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Nanocomposite synthesis and characterization of Kesterite, Cu_2ZnSnS_4 (CZTS) for photovoltaic applications

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Abstract

Nanocomposite processing of binary metal chalcogenide solids has led to the synthesis of Kesterite, Cu_2ZnSnS_4 (CZTS), which is an important emerging material for thin film photovoltaic devices. Nanophase precursors are combined in stoichiometric ratios and annealed in a 350–500 °C sulfur-rich nitrogen atmosphere to form CZTS. Processing methods for CZTS in the literature are either energy-intensive, requiring the sequential sputtering of metal layers at 700 °C, followed by an annealing step in a sulfur-containing atmosphere at 500 °C, or the use of chemicals and solvents that are detrimental to the environment. The presence of CZTS is clear in the resulting powders as confirmed by both XRD and UV–Vis analysis. Our results show that increasing the annealing temperature of the nanophase precursor mixture led to a higher level of CZTS purity and that a copper-poor and zinc-rich environment produced the purest CZTS. Tin disulfide, SnS_2, precursors produced a purer CZTS than when tin monosulfide, SnS, was used, because the latter is more volatile and decomposes at lower temperatures than the former. This synthetic route is more cost effective and environmentally friendly, avoiding the use of long processing times and harsh solvents.

Keywords: B. Nanocomposites; CZTS; Hydrothermal powders; Chemical preparation

1. Introduction

Kesterite Cu_2ZnSnS_4, or copper zinc tin sulfide (CZTS), is a quaternary semiconducting material which has been generating interest over the past decade for applications in thin film photovoltaics. CZTS offers favorable optical and electronic properties that are advantageous for thin film applications, and is composed of abundant, non-toxic elements. The current record for CZTS photovoltaic efficiency is 10.1% [1] using a hydrazine-based solution for spin-coating a molybdenum-coated substrate, although higher efficiencies are necessary for the commercialization of CZTS. Current processing methods for CZTS are either expensive or detrimental to the environment [1–4], requiring harsh organic solvents and/or energy-intensive procedures. Nanocomposite techniques, the synthesis of a desired material using nanoparticle precursors, present a unique alternative to explore crystal growth in complex chalcogenide alloys, as demonstrated in the literature [5], and could allow for the large-scale deployment of CZTS-based thin film photovoltaics for energy generation. The use of stable, solid phase precursors and environmentally benign, inexpensive processing methods may allow for successful scalability of low cost CZTS.

The primary objective of this work is to use nanocomposite synthesis methods and aqueous processing of phase-pure CZTS to yield a low energy processing method with a low environmental impact of processing. The usefulness of the nanocomposite approach must be evaluated by comparing the resulting powders with products of traditional syntheses. The nanocomposite approach capitalizes upon available free energies in nanoparticles; excess free surface energy permits faster sintering times at lower temperatures than conventional ceramic processing techniques involving heat [6]. Furthermore,

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the reliance upon sintering in nanocomposite processing not only eliminates the need for harsh chemicals, but improves the crystallinity of the resulting powders [7].

There were three goals that were used to quantify the usefulness of the nanocomposite approach for the processing of CZTS: (1) precursor identification, (2) identification of temperature effects, and (3) identification of stoichiometric effects. There have been several discrepancies in the literature regarding the appropriate solid phase precursors for the nanocomposite synthesis of CZTS [5,8]. The use of tin monosulfide has been shown to produce CZTS powders [5] according to the following reaction:

$$2CuS+ZnS+SnS \rightarrow Cu_2ZnSnS_4$$

However, this is a problematic approach because tin monosulfide evaporates at temperatures above 200 °C [8], and all processing of CZTS is carried out at temperatures in excess of 200 °C. The use of SnS_2 may eliminate this problem. Second, it has been widely documented throughout the literature that monophase CZTS is very difficult to synthesize, and most examples of CZTS in the literature have at least minor quantities of reaction intermediates, most notably Cu_2SnS_3 [3]. It is worthwhile, then, to investigate whether processing temperature has any influence on the purity of the resulting CZTS product. This may also be effective in reducing the processing temperatures of CZTS, particularly because nanophases have lower melting and phase-change temperatures than bulk materials. The use of nanophase precursors also increases the surface area for the reaction, allowing for faster interdiffusion of species. Finally, the literature has suggested that the optimal growth conditions for CZTS may not combine the precursor metals in their strict stoichiometric ratios of 2:1:1. Excess copper is likely to form binary and ternary copper chalcogenide phases; it has been shown that copper-poor, zinc-rich conditions may be necessary, and that the optimized stoichiometric ratio is 1.332 Cu:0.914 Zn:0.75 Sn [9]. Thus far, these results have only been applied to the traditional processing methods, such as sequential metal deposition, followed by sulfurization; it has yet to be seen if these findings apply to a nanocomposite processing method.

2. Experimental

2.1. Precursor optimization

CZTS was made from binary chalcogenide precursors, each of which was synthesized via the microwave-assisted hydrothermal processing methods. The synthesis of each of the precursors, CuS, ZnS, SnS_2, and SnS, was developed to attain stable solutions of nanophase precursors, controlling: temperature, processing time, and the stoichiometry of the hydrothermally processed solution. Two temperatures and two processing times were tested for each precursor; the presence of excess sulfur was also experimentally varied to determine whether the presence of excess sulfur is necessary for successful synthesis.

It was determined that intermediate-temperature processing of anhydrous copper (II) chloride and sodium sulfide is ideal for CuS synthesis, which means that hydrothermal processing should occur at 80 °C. At temperatures lower than 80 °C, excess sulfur is present in the samples. The excess sulfur due to both lower temperature processing and excess quantities of sodium sulfide is not incorporated into the sample as covellite, but is a mixture of sulfur-containing species, such as $Cu_{1:8}S$ and S_8. Processing time is not a critical factor for covellite formation, as CuS was successfully prepared using both 24 h and 4 h processing times via conventional hydrothermal methods. Intermediate-temperature, 80 °C microwave-assisted processing of zinc chloride and sodium sulfide is ideal for ZnS. At temperatures greater than 80 °C, oxidation occurs. By experimentally varying the ratio of sodium sulfide to zinc chloride, it can be concluded that an excess of sulfur is advantageous to prevent the oxidation of the zinc to zinc oxide. Furthermore, longer microwave processing times of 30 min are necessary to fully incorporate the sulfur into the zinc sulfide structure to form monophase ZnS. Intermediate-temperature processing of anhydrous tin (IV) chloride and sodium sulfide at 80 °C is ideal for SnS_2 synthesis. At temperatures greater than 80 °C, sulfur may not be fully incorporated into the samples due to its volatilization into the head space of the reaction vessel during processing; $Sn_{0:9}S_{1.8}$ was found as a secondary phase in samples processed at higher temperatures. Increasing the ratio of sodium sulfide to tin (IV) chloride does not improve the incorporation of sulfur into the tin disulfide product. Such samples have an amorphous character and lack the ordered crystallinity of SnS_2. Longer microwave processing times of 30 min are necessary to fully incorporate the sulfur into the tin disulfide structure to form monophase SnS_2. Higher processing temperatures of 100 °C were necessary for the hydrothermal processing of anhydrous tin (II) chloride and sodium sulfide into tin monosulfide, SnS. Lengthy processing times of 1 h are essential for the full incorporation of sulfur into the tin monosulfide structure; shorter processing times resulted in the presence of various sulfur phases in the SnS samples due to incomplete reaction of the reagents into tin monosulfide. The presence of excess sulfur during sample preparation improved the crystallinity of the resulting powders.

For the synthesis of pure-phase CZTS (Table 1), CuS nanoparticles were made via conventional hydrothermal processing at 80 °C for 4 h. ZnS nanoparticles were prepared using microwave-assisted hydrothermal processing techniques at 80 °C for 30 min in the presence of 30% excess sulfur. SnS_2 nanoparticles were prepared using microwave-assisted hydrothermal processing at 80 °C for 30 min, while the SnS nanoparticles were prepared at 100 °C using microwave-assisted hydrothermal processing for 1 h, in the presence of 30% excess sulfur. The microwave-assisted experiments were performed using 2.45 GHz frequency with a MARS5 microwave system (CEM Corporation, Matthews, NC) at a power setting of 300 W with a ramping time of 5 min.

2.2. CZTS synthesis

The CuS, ZnS, SnS_2, and SnS precursors were combined in the stoichiometric ratios listed in Table 1, and annealed at temperatures that correspond to their row in the table. After weighing out the necessary amount of sample, the resulting

Table 1
The experimental matrix for the synthesis of CZTS.

Temperature (°C)	CuS (mmol)	ZnS (mmol)	SnS_2 (mmol)	SnS (mmol)
300	1.332	0.915	0.750	–
350	1.332	0.915	0.750	–
400	1.332	0.915	0.750	–
450	1.332	0.915	0.750	–
500	1.332	0.915	0.750	–
300	1.332	0.915	–	0.750
350	1.332	0.915	–	0.750
400	1.332	0.915	–	0.750
450	1.332	0.915	–	0.750
500	1.332	0.915	–	0.750
300	2.000	1.000	1.000	–
350	2.000	1.000	1.000	–
400	2.000	1.000	1.000	–
450	2.000	1.000	1.000	–
500	2.000	1.000	1.000	–
300	2.000	1.000	–	1.000
350	2.000	1.000	–	1.000
400	2.000	1.000	–	1.000
450	2.000	1.000	–	1.000
500	2.000	1.000	–	1.000

powder was thoroughly mixed and ground for approximately 20 min to ensure thorough dispersion of the powders. A sintering boat of finely ground elemental sulfur was loaded into the tube furnace closest to the gas inlet, followed by a sintering boat containing the sample. The sample was centered in the tube furnace, to ensure precise temperature control, while the sulfur was located directly adjacent to the furnace opening. A nitrogen tank was attached to the furnace, and adjusted to a slow, steady bubble rate to produce a sulfur-rich atmosphere. The tube furnace was quickly ramped up to temperature and held at the reaction temperature for 2 h.

2.3. *CZTS characterization*

X-ray diffraction patterns were determined using a PANalytical X'Pert Pro MPD configured in focusing geometry, or power mode. A 10 mm beam mask was used, along with a 0.5 fixed antiscatter slit. A multi-purpose sample stage was used to mount a zero-background sample holder, and patterns were collected over a range spanning from 5° to 70°. The instrument step size was 0.02°; a step was taken every 100 s. XRD patterns of CZTS, Cu_2SnS_3, and ZnS are strikingly similar. CZTS can be distinguished from Cu_2SnS_3 and ZnS by the presence of small peaks at 37.1°, 38°, and 44.9° [3]; however, this does not preclude the presence of Cu_2SnS_3 and ZnS in the powders. Cu_2SnS_3 and ZnS may be present as major byproducts of CZTS synthesis, and care must be taken to ensure that the results of the synthesis are, indeed, CZTS.

UV–Vis characterization via band gap analysis was used as a second means of ensuring the purity of the final product. UV–Vis spectra were determined using a Perkin-Elmer Lambda 950 UV/VIS/NIR Spectrophotometer. A 150 mm integrating sphere attachment in diffuse reflectance mode was used for collection; this instrument is accurate over a 250–2500 nm range. For our purposes, a scan range of 600–1200 nm was used; midway through data collection, the scan range was expanded to encompass a range of 500–1500 nm. The step size was 2 nm. A photomultiplier tube was used as the detector in the ultraviolet and visible regions of the scan range, while PbS was used in the near infrared region.

Particle size and morphology were determined by scanning electron microscopy (SEM) using a Hitachi S-3500N SEM with energy-dispersive x-ray, orientation imaging microscopy, and backscatter electron detectors. The nanocomposite powder samples were fixed to carbon tape and analyzed. Spatial resolution of the instrument is 4 nm. Particle size and morphology were also determined by transmission electron microscopy (TEM). For TEM analyses, the nanocomposite powders were dispersed in alcohol, dropped onto copper grids that were coated with collodian and carbon films and then dried in air. The TEM images were obtained from a JEM-2010 instrument (JEOL, Tokyo, Japan) at an acceleration voltage of 200 kV.

Surface areas were determined by multipoint nitrogen adsorption at liquid nitrogen temperature using an Autosorb-1 instrument made by Quantachrome Company. The Brunauer, Emmett and Teller (BET) surface areas were obtained using several values of adsorption in the P/P_0 range of 0.05–0.25.

3. Results and discussion

Three effects were examined using the experimental matrix in Table 1—processing temperature, stoichiometry of the binary sulfide precursors, and the tin source for CZTS formation. By systematically varying these three factors, it was found that CZTS can be successfully synthesized using a nanocomposite approach. Although there are several sets of nanocomposite processing conditions under which CZTS will be produced, it was found that nearly monophase CZTS results from a copper-poor, zinc-rich composition at 400 °C using CuS, ZnS, and SnS_2 as precursors. The XRD pattern of this sample is shown in Fig. 1; the small peaks indicative of CZTS formation at 37.1° (202), 38.0° (211), and 44.9° (105 and 213) are present in this sample. In addition, prominent peaks include the peak at 28.5°, which corresponds to an orientation of (112), the peak at 47.4° corresponding to both (220) and (204), and the third peak at 56.2°, which corresponds to an orientation of (116). (The CZTS peaks matched with the standard Kesterite pattern with a PDF number of 04-003-8816).

To conclude that we have nearly monophase CZTS, UV–vis analysis was performed on the sample as well. Diffuse reflectance spectra were collected for each sample, and Kubelka–Munk transformations were performed on each data set to estimate absorption profiles [10]. The band gap of the sample was found to exhibit a direct optical transition with a band gap of 1.32 eV, as can be seen in Fig. 2. This band gap indicates that CZTS is the dominant phase in the sample because the other phases likely to occur are ZnS, which has a band gap of 2.8 eV, and Cu_2SnS_3, which has a band gap of 0.96 eV; CZTS synthesized via the traditional methods has a direct transition band gap of between 1.0 and 1.62 eV [11].

3.1. Precursor effect

It was found that the use of tin disulfide, rather than tin monosulfide, is conducive to the formation of CZTS. Tin disulfide produces powders of significantly higher purity than those produced using tin monosulfide as a precursor. Tin monosulfide decomposes due to the loss of sulfur and evaporates at temperatures above 200 °C; the CZTS will dissociate during processing, which leads to the formation of multiple phases. As can be seen from the XRD patterns found in Fig. 3, some samples decomposed to a very significant extent and formed secondary phases (34.0° and 45.5°), making phase identification a challenge.

3.2. Temperature effects

It was found that as the annealing temperature of the sample is increased, the purity of the CZTS will also increase. There are less extraneous peaks present in addition to the CZTS peaks that are expected in the pattern, as shown in Fig. 4.

Melting and phase transformation temperatures of a material decrease significantly with crystal size, such that nanophases have vastly different properties than bulk materials. It is possible to synthesize phase-pure CZTS at such low temperatures because the precursor particle sizes are on the nanometer scale. Additionally, the large surface areas of the nanoparticle precursors provide a very large surface on which a reaction can occur. A faster diffusion of particles can occur, which means that the reaction requires a decreased external supply of energy [6].

3.3. Stoichiometric effects

The ratio in which the precursors are combined improves the purity of the resulting CZTS, as shown in Fig. 5. If the precursors are combined in strict stoichiometric ratios (2:1:1 (mole) of CuS:ZnS:SnS_2), the resulting powder product has significantly more byproduct phases. When samples are annealed from precursors in a 2:1:1 ratio, binary and ternary copper-containing phases (usually copper chalcogenides) are present in the final samples, indicating the need to minimize the copper content of the samples. In contrast, for conditions where the precursors are combined in a copper-poor, zinc-rich environment, the resulting powder contains fewer byproducts and unreacted precursors. This result confirms simulation research by Chen et al. [12] and Guo et al. [9].

3.4. Particle size

The optimized CZTS was determined to have particles of spherical morphology clumped into aggregates. The average

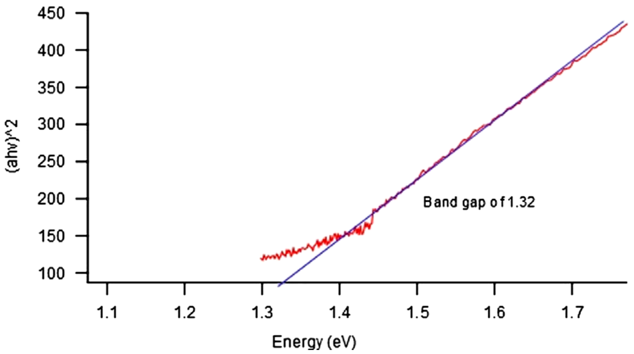

Fig. 2. The UV–vis spectrum and Kubelka–Munk transformation of the optimized CZTS.

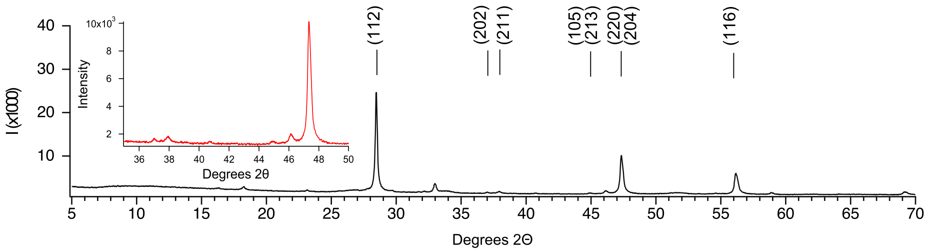

Fig. 1. The XRD pattern of CZTS synthesized at 400 °C in a copper-poor, zinc-rich environment using SnS_2.

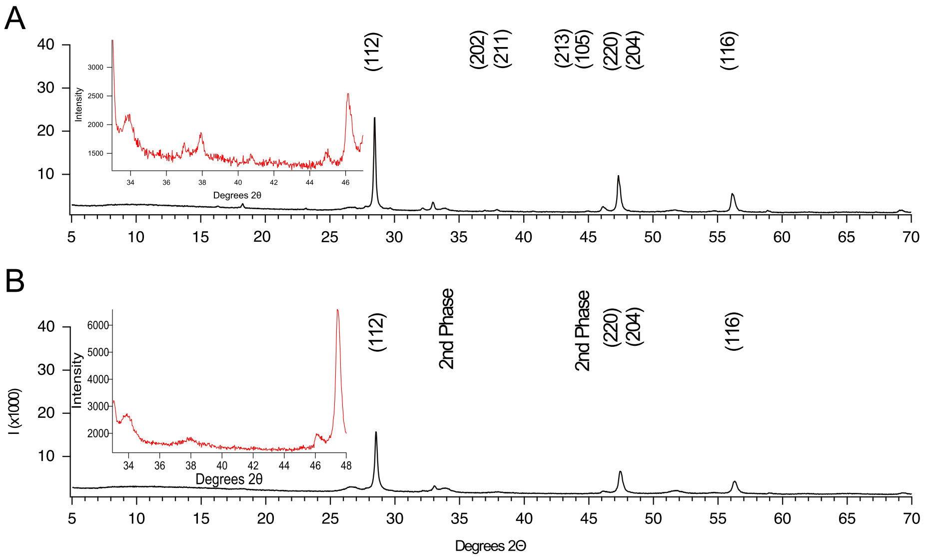

Fig. 3. The XRD patterns of CZTS synthesized at 450 °C in a copper-poor, zinc-rich environment. In (A) SnS_2 is used as a precursor, and in (B) SnS is used as one of the synthetic precursors.

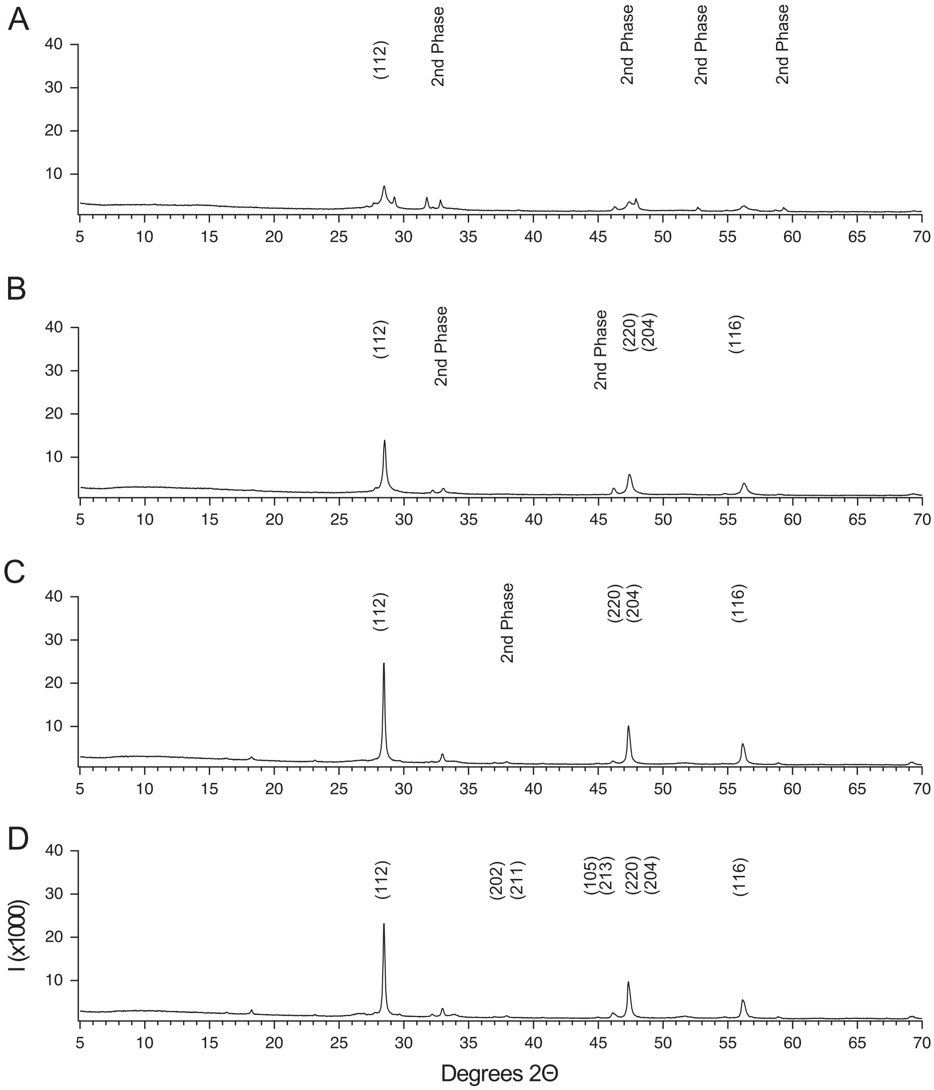

Fig. 4. The XRD patterns of copper-poor, zinc-rich, SnS_2-containing samples annealed at several different temperatures: (A) 300 °C, (B) 350 °C, (C) 400 °C, and (D) 450 °C.

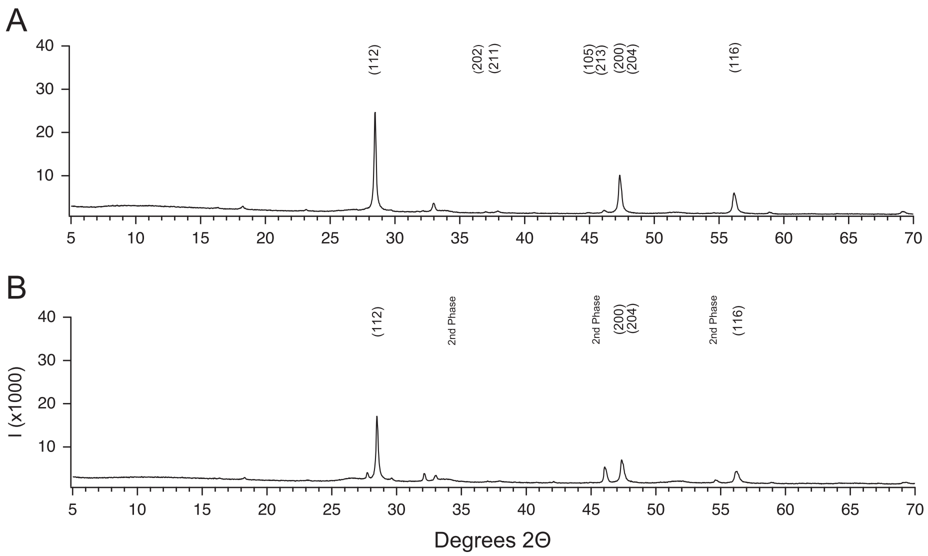

Fig. 5. The XRD patterns of a copper-poor, zinc-rich CZTS (A) and stoichiometric-ratio (2:1:1) prepared CZTS (B) annealed at 400 °C.

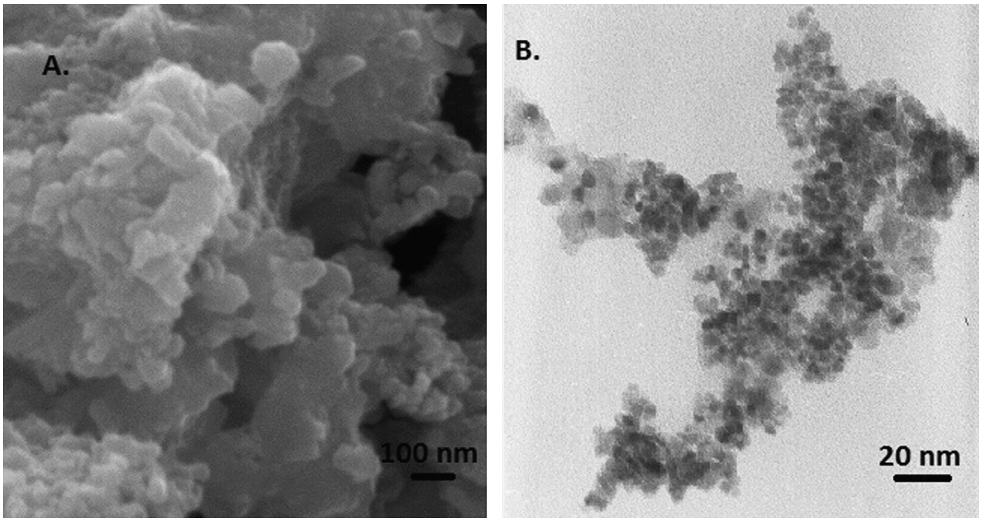

Fig. 6. (A) SEM, and (B) TEM images of the optimized CZTS.

particle size, as can be seen in the SEM and TEM image of Fig. 6, is between 5 and 10 nm.

3.5. Surface area analysis

The surface area of the optimized CZTS was determined to be 15 m^2/g; the surface areas of CuS, ZnS, and SnS$_2$ are 27, 124, and 105 m^2/g, respectively. The precursors have a higher surface area, especially when compared to the final CZTS product, which means that the nanocomposite approach was successful in the synthesis of CZTS. The high surface energies of the precursors derived from their large surface areas were likely used to reduce the required energy to run the CZTS synthesis reaction. Thus, a decreased external supply of heat was required for the successful synthesis of CZTS, as has been previously demonstrated in reducing the crystallization and densification temperatures of many nanocomposite oxide gel systems [13–16].

4. Conclusions

CuS, ZnS, SnS, and SnS$_2$, synthesized by microwave-assisted hydrothermal methods, were combined in stoichiometric ratios and annealed in a 350–500 °C sulfur-rich nitrogen atmosphere to form CZTS. The presence of CZTS of nominal chemical composition is clear in the resulting powders as confirmed by both XRD and UV–vis analysis. It was found that increasing the annealing temperature of the nanocomposite corresponds to a higher level of purity of the resulting CZTS powders. The nanophase precursors have a high surface area, and therefore a high surface energy; this high surface energy was used to reduce the heat necessary to synthesize CZTS. It was also found that a copper-poor, zinc-rich environment produces the purest CZTS powders. If the precursors are combined in a strictly stoichiometric ratio, byproducts, primarily ZnS and Cu$_2$SnS$_3$, will form; this problem is minimized in a copper-poor, zinc-rich system. Tin disulfide precursors produce a purer CZTS, despite studies concluding the successful use of tin monosulfide as a precursor. Tin monosulfide decomposes during CZTS processing due to the volatilization of sulfur and its subsequent evaporation; this decomposition will lead to the formation of multiple phases in addition to the desired CZTS product.

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