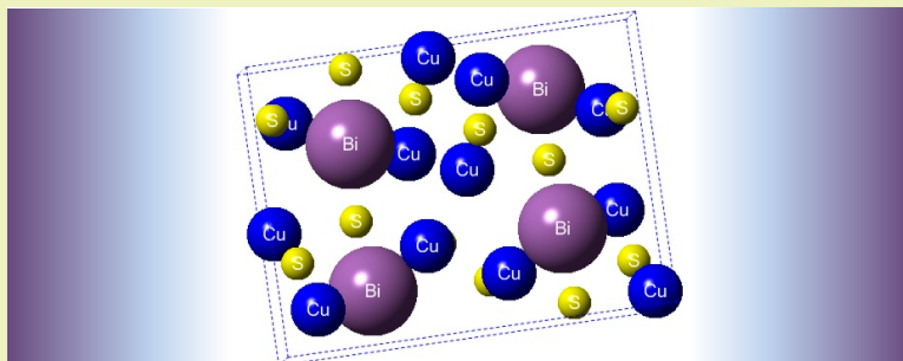


Solvothermal Synthesis of Cu_3BiS_3 Enabled by Precursor Complexing

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ABSTRACT: Copper bismuth sulfide, Cu_3BiS_3 , has been prepared by a solvothermal method that relies on precursor complexing to achieve the desired ternary chalcogenide preferentially over possible binary sulfides in the system. The complexing agent *L*-cystine also simultaneously donates sulfur to the compound when the complexes are dissociated at a single temperature. This low temperature and use of nitrate salts instead of the commonly employed but less “green” chloride salts provide a path toward cleaner methods. The reaction progression has been characterized by X-ray powder diffraction of sequential samples and shows complete reaction of reagents to form the Wittichenite phase. Spectroscopy analysis reveals confirmation of a direct bandgap at approximately 1.5 eV. Microscopy images reveal varying morphology dominated by nanorods and including particles with aspect ratios approaching 1:1. A low-temperature Cu_3BiS_3 synthesis employing *L*-cystine as a sulfur source and complexing agent, nitrate salt precursors, and pure ethylene glycol has been demonstrated.

KEYWORDS: Cu_3BiS_3 , Nanoparticles, Complexing, *L*-Cystine, Solvothermal, Energy storage and conversion

INTRODUCTION

Increasing attention is being directed toward the development of alternative and earth-abundant semiconductors for photovoltaic and other optoelectronic applications. One promising class is the I–V–VI family that includes Cu_3BiS_3 . Naturally occurring in the “Wittichenite” mineral form,¹ the compound is stable for a broad range of processing temperatures.^{2,3} As such, various techniques have been employed to synthesize Cu_3BiS_3 and other ternary sulfide films and nanostructures. Sputtering,^{4–9} coevaporation,^{10–12} and solid-state reactions^{9,13,14} have been successful in producing stoichiometric compounds depending on the nature of the processes. Solution-based syntheses of both hydrothermal¹⁵ and solvothermal^{9,16–20} routes have been demonstrated with a range of precursors. While most rely on thermal heating to exceed the reaction threshold, microwave heating has also been demonstrated.²⁰

Solution-based synthesis of ternary chalcogenides also brings with it the risk of producing counterproductive binary compounds. Strong reducers are often employed to facilitate and expedite ternary syntheses, but their toxicity is a growing concern if any process is to be scaled for manufacturing. In a rising trend toward green synthesis, the employment of biological complexing agents has been successful. The use of *L*-cystine as a sulfur donor was demonstrated for Sb_2S_3 ,¹⁷ and its use as a complexing agent for the ternary Cu_3SbS_3 system

followed quickly.¹⁹ The Cu_3BiS_3 morphologies produced in a similar fashion have resulted in varying morphologies, including dendrites,^{14,20} rods,²¹ and flower (or coral) like structures.^{18,22} There remains until now a lack of Cu_3BiS_3 synthesis employing a solvothermal system, *L*-cystine as a sulfur donor and a complexing agent, radiant heating, and nitrate salt precursors; this new and useful method is presented here.

EXPERIMENTAL SECTION

Reagents. All chemicals in this work were used as obtained and include entirely (i) copper(II) nitrate trihydrate, 99–104% purity, purchased from Sigma-Aldrich; (ii) bismuth(III) nitrate pentahydrate, 99.99% purity, purchased from Sigma-Aldrich; (iii) *L*-cystine, 99.5% purity, purchased from Sigma-Aldrich; (iv) ethylene glycol, $\geq 99\%$ purity, purchased from Sigma-Aldrich; and (v) absolute ethanol, 99.99% purity, purchased from Fischer Scientific.

Preparation. In a typical procedure, 3 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3(\text{H}_2\text{O})$ was dissolved in 50 mL ethylene glycol and 3 mmol *L*-cystine was added by stirring. Separately, 1 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5(\text{H}_2\text{O})$ was dissolved in 50 mL ethylene glycol and 1 mmol *L*-cystine was added by stirring. The two solutions were added under stirring to a two-necked flask fitted with a reflux column to prevent solvent loss. The flask was

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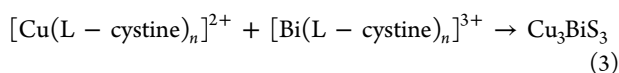
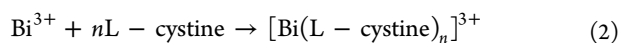
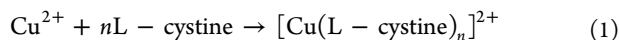
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fitted with a thermometer and heated by mantle. Upon heating to 153 °C, the blue solution changed to brown/black, and the synthesis continued at 187 ± 3 °C for 4 h. Regular aliquot sampling of the particle suspension was collected by a glass pipet. After cooling to room temperature, the precipitates were washed in absolute ethanol and either dried to a powder or drop cast in suspension onto soda-lime glass.

Instrumentation. The X-ray diffraction patterns for the time-sampled study were recorded using Cu K α radiation with a wavelength of 1.54 Å on a Siemens Kristalloflex diffractometer controlled by MDI Data Scan. The scan range was 10°–70° with a step size of 0.02° and a 2.3 s dwell time. The absorbance spectra of a particle solution were collected on a PerkinElmer UV–vis Lambda 850 spectrometer. Microstructure details were obtained from uncoated powder samples with a field-emission scanning microscope (FESEM), model Zeiss Sigma.

RESULTS AND DISCUSSION

The reaction proposed here is built on the work of Jiasong,¹⁹ wherein the antimony-based system is complexed in a similar manner. Pure ethylene glycol (EG) is used as solvent to allow for a reaction suitable for benchtop heating. The high boiling point of the solvent allows for heating in the presence of a reflux tube to capture lost vapor, a process that would not be as effective with the depressed boiling point of EG–H₂O mixtures. Independent from each other, the dissolved copper nitrate hydrate supplied copper ions complex with the dissolved L-cystine (eq 1), and the dissolved bismuth nitrate hydrate supplied bismuth ions complex with the dissolved L-cystine (eq 2). After combination under heating and stirring in the reflux column fitted three-necked flask, the complexed metal ions receive donated sulfur from the L-cystine and reacted to form Cu₃BiS₃.



The reaction initiation appears at 153 °C as a quick sweeping color change from the azure blue of the copper ion-containing solution through amber to a dark brown within minutes. Continued growth and purification is assumed from the analysis of XRD patterns of drop cast precipitate collected progressively during the synthesis (Figure 1). At 1 h post-nucleation, no evidence exists for the presence of the Wittichenite crystal, but the small particle size may inhibit diffraction sufficient for XRD detection. At 1.5 h, characteristic Cu₃BiS₃ peaks appear as well as a strong peak around 28 deg 2 θ . This intense peak that diminishes through 2.5 h and disappears by 3.5 h is proposed to be a H₂S intermediary²³ that is seen in other reactions. By 3.5 h, all of the diffraction peaks can be indexed as those from the known Wittichenite crystal (Figure 2). Continued heating and stirring of the solution to 4.0 h results in strengthening of XRD peaks and likely indicates the growth of individual particles.

UV–vis analysis of a particle solution in ethanol and a subsequent conversion of data into a Tauc plot (Figure 3) allows for an estimation of the bandgap.²⁴ A curve fit of the linear region extended to the X intercept provides a bandgap estimated at 1.5 eV, in good agreement with published values.^{4,7,12,22}

The structure of the nanoparticles is varied and includes rods and more spherical particles approaching an aspect ratio of 1:1

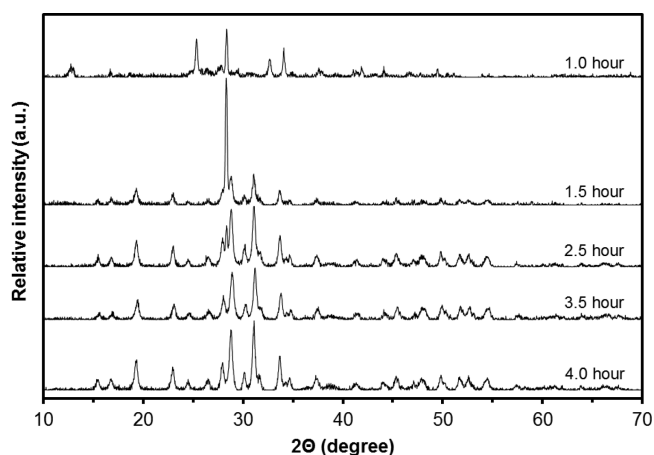


Figure 1. XRD pattern of precipitate as synthesized at various stages during reaction.

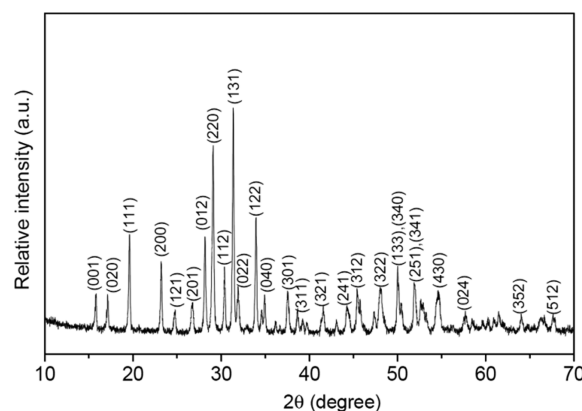


Figure 2. XRD reference pattern for pure Cu₃BiS₃ Wittichenite crystal.

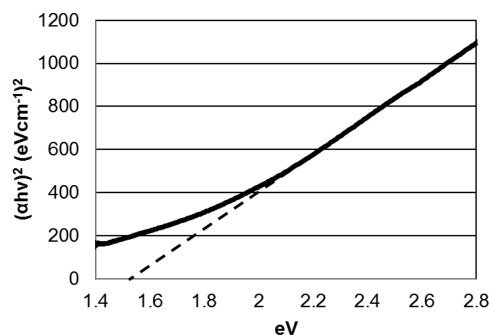


Figure 3. Tauc Plot from UV–vis spectrum of precipitate as synthesized 4 h into reaction with estimated intercept at direct band gap of 1.5 eV.

(Figure 4). There exist regions of higher concentration for each particle type, and this may indicate two different growth processes occurring during synthesis. The rods are on the order of 100–300 nm wide and up to 2 μm in length. The more spherical particles are 50–150 nm in diameter. As no substrate was provided for growth, there is no ordering or alignment of the rod shapes.

The nucleation and growth of spherical particles is expected in the absence of any substrate or seeding nucleus. The presence of rod structures may best be attributed to the spontaneous formation of one or more screw dislocations within a growing sphere that result in nanowire growth.²⁵

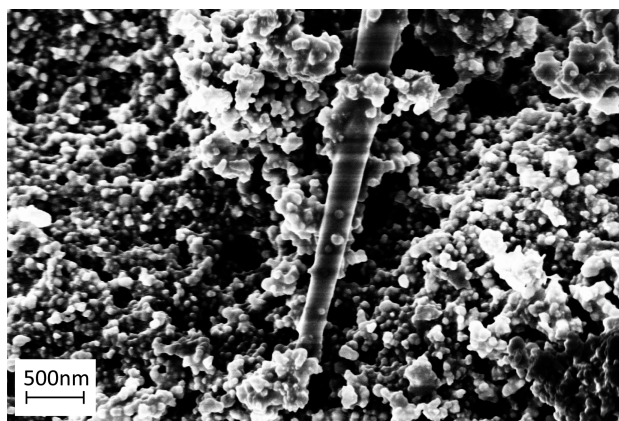


Figure 4. SEM image (50 kX) of as grown spherical particles and rods within Cu_3BiS_3 nanostructure.

CONCLUSION

Cu_3BiS_3 nanoparticles have been successfully synthesized through the use of a complexing agent in a solvothermal process. Benchtop conductive heating drives the reaction of nitrate precursors complexed with L-cystine, which also serves as the sulfur source. XRD patterns confirm a pure Wittichenite crystal structure. UV-vis spectra confirm a bandgap of approximately 1.5 eV, and SEM image analysis reveals particles on the scale of 20–500 nm. This method will be employed to investigate doping and device possibilities for this and other ternary chalcogenides.

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Notes

The authors declare no competing financial interest.

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