

Solvothermal reaction route to nanocrystalline semiconductors AgMS_2 ($\text{M} = \text{Ga}, \text{In}$)

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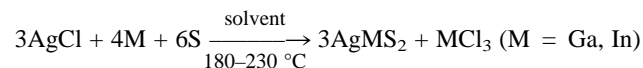
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Nanocrystalline semiconductors AgGaS_2 and AgInS_2 with particle sizes ranging from 5 to 12 nm are prepared by a solvothermal reaction in the temperature range 180–230 °C.

The study of nanometre sized crystallites provides an opportunity to observe the evolution of material properties with size.¹ Studies of semiconductor nanostructures with size-dependent optical and electronic properties are motivated by potential applications which include quantum-dot lasers and high-speed non-linear optical switches.^{2,3} Therefore, current attention has focussed on the development of new methods for the preparation of nanocrystalline semiconductors.

I–III–VI₂ chalcopyrite semiconducting compounds such as AgGaS_2 and AgInS_2 have been shown to be useful linear and non-linear optical materials.^{4,5} The band gaps and optical properties of many of these ternary sulfur containing chalcopyrites have been reported.^{6,7} Considerable progress has been made in the synthesis of I–III–VI₂ semiconductor crystallites.^{8,9} However, the reported preparative routes were traditional solid-state reaction methods which require high processing temperatures (800–1000 °C), long reaction times, and special apparatus. Vacancies or interstitial defects in the chalcopyrite lattice cause these compounds to have poor crystal quality and poor optical transparency.¹⁰ As we know, different preparative methods have important effects on the resulting microstructure and physical properties of materials. Recently, various solution chemical synthesis techniques have been utilized to prepare some fascinating materials. This chemical method allows the particle size and their distribution as well as their morphology to be controlled.¹¹

Herein, we report a solvothermal synthetic route to the I–III–VI₂ nanocrystalline compounds AgGaS_2 and AgInS_2 in the temperature range 180–230 °C by using AgCl , Ga (or In) and S as the reactants. The synthetic reaction was carried out in an autoclave and can be represented by eqn. (1).



In this process, the coordinating solvent plays an important role in the formation of AgGaS_2 and AgInS_2 .

In a typical procedure, analytical grade AgCl (1.0 g), Ga (0.648 g) or In (1.068 g), and S (0.447 g) were put into an autoclave of 50 mL capacity and then the autoclave was filled with ethylenediamine up to 85% of the total volume. The autoclave was maintained at 180–230 °C for 10 h and then allowed to cool to room temperature. The precipitates were filtered off and washed sequentially with CS_2 , absolute ethanol, dilute acid, aqueous ammonia solution and distilled water, to remove the residual impurities (*e.g.* elemental sulfur and chloride). After drying in a vacuum at 70 °C for 2 h, a final dark yellow product was obtained.

The obtained samples were characterized by X-ray powder diffraction (XRD), operating on a Japan Rigaku Dmax- γ A X-ray diffractometer with graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology and particle size of the

final products were determined by transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. X-Ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromated $\text{Mg-K}\alpha$ radiation as the excitation source.

Fig. 1(a) shows the XRD pattern of an AgGaS_2 sample prepared by the solvothermal synthetic process. All the peaks could be indexed to the tetragonal AgGaS_2 phase with cell constants $a = 5.7538$ and $c = 10.3026 \text{ \AA}$, in agreement with reported data in the literature.¹² No characteristic peaks of other impurities such as Ga or Ag_2S , were observed. Fig. 1(b) shows the XRD pattern of an AgInS_2 sample. All the reflections could be indexed to the pure chalcopyrite phase AgInS_2 with lattice parameters $a = 5.8652$ and $c = 11.1992 \text{ \AA}$, in good agreement with the literature values.¹³ The broadened nature of these diffraction peaks indicate that the grain sizes of the samples are on the nanometre scale. The average sizes of the particles are 6 and 10 nm, for AgGaS_2 and AgInS_2 , respectively, as estimated by the Scherrer equation.

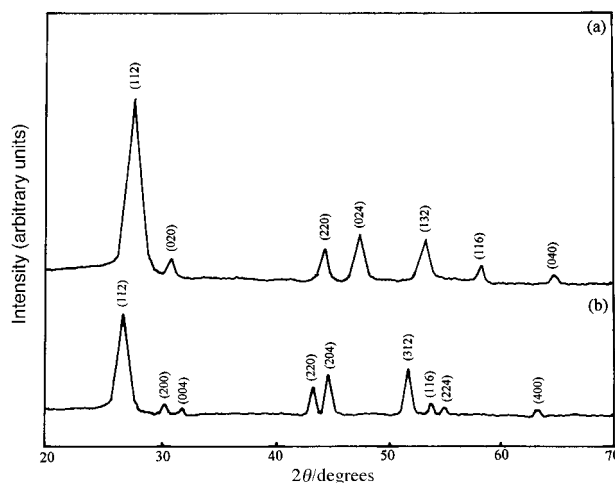


Fig. 1 XRD patterns of samples of (a) AgGaS_2 and (b) AgInS_2 prepared by solvothermal reaction.

The quality of the samples was also characterized by XPS. No obvious impurities, *e.g.* chloride ion or elemental sulfur, could be detected in the samples, indicating that the level of impurities is lower than the resolution limit of XPS (1 at%). Quantification of the XPS peaks gave $\text{Ag}:\text{Ga}:\text{S}$ atomic ratios of 1:1.08:2.10.

Fig. 2 shows TEM images of as-prepared nanocrystalline AgGaS_2 and AgInS_2 . It can be seen that the samples consist of uniform spherical particles. The diameters of the particles are in the range 5–7 and 9–12 nm, respectively, in accord with the XRD results.

It is well known that solvents can influence the reaction pathway. In our experiments, different solvents were tested and the results revealed that the coordinating ability of the solvent played an important role in the formation of nanocrystalline

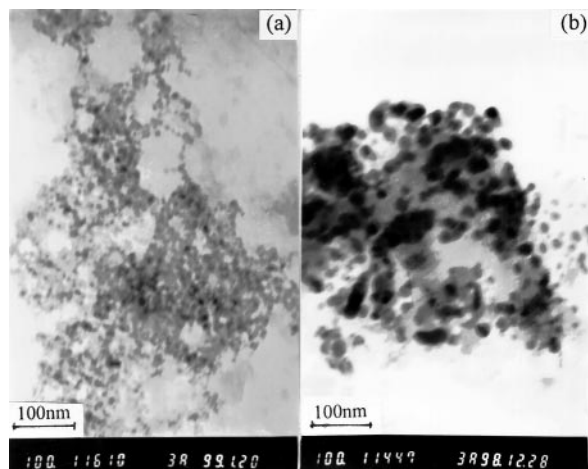


Fig. 2 TEM images of (a) AgGaS₂ and (b) AgInS₂ as in Fig. 1.

AgGaS₂. Ethylenediamine, a bidentate solvent, was selected due to its strong N-chelation ability and basicity. It can act as a bidentate ligand to form a relatively stable Ag⁺ complex, which can incorporate dissolved sulfur as seen for other amine solvents.^{14,15} As the temperature was increased, Ga melted and the formation of AgGaS₂ may be through a liquid-solution diffusion process. This route thus differs substantially from solid state reactions which require high temperature to overcome higher activation energy barriers. When pyridine, showing weaker binding and basicity, was used as solvent, keeping the other reaction conditions constant, the reaction was incomplete and the product purity was lower. A non-polar solvent, benzene, having no chelating ability or basicity, was also tried. According to XRD analysis, the reaction in benzene did not produce AgGaS₂, and the product was mostly unreacted AgCl and Ga. The influence of reaction temperature and time on the formation of AgGaS₂ were also studied. The optimum conditions for the formation of nanocrystalline AgGaS₂ is at a temperature of 180–230 °C for 10 h. If the temperature was lower than 150 °C, or the time was shorter than 5 h, the crystallinity of the AgGaS₂ was lower. If the temperature was

higher than 250 °C or the time longer than 12 h, the particles were larger and the product was contaminated by carbonization of the solvent.

In summary, we have succeeded in the synthesis of nanocrystalline AgGaS₂ and AgInS₂ by solvothermal reaction. The structure and property of the solvent can strongly influence the reaction process. The method presented herein provides uniform particles with narrow size distribution which may be further enhanced by use of other solvents. This method can be readily employed to prepare other nanocrystalline I–III–VI₂ materials such as AgMSe₂, CuMS₂ (M = Ga, In). A detailed study on this synthesis method is in progress.

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