Solvothermal Preparation of Silver Chalcogenides Ag_2E(E=S,Se,Te)

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(Received July 27, 1998; CL-980566)

Well crystallized silver chalcogenides were synthesized by a solvothermal reaction of silver oxalate $Ag_2C_2O_4$ with chalcogens in organic solvents at relatively low temperature (140 ℃-180 ℃). It was found that both solvents and temperature have significant influence on the synthesis of silver chalcogenides.

The synthesis of binary metal chalcogenides of groups IB and IIB has been the focus of much attention recently.[1,2] These materials have wide applications in semiconductors, pigments,[1] luminescence devices,[1] solar cells, IR detectors, and optical fiber communications.[4]

Conventionally, metal chalcogenides are synthesized by the reaction of the elements at elevated temperature, typically 500 ℃ -600 ℃, in evacuated tubes,[1,5,6] or by reaction of aqueous metal salt solutions with toxic and malodorous gas H_2E.[5,7] Synthesis *in situ* of nanosized silver sulfide particles in reverse micelles was also reported.[8,9] Korczynski *et al* [10] reported one method for the preparation of heavy metal selenides based on heavy metal salt reactions with K_2Se in aqueous media, which required excess metallic Al to prevent Se co-precipitation with selenides and H_2 atmosphere to avoid K_2Se oxidation. The obtained metal selenides via this method showed deviation from their theoretical compositions.[10] Parkin *et al* [1,2] reported a new method for the synthesis of metal chalcogenides by a reaction between metal and E in liquid ammonia at room temperature. Crystalline Ag_2S and Ag_2Se powders were obtained at room temperature.[1] The predominant product was Ag_2Te with 5-10% of Ag_7Te_4.[2]

In this letter, we report a novel solvothermal approach to crystallized Ag_2E by a reaction between $Ag_2C_2O_4$ and E in organic solvents. The so-called solvothermal process is similar to the hydrothermal process, except that organic solvent substitutes for water. The reactions can be expressed as the following equation :

$$Ag_2C_2O_4 + E \xrightarrow{\text{solvent}} Ag_2E + 2CO_2\uparrow \qquad (1)$$

In a typical procedure, 0.01mol analytical E and 0.01mol $Ag_2C_2O_4$ was put into a Teflon-lined autoclave of 100 ml capacity, which was filled with pyridine(py), ethylenediamine(en) or tetrahydrofuran(THF) up to 80% of the total volume. The autoclave was maintained at 140 ℃ for 12 h and then air cooled to room temperature. The precipitate was filtered, washed respectively with ethanol, distilled water, diluted HNO_3 solution, and absolute ethanol to remove the impurities. The product was dried in vacuum at 70 ℃ for 4 h.

Table 1. The solvent and temperature effects on the formation of silver chalcogenides by the present solvothermal route

Sample No.	Reagents	Solvent	Reaction temperature and time	Crystalline phase
1	$Ag_2C_2O_4$ + S	en	140 ℃, 12 h	Ag_2S
2	$Ag_2C_2O_4$ + S	py	140 ℃, 12 h	Ag_2S
3	$Ag_2C_2O_4$ + S	THF	140 ℃, 12 h	Ag_2S
4	$Ag_2C_2O_4$ + Se	en	140 ℃, 12 h	Ag_2Se
5	$Ag_2C_2O_4$ + Se	py	140 ℃, 12 h	Ag_2Se^a + Se
6	$Ag_2C_2O_4$ + Se	py	160 ℃, 12 h	Ag_2Se^a + Ag
7	$Ag_2C_2O_4$ + Se	THF	140 ℃, 12 h	Ag_2Se^a + Se
8	$Ag_2C_2O_4$ + Te	en	180 ℃, 12 h	Ag_2Te^a + Ag
9	$Ag_2C_2O_4$ + Te	en	160 ℃, 12 h	Ag_2Te + Ag^a
10	$Ag_2C_2O_4$ + Te	py	180 ℃, 12 h	Ag_2Te + Ag^a
11	$Ag_2C_2O_4$ + Te	THF	180 ℃, 12 h	Ag_2Te + Ag^a

[a] indicates the dominant phase in the sample.

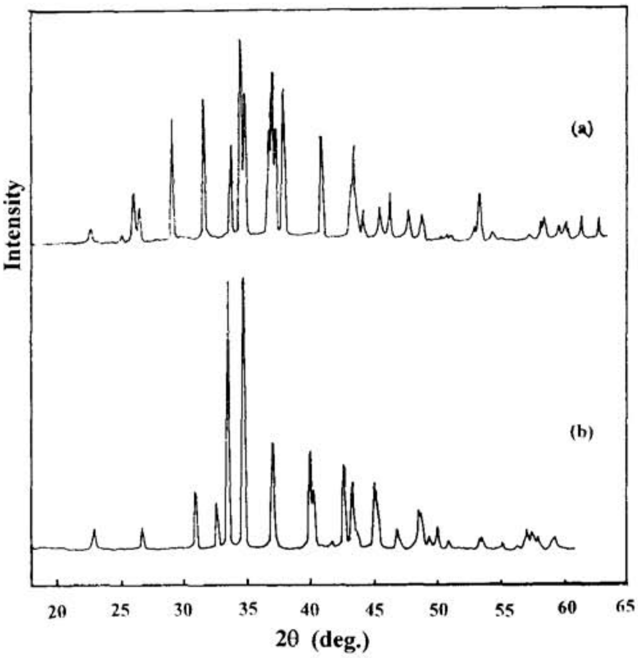

Figure 1. X-Ray diffraction spectra for the produced Ag_2E powders: (a) Ag_2S powders synthesized in py at 140 ℃ for 12 h; (b) Ag_2Se powders synthesized in en at 140 ℃ for 12 h.

The specific experimental conditions and results are summarized Table 1. The results showed that the reaction of $Ag_2C_2O_4$ with E in different solvents such as en, py, and THF can produce crystallized Ag_2E. X-ray diffraction patterns in Figure 1(a) and 1(b) show that the produced Ag_2S powders in py (sample 2) and Ag_2Se powders in en (sample 4) are pure monoclinic phase and orthorhombic phase, respectively, with cell constants a=0.4226, b=0.6929, c=0.7860 nm, with the value of angle between *a* and *c* axis β=99.65° for Ag_2S, and a=0.4331, b=0.7059, c=0.7758 nm for Ag_2Se, which are close to the literature data (JCPDS Card, Files: 14-72, 24-1041). As shown in Table 1, the product obtained in en at 180 ℃ for 12 h (sample 8) is a mixture phase of Ag_2Te and Ag. The dominant phase can be indexed as monoclinic Ag_2Te with cell constants a=0.81690, b=0.8937, c=0.80581 nm, with the value of angle between *a* and *c* axis β=112.830°, which are also close to the reported data (JCPDS Card File: 34-142). No Ag_7Te_4 was detected in the products via the present route. This result is different from that reported by Parkin *et al.*[2]

Transmission electron micrograph(TEM) in Figure 2(a) shows that the Ag_2S powders synthesized in py consist of agglomerates of spherical particles with an average size of about 200 nm. Scanning electron micrograph(SEM) in Figure 2(b) indicates that the produced Ag_2Se powders in en display flake-like morphology. Elemental analysis shows that the products Ag_2S and Ag_2Se are in chemical composition.

The effects of solvents on the synthesis of crystalline Ag_2E were investigated. Pure Ag_2S powders (samples 1-3) were prepared in en, py, and THF. Similarly, pure Ag_2Se powders (sample 4) were obtained in en. However, X-ray diffraction patterns indicated that the dominant phase for the samples synthesized in py or THF (samples 5 and 7) was Ag_2Se, but a small amount of unreacted Se in the samples was detected. Its amount in the sample 5 obtained in py is smaller than that of the sample 7 in THF. These results demonstrated that solvents give significant influence on the solvothermal reaction, and the reaction in en proceeds more completely than those in py or THF. The result of solvent effects on the completeness of the solvothermal reaction between $Ag_2C_2O_4$ and Te is also consistent with those for Ag_2Se.

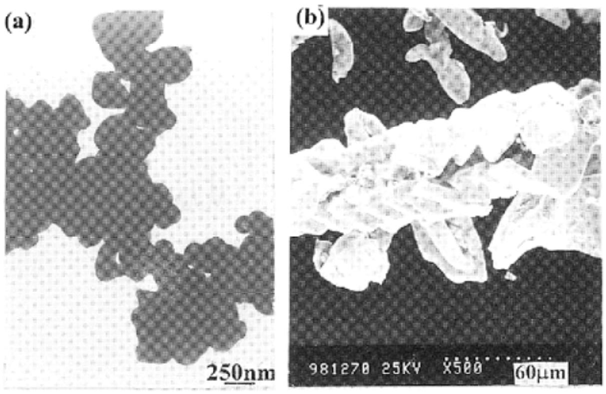

Figure 2. TEM of Ag_2S and SEM of Ag_2Se powders: (a) TEM of Ag_2S powders synthesized in py at 140 ℃ for 12 h; (b) SEM of Ag_2Se powders synthesized in en at 140 ℃ for 12 h.

The temperature is also an important factor for the synthesis of Ag_2Se and Ag_2Te. Higher temperature is more favorable for the reaction, whereas, it leads to the decomposition of silver oxalate. For example, the dominant phase of sample 5 synthesized in py is Ag_2Se, but some Se was detected by XRD. If the temperature is above 150 ℃, no elemental Se was detected (sample 6). But, a small amount of metallic Ag was detected. It is well-known that silver oxalate will decompose to Ag and CO_2 when temperature exceeds 140 ℃:

$$Ag_2C_2O_4 \rightarrow Ag + 2CO_2 \uparrow \qquad (2)$$

Similar phenomenon was also observed in the synthesis of Ag_2Te. It is interesting to note that no Te was detected for the reaction of $Ag_2C_2O_4$ with Te (samples 8-11) if temperature exceeds 160 ℃. This means that high temperature is more favorable for the synthesis of crystallized Ag_2Te.

In summary, we provides a convenient route to prepare silver chalcogenides by a novel solvothermal reaction between silver oxalate and chalcogens. Both solvents and temperature have significant effects on the synthesis of Ag_2E. The present method is expected to prepare other important metal chalcogenides.

We acknowledge the Huo Ying-dong Foundation for young teachers, the National Outstanding Youth Fund, and Anhui Provincial Foundation of Natural Science Research.

References and Notes

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