Preparation of $Cu_2ZnSn_{(1-x)}Ge_xS_4$ Single Crystals by Molten Salt Method

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Keywords: $Cu_2ZnSn_{(1-x)}Ge_xS_4$ single crystals, Molten salt method, Solar cells, Semiconductors.

Abstract. $Cu_2ZnSn_{(1-x)}Ge_xS_4$ (CZTGS) Single crystals have been produced within a sealed quartz ampoule via molten salttechnique using CsCl as the molten flux. The synthesized crystals have been analyzed with X-ray diffraction (XRD), Raman, scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscope (TEM) for compositional and structural characterizations. XRD patterns and Raman spectra showed that the CZTGS crystals exhibit pure kesterite phase with (112) preferred orientation. The optical properties of the single crystals have been analyzed by UV−vis spectra. The synthesized crystals have suitable properties and are feasible candidates of absorber materials in solar cells.

Introduction

Chalcopyrite semiconductors like $CuInSe_2$ and $CuIn_{1-x}Ga_xSe_2$ (CIGS) have been proved to be successful candidates for the absorber layers in thin film solar cells. It is reported that the conversion efficiency of CIGS solar cells has exceeded 22%.[1] However, the CIGS solar cells utilize expensive elements like indium and gallium, which blocks the large-scale production and application of cost-effective photovoltaic technology. Cu_2-II–IV–VI_4 quaternary semiconductors such as Cu_2ZnSnS_4 (CZTS), Cu_2FeSnS_4 (CFTS), $Cu_2ZnSn(S,Se)_4$ (CZTSSe) and their solid solutions have attracted general attention to provide an alternative to CIGS due to Sn, Zn and Fe with relatively low toxicity and high abundance on the earth. Cu_2ZnSnS_4 (CZTS) is a promising material for low-cost thin-film solar cells owing to the suitable optical band-gap energy of about 1.5 eV and large absorption coefficient over 10^4 cm^{-1} [2].Therefore, variety of methods based on vacuum and non-vacuum techniques such as pulsed laser deposition [3], chemical vapor deposition [4], electrodeposition [5], thermal evaporation [6] and sputtering [7], have been utilized to fabricate CZTS thin films. Recently, new CZTS solar cell efficiency record of 12.6% has been achieved . However, Se substitution leads to a smaller band gap which is negative for open circuit voltage and multi-junction device application.

Recently, partially substituting Sn with Ge has been investigative to modulate the bandgap of CZTS or CZTSSe for photovoltaic application [8-10]. The bandgap of $Cu_2ZnSn_{1-x}Ge_xS_4$(CZTGS) compounds can be tuned from ~1.5 to ~2.25 eV by varying the atomic ratio *x* of Ge/(Ge+Sn) [8]. This tuneable bandgap for achieving graded-band-gap single-junction solar cells and also multi-junction devices as those reported in CIGS solar cells [11]. Ford et al. [8]has reported a

tunable band gap $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ nanocrystals solar cells with a conversion efficiency of 6.8%, while a thorough understanding of the basic properties of CZTGS single crystal is essential for the successful utilization of these compounds in high efficiency solar cells. Molten salt method that employ isothermal recrystallization of initial powders in different molten fluxes appears to be a relatively simple, inexpensive and a convenient method to produce CZTGS powders with an improved crystal structure. The shape and size of the crystals can be conveniently controlled by the temperature and duration of the recrystallization process. In this paper, we report for the first time the synthesis of high-quality CZTGS single crystals in the cesium chloride molten flux using copper (Cu), zinc sulphide (ZnS), tin (Sn), germanium (Ge) and sulphur (S) powders as the raw materials. The morphology, structure, composition, electrical and optical properties of the single crystals were also investigated. We have investigated the synthesis conditions and properties of the single crystals in order to determine the optimal preparation conditions for the realization of CZTGS crystals as the absorber material in solar cell.

Experimental Details

Cu, ZnS, Sn, Ge, S and CsCl were purchased from Aladdin. All reagents were of analytical grade and used without further purification. $Cu_2Zn (Sn_{1-x}Ge_x) S_4$ microcrystal was synthesized by the molten salt method using CsCl as the molten flux. In a typical synthesis, 10 mmol Cu, 5 mmol ZnS, 5 mmol Sn and Ge, 40 mmol S and 25 mmol CsCl was ground evenly in an agate mortar. The mixture were sealed in evacuated quartz ampoules and annealed at 750 ℃ for 72 h. Then, evacuated quartz ampoules were quenched to room temperature. The products were washed several times with deionized water and dried at 80℃ for 6 h. the morphology and microstructure of the prepared samples was observed with a field emission scanning electron microscope (SEM, Hitachi S-4800). The elemental composition was determined by energy dispersive X-ray microanalysis (EDX) attached to the scanning electron microscope equipped with a Bruker AXS XFlash detector 4010. The crystal structure of the particles was identified by a Rigaku D/max-IIIC X-ray diffraction (XRD) with Cu-Ka radiation (λ=0.154 nm). The phases of the samples were characterized using Thermo Almega XR Raman spectrometer with 632 nm incident light. The optical properties of particles were analyzed by UV–vis diffuse reflectance spectrum (UV–vis DRS, Hitachi-U3010) with an integrating sphere. The electrical resistivity of the crystals was measured by pressing individual grains between two *In contactors*.

Results and Discussion

The energy dispersive X-ray microanalysis (EDX) was used to analyze the degree of stoichiometry of the studied single crystals. Here we label $Cu_2ZnSn_{1-x}Ge_xS_4$ crystals of x=0.25, 0.5, 0.75, 1 as S1, S2, S3 and S4, respectively. As can be seen in *Table 1*, composition of the samples is closed to stoichiometric (with a slight Cu deficiency).

Table 1 Chemical composition of $Cu_2ZnSn_{1-x}Ge_xS_4$ single crystals measured by EDX.

Sample	Cu (at%)	Zn (at%)	Sn (at%)	Ge (at%)	S (at%)
S1	28.81	14.92	9.45	3.10	43.72
S2	26.81	12.24	6.42	6.16	48.38
S3	22.70	12.13	3.10	9.31	52.77
S4	22.58	12.05	0	11.59	53.78

XRD patterns of the as-synthesized $Cu_2ZnSn_{1-x}Ge_xS_4$ single crystals in dependence of the x value were recorded in *Fig. 1a*. As observed in the XRD spectrum, the most intense peak contributed to (112) orientation of the kesterite phase $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ single crystals [8]. And with the Ge content increased, the diffraction peaks of (112) orientation shifted to higher angle. This can be explained by the replacement of large Sn atoms by smaller Ge atoms. Lattice shrinkage with increasing substitution for the smaller Ge atoms results in a systematic shift in the diffraction peaks to higher angles [12]. Besides, the most intense (112) orientation peak appeared when x=0.5, which indicated that a half substitution of Sn atoms by Ge atoms contributed to a higher crystalline of CZTGS single crystals.
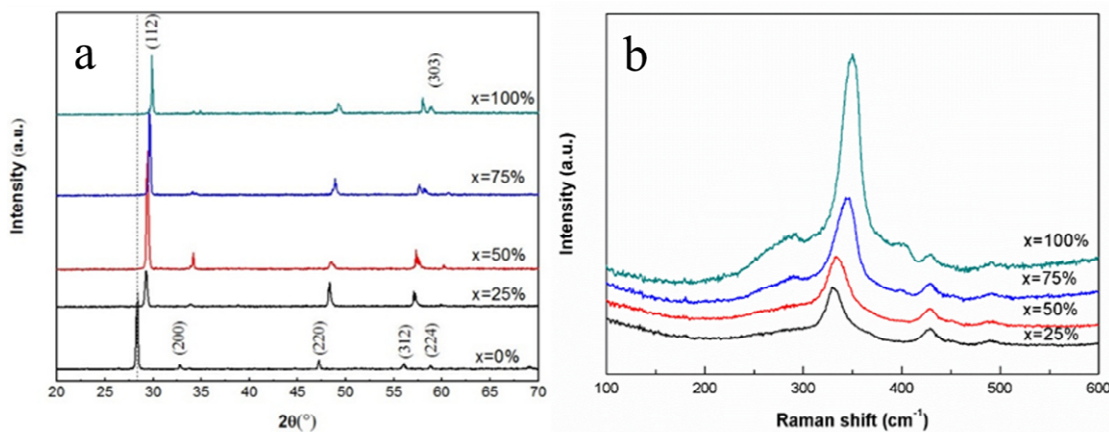

Fig. 1 (a) The X-ray diffraction patterns of the as-synthesized CZTGS single crystals; (b) Raman spectra of the as-synthesized CZTGS single crystals

To confirm the purity of the crystals, the samples were further analyzed using Raman scattering, which is shown in *Fig. 1b*. For crystals of x=0.25, the most intense peak at ~336 cm^{-1} is found, which performs a slight blue-shift compared to the peak of pure CZTS crystals and is consistent with the characteristic peaks of CZTGS. As the Ge content increased, the intense peak suffered from a larger blue-shift while the position of other peaks unchanged. These results indicate that the obtained crystals are pure CZTGS when part of initial Sn was substituted by Ge, which is corresponding with the XRD results.

Fig. 3 depicts UV-vis data for CZTGS nanocrystals with Ge/(Sn+Ge) ratios of 0.0, 0.5 and 1.0. The band gap is observed to increase with increasing Ge content of the synthesis precursors. The expected band gap for CZTS is ~1.5 eV, whereas the band gap for CZGS has been reported to be 2.05-2.25 eV[13]. Linear extrapolation of the crystal light absorption versus the photon energy is typically used to determine the effective band gap. Specifically, the band gap of the CZTGS particles was estimated from the plot of *(αhν)^2* versus *hν* (*α = absorptivity, h = Planck's constant and ν = frequency*) which was derived from the corresponding UV-vis absorption spectrum. As

shown in *Fig. 3*, if the CZTS data are extrapolated to yield a bandgap of 1.52 eV, then the CZGS crystals would have a band gap of 2.25 eV. Note that this band gap is similar to previously reported for bulk Cu_2ZnGeS_4 (CZGS). And the CZTGS data are extrapolated to yield a bandgap of 1.94 eV, which is between those of CZTS and CZGS.
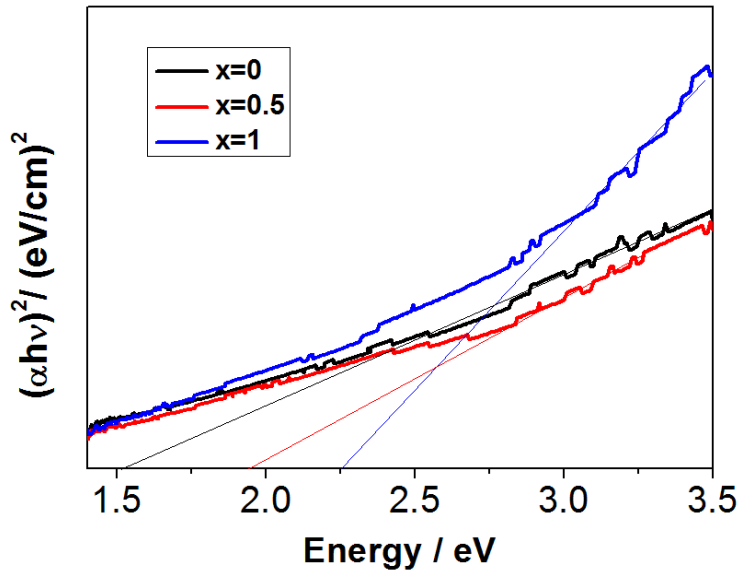

Fig. 2 UV-vis data depicting the increasing onset of absorption with increasing Ge content in CZTS (black), CZTGS (red), and CZGS (blue).

The SEM image for a typical morphology of the prepared CZTGS samples is shown in *Fig. 4*. It is noticeable that the sizes of the CZTGS crystals were about 50–100 μm and dominant columnar shapes were found among the particles. It can also be found that the connection between two sides is smooth due to the drastic friction in molten salt at high temperature.
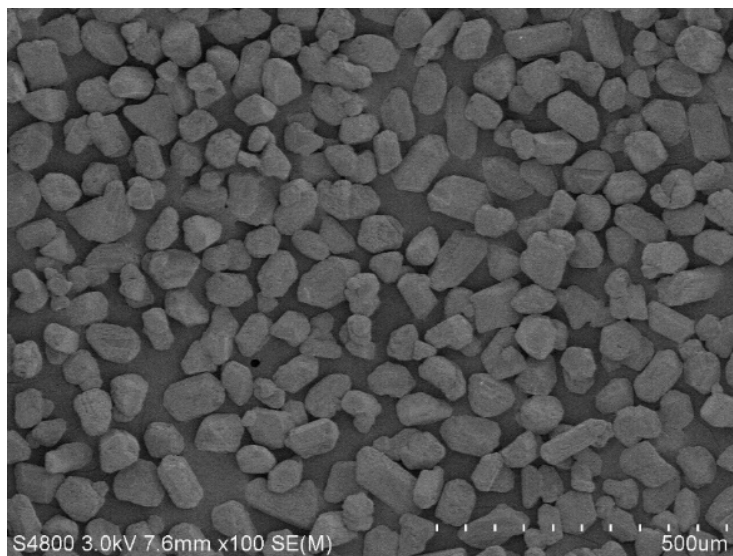

Fig. 3 SEM image of typical CZTGS crystals

Conclusions

In this paper, micron-sized $Cu_2ZnSn_{1-x}Ge_xS_4$ (CZTGS) single crystals were fa-bricated by molten salt method using Cu, ZnS, Sn, Ge, and S as raw materials and using CsCl as flux for the first time.

The stoichiometric ratio of CZTGS single crystals are controllable in molten salt method. The average size of the CZTGS single crystals was about 50–100 μm and their band gap could be adjusted from 1.52 eV to 2.25 eV. The as-prepared sample can be used to fabricate absorb layer of solar cell through printing or other methods. In this way, molten salt method can be widely used in thin film solar cells.

Acknowledgements

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