## Retraction for CrystEngComm:

#### The synthesis of Cu<sub>2</sub>Zn(Ge<sub>x</sub>Sn<sub>1-x</sub>)Se<sub>4</sub> nanocrystals with tunable band gaps

Kai Zhong, Si Heng Lu, Hao Wang, Yu Xiu Sun, Hui Juan Zheng, Jing Bing Liu and Hui Yan

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We, the named authors, hereby wholly retract this *CrystEngComm* article due to data fabrication in Fig. 4 and 6. One of the spectra in Fig. 4, corresponding to nanocrystals of varying Sn/Ge content, has been copied and shifted within the figure: the purple spectrum (x = 1) is the copy of the black spectrum (x = 0). One of the plots in Fig. 6b, corresponding to nanocrystals of varying Sn/Ge content, has been copied and shifted: the blue curve (x = 0.3) is the copy of the green curve (x = 0.7).

An investigation by Dr Yongping Lei (Professor and Chairman of College Council of the College of Materials Science and Engineering, Beijing University of Technology, China) determined that Kai Zong was responsible for these instances of data fabrication. Hao Wang, as his tutor and also corresponding author, is responsible for the duty of supervision and management. Other co-authors accept joint responsibility for the preparation of article. Please allow us to sincerely apologise to all readers and the Editorial Office.

Signed: Kai Zhong, Si Heng Lu, Hao Wang, Yu Xiu Sun, Hui Juan Zheng, Jing Bing Liu, Hui Yan, 25 November 2013.

This retraction is endorsed by Jamie Humphrey, Editor, *CrystEngComm*. Retraction published 13 December 2013.

# CrystEngComm

# PAPER

# The synthesis of $Cu_2Zn(Ge_xSn_{1-x})Se_4$ nanocrystals with tunable band gaps

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 $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$  (CZTGSe) nanocrystals with tunable band gaps have been synthesized via a hot-

injection method. The band gaps of the nanocrystals were demonstrated to be linearly tuned from 1.33 to

1.63 eV by adjusting the composition parameter x of the Ge/(Ge + Sn) ratio from 0.0 to 1.0. This indicates

that the tunable band gap CZTGSe can be a potential substitute for Cu<sub>2</sub>ZnSnSe<sub>4</sub> (CZTSe) nanocrystal

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# Introduction

The optical band gap plays a significant role to determine the optical and electrical properties of photovoltaic (PV) applications. An ideal material for a thin film solar cell absorber layer should have an optical band gap of around 1.3–1.5 eV.<sup>1</sup> The  $Cu_2In_xGa_{1-x}Se_2$  (CIGSe) thin film solar cell with a band gap of about 1.1–1.2 eV has attracted much attention in recent years,<sup>2,3</sup> however, the relatively low band gap energy and limitations in the supply of In and Ga are projected to restrict the production capacity.

photovoltaic devices in the future.

Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) is receiving increased attention for use in low-cost thin-film PVs due to its optimal band gap energy (1.4-1.5 eV), relatively low toxicity, high absorption coefficient  $(>10^4 \text{ cm}^{-1})$ , and more importantly, the earth abundant content of elements, compared with CIGSe.4-7 Though the CZTS solar cells have reached a power conversion efficiency of 8.4%,8 it is still difficult for them to meet commercial demand.9 Recently, the achievement of beyond 11.1% efficient laboratory scale  $Cu_2ZnSn(S_{1-x}Se_x)_4$  (CZTSSe) devices using a non-vacuum, hydrazine-based deposition process has been reported.<sup>10</sup> The inclusion of Se in CZTS increases the lattice parameters to facilitate enhanced grain growth, passivate the grain boundaries to reduce the potential barriers for grain-tograin carrier transport, and alter the band gap energy of CZTSSe.<sup>11-13</sup> CZTSSe has a direct band gap around 1.04-1.5 eV,<sup>11,14,15</sup> by varying the ratio of Se/(S + Se), which is similar to the previous reports of  $Cu_2Ge(S_{3-x}Se_x)$  and  $Cu_{2-x}S_ySe_{1-y}$ .<sup>16,17</sup> As the ratio of Se/(S + Se) increases, the CZTSSe devices exhibit a better performance. However, the higher ratio of Se/(S + Se)

decreases the band gap, which is around 1.04–1.1 eV. To contend with its kesterite-based predecessor CZTS, this value must be improved. Besides, the low band gap energy will generate a large short circuit current, which would release a large amount of heat to affect the service life and security of the devices.

Similar to CIGSe, which widens the band gap by incorporating Ga into the CuInSe<sub>2</sub> device,<sup>18,19</sup> Hillhouse<sup>20,21</sup> et al. discovered that the band gap tuning of the CZTS devices was possible by substituting Ge for some of the Sn, which tuned the band gap to 1.94 eV. We predict that a similar band gap tuning to CZTSe may also be feasible. The substitution of Sn with Ge is an ideal route, for CZTSe, first principle calculations have indicated that the smaller Ge atoms strengthen the s-s and s-p level repulsion between the Ge and Se atoms and should result in an increase in the anti-bonding conduction band minimum.<sup>22,23</sup> Mitzi et al. have recently prepared CZTGSe solar cell devices with a 9.1% conversion efficiency by using a hydrazine-based deposition process.<sup>24</sup> Moreover, the band gap tunability of mixed chalcogenides offers an alternative to the quantum-confinement effect, as this effect is generally lost when the nanocrystals are annealed into dense films.<sup>2,25</sup>

There are previous reports on the synthesis of  $Cu_2ZnGeSe_4$  (CZGSe) compounds.<sup>26,27</sup> However, such compounds have not been researched in the band gap tuning with different Ge/(Ge + Sn) ratios. Herein, our work focuses on the synthesis of CZTGSe nanocrystals with tunable band gaps by varying the Ge/(Ge + Sn) ratio from 0.0 to 1.0 resulted in a tunable band gap of 1.33 to 1.63 eV, respectively. This proves that the CZTGSe nanocrystals are an ideal candidate for an absorber material and would facilitate thin film solar cells to achieve a higher efficiency in the near future.

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## **Experimental section**

#### Chemicals

Copper(I) iodide (CuI, Aldrich, 99.99%), zinc(II) acetate  $(Zn(OAc)_2 \cdot 2H_2O, Fisher)$ , tin(IV) chloride pentahydrate (SnCl<sub>4</sub> · 5H<sub>2</sub>O, Aldrich), germanium(IV) chloride (GeCl<sub>4</sub>, Alfa Aesar, 99.9999%), selenium powder (Se, Strem, 99.99%), sodium borohydride (NaBH<sub>4</sub>, Alfa Aesar, 98%) and oleylamine (Aladdin, 80–90%) were purchased. All chemical reagents were used as received without further purification.

#### Cu2ZnSnSe4 nanocrystal synthesis

The synthesis of the CZTSe nanocrystals was carried out using a hot-injection method adapted from a previous report.<sup>7</sup> Oleylamine was degassed for 1 h with N2 before reaction. All reaction conditions were kept inert to prevent the formation of an oxide. The target composition, deviated from stoichiometry with Cu/(Zn + Sn) = 0.8 and Zn/Sn = 1.2 which was based on the highest solar cell efficiencies.<sup>4,28,29</sup> 0.18 mmol CuI, 0.12 mmol Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O and 0.1 mmol SnCl<sub>4</sub>·5H<sub>2</sub>O were dissolved in 5 mL oleylamine in a three-neck round bottom reaction flask and then heated up to 180 °C. At the same time, in a 10 mL scintillation vial, 0.7 mmol Se powder, 0.4 mmol NaBH<sub>4</sub> and 3 mL OLA were sonicated until Se had dissolved. The reaction solutions were mixed by injecting the Se powder solution into the former salt solution. Following the injection, the temperature dropped to around 150 °C. The growth temperature of the reaction solution was increased from 150  $^\circ C$  to 270  $^\circ C$  and kept at 270  $^{\circ}$ C for 1 h.

#### $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ nanocrystal synthesis

The synthesis procedure of the CZTGSe nanocrystals is similar to that of CZTSe nanocrystals except that 0.1 mmol  $SnCl_4 \cdot 5H_2O$  was substituted by a 0.1 mmol mixture of GeCl<sub>4</sub> and  $SnCl_4 \cdot 5H_2O$ . The amount of GeCl<sub>4</sub> added depends on the desired Ge/(Ge + Sn) ratio of 0.3, 0.7 and 1.0. Note that the GeCl<sub>4</sub> solution required mild heating around 40 °C to prevent gelling. The reaction was held at 290 °C for 1 h while other reaction parameters were kept the same as CZTSe.

When the reaction was completed, the flask was removed from the heating mantle and naturally cooled down to room temperature. The black product with an amount of ethanol was collected and centrifuged at 8000 rpm for 5 min and the upper clear solution was discarded. Then, hexane was added to disperse the nanocrystals. The dispersion was centrifuged at 5000 rpm for 10 s, the larger nanocrystals and aggregates were discarded while the black colloidal solution was transferred into another centrifuge tube where slurries formed after the addition of isopropanol. Those slurries were centrifuged again at 8000 rpm for 5 min and the nanocrystals accumulated at the bottom of the centrifuge tube once again, the washing process was repeated three times.

#### Materials characterization

The nanocrystals dispersed in hexane were dropped on carbon supported Cu grids for transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observation, which were performed using a JEM-2100 with an acceleration voltage of 200 kV. The TEM was equipped with a Princeton Gamma Tech Prism 2000 energy-dispersive X-ray spectroscopy (EDS) detector, and used for the elemental analysis of the CZTGSe nanocrystals. The X-ray powder diffraction (XRD) patterns were measured with a German Bruker AXS D8 ADVANCE diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5405$  Å). The operation voltage and current were kept at 40 kV and 40 mA, respectively. All structural refinements were carried out using the Rietveld refinement technique with the Fullprof software suite.<sup>30</sup> Raman spectra (LabRam HR800) were recorded using the 488 nm laser line with the laser power of 100 mW. UV-Vis-NIR spectra were obtained from 300-1500 nm on a Shimadzu UV-3101PC spectrophotometer at room temperature. All solutions were prepared in hexane.

# **Results and discussions**

The compositions of the CZTGSe nanocrystals measured by the EDS detector are listed in Table 1. The calculated composition of the Ge and Sn and the obtained Ge : Sn ratios in the final CZTGSe nanocrystals are in close agreement. This indicates that the synthetic route allowed for the delicate adjustment of the Ge content in the CZTGSe nanocrystals with controlled ratios of Ge/(Ge + Sn).

Fig. 1(a) displays the XRD data for a series of CZTGSe nanocrystals synthesized with different Ge/(Ge + Sn) precursor ratios of 0.0, 0.3, 0.7 and 1.0, respectively. At x = 0.0, the experimental pattern agrees well with the standard pattern of Cu<sub>2</sub>ZnSnSe<sub>4</sub> (JCPDS no. 52-0868), which has a tetragonal structure with three major diffraction peaks of the (112), (204) and (312) planes. As the ratio of Ge/(Ge + Sn) increases, all the diffraction peaks move to larger  $2\theta$  values (Fig. 1(b)). Such a systematic shift is due to the contraction of the lattice parameters by substituting the larger Sn atoms (1.72 Å) with the smaller Ge atoms (1.52 Å) in the CZTGSe lattice. Eventually, at x = 1.0, the diffraction pattern agrees well with Cu<sub>2</sub>ZnGeSe<sub>4</sub> (JCPDS no. 52-0867). No secondary phases are detected in each sample with different Ge contents from the

Table 1 The composition analysis of the Cu<sub>2</sub>ZnSn<sub>1-x</sub>Ge<sub>x</sub>Se<sub>4</sub> nanocrystals

Calcd composition	Cu : Zn : Ge : Sn : Se ratio determined by EDS
$Cu_2 ZnSnSe_4 (x = 0)$	1.92:1.03:0.92:3.83
$Cu_2Zn(Ge_{0.3}Sn_{0.7})Se_4$ (x = 0.3)	1.82: 1.12: 0.28: 0.71: 4.02
$Cu_2Zn(Ge_{0.7}Sn_{0.3})Se_4(x = 0.7)$	2.02:1.22:0.69:0.33:4.11
$Cu_2ZnGeSe_4 (x = 1)$	2.02:1.12:1.03:3.91

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Paper



Fig. 1 (a) The XRD patterns of the  $Cu_2ZnSn_{1-x}Ge_xSe_4$  nanocrystals for various values of x. The standard XRD patterns for CZTSe and CZGSe are shown below. (b) The diffraction peak of the (112) plane for various values of x. (c) The Rietveld fit of the obtained  $Cu_2ZnGeSe_4$  nanocrystals.

XRD data. To eliminate the deviation of the sample displacement influence, Fullprof 2012 software is used to refine the lattice parameters of CZGSe (Fig. 1(c)). According to the Rietveld refinement result, the lattice parameters are a =5.561 Å and c = 11.109 Å. The pattern factor  $R_{\rm p}$ , the weighted pattern factor  $R_{wp}$ , and the expected pattern factor  $R_{exp}$  are 5.15%, 6.68% and 2.55%, respectively. The interplanar spacings of the CZTGSe nanocrystals for each composition are estimated from the  $2\theta$  of the strongest (112) peaks by Bragg's Law. Upon calculation, the values of  $d_{(112)}$  are plotted as shown in Fig. 2. It can be concluded that as the Ge/(Ge + Sn)ratio rises, there is a decreasing tendency of the interplanar spacings due to the lattice contraction. The CZTGSe lattice parameters *a* and *c* (in Fig. 3) are calculated as a function of xfrom the XRD data and are found to vary linearly with the Ge content, as expected by the basis of Vegard's Law. This confirms that the CZTGSe nanocrystals have a homogeneous solid solution.

In addition to the XRD analysis, Raman spectra are useful to investigate the phase purity. Fig. 4 shows the Raman spectra of the CZGTSe nanocrystals with different Ge/(Ge + Sn) ratios. At x = 0.0, the spectrum presents a main band at 196 cm<sup>-1</sup>, and two sub bands at 173 and 235 cm<sup>-1</sup>, which match well with those generally observed in the Raman spectra of the tetragonally structured CZTSe.<sup>31–33</sup> As the Ge content increases from 0.0 to 1.0, a slight blue shift of the three bands is



Fig. 2 The interplanar spacings of the (112) plane for various values of x.



Fig. 3 A plot of the lattice parameters a and c for various values of x.

observed. Because of the different ion radii and masses of  $Ge^{4+}$  and  $Sn^{4+}$ , the replacement of Sn by the smaller Ge will result in the movement of the Ge cation closer to the selenium atoms, thereby shrinking the Ge–Se bond and increasing the vibrational frequencies. The blue shift of the three bands can be explained as a result of the increase of distortion in the CZTGSe structure.<sup>34</sup> The Raman spectrum at x = 1.0 shows an intense band at 204 cm<sup>-1</sup> and a weak band at 180 cm<sup>-1</sup>, which is consistent with previous report for CZGSe.<sup>35</sup> With these



**Fig. 4** The Raman spectra of the  $Cu_2ZnSn_{1-x}Ge_xSe_4$  nanocrystals for various values of *x*.

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**Fig. 5** (a), (c), (e), and (g) TEM images of  $Cu_2ZnSn_{1-x}Ge_xSe_4$  nanocrystals with x = (a) 0.0, (c) 0.3, (e) 0.7, and (g) 1.0. Inset: size distribution of each sample. (b), (d), (f), and (h) HRTEM images of the  $d_{(112)}$  lattice fringes correspond to the TEM images.

identifications, the as-obtained CZTGSe can be considered as a solid solution without secondary phases.

The TEM images in Fig. 5(a), (c), (e) and (g) reveal the morphologies and sizes of the obtained CZTGSe nanocrystals which are fairly monodisperse and appear to be highly faceted with polyhedral geometries. The dimensions of the samples with Ge/(Ge + Sn) precursor ratios of 0.0, 0.3, 0.7 and 1.0, respectively, fall in the range of 19.3 to 15.4 nm. The histogram

of the size distribution of each sample is shown in the inset of Fig. 5(a), (c), (e) and (g) and is obtained by measuring 210 individual nanocrystals. Narrow size distributions, with dispersions around 10% are systematically obtained. Fig. 5(b), (d), (f) and (h) show HRTEM images, highlighting the lattice fringes of the individual  $Cu_2Zn(Ge_rSn_{1-r})Se_4$ nanocrystals. The interplanar spacings are calculated by averaging measurements from multiple fringes on each particle and from multiple particles. At x = 0.0, the measured interplanar spacing is  $3.28 \pm 0.02$  Å, corresponding to the ideal distance of the Cu<sub>2</sub>ZnSnSe<sub>4</sub> (112) crystal plane. As the Ge content increases from 0.0 to 1.0, the values of the interplanar spacings decrease. For x = 1.0, the measured lattice fringe with an interplanar spacing was 3.18 + 0.02 Å, which represents the (112) crystal plane of Cu<sub>2</sub>ZnGeSe<sub>4</sub>. All the values of the interplanar spacings correspond well with those calculated from the XRD data by Bragg's Law.

Fig. 6(a) illustrates the UV-vis spectra for the CZTGSe nanocrystals with different Ge/(Ge + Sn) ratios. The absorption spectra are measured using the liquid phase method. The CZTGSe nanocrystals are dispersed in hexane by ultrasound for several minutes, and then, the final dispersion is transferred to the cuvette to measure the absorption spectra. The optical absorption edge shows an obvious blue shift to a higher energy as the ratio of Ge/(Ge + Sn) increases from 0.0 to 1.0. The band gap energies  $(E_g)$  (Fig. 6(b)) are calculated by plotting the square of  $\alpha h \gamma$  as a function of  $h \gamma$  and extrapolating the linear portion to the x intercept, where  $\alpha$  is the absorption coefficient obtained from the UV-vis spectra of solutions of the CZTGSe nanocrystals, and  $h\gamma$  is the photo energy. The  $E_{g}$ values determined from the optical absorption of the CZTGSe nanocrystals range from 1.33 eV for x = 0.0 to 1.63 eV for x =1.0, which are comparable to the experimental bulk values reported for CZTSe and CZGSe, respectively.7,36,37 It can be clearly observed from Fig. 6(c) that the band gaps of the CZTGSe nanocrystals almost linearly increase with the increasing composition x. The band gap of the CZGSe nanocrystals is slightly lower than that of the CZGS nanocrystals, which has been reported to be 1.94 eV<sup>20</sup> and 2.2 eV.<sup>38</sup> The similar band gap tuning is previously observed from CZTS to CZTSe.<sup>7,15</sup> Note that at x = 0.7, the value of the band gap is



**Fig. 6** (a) The UV-vis absorption spectra for the  $Cu_2ZnSn_{1-x}Ge_xSe_4$  nanocrystals as a function of the Ge/(Ge + Sn) ratio, (b) the band gap data depicting the increasing onset of absorption with x = 0.0, 0.3, 0.7 and 1.0, and (c) the band gap energies determined from the optical absorption of the  $Cu_2ZnSn_{1-x}Ge_xSe_4$  colloidal nanocrystals.

determined to be 1.52 eV, which approaches the optimum value for solar photoelectric conversion. As expected, these CZGSe nanocrystals indeed display tunable band gaps in an range of 1.33 to 1.63 eV, indicating that the band gaps of the CZTGSe nanocrystals are mainly effected by the Ge/(Ge + Sn) ratio.

# Conclusion

In conclusion, we have synthesized  $Cu_2Zn(Ge_xSn_{1-x})Se_4$ nanocrystals by a hot-injection method through tuning the Ge/(Ge + Sn) ratio of the precursor. The diameters of the CZTGSe nanocrystals mainly range from 15.4 to 19.3 nm. The lattice parameters are found to be composition-dependent, and follow Vegard's Law. As expected, varying the value of the Ge/(Ge + Sn) ratio from 0.0 to 1.0 resulted in a tunable band gap of 1.33 to 1.63 eV, which was verified by the UV-vis absorption spectra. Note that at x = 0.7, the value of the band gap is determined to be around 1.52 eV, which approaches the optimum value for solar photoelectric conversion. The synthesis of the pure CZTGSe nanocrystals reported herein provides a way for probing the effect of Ge inclusion in mixedchalcogenide thin films and may render CZTGSe as a promising candidate for photovoltaic applications in the future.

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