



# Synthesis of binary and multinary metal sulphides by precipitation and their characterisation



Pritty Rao<sup>a</sup>, Sanjiv Kumar<sup>b,\*</sup>, Naina Raje<sup>c</sup>, R.B. Tokas<sup>d</sup>, N.K. Sahoo<sup>d</sup>

<sup>a</sup> Solid State Physics Laboratory, DRDO, New Delhi 110054, India

<sup>b</sup> National Centre for Compositional Characterisation of Materials, BARC, Hyderabad 500062, India

<sup>c</sup> Analytical Chemistry Division, BARC, Mumbai 400085, India

<sup>d</sup> Atomic and Molecular Physics Division, BARC, Mumbai 400085, India

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## ABSTRACT

CuS, In<sub>2</sub>S<sub>3</sub>, CuInS<sub>2</sub> and CuGaS<sub>2</sub> semiconductors have been synthesised in powder form by precipitation reaction using Na<sub>2</sub>S·3H<sub>2</sub>O as a precipitating agent. Precipitated at about 313 K in aqueous medium, the powders of CuS crystallise in covellite (hexagonal) phase and those of In<sub>2</sub>S<sub>3</sub>, CuInS<sub>2</sub> and CuGaS<sub>2</sub> in tetragonal phase on heat treatment in argon atmosphere. The formation of CuS or In<sub>2</sub>S<sub>3</sub> takes place due to the reaction between the metal and bisulphide ions in aqueous phase while that of CuInS<sub>2</sub> or CuGaS<sub>2</sub> involves solid state reaction between CuS and In<sub>2</sub>S<sub>3</sub> or Ga<sub>x</sub>S<sub>y</sub> during heat treatment and is accompanied with the evolution of SO<sub>2</sub> gas. The powders are nearly monophasic, exhibit nanometric morphology and bear their respective stoichiometric compositions. The direct band gaps of CuS, In<sub>2</sub>S<sub>3</sub>, CuInS<sub>2</sub> and CuGaS<sub>2</sub> measure 2.06, 2.3, 1.34 and 2.38 eV respectively. The method is simple and is extended to the synthesis of CuIn<sub>0.8</sub>Ga<sub>0.2</sub>S<sub>2</sub> as well.

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## 1. Introduction

Metal chalcogenides are an important class of materials with unique chemical, electrical and optical properties and have found applications in a wide range of fields that include catalysis, energy storage and conversion, and optoelectronic devices [1–5]. Among chalcogens (S, Se, Te), sulphur is non-toxic, has the highest natural abundance and is the cheapest. As a result, sulphides have attracted considerable interest in recent years. Sulphur, like other chalcogens, forms binary, ternary or quaternary compounds with different metals. Copper sulphide (CuS), an I–VI and indium sulphide (In<sub>2</sub>S<sub>3</sub>), a III–VI compound semiconductor are important binary sulphides. CuS is a promising material for various semiconductor devices such as solar cells [6], photodetectors [7] and gas sensors [8]. It exhibits metallic character and acquires superconducting properties at 1.6 K [9]. Due to high electronic conductivity (10<sup>3</sup> S cm<sup>-1</sup>), CuS is also a candidate cathode material in lithium rechargeable batteries [10,11]. Similarly, In<sub>2</sub>S<sub>3</sub> is a useful photovoltaic material and is a strong contender for buffer layers in lieu of toxic CdS in heterojunction solar cells [12]. Interestingly, CuS and In<sub>2</sub>S<sub>3</sub> constitute CuInS<sub>2</sub>, an I–III–VI<sub>2</sub> ternary compound semiconductor with established 11.4% photoconversion efficiency

[13]. Meanwhile copper indium gallium sulphide (CuInGaS<sub>2</sub>), a quaternary compound semiconductor obtained by the partial substitution of In<sup>+3</sup> in CuInS<sub>2</sub> lattice with Ga<sup>+3</sup> has been reported to exhibit 12.3% photoconversion efficiency [14,15]. In fact, CuInGaS<sub>2</sub> can be considered to be an intermediate of CuInS<sub>2</sub> (band gap, E<sub>g</sub> ~1.5 eV) and CuGaS<sub>2</sub> (E<sub>g</sub> ~2.5 eV) and its E<sub>g</sub> can be tuned in 1.5–2.5 eV range by varying the relative content of Ga in the compound. CuGaS<sub>2</sub>, on the other hand, is a promising host for intermediate band gap solar cells with transition metal (Ti, Cr, Fe) dopants introducing band of states inside the fundamental gap [16,17].

The synthesis of stoichiometric and phase singular chalcogenides is crucial for realising their potential. As a result, the synthesis of these materials as bulk powders and also as thin films has been a subject of numerous investigations. Between the two, bulk chalcogenides are of special interest since these not only can serve as precursors for the deposition of films by physical vapour techniques but can also be, in an economical and facile way, directly paste coated or ink-jetted on different kinds of substrates [18,19]. Moreover these can be used in the fabrication of heterojunction devices and electrodes, and as catalysts. Solid state as well as wet chemical methods have been employed to synthesise chalcogenide powders, though, the latter are often preferred due to lower processing temperatures and better control over reactivity, particle size and homogeneity. More importantly due to high migrating activity of group I elements, high vapour

\* Corresponding author.

E-mail address: [sanjucm@rediffmail.com](mailto:sanjucm@rediffmail.com) (S. Kumar).

pressure of group VI elements and miscibility gap in phase diagram, the synthesis of stoichiometric ternary or quaternary chalcogenides from the constituent elements by solid state route is difficult.

Hydrothermal, solvothermal, sonochemical and sol-gel methods are some of the frequently used solution-based approaches for the synthesis of chalcogenides with a variety of morphological features [20–22]. Though conducted at lower temperatures ( $\leq 473$  K), these methods often utilise hazardous and toxic organic chemicals with the duration of synthesis typically being several ( $>10$ ) h. Obviously there is a need of a simpler, rapid and green route for the preparation of the chalcogenides. In this paper we report a precipitation based approach for the preparation of CuS,  $\text{In}_2\text{S}_3$ ,  $\text{CuInS}_2$ , and  $\text{CuGaS}_2$  in powder form using sodium sulphide ( $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$ ), a common and rather benign chemical, as the precipitating agent. The chalcogenides are (poly) crystalline and monophasic and bear nearly stoichiometric compositions. To the best of our knowledge this is the first report wherein a method or  $\text{Na}_2\text{S}$  (as a source of sulphide) has been used to synthesise binary, ternary as well as quaternary chalcogenide semiconductors. It is worthwhile mentioning that  $\text{Na}_2\text{S}$  is not as widely employed as thiourea and thioacetamide in the preparation of sulphides, apparently to avoid any contamination of the products with sodium. However, Na reportedly has beneficial influence on the photoconversion efficiency of chalcogenides and therefore its presence, if at all, may rather be advantageous.

## 2. Experimental

### 2.1. Synthetic procedure

Cu, Ga and In metals ( $>99.9\%$  purity) were used in the synthesis of the chalcogenides. Cu was dissolved in 50% nitric acid ( $\text{HNO}_3$ ), Ga in concentrated  $\text{HNO}_3$  and In in concentrated hydrochloric acid

(HCl).  $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$  was dissolved in deionised water. The metal solutions were evaporated to dryness and the residues were taken in dilute HCl. For the preparation of  $\text{CuS}$ ,  $\text{Cu}^{2+}$  ions and  $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$  were taken in 1: 1.1 molar ratio while for  $\text{In}_2\text{S}_3$ ,  $\text{In}^{3+}$  ions and  $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$  were used in 1: 1.65 molar ratio. The precipitation was affected by the addition of sulphide solution to that of metal ion at  $\sim 300$  K. The preparation of  $\text{CuInS}_2$ ,  $\text{CuGaS}_2$  or  $\text{CuIn}_x\text{Ga}_{1-x}\text{S}_2$  involved two steps. In the first step the solutions of the respective metals ions were mixed in 1:1 molar ratio or in molar proportions as required by the stoichiometry of the compound and heated up to about 310 K for homogenisation while in the second step the sulphide solution was added to solution of metal ions for precipitation. As in the case of  $\text{CuS}$  or  $\text{In}_2\text{S}_3$ , the molar concentration of sulphide ions was 10% in excess of the requisite content. In all preparations the addition of  $\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$  was accompanied with stirring. Though the precipitation occurred almost instantaneously, stirring was continued for an hour for the completion of the process. The precipitates were subsequently filtered and washed copiously with warm water to remove sodium and chloride ions. These were finally washed with isopropanol for easiness in drying which involved heating the  $\text{In}_2\text{S}_3$  precipitate at 373 K and the rest at 393 K for 2 h in a tubular furnace in flowing argon gas. The powder thus obtained was heated in 473–693 K temperature range for 1–2 h under flowing argon in a temperature programmable furnace with a typical heating rate of  $5^\circ/\text{minute}$ . The powders were allowed to cool naturally and were removed from the furnace at about 340 K.

### 2.2. Structural, morphological, optical and thermal analyses

The phase constitution of the powders was examined by X-ray diffraction (XRD) (Rigaku Ultima IV diffractometer) using  $\text{CuK}\alpha$  X-rays. The lattice parameters of the compounds were determined from the diffractions patterns using the formulations of the

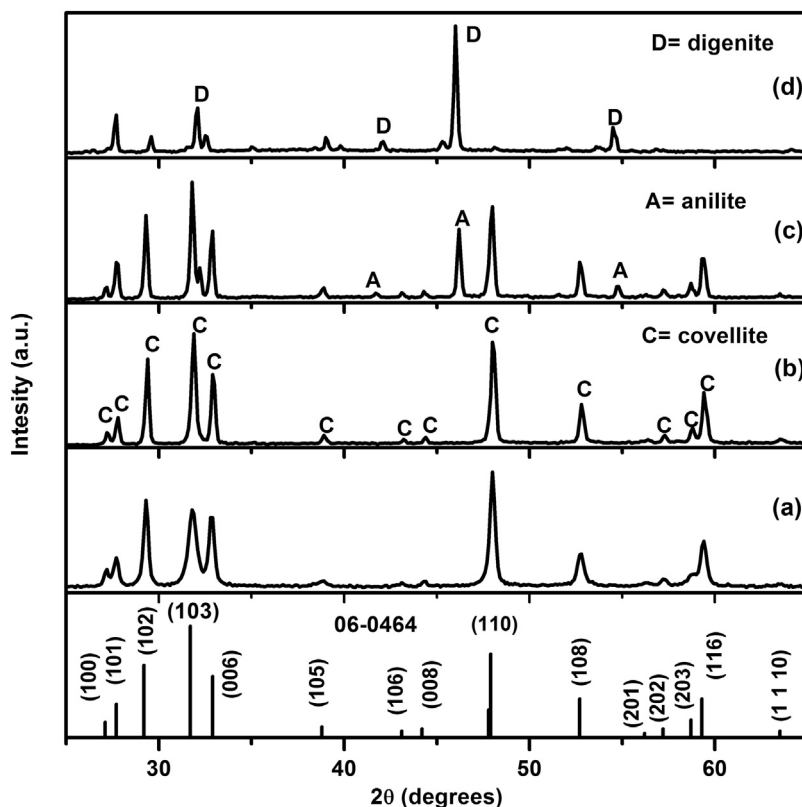


Fig. 1. XRD patterns of CuS powder heat treated at (a) 473 K, (b) 523 K, (c) 623 K and (d) 673 K under argon atmosphere.

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