Supporting Information

Rubidium Fluoride Assisted High-efficiency Cu₂(Zn,Cd)SnS₄ Solar Cells by Co-evaporation/annealing Method

Shijin Wangᵃᵇ, Lan Huangᵇ, Zi Yeᵇ, Lan Zhongᵇ, Guilin Chenᶜ,*, Jianmin Liᵃ*, and Xudong Xiaoᵃᵇ,*

ᵃ: School of Physics and Technology, Wuhan University, Wuhan 430072, China.
ᵇ: Department of Physics, The Chinese University of Hong Kong, Shatin 999077, Hong Kong.
ᶜ: College of Physics and Energy, Fujian Normal University, Fuzhou 350007, China.

E-mail: ljmphy@whu.edu.cn, glchen@fjnu.edu.cn, xdxiao@phy.cuhk.edu.hk, xdxiao@whu.edu.cn.

Corresponding authors: Jianmin Li (Dr. Li), Guilin Chen (Prof. Chen), Xudong Xiao (Prof. Xiao)
Literature reviews

Table S1  Parameters of Rb-doped kesterite solar cells.

<table>
<thead>
<tr>
<th>Alkali</th>
<th>Absorber</th>
<th>Comparison</th>
<th>PCE (%)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbF: Rb doped absorber target</td>
<td>CZTSSe</td>
<td>undoped</td>
<td>6.25</td>
<td>300.4</td>
<td>62.6</td>
<td>33.2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>doped</td>
<td>8.41</td>
<td>317</td>
<td>70.2</td>
<td>37.8</td>
<td></td>
</tr>
<tr>
<td>RbCl: Solution-based</td>
<td>CZTSSe</td>
<td>undoped</td>
<td>4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>doped</td>
<td>6.35</td>
<td>360</td>
<td>49.9</td>
<td>35.2</td>
<td></td>
</tr>
<tr>
<td>RbOH•xH$_2$O: Solution-based</td>
<td>CZTSSe</td>
<td>undoped</td>
<td>4.13</td>
<td>407</td>
<td>41.32</td>
<td>24.56</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>doped</td>
<td>5.41</td>
<td>401</td>
<td>53.2</td>
<td>25.39</td>
<td></td>
</tr>
<tr>
<td>RbF: Solution-based</td>
<td>CZTSSe</td>
<td>undoped</td>
<td>6.4</td>
<td>426.0</td>
<td>48.5</td>
<td>30.8</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>doped</td>
<td>5.7</td>
<td>441.1</td>
<td>44</td>
<td>29.6</td>
<td></td>
</tr>
</tbody>
</table>

Interestingly, the impacts of Rb-doping are still unclear. In reference [1], [2], and [3], one can see an improvement in efficiency after Rb-doping. Nevertheless, the change of performance parameters is not in the same direction. For example, in reference [1], it is clear that $V_{OC}$, $J_{SC}$, and $FF$ all are improved after Rb incorporation, while in reference [3], the $V_{OC}$ decreases. More impressively, the Rb-doping in reference [4] shows a negative effect on device performance with an improved $V_{OC}$. All these works indicate that the role of Rb in CZTSSe is complicated.
Table S2 Efficiency evolution based on pure sulfide CZTS solar cells fabricated by thermal evaporation method in recent ten years.

<table>
<thead>
<tr>
<th>Years</th>
<th>Efficiency (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>4.1</td>
<td>5</td>
</tr>
<tr>
<td>2010</td>
<td>6.81</td>
<td>6</td>
</tr>
<tr>
<td>2011</td>
<td>8.4</td>
<td>7</td>
</tr>
<tr>
<td>2014</td>
<td>2.56</td>
<td>8</td>
</tr>
<tr>
<td>2015</td>
<td>2.72</td>
<td>9</td>
</tr>
<tr>
<td>2015</td>
<td>4.61</td>
<td>10</td>
</tr>
<tr>
<td>2016</td>
<td>5.23</td>
<td>11</td>
</tr>
<tr>
<td>2017</td>
<td>2.25</td>
<td>12</td>
</tr>
<tr>
<td>2018</td>
<td>8.98</td>
<td>13</td>
</tr>
<tr>
<td>2019</td>
<td>5.6</td>
<td>14</td>
</tr>
<tr>
<td>2020</td>
<td>7.28</td>
<td>15</td>
</tr>
<tr>
<td>2020</td>
<td>8.31</td>
<td>16</td>
</tr>
<tr>
<td>2021</td>
<td>0.61</td>
<td>17</td>
</tr>
</tbody>
</table>

Sn concentration optimization

Figure S1 Device efficiency statistics for CCZTS solar cells with different Sn concentrations.
Cd concentration optimization

Figure S2 Device efficiency statistics for CCZTS solar cells with different Cd concentrations.

The substrate temperature optimization for precursor

Figure S3 Device efficiency statistics for CCZTS solar cells with precursors deposited under different substrate temperatures.
Post-annealing treatment process optimization

Figure S4 Device efficiency statistics for CCZTS solar cells related to (a) 1st step H$_2$S pressure, (b) 1st step annealing time, (c) 2nd step annealing time, and (d) 2nd step annealing temperature.

Composition information of films

Table S3 Composition information of the absorbers under different Rb source temperatures.

<table>
<thead>
<tr>
<th>RbF source temperature</th>
<th>Cd/(Cd+Zn)</th>
<th>(Cd+Zn)/Sn</th>
<th>Cu/(Cd+Zn+Sn)</th>
<th>Rb/(Rb+Cu)</th>
<th>Denotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>0.32</td>
<td>1.17</td>
<td>0.74</td>
<td>0</td>
<td>control</td>
</tr>
<tr>
<td>450°C</td>
<td>0.33</td>
<td>1.21</td>
<td>0.74</td>
<td>0.53%</td>
<td>Rb-0.53%</td>
</tr>
<tr>
<td>460°C</td>
<td>0.33</td>
<td>1.21</td>
<td>0.73</td>
<td>0.87%</td>
<td>Rb-0.87%</td>
</tr>
<tr>
<td>470°C</td>
<td>0.33</td>
<td>1.19</td>
<td>0.73</td>
<td>1.19%</td>
<td>Rb-1.19%</td>
</tr>
<tr>
<td>500°C</td>
<td>0.33</td>
<td>1.18</td>
<td>0.75</td>
<td>2.16%</td>
<td>Rb-2.16%</td>
</tr>
</tbody>
</table>

For all absorbers, the ratios of Cd/(Cd+Zn), (Cd+Zn)/Sn, and Cu/(Cd+Zn+Sn) are controlled within narrow ranges of 0.32-0.33, 1.17-1.21, and 0.73-0.75, respectively. As expected, with the increasing RbF source
temperature, the Rb/(Rb+Cu) ratio increases. In this work, the Rb/(Rb+Cu) ratio is controlled from 0 to 2.16% after washing away the extra Rb on the crystalized CCZTS surface. For clear expression, the samples with RbF cap layer under 450°C, 460°C, 470°C and 500°C are denoted as “Rb-0.53%”, “Rb-0.87%”, “Rb-1.19%”, and “RbF-2.16%”, respectively.

49  **SIMS measurement**

![SIMS measurement](image)

Figure S5 Elemental distribution of Cu, Zn, Cd, Sn, S, and Mo in (a) “control” and (b) “Rb-0.87%”. An enlarged plot at the rear interface for both cells: (c) all elements, (d) Sn, (e) Cd, and (f) Cu.
Performance boxplots

Figure S6 Statistic boxplots of $V_{OC}$, $J_{SC}$, and $FF$ for the CCZTS thin-film solar cells prepared with an RbF layer deposited from a Knudsen cell with varied doping concentration.

Urbach energy calculation

The value of Urbach energy ($E_U$) derived from EQE response could characterize the band tail states of the CCZTS films, which provides an estimation of tail states by the following equation: 16, 18

$$\ln(\text{EQE}) = c + \frac{h\nu}{E_U}$$  \hspace{1cm} (1)

where $c$ is a constant and $h\nu$ is the bandgap energy.
Figure S7 Dark J-V curves for the CCZTS thin-film solar cells prepared with an RbF layer deposited from a Knudsen cell with varied doping concentration.

The diode quality factor \( A \) and the reverse saturation current density \( J_0 \) could be estimated by the following equation:

\[
\ln J = \ln J_0 + \frac{qV}{AKBT}
\]

(2)

where \( q \), \( k_B \), and \( T \) are the elemental charge, Boltzmann constant, and temperature, respectively. According to it, \( J_0 \) can be derived by extending the fitting line in the graph to 0 V, and \( A \) can be calculated from the slope of the curve. Quantitatively, the \( V_{OC} \) gain between two devices can be calculated using the following equations:

\[
V_{OC} = \frac{AKT}{q} \ln \left( 1 + \frac{J_{SC}}{J_0} \right) \approx \frac{AKT}{q} \ln \left( \frac{J_{SC}}{J_0} \right)
\]

(3)

\[
\Delta V_{OC} = \frac{AKT}{q} \ln \left( \frac{J_{Rb}^{0.87\%}}{J_{control}^{0.87\%}} \times \frac{J_{control}^{0\%}}{J_{SC}} \right)
\]

(4)
**C-V measurement**

From C-V measurement, the relation between junction width and the charge density can be extracted and the built-in potential \((V_{bi})\) according to the following equations:

\[
N_{C-V} = \frac{C^3}{qS^2\varepsilon_0\varepsilon_r} \left(\frac{dC}{dV}\right)^{-1}
\]  

(5)

\[
W_d = \frac{S\varepsilon_0\varepsilon_r}{C}
\]  

(6)

\[
\frac{1}{C^2} = \frac{2}{\varepsilon_0\varepsilon S^2 N} (V_{bi} - V)
\]  

(7)

Here, \(C\), \(S\), \(V\), \(\varepsilon_0\), \(\varepsilon_r\), \(N\) and \(q\) are measured capacitance, effective area of the solar cell, positive/negative for forward/reverse bias, and the vacuum permittivity, the relative dielectric constant of CCZTS film, the carrier density, and elemental charge, respectively.

**Figure S8** \(C^2\)-voltage curves for “control” and “Rb-0.87%”.

Band offset measurement and calculation

Figure S9 XPS depth profile of Cu, Cd, Zn, Sn, and S at CdS/CCZTS:Rb interface starting from bulk CdS into bulk CCZTS:Rb. The etched depth is referred to Ta$_2$O$_5$ standard sample.

The elemental depth profiles of Cd, Cu, Zn, Sn, and S from CdS to CCZTS:Rb are detected by moderately sputtering with Ar$^+$ ions (1000 eV). According to the composition variation, three areas (bulk CdS area, interface area, and bulk CCZTS area) can be readily identified. With the known approach, the valence band offset (VBO) and the conduction band offset (CBO) of the CCZTS/CdS heterojunction can be calculated as shown below:\textsuperscript{19,20}

\begin{equation}
VBO = E_{VBM}^{CdS} - E_{VBM}^{CCZTS} + \Delta E
\end{equation}

\begin{equation}
CBO = E_{g}^{CdS} - E_{g}^{CCZTS} - VBO
\end{equation}

where $E_{VBM}^{CdS}$, $E_{VBM}^{CCZTS}$, $\Delta E$, $E_{g}^{CdS}$, and $E_{g}^{CCZTS}$ are the positions of valence band edges of bulk CdS and bulk CCZTS, band bending, the bandgap of CdS and CCZTS, respectively.
Figure S10 The XPS valence band spectroscopy of the bulk CdS and bulk CCZTS or CCZTS:Rb for "control" and "Rb-0.87%". The negative sign means the position is lower than the Fermi level.

It is clear to see that the $E_{VBM}$ (relative to Fermi level) of bulk CdS and bulk CCZTS:Rb are at -1.59 eV and -0.61 eV, respectively, and that of bulk CdS and bulk CCZTS of "control" are at -1.66 eV and -0.50 eV, respectively.

Figure S11 The XPS peaks of the concerned element in the bulk and at the interface calibrated by C peak (284.8 eV). (a-e) for "control", and (f-j) for "Rb-0.87%".

To calculate VBO, $\Delta E$ appears ultimately necessary, which can be easily derived by the well-known formula:

$$\Delta E_{CL} = (\Delta E_C^a - \Delta E_C^a(i)) + (\Delta E_C^b(i) - \Delta E_C^b)$$

(10)
\[ \Delta E = \frac{(\Delta E_{Cd/Cu} + \Delta E_{Cd/Zn} + \Delta E_{Cd/Cd} + \Delta E_{Cd/Sn})}{4} \]

(11)

where \( \Delta E_{CL}^a \) and \( \Delta E_{CL}^b \) are the core level energies of two selected elements in the bulk absorber (CCZTS or CCZTS:Rb) and in the bulk buffer (CdS), and \( \Delta E_{CL}^a(i) \) and \( \Delta E_{CL}^b(i) \) are the core level energies of the corresponding element at the interface. In the present case, the Cd is chosen in CdS and Cu, Zn, Cd, and Sn are selected in CCZTS or CCZTS:Rb. The XPS peaks of each element in the bulk and at the interface are plotted in Figure S5. These figures provide the peaks shift values of (Cd/Cu), (Cd/Zn), (Cd/Cd) and (Cd/Sn) as discussed in the article. The associated values are summarized in Table S4.

Table S4: XPS peak positions of all elements at the interface or in the bulk CdS and CCZTS films of “control” and “Rb-0.87%” after calibration by C peak (284.8 eV).

<table>
<thead>
<tr>
<th>Samples</th>
<th>location</th>
<th>Cd 3d</th>
<th>Cu 2p</th>
<th>Sn 3d</th>
<th>Zn 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>405.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Rb-0.87%”</td>
<td>interface</td>
<td>405.38</td>
<td>932.83</td>
<td>486.58</td>
<td>1021.94</td>
</tr>
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<td></td>
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<td>405.39</td>
<td>932.94</td>
<td>486.68</td>
<td>1022.03</td>
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<td></td>
<td></td>
<td>405.28</td>
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<tr>
<td>control</td>
<td>interface</td>
<td>405.29</td>
<td>932.71</td>
<td>486.47</td>
<td>1021.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>405.38</td>
<td>932.91</td>
<td>486.61</td>
<td>1021.95</td>
</tr>
</tbody>
</table>

These data are extracted from Figure S11 and used for calculating the band bending value. The values for (Cd/Cu), (Cd/Zn), (Cd/Cd) and (Cd/Sn) in CCZTS:Rb are estimated to be 0.11 eV, 0.09 eV, 0.01 eV, and 0.1 eV, correspondingly, resulting in an overall average band bending value of 0.08 eV by using Equation (11).

With the same method, the bending for “control” is estimated to be 0.15 eV. The decreased \( \Delta E \) by Rb-doping should be attributed to the reduced defect states in bulk or at the interface of CCZTS film.
Figure S12 Plot of $[h\nu\times\ln(1-EQE)]^2$ versus $h\nu$ of “control”, “Rb-0.87%”, and “Rb-2.16%”.

This plot gives information on the bandgap value of the absorber. The three absorbers share the same bandgap with 1.38 eV, suggesting the Rb-doping in this work does not affect the bandgap. This may be explained by the low Rb-doping concentration.

Figure S13 (a) Transmittance spectra of CdS thin film directly deposited onto glass. (b) The plots of the differential of the transmittance to wavelength versus wavelength.

The differential curve in (b) exhibits a peak located at 514 nm, suggesting there is a strong absorption peak of CdS. Thus, the bandgap of CdS can be calculated to be 2.41 eV.

By combining the valence band edges of buffer and absorber, and the overall average band bending, the valence band offset (VBO) at CCZTS/CdS and CCZTS:Rb/CdS interface can be calculated to be -1.01 eV and -0.90 eV based on Equation (8). Therefore, the conduction band offset (CBO) can be derived to be 0.02 eV for CCZTS and 0.13 eV for CCZTS:Rb by Equation (9). Here, the bandgap of 1.38 eV for CCZTS film and of 2.41 eV for CdS are used.
SEM images

Figure S14 Cross-view SEM image of “Rb-2.16%”.

The FWHM of absorber of “Rb-2.16%” is 0.82, lower than those of “control” and “Rb-0.87%”, suggesting the bulk crystallinity is improved under higher Rb-doping concentration.

EDX mapping

Figure S15 (a) Top surface morphology and (b) EDX mapping of Zn element for “Rb-2.16%”.

One can notice that there are lots of Zn-related particles on the top surface of the absorber.
Figure S16 Schematic diagram of the role of ZnS particles at the interface of CCZTS/CdS.

This schematic is used for analyzing the mechanism of the ZnS-induced interface recombination. It is well-known that the ZnS is a high resistive semiconductor with higher CBM and lower VBM than those of CCZTS and CdS. Thus, the ZnS at the interface will act as a barrier for electrons and hole transport. As described, the electrons and holes will accumulate at the interface, leading to a high recombination.