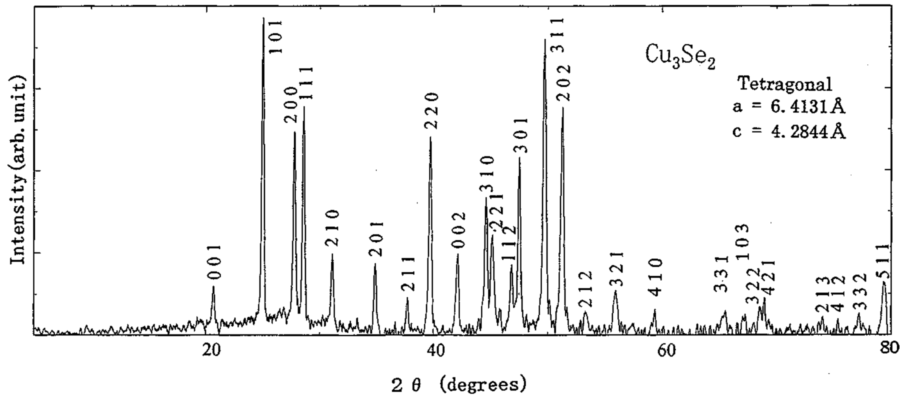

FIG. 2. X-ray diffraction pattern of Cu_3Se_2, which was obtained by irradiating the elemental mixture of 3Cu and 2Se in methanol with ultrasound at 28 kHz for 8 h.

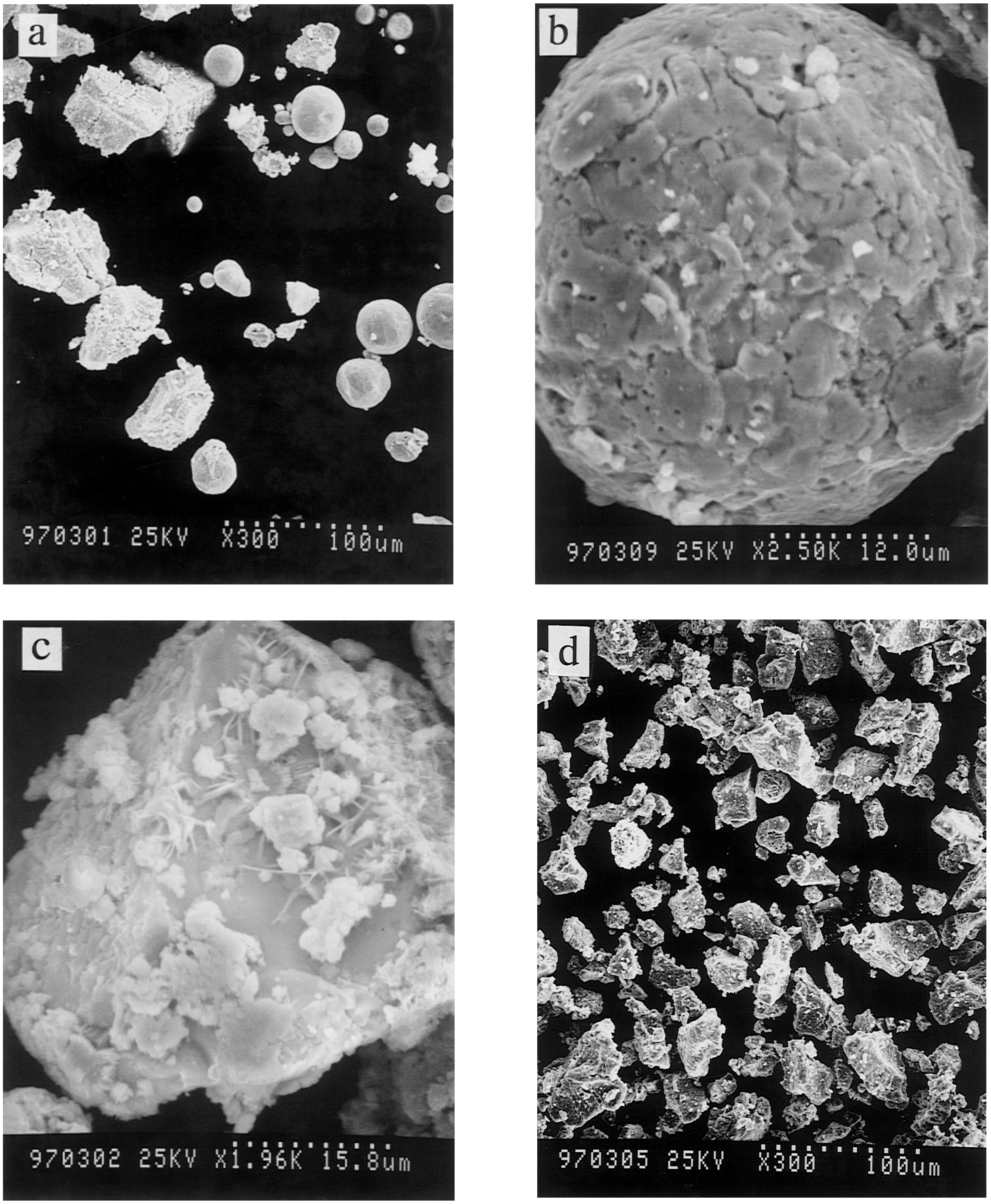

FIG. 3. SEM images of Cu_3Se_2 after different ultrasonic irradiation times: (a) initial mixture of Cu and Se powders, (b) Cu particle after irradiation for 0.5 h, (c) Se particle after irradiation for 0.5 h, and (d) the final product after irradiation for 8 h.

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