11.39% efficiency Cu$_2$ZnSn(S,Se)$_4$ solar cells from scrap brass

Yining Pan$^1$ | Chang Yan$^1$ | Xiangyun Zhao$^1$ | Wangxian Chen$^1$ | Kaiwen Sun$^1$ | Qing Wu$^2$ | Liming Ding$^3$ | Fangyang Liu$^1$

$^1$ School of Metallurgy and Environment, Central South University, Changsha, P. R. China
$^2$ Information and Network Centre, Central South University, Changsha, P. R. China
$^3$ Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing, P. R. China

Correspondence
Fangyang Liu, School of Metallurgy and Environment, Central South University, Changsha 410083, P. R. China.
Email: liufangyang@csu.edu.cn

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Kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) is one of the most promising next-generation thin-film photovoltaic materials due to its environmental friendliness and earth-abundant constitutions, excellent optoelectronic properties (high absorption coefficient $> 10^4$/cm and tunable band gap 1.0–1.5 eV) and high theoretical efficiency (32%).$^{1,2}$ In 2014, 12.6%$^3$ efficiency was achieved by the IBM group using the hydrazine method. Based on the sputtering process, 12.62%$^4$ efficiency for CZTSSe and 12.5%$^5$ efficiency for CZTSe have been achieved in recent years. However, the highest efficiency has stuck around 12.6% for several years. Lately, a breakthrough with certified 13% power conversion efficiency (PCE) has been demonstrated for CZTSSe thin-film solar cells, surpassing the dust-covered efficiency record since 2014.$^{1,6}$ Along with the efficiency advancement of kesterite solar cells, a cost-effective fabrication process with low carbon footprint plays an increasingly important role considering the near-future industrialisation of this kind of solar cell with low energy payback time. Normally, the synthesis of high-quality CZTSSe materials demands high-purity raw materials, that is, copper (Cu), zinc (Zn), and tin (Sn) compounds. However, environmental concerns are raised regarding the procedures to mine and refine copper and zinc for synthesizing CZTSSe materials. Both the copper and zinc metallurgy require a high-temperature process of over 1000°C that generates greenhouse gases, which contribute significantly to energy consumption and carbon footprint. From 2015 to 2019, the average annual global refined copper production and slab zinc production were 23.62 and 17.18 million tons, respectively.$^7$ The environment has been burdened with the mining and refining of Cu and Zn, while the industrialization of CZTSSe solar cells with possible terawatt production scales may exacerbate environmental conflicts. Therefore, low-cost fabrication processes, using alternative copper and zinc sources with low carbon footprints, are critical for the future large-scale production of CZTSSe-based solar cells.

An alternative, readily available copper and zinc source for synthesizing CZTSSe materials with a low carbon footprint is scrap brass. The main composition of brass is the copper and zinc alloy, which can readily provide the raw materials for the CZTSSe photovoltaic materials. Typically, there are two mainstream processes for recycling...
brass. The first one is to remelt directly to produce brass products. However, this pyrometallurgical process is not beneficial to carbon neutrality. Thus, the second environmentally responsible hydrometallurgical approach attracts more attention because of its low energy cost and greenhouse gas emissions. The main procedure of the traditional hydrometallurgical method to recycle brass is to separate the copper and zinc, resulting in a long process and high expenditure on chemicals. The recycling process could be simplified and cost competitive if the copper and zinc separation procedures were eliminated. Preparation of CZTSSe precursor solution with the scarp brass as raw materials could readily exclude the separation procedure since the precursor solution for synthesizing CZTSSe absorber film uses the mixture of copper salt and zinc salt. Herein, we propose an environmental friendly process to recover copper and zinc from scrap brass. The recovered product can be directly used as the precursor salts to fabricate efficient CZTSSe thin-film solar cells. The best PCE of the device using the proposed ecofriendly process is 11.39% which is close to the PCE of our champion device fabricated by high-purity chemicals (12.18%). The concept of fabrication of CZTSSe-based thin-film solar cells by recycled scrap brass, combining photovoltaics and metallurgy, is proposed for the first time. This technique not only provides a cost-effective way to produce high-efficiency CZTSSe thin-film solar cells and boost the recycling rate of brass, but also enables the society to accelerate towards “the net-zero emission 2050.”

The synthesis route of CZTSSe thin-film solar cells from scrap brass is shown in Figure 1. The process includes three major steps: (1) leaching the harvested scrap brass by oxidative ammonia method; (2) synthesizing copper acetate and zinc acetate; and (3) fabricating solar cells with the synthesized salts. Specifically, the scarp brass products like taps, keys, and pipes were washed with detergent and then smashed and ground into foils and particles. The rinsed brass foils and particles were added into aqueous solution of NH₄OH, H₂O₂, and (NH₄)₂CO₃ in a round-bottom flask. The function of ammonia is to react with brass to form the Cu(NH₃)₄²⁺ and Zn(NH₃)₄²⁺ complexes. During the complexing process, H₂O₂ was introduced as the oxidizing agent as the reaction rate of metal oxides with ammonia is much faster than that of metal with ammonia. During the reaction, the ammonium ions from NH₄OH are consumed to form the complexes, resulting in decreased solution pH. Thus, (NH₄)₂CO₃ in the leaching solution provides the extra ammonium ions and stabilizes the pH >9.2 during the reaction. This pH range enables the selective extraction of the Cu and Zn from the brass and separates them from impurities like aluminum (Al) and iron (Fe) that would be left in the slag. The leaching solution was heated and stirred to accelerate the reaction. After leaching, all brass particles and foils dissolved into the solution, and a dark blue solution was acquired. To optimize the leaching conditions, we investigated the effects of reaction temperature, stirring speed, and reaction time on the leaching efficiency and impurity in the production. Figure 2 shows the leaching efficiency at different leaching conditions. The leaching process is an endothermic reaction, and thus, the leaching efficiency can be readily promoted by elevating the system temperature from 30 to 70°C. The leaching efficiency
was saturated at around 70°C, and the further temperature increase only showed a slight improvement in leaching efficiency. Therefore, 50°C was chosen as the optimal temperature, considering the energy consumption. The stirring reduced the temperature and concentration gradient of the reaction, and the higher stirring rate led to a more uniform composition of the leaching solution. When the stirring rate increased from 200 to 400 rpm, the leaching rate of both Cu and Zn increased subsequently. However, when the stir rate reached 400 rpm, some foils and particles adhered to the inner wall of the flask and above the liquid level, which would require additional processing to immerse them back to the solution. Correspondingly, 300 rpm seemed to achieve the balance of decent leaching rate without the above-stirring issue, thus, being adopted as the optimum stir rate. Reaction time was studied from 30 to 90 min. Thirty minutes is insufficient for the reaction since undissolved brass was observed, and the leaching efficiencies for Cu and Zn were lower than 80%. A longer reaction time would enable the completion of the reaction. Ninety minutes of leaching witnessed the highest leaching efficiency. However, longtime leaching seemed to facilitate the impurity dissolving process that needs to be paid attention to. As tabulated in Supporting information Table S1, the reaction temperature and the stirring speed have negligible effects on the impurity content. Nonetheless, the long reaction time increases the Al and Fe concentration in the leaching solution, which may be due to the redissolution of impurity back into the solution since the pH decreased resulting from the ammonia evaporation. Consequently, the optimum leaching reaction time is 60 min considering the balance of leaching efficiency and solution purity. According to the above discussion, the optimal experimental parameters are as follows: temperature of 50°C, stirring rate of 300 rpm, and the leaching time of 60 min. The total amount of the impurity ions in the scarp brass is 1452 ppm (wt.), and that in the obtained salt is 315 ppm (wt.), indicating the leaching process eliminates most of the undesirable impurities. It is worthy of mentioning that not all impurities are detrimental. The potassium (K) and lithium (Li) ions are beneficial for crystalline growth and defect passivation and, thus, exert a positive effect on the device efficiency. The Sn ions are the essential ingredients for the precursor solution. Hence, the unfavorable ions in the obtained salt account for a meager percentage. Thus, these obtained salts are directly used for synthesizing CZTSSe film without further purification.

After the complete dissolution of brass, the leaching solution was boiled to decrease the pH value and recycle the ammonia for the subsequent leaching. The after-boiling product was immersed in the acetate solution to form the metal acetate salt solution. To obtain the copper acetate and zinc acetate, we evaporated the solvent to recrystallize metal salts. As shown in Supporting information Figure S1, the X-ray diffraction (XRD) of as-obtained copper and zinc salt is complicated. Comparing the XRD spectra of the as-obtained salt with XRD patterns of Cu(CH3COO)2, Cu(CH3COO)2\(\cdot\)H2O, and Zn(CH3COO)2\(\cdot\)2H2O, we confirmed that the as-obtained salt was the mixture of copper acetate, copper acetate monohydrate, and zinc acetate dihydrate. A further precursor solution metal composition was adjusted by adding zinc acetate dihydrate and tin (II) chloride to maintain the precursor composition of CTZSSe at Zn/Sn = 1.2 and Cu/(Zn+Sn) = 0.75,14–16 which is a desirable composition of efficient CZTSSe solar cell.

The Raman spectra of the precursor and synthesized CZTSSe absorber prepared by as-obtained salt from scrap brass are shown in Figure 3A. Compared with the film fabricated by purchased chemicals,8 both precursor samples show the Cu2ZnSnS4 (CZTS) characteristic peak (327/cm), and both absorbers exhibit the CZTSSe characteristic peak (176, 196, and 236 cm\(^{-1}\)). The Raman patterns of CZTSSe from scarp brass demonstrate a similar crystallinity as that of the high-purity chemicals according to the FWHM of the corresponding Raman peaks. The morphology of the absorber fabricated from as-obtained salt is shown in Figure 3B. The absorber fabricated from as-obtained salt is composed of densely packed grains, and the size of the grains ranges from hundreds of nanometers to 5 microns. Compared with the morphology of the films fabricated by high-purity chemicals,8 the size distribution of the film by scrap brass is not as uniform as that of counterpart films, and more relatively small grains (<1 \(\mu\)m) are observed. The tropology measured by high-angle annular dark-field (HAADF) scanning transmission electron
microscopy (STEM) is displayed in Figure 3C. The trilayer-structure absorber is comprised of a dense large-grain layer (thickness around 550 nm), a loose large-grain layer (thickness around 800 nm), and a fine-grain layer (thickness around 250 nm), from top to bottom. Even though the top surface layer of the absorber is compact and smooth, the middle layer beneath the top layer is loose, and voids are detected. The voids in the loose large-grain layer may block the transportation of carriers. The fine-grain layer is compact without voids observed, but the fine-grain leads to a significant number of grain boundaries which are considered as the recombination centre. Even though the topology of the absorber is dissimilar, the vertical distribution of elements in the absorber region, as manifested in Figure 3D, is steady without any fluctuation, indicating high uniformity of the composition in the absorber region. In the region between 0.8 and 1.0 μm, the ratios of Cu, Sn, and Se decrease while the ratios of Zn and S increase, which indicates that tiny ZnS is present within the film, compared to CZTSSe film from high purity chemical source, where this impurity is not apparent.

The current density-voltage (J-V) characteristics of devices based on scrap brass and on purchased chemicals are shown in Figure 4A, and the device performance parameters extracted from J-V curves are tabulated in Table 1. Compared with the champion device fabricated by high-purity chemicals, the device fabricated by scrap brass demonstrates better open-circuit voltage (Voc) at 487.4 mV and fill factor (FF) at 67.58%. The culprit for the slightly lower efficiency (η) of 11.39% is the lower short-circuit current density (Jsc) 34.56 mA/cm². The obtained salts from the scrap brass were also applied in the pure sulfur CZTSSe-based thin-film solar cells, which also acquired a decent efficiency of 10.33%. The parameters of this photovoltaic device are certified by the National PV Industry Measurement and Testing Center (Supporting information Figure S2 for best CZTSSe-based thin-film cell and Fig S3 for the best CZTS one). The low Jsc may attribute to the loosened grain in the loose large-grain layer with the presented voids, which is detrimental to the correct collection in the deep region. Another possible reason lies in the impurities that remain. Even though the vertical elemental distribution of the main content of the CZTSSe absorber is stable, the impurity dispersal in the absorber is not studied. A more precise and accurate characterization method should be applied to explore the impact of the impurities. The poor...
FIGURE 4 Device characterisation of the champion CZTSSe-based thin-film solar cell fabricated from scrap brass. (A) J-V curve of the champion CZTSSe solar cell fabricated by scrap brass and purchased chemicals; (B) EQE curve of the champion CZTSSe solar cell fabricated by scrap brass; (C) TRPL characteristic of the CZTSSe thin-film solar cell fabricated by scrap brass (the excitation wavelength is 470 nm); and (D) C–V profiling and DLCP profiling for the CZTSSe thin-film solar cell fabricated by scrap brass.

TABLE 1 Device parameters of the best-performing devices from different raw material sources

| Device by purchased chemicals (CZTSSe) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm²) | FF (%) | $\eta$ (%) | $R_s$ (Ω cm²) | $R_{sh}$ (Ω cm²) |
|---------------------------------------|---------------|-------------------|--------|------------|---------------|-----------------|
| Device by scrap brass (CZTSSe)        | 487.40        | 34.56             | 67.58  | 11.39      | 0.59          | 663.96          |
| Device by scrap brass (CZTS)           | 835.20        | 20.03             | 61.39  | 10.33      | 1.05          | 594.17          |
| Previous world champion device (CZTSSe) | 513.40        | 35.20             | 69.80  | 12.60      | 0.72          | 621.12          |
| World champion device (CZTS)           | 730.30        | 21.74             | 69.27  | 11.01      | 2.58          | 1020.41         |

The response of external quantum efficiency (EQE) at the long-wavelength region, as illustrated in Figure 4B, is further proved poorly collected in the deep area and also consistent with relatively short minority carrier lifetime (Figure 4C) and dominated bulk recombination (Figure 4D). The lifetime $\tau_2$ extracted from the time-resolved photoluminescence (TRPL) measurement is 6.05 ns, interpreted the decent collection of carriers, but the lifetime is lower than that of the device fabricated by the high-purity chemicals ($\tau_2 = 6.23$ ns). The lower lifetime may be attributed to one or both of the following reasons: impurity in the absorber; loosen microstructure at the middle of the film. The minute difference between carrier concentration $N_{C-V}$ and drive-level density $N_{DL}$ at zero bias confirms the few traps at the CZTSSe/CdS interface. Thus, the main reason for the efficiency deficit is the inferior quality of the absorber.

In summary, we developed an environmental friendly synthesis method to reuse scrap brass for the fabrication of CZTSSe thin-film solar cells. Cu and Zn content could be extracted and collected by a mild process.
without any hazardous emission. The photovoltaic performance of solar cells fabricated by scrap brass is 11.39%, close to the efficiency of 12.18% by purchasing high-purity chemicals. Fabrication of CZTSSe solar cells from recycled brass is cost competitive, environmentally responsible, and it is of great significance for the industrialisation of CZTSSe thin-film solar cells. The process elaborated in this work provides a new way to recycle scrap brass and has a positive impact on metal recycling and environmental protection.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

**ORCID**

Liming Ding https://orcid.org/0000-0002-0580-7888
Fangyang Liu https://orcid.org/0000-0001-6437-9150

**REFERENCES**

1. Gour KS, Karade V, Babar P, et al. Potential role of kesterites in development of earth-abundant elements-based next generation technology. Solar RRL. 2021;5(4). https://doi.org/10.1002/solr.202000815.

2. Giraldo S, Jehl Z, Placidi M, Izquierdo-Roca V, Pérez-Rodriguez A, Saucedo E. Progress and perspectives of thin film kesterite photovoltaic technology: a critical review. Adv Mater. 2019;31(16):1806692. https://doi.org/10.1002/adma.201806692.

3. Wang W, Winkler MT, Gunawan O, et al. Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. Adv Energy Mater. 2014;4(7):1301465. https://doi.org/10.1002/aenm.201301465.

4. Son D-H, Kim S-H, Kim S-Y, et al. Effect of solid-H2S gas reactions on CZTSSe thin film growth and photovoltaic properties of a 12.62% efficiency device. Journal of Materials Chemistry A. 2019;7(44):25279–25289. https://doi.org/10.1039/C9TA08310C.

5. Li J, Huang Y, Huang J, et al. Defect control for 12.5% efficiency Cu2ZnSnSe4 kesterite thin-film solar cells by engineering of local chemical environment. Adv Mater. 2020;32(52):e2005268. https://doi.org/10.1002/adma.202005268.

6. NREL. Best research-cell efficiencies revision 201726. 2021. https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies-rev201726.pdf

7. Brown T, Idoine N, Wrighton C, World mineral production 2015–19. 2019.

8. Zhao X, Pan Y, Zhuo C, et al. Ambient air-processed Cu2ZnSn(S,Se)4 solar cells with over 12% efficiency. Sci Bulletin. 2021;66(9):880–883. https://doi.org/10.1016/j.scib.2020.12.030.

9. Haass SG, Andres C, Figi R, et al. Complex interplay between absorber composition and alkali doping in high-efficiency kesterite solar cells. Adv Energy Mater. 2018;8(4):1701760. https://doi.org/10.1002/aenm.201701760.

10. Hsieh Y-T, Han Q, Jiang C, et al. Efficiency Enhancement of Cu2ZnSn(S,Se)4 solar cells via alkali metals doping. Adv Energy Mater. 2016;6(7):1502386. https://doi.org/10.1002/aenm.201502386. n/a-n/a. 1502386.

11. Zhou J, Xu X, Duan B, et al. Regulating crystal growth via organic lithium salt additive for efficient Kesterite solar cells. Nano Energ. 2021;89:106405. https://doi.org/10.1016/j.nanoen.2021.106405.

12. Altamura G, Wang M, Choy K-L. Influence of alkali metals (Na, Li, Rb) on the performance of electrostatic spray-assisted vapor deposited Cu2ZnSn(S,Se)4 solar cells. Sci Rep-Uk. 2016;6:22109. https://doi.org/10.1038/srep22109.

13. He M, Zhang X, Huang J, et al. High Efficiency Cu2ZnSn(S,Se)4 solar cells with shallow LiZn acceptor defects enabled by solution-based Li post-deposition treatment. Adv Energy Mater. 2021;11(13):2003783. https://doi.org/10.1002/aenm.202003783.

14. Larramona G, Levecenko S, Bourdais S, et al. Fine-tuning the Sn content in CZTSSe thin films to achieve 10.8% solar cell efficiency from spray-deposited water–ethanol-based colloidal inks. Adv Energy Mater. 2015;5(24):1501404. https://doi.org/10.1002/aenm.201501404.

15. Kumar M, Dubey A, Adhikari N, Venkatesan S, Qiao Q. Strategic review of secondary phases, defects and defect-complexes in kesterite CZTS-Se solar cell. Energy Environ Sci. 2015;8(11):3134–3159. https://doi.org/10.1039/C5EE02153G.

16. Ge S, Xu H, Huang Y, et al. Surprising efficiency enhancement of Cu2ZnSn(S,Se)4 solar cells with abnormal Zn/Sn ratios. Solar RRL. 2020;4(11):2000325. https://doi.org/10.1002/solr.202000325.

17. Mondal A, Scheinert C, Radich JG. Carrier lifetime and charge separation in K+ doped CZTS nanocrystals. ACS Applied Energy Materials. 2019;2(1):250–259. https://doi.org/10.1021/acsaem.8b01168.

18. Ahn K, Kim S-Y, Kim S, et al. Flexible high-efficiency CZTSSe solar cells on stainless steel substrates. J Material Chem A. 2019;7(43):24891–24899. https://doi.org/10.1039/C9TA08265D.

19. Yan C, Huang J, Sun K, et al. Cu2ZnSnS4 solar cells with over 10% power conversion efficiency enabled by heterojunction heat treatment. Nat Energy. 2018;3(9):764–772. https://doi.org/10.1038/s41560-018-0206-0.

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