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Solution synthesis of $CuSbS_2$ nanocrystals: A new approach to control shape and size

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ABSTRACT

Chalcostibite copper antimony sulfide ($CuSbS_2$) micro- and nanoparticles with a different shape and size have been prepared by a new approach to hot injection route. In this method, sulfur in oleylamine (OLA) is employed as a sulfonating agent providing a simple route to control the shape and size of the particles, which enables the optimization of $CuSbS_2$ for a variety of applications. The sulfur to metallic precursor ratio appears to be one of the most effective parameters along with the temperature and time for controlling the size and morphology of the particles. The growth mechanism study shows in addition to the $CuSbS_2$ phase the presence of not previously observed intermediate phases (stibnite (Sb_2S_3) and famatinite (Cu_3SbS_4)) at the initial stage of the reaction. By increasing the ratio of sulfur to copper and antimony, wider and thinner $CuSbS_2$ particles are obtained. The particles have nanoplate and nanosheet morphology with a good shape and size uniformity. Coalescence of very thin nanosheets occurs with increasing reaction time eventually leading to formation of thicker particles which can be called nanobricks. Band gap determinations demonstrate that the obtained $CuSbS_2$ particles have both direct (1.51–1.57 eV) and indirect (1.44–1.51 eV) bandgaps. Transmission Electron Microscopy (TEM) studies revealed that the preferred growth directions are along the basis axes of the unit cell ([100] and [010]). Optical and structural properties of the obtained $CuSbS_2$ particles are indicative for their great potential in different generations of solar cells and supercapacitor applications.

1. Introduction

Semiconductor nanocrystals have attracted considerable attention owing to their wide range of applications in photodetectors [1–3], light emitting diodes [4,5], biology [6] supercapacitors [7,8], and solar cells [9–11]. Different kinds of semiconductors have been developed for each purpose [12]. Interesting candidates among those specifically aimed for solar cell applications are ternary and quaternary copper-based chalcogenide semiconductors, because they have high absorption coefficients and appropriate band gaps for light absorption. Within ternary chalcogenide semiconductors chalcostibite ($CuSbS_2$) is an emerging one due to its suitable bandgap. It is relatively less explored in comparison with $CuInS_2$ [13,14], $Cu(InGa)Se_2$ [15], and Cu_2ZnSnS_4 [16,17] and has been demonstrated as a promising alternative, because all elemental components of $CuSbS_2$ are earth abundant and economical, as the price of antimony is much lower than that of indium [18]. First-principle calculations using density functional theory have indicated $CuSbS_2$ as a new promising candidate for a p-type absorber material [19]. The results of the calculations suggest that $CuSbS_2$ has a strong light absorption coefficient ($\alpha > 1 \times 10^4$ cm^{-1}), and suitable electrical properties, both of which are essential for solar cell application [20,21]. $CuSbS_2$ crystallizes in an orthorhombic crystal system with a *Pnma* space group [22]. It is chemically quite similar to $CuInS_2$ but structurally very different due to its low valence state of antimony [23]. Theoretical simulations predict that $CuSbS_2$ has an indirect band gap, but experimental investigations show that the material has a direct band gap. However, many key parameters of $CuSbS_2$, such as the conduction band and valence band positions have not been fully investigated [21,24]. Studies of

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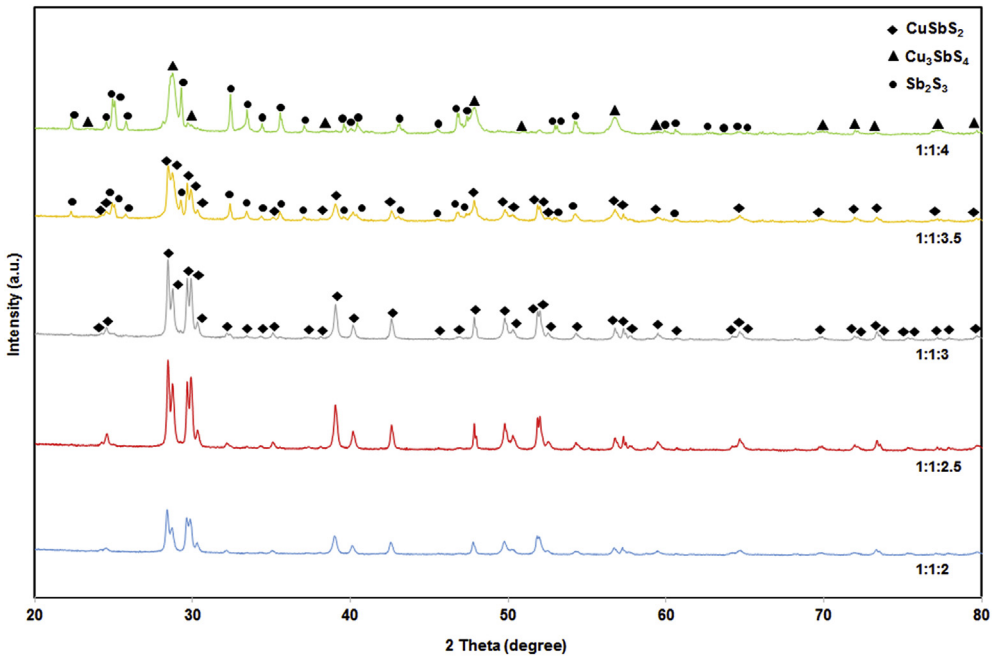

Fig. 1. XRD patterns of powders synthesized at 260 °C with different sulfur ratios.

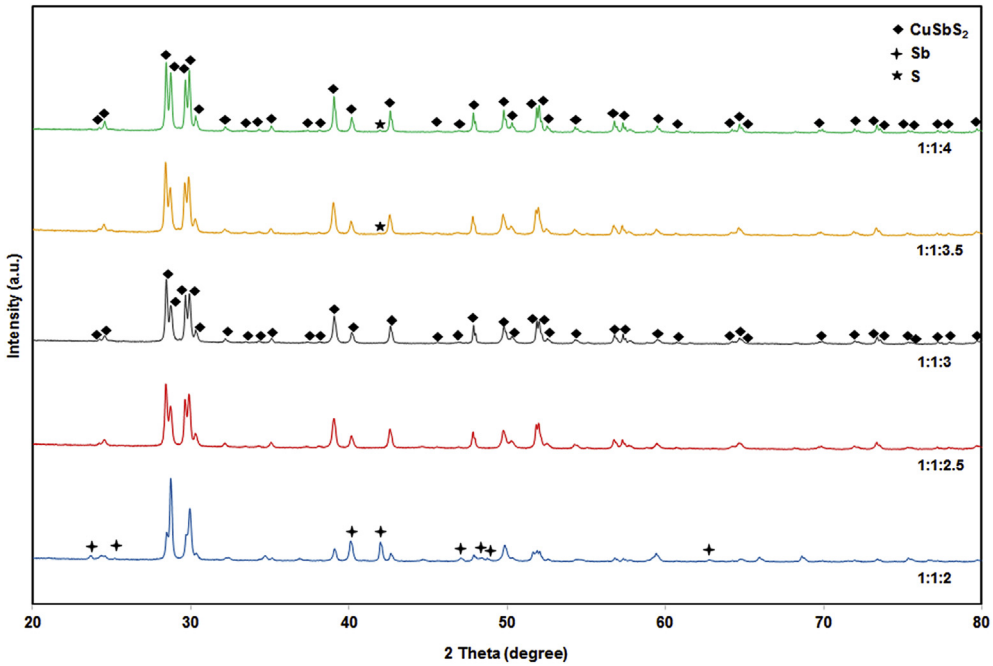

Fig. 2. XRD patterns of powders synthesized at 260 °C with different sulfur ratios.

this material as a potential absorber for sustainable and scalable thin film solar cells have been conducted, but still more research and investigation needs to be done in order to fully characterize the properties of these materials [25–28].

Table 1
Summary of powder X-ray diffraction measurements for samples.

Sample	Cu:Sb:S	Reaction temperature (T) (℃)	a (Å)	b (Å)	c (Å)
A	1:1:2	240	6.021	3.801	14.505
B	1:1:2.5	240	6.024	3.800	14.506
C	1:1:3	240	6.024	3.800	14.504
D	1:1:2.5	260	6.024	3.800	14.507
E	1:1:3	260	6.023	3.798	14.503

In recent years, characterization of $CuSbS_2$ thin films deposited by sputtering [29], thermal evaporation [30,31], and chemical bath deposition [32] have been published, but there are only a few studies on the synthesis of $CuSbS_2$ in powder form. In the synthesis of ternary materials, controlling the reaction condition, which is directly related to the synthesis method is essential. Many efforts have been focused on the nanoparticle formation mechanism, and many reliable and reproducible synthesis approaches have been developed [33,34]. Solvothermal, hydrothermal and hot injection methods have already been reported for the formation of $CuSbS_2$