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ABSTRACT

Reaction pathway investigations of the solvothermal preparation of nanocrystalline $CuIn_{1-x}Ga_xSe_2$ in triethylenetetramine reveal the early formation of a previously unreported $Cu_{2-x}Se(s)$ intermediate. Over 24 hours, this reacts with In and Se species to form $CuInSe_2(s)$. If Ga is present, the reaction proceeds over an additional 48 hours to form $CuIn_{1-x}Ga_xSe_2$. Adding ammonium halide salts reduces the $CuInSe_2$ formation time to as little as 30 minutes. It is proposed that in these cases, $Cu_{2-x}Se$ particle growth is limited via a competitive Cu-halide complex formation. The smaller $Cu_{2-x}Se$ particles may react and form $CuInSe_2$ more rapidly. A reaction pathway scheme consistent with experimental results and previous literature reports is proposed.

INTRODUCTION

For some time, the chalcopyrite semiconductors $CuInSe_2$ (CIS) and $CuIn_{1-x}Ga_xSe_2$ (CIGS) have been leading thin-film material candidates for incorporation in high-efficiency photovoltaic devices [1-4]. Interest in the development of more cost-effective, non-vacuum film production techniques has stimulated research in the solution-based preparation of nanocrystalline CIS and CIGS. Reported nanocrystal preparations involve solvothermal processes in which constituent elements or their salts are heated in a solvent. While a variety of reaction conditions have successfully yielded nanocrystalline CIS [5-10], and to a lesser extent CIGS [11, 12], no systematic study of the solvothermal reaction mechanism(s) or structure-activity relationships has been conducted. A better mechanistic understanding of this solvothermal preparation may lend insight into the synthesis of new $CuIn_{1-x}M_xSe_2$ (M = Ga, Al, B) chalcopyrite materials.

Most early reported procedures for solvothermal CIS and CIGS formation involved superheating a sealed container of Cu, In, Ga, and Se sources in ethylenediamine (en) solvent at 140-280 °C for 15-36 hours [5-8]. The reaction directly yields nanocrystals. Proposed mechanisms for these solvothermal processes involve the formation of separate indium and gallium selenide species that react with a solvated Cu^+ complex to form CIS or CIGS. Following initial Cu^{2+} and Se reduction, CIS formation is proposed to occur as follows [9, 12]:

$$2\ InCl_3 + 3\ Se^{2-} \rightarrow In_2Se_3 + 6\ Cl^- \quad (1)$$
$$In_2Se_3 + Se^{2-} \rightarrow 2\ InSe_2^- \quad (2)$$
$$InSe_2^- + [Cu(en)_2]^+ \rightarrow CuInSe_2 + 2\ en \quad (3)$$

In the formation of CIGS isometric nanoparticles, it has been proposed that $[Cu(en)_2]^+$ reacts with separately-formed In_2Se_3 and Ga_2Se_3 phases [12]. While reported mechanism proposals are consistent with the CIS and CIGS solvothermal preparations, there has been no experimental evidence of any of the proposed intermediates.

Solvent selection is proving to be important in the engineering of CIS and CIGS nanocrystal size and morphology. Early attention focused on en because of possibilities that the square-planar geometry of the $[Cu(en)_2]^+$ intermediate complex would promote one-dimensional nanorod growth [9]. More recent reports [10, 13] describe the use of surfactant-based phosphine and amine solvents such as trioctylphosphine (TOP), tributylphosphine (TBP), octadecylamine, and oleylamine in order to control the growth rate of newly formed nanocrystals. Generally, the bulk of the solvent molecules and the size of stabilized nanoparticles are inversely related [14]. Stabilization of small nanoparticles seems to be related to formation reaction rate. Using these surfactant-based solvents, CIS and CIGS formation reaction times of 30-60 minutes have been reported [13].

An advantage of using en and chemically similar solvents that coordinate strongly to transition metals in molecular complexes is that reaction intermediates may be better shielded from oxidation in open-air syntheses. We have recently demonstrated the first open-air solvothermal preparation of nanocrystalline $CuIn_{1-x}Ga_xSe_2$ of wide-ranging Ga/In ratios (x = 0, 0.21, 0.35, 0.79, 1) [15]. At all compositions, morphologies consist of a mixture of isometric nanocrystalline growths (10-40 nm diameters), larger plates (50-100 nm diameters) and nanorods (see Fig. 1).

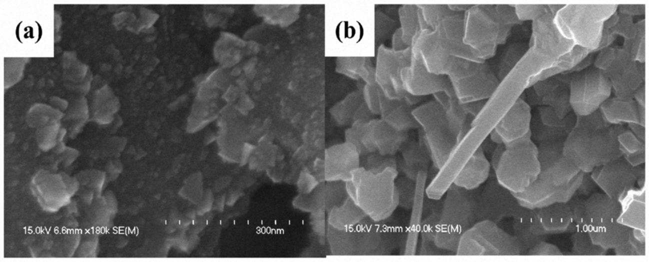

Fig. 1. SEM images of (a) $CuIn_{0.79}Ga_{0.21}Se_2$ and (b) $CuGaSe_2$ nanocrystals prepared solvothermally [15].

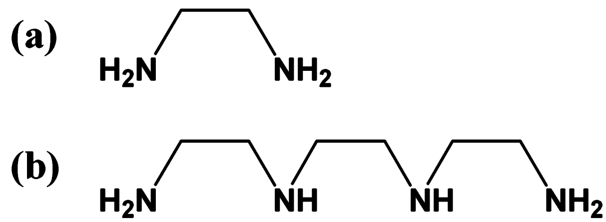

Fig. 2. Molecular structures of (a) ethylenediamine and (b) triethylenetetramine

In this paper, we report studies of the solvothermal reaction pathway in triethylenetetramine (trien). This solvent is chemically similar to en (see Fig. 2) but has a higher boiling point (267 °C) that appears to be necessary to incorporate Ga in the chalcopyrite crystalline lattice and form CIGS [12]. In the CIS preparation, the initial formation of a previously unreported $Cu_{2-x}Se$ solid-state intermediate is observed. Over time, this compound reacts with Se and one or more In species to form CIS. If Ga is present, conversion to CIGS proceeds. The reaction rate is accelerated by the presence of soluble ammonium and halide salts in the reaction mixture. A reaction pathway scheme that is consistent with our results and previous literature is proposed.

EXPERIMENTAL

Desired stoichiometric quantities of $CuCl_2$, $InCl_3$, $GaCl_3$, and Se were combined in triethylenetetramine (trien) solvent and refluxed with stirring for times ranging from five minutes to 48 hours. The reaction mixture was cooled to room temperature and centrifuged. Following the decanting of the solvent, the remaining black solid was washed with methanol and deposited onto a glass or Mo-glass substrate via spin coating from a methanol/CH_2Cl_2 suspension. Products were characterized by micro-Raman spectroscopy, Auger electron spectroscopy (AES), X-ray diffraction (XRD), and scanning electron microscopy (SEM). In reaction rate acceleration investigations, the reaction mixture included a 2- to 18-mole excess (relative to Cu) of NH_4Cl or other salt in the reaction mixture.

RESULTS AND DISCUSSION

Solvothermal Reaction Pathway for CIS and CIGS Formation

We have gained information about the CIS preparation reaction pathway in trien solvent from the analysis of stable solid-state intermediates. Upon combining stoichiometric quantities of $CuCl_2$, $InCl_3$, and Se in trien, Raman peak(s) for $Cu_{2-x}Se$ (~ 255 cm^{-1}) [16] are observable within five minutes. At this point, Se (~ 235 cm^{-1}) [17] and $Cu_{2-x}Se$ solids are observable by Raman spectroscopy (Fig. 3a). From XRD spectroscopy, this $Cu_{2-x}Se$ phase is identified as berzelianite ($Cu_{1.8}Se$), the same composition that was use to model copper-deficient Cu_2Se XRD signal phase fitting in *in-situ* XRD studies of solid-state CIGS formation reactions [18].

No Se XRD signals appear, indicating that at this point, the Se in the sample is amorphous. As the reaction

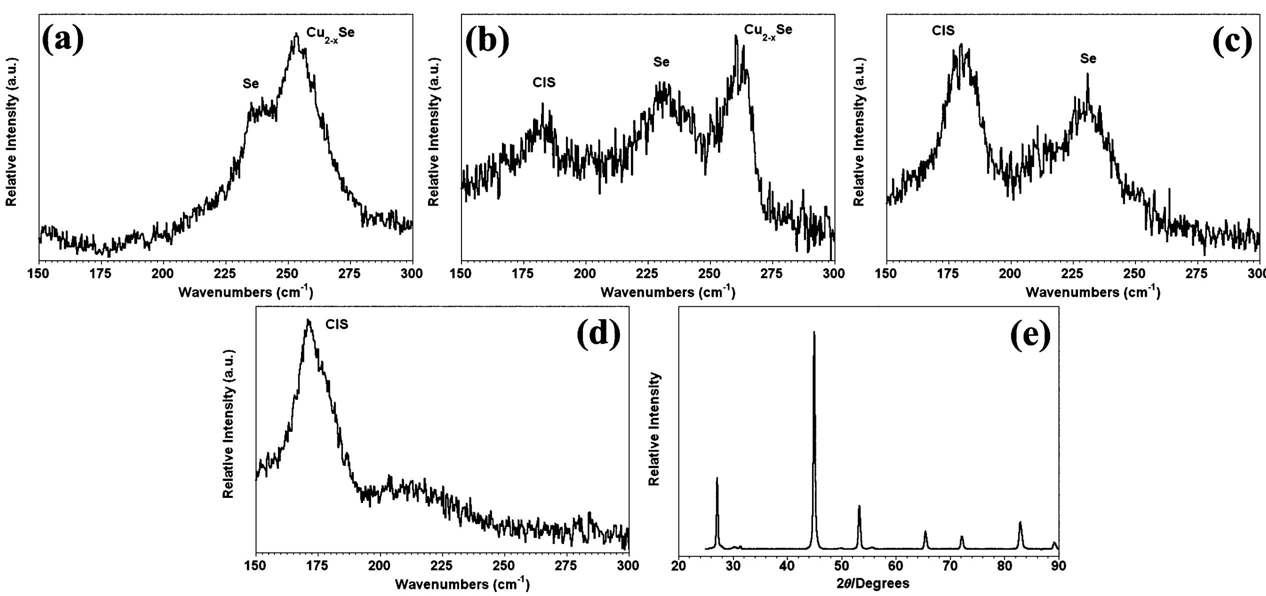

Fig. 3. Raman spectra of solid products from reaction between $CuCl_2$, $InCl_3$, and Se in refluxing trien after reactions times of (a) 5 min, (b) 1 hr, (c) 6 hr, and (d) 24 hr reaction times. (e) XRD pattern of same material as in (d).

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progresses, a CIS Raman peak (~ 170 cm^{-1}) [19] starts to grow in after 1 hour (Fig. 3b). As CIS forms, the $Cu_{1.8}Se$ peak disappears within six hours (Fig. 3c). After 24 hours, all Se has been reacted (Fig. 3d), and the XRD spectrum shows only CIS (Fig. 3e).

Neither Raman spectroscopy nor XRD indicate the presence of any solid-state In species. This lends support to the formation of $InSe_2^-$ as in (2) or a solvated complex such as $[In(trien)_x]^{3+}$, as amines are known to coordinate to In^{3+} as labile ligands [20]. Nuclear magnetic resonance (NMR), electrochemical, and spectroscopic studies of soluble reaction species are in progress.

Studies of CIGS solvothermal formation indicate that the reaction initially proceeds to CIS as described above (Figs. 3a-d) followed by a slow reaction with one or more soluble Ga species to form CIGS. This is consistent with reported $[Ga(amine)_x]^{3+}$ formation constants that are two orders of magnitude larger than those for analogous $[In(amine)_x]^{3+}$ complexes [20]. In reported solid-state mechanisms, separately-crystallized CIS and CGS interdiffuse to form CIGS [21]. From solvothermal reaction products, we have seen no evidence of simultaneously present CIS and CGS Raman and XRD signals.

The formation of $Cu_{2-x}Se(s)$ is absent from previously proposed solvothermal mechanisms and raises questions about the stability of $[Cu(amine)_x]^+$ complexes in this reaction pathway. While metal-solvent complexes may be important intermediates in the reduction of Cu and the fast formation of $Cu_{2-x}Se(s)$, it is more likely that this solid-state species is the immediate precursor to CIS.

Reaction Acceleration Effects of Added Ionic Salts

The role of specific starting material counterions or solution ionic strength in solvothermal CIS preparations has not been investigated. Given that solution-phase charged complexes may be important in solvothermal preparation mechanisms, it is feasible that solution ionic strength or counterion presence could affect the stability of these complexes during the reaction. The reported process for electrodeless deposition of CIGS from aqueous solution employs a 10-fold excess of LiCl as a "background electrolyte" [22]. Most likely, this facilitates the various redox reaction steps involved in the CIGS deposition.

$CuCl_2$, $InCl_3$, and Se were reacted in refluxing trien solvent that contained a 2- to 18-times mole excess (relative to Cu) of an ammonium or halide salt. Reaction rates are greatly accelerated. Pure CIS (as determined by Raman and XRD spectroscopy) can be prepared in as little as 30 minutes when an 18-fold NH_4Cl excess is present. This compares to 24 hours without any NH_4Cl in the reaction mixture. Tables 1 and 2 summarize the CIS reaction completion times when various salts are present in the reaction mixture.

Table 1. Solvothermal CIS Formation Times, in Hours, with added Ammonium Salts

equiv present[a]	NH_4Cl	NH_4Br	NH_4I	NH_4PF_6
0	24	24	24	24
2	6	8	14	24
6	1	4	6	24
18	0.5	1	2	24

[a]molar equivalents relative to Cu

CIS formation times vary with the nature of halide ion (Cl^-, Br^-, I^-) in the added ammonium salt. Halide ions are known to form complexes with Cu^+ and In^{3+} [23, 24], and the reaction times correlate inversely with the relative stabilities of $[Cu(amine)_3X]$ (X = Cl-, Br-, I-) complex formation [25]. The presence of PF_6^-, a non-coordinating anion, does not accelerate the reaction. This supports the idea of Cu- and/or In-halide complex formation in the reaction pathway.

Table 2. Solvothermal CIS Formation Times, in Hours, with added Chloride Salts

equiv present[a]	NH_4Cl	$(CH_3)_4NCl$	$CaCl_2$
0	24	24	24
2	6	14	n.d.[b]
6	1	6	n.d.
18	0.5	2	12

[a]molar equivalents relative to Cu
[b]not determined

CIS formation times also vary with the nature of the cation in the added salt. Effects of NH_4^+ and $(CH_3)_4N^+$ may be directly compared. It is unlikely that the greater rate acceleration effect of NH_4^+ is due to proton transfer to trien followed by NH_3 complexation to Cu or In, as NH_3 is less basic (pK_b = 4.75) [26] than trien (pK_b = 3.21) [27]. It is possible that with its larger charge density (smaller ion size), NH_4^+ may better stabilize a negatively-charged Cu- and/or In-halide complex in the reaction pathway. This would imply that the presence of smaller inorganic cations may accelerate the reaction to a greater extent. Unfortunately, $CaCl_2$ was only slightly soluble in the reaction mixture, while $MgCl_2$, NaCl and KCl were insoluble.

Proposed Reaction Pathway Scheme

A modified CIS/CIGS solvothermal preparation reaction pathway scheme based on our experimental results and previously reported literature is proposed in Figure 4.

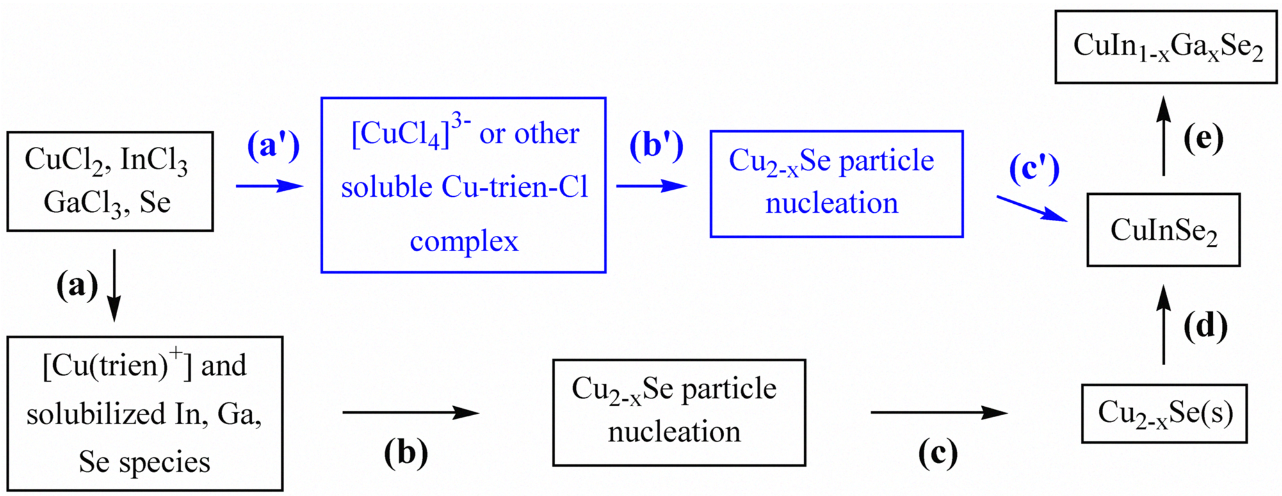

Fig. 4. Proposed reaction pathway scheme for the solvothermal preparation of nanocrystalline $CuIn_{1-x}Ga_xSe_2$ in triethylenetetramine. See the text for descriptions of the lettered steps. The blue pathway steps (a'), (b'), and (c') are proposed to be adopted in place of steps (a) through (d) when NH_4Cl is present in the reaction mixture.

Step (a) – Solubilization of source elements. Upon combining $CuCl_2$, $InCl_3$, $GaCl_3$, and Se in trien, the solution immediately turns deep blue, indicative of $[Cu(trien)]^+$ formation. Se appears to slowly dissolve at room temperature. Amine solvents are known to activate and solubilize Se as $Se(amine)_x$ complexes [28]. Upon heating, $InCl_3$ and $GaCl_3$ dissolve, presumably as amine complexes, such as $[In(trien)]^{3+}$ and $[Ga(trien)]^{3+}$, and/or as selenide ions such as the previously proposed $InSe_2^-$ [9, 12]. No In or Ga species were observed in solid-state intermediates by Raman, XRD, or AES. This indicates that such intermediates remain in solution until the CIS formation step.

Step (b) – $Cu_{2-x}Se$ particle nucleation. Molecular clusters of $Cu_{2-x}Se$ form upon reaction of solvated Cu and Se species. The first black $Cu_{2-x}Se$ precipitate is observed with the reaction mixture reaches the trien boiling point (267 °C).

Step (c) – $Cu_{2-x}Se$ particle growth. In trien solvent under reflux conditions, this growth is expected to proceed rapidly. Without long carbon chains in their molecular structures, the trien molecules cannot stabilize [14] newly formed $Cu_{2-x}Se$ particles and prevent growth through addition of $Cu_{2-x}Se$ molecular clusters.

Steps (d) and (e) – CIS and CIGS formation. Over a period of 24 hours at reflux temperature, the solid $Cu_{2-x}Se$ reacts with solution-phase In to form CIS nanocrystals. If Ga is present, it will react with CIS over an additional 48 hours at reflux temperature to form CIGS.

Connection between Reaction Rates and Intermediate $Cu_{2-x}Se(s)$ Particles. Surfactant-based solvents have recently been reported to accelerate CIS and CIGS nanoparticle formation [13]. Although no explanation for this has been proposed, it is reasonable that through increased accessible surface area, smaller $Cu_{2-x}Se$ particles would react with dissolved In faster than larger $Cu_{2-x}Se$ particles would react. Because surfactant-based solvents can stabilize nanoparticles at earlier stages in their growth, nanoparticle intermediates in CIS/CIGS solvothermal preparation reactions would react faster in surfactant-based solvents than in non-surfactants like en and trien.

Reaction Acceleration Effects of Added Salts. If the accelerated CIS formation reaction times in Tables 1 and 2 stem from the stabilization and subsequent reaction of smaller $Cu_{2-x}Se$ intermediate particles, the addition of ammonium halide salts would appear to have a "surfactant" effect on the reaction. Because the halide ions are negatively charged, it is not reasonable to propose that they stabilize newly-formed $Cu_{2-x}Se$ nanoparticles through a capping phenomenon. Considering our evidence of Cu-halide complex formation, the growth of $Cu_{2-x}Se$ particles may be inhibited by a competitive Cu-halide complex formation mechanism (steps (a') and (b') in Figure 4). This would result in an accelerated reaction (step (c') in Figure 4) of smaller intermediate $Cu_{2-x}Se$ particles with In.

CONCLUSION

Reaction pathway studies of the solvothermal preparation of nanocrystalline $CuIn_{1-x}Ga_xSe_2$ in triethylenetetramine have resulted in experimental evidence of a solid-state $Cu_{2-x}Se$ intermediate and reaction rate acceleration by added ammonium halide salts. The proposed reaction pathway scheme features solubilization of Cu, In, Ga, and Se starting materials, rapid nucleation and growth of $Cu_{2-x}Se(s)$ particles, and subsequent reactions of these with a soluble In species, forming CIS, followed by reaction with a soluble Ga species, forming CIGS. Halide anions from added ammonium salts are believed to accelerate the reaction by limiting $Cu_{2-x}Se$ particle growth through a competitive Cu-halide complex formation step. The smaller $Cu_{2-x}Se$ particles may react faster with In to form CIS. Further experimental work, including microscopy of $Cu_{2-x}Se(s)$ intermediates formed under different experimental conditions, investigation of surfactant-based solvent effects on reaction rate, and identification of soluble In and Ga intermediate species, to test the validity of this reaction scheme is underway.

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