Materials Research Proceedings 64 (2026) 664-671 https://doi.org/10.21741/9781644904091-83

Lithium Incorporation into Sol-Gel-Processed Chalcogenide Photovoltaic Absorbers: A Simple and Efficient Strategy

Naoufal ENNOUHI[1,a], Nisar ALI[1,b], Rosemary CHITI[1,c], Otman ABIDA[1,d], Bakhtiar ULHAQ[2,e]

[1]African Sustainable Agriculture Research Institute (ASARI), Mohammed VI Polytechnic University, 70000, Laayoune, Morocco

[2]Mechanical Engineering Department, College of Engineering, Prince Mohammad Bin Fahd University, Alkhobar 31952, Saudi Arabia.

[a]Naoufal.ENNOUHI-EXT@um6p.ma, [b]nisar.ali@um6p.ma, [c]Rosemary.CHITI@um6p.ma, [d]otman.abida@um6p.ma, [e]bakhtiarjadoon@gmail.com

Keywords: Kesterite, ACZTS, Lithium Doping, Sol-Gel, Thin Films, Photovoltaics

Abstract. Lithium doping is one of the most successful approaches used recently to improve the properties of kesterite materials and the performance of their solar cells. However, doping in sol-gel-derived kesterite is still limited to dopant incorporation during solution preparation. Here, we present a simple strategy to incorporate lithium into kesterite absorbers by depositing thin Li-containing layer onto kesterite precursors via the spin-coating method. Compared with conventional doping approach, this method led to enhanced film quality. Comprehensive structural and morphological analysis was performed via X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Our results confirmed a significant improvement in crystallinity, a reduction in Cu/Zn disorder, and the growth of larger and well-defined grains. Optical characterization confirmed the improved bandgap and a reduction in the defect density following lithium incorporation via the proposed strategy. The findings reported in this work demonstrate that doping via surface deposition represents a promising approach for enhancing the properties of kesterite thin films prepared using sol-gel method and can be a promising approach for developing highly efficient kesterite-based solar cells if carefully controlled.

Introduction

Kesterite materials such as $Cu_2ZnSnSSe_4$ (CZTSSe) have been proposed in the last few years as an alternative to commercialized CIGS solar cells due to their earth-abundant constituents and their higher optoelectronic properties [1] [2]. However, despite the progress reported in the last years for kesterite solar cell, the record efficiency remains limited to a higher open circuit voltage (V_{OC}) deficit originating from the high density of defects and the resistive Kesterite/CdS interface [3]. Recently, a wide range of strategies have been used to address these limitations, such as doping and alloying, which show a significant potential in reducing atomic disorder, enhance crystallinity, and improve carrier collection [4].

Alkali-metals doping and silver alloying have been shown to be the most successful approaches used in the last few years to enhance the properties of kesterite solar cells, and efficiencies beyond 15% have been achieved by combining sodium or lithium doping and silver alloying [5]. These effects can translate into larger grains and reduce the density of detrimental defects when properly coordinated with annealing conditions and precursor chemistry [6]. In parallel, alkali-metal diffusion from soda-lime glass (SLG) through porous Mo back contacts or introduction during the preparation process [7] promotes liquid-phase-assisted grain growth during annealing and passivates grain boundaries, thereby improving the film morphology and electronic quality [8].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 license. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under license by Materials Research Forum LLC.

Materials Research Proceedings 64 (2026) 664-671 https://doi.org/10.21741/9781644904091-83

Among alkalis, lithium (Li) is particularly compelling: its ionic radius closely matches that of Cu, enabling Li to occupy Cu vacancies and form shallow acceptors (e.g., Li_{Zn}) that increase the hole density and can lower disorder, with multiple reports linking Li to enhanced crystallinity and Voc improvements [9]. The methods for incorporating alkali metals into kesterite materials vary according to the deposition technique employed in the creation of kesterite materials. In solution-processed kesterite materials, such as those produced via the sol-gel method, alkyl metal salts are employed during solution preparation [10,11]. In contrast, in physical vapor deposition techniques, a thin layer of alkali metal (e.g., NaF, LiF, etc.) is typically employed [12,13]. In solution-processed kesterite approaches, the incorporation of alkali metals commences in the solution phase, subsequently resulting in a homogeneous distribution of these alkali-metals within the precursors, which are then subjected to an annealing process. In contrast, in physical methods, alkali metal layers can be deposited at varying positions and thicknesses, and during the annealing process, alkali metals can diffuse into the absorber in different ways. Furthermore, these diffusion methods of alkali metals significantly impact the final properties of the absorbers, thereby enhancing the flexibility in doping kesterite materials. [14]. Nevertheless, the capacity to alter the diffusion of alkali metals into kesterite absorbers is not inherent to solution deposition techniques, where alkali metals are employed in the solution. Moreover, when FTO is used as the back contact (instead of Mo/SLG), parasitic alkali diffusion from SLG is strongly suppressed; consequently, any alkali-related effects can be attributed to the intentionally introduced dopant, simplifying interpretation.

In this work, we therefore evaluate a simple postdeposition Li incorporation strategy for sol–gel–processed ACZTS absorbers: a thin Li-containing layer is deposited directly on top of the dried ACZTS precursor prior to sulfurization. We benchmark this method against conventional solution-phase Li doping under identical precursor chemistries and annealing protocols. A multimodal characterization suite, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-visible spectroscopy, reveals the structural, morphological, and optical impacts of the Li incorporation route on ACZTS, with particular attention to crystallinity, Cu/Zn disorder, grain growth, and band-tailing (Urbach energy). The results highlight the advantages of the postdeposition route in delivering denser microstructures, larger grains, and reduced disorder, which are key prerequisites for closing the Voc gap in kesterite photovoltaics. The control of alkali-metals incorporation using the post-deposition method seems to be difficult for controlling the doping profile compared to solution phase doping. However, this work represents the first proof-of-concept, and by controlling the thickness, annealing and pre-heating temperatures, as well as the position of Li-containing layers, it is possible to achieve more controllable lithium incorporation compared the homogeneous distribution of these alkali-metals in the solution phase. Therefore, further advanced work should be carried out using this approach to improve Li diffusion and enhance control over this method

Materials Research Proceedings 64 (2026) 664-671 https://doi.org/10.21741/9781644904091-83

Experimental Details

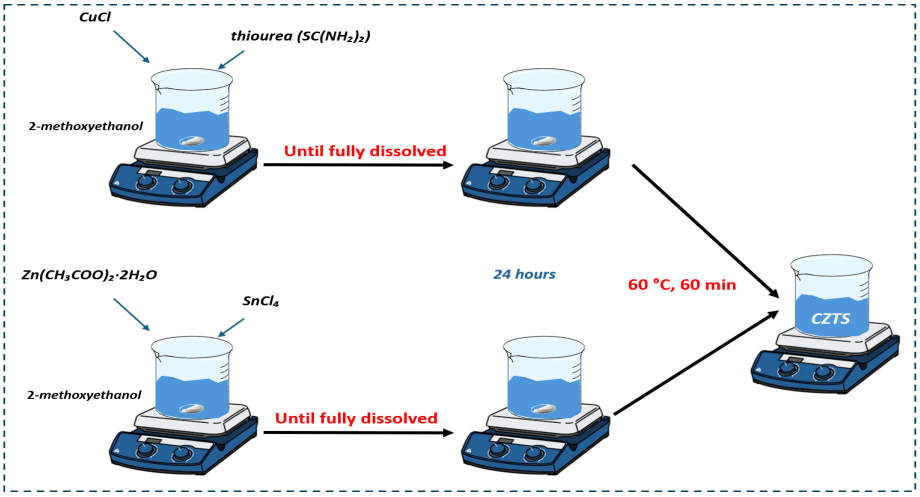

Figure 1: *Process used to prepare the ACZTS sol–gel solution*

ACZTS precursor solutions were prepared via a sol–gel route from CuCl, Zn(CH3COO)2·2H2O and SnCl4 in 2-methoxyethanol following the protocol summarized in Figure 1 and then filtered (0.45 µm). Films were deposited on UV-ozone--treated FTO/SLG by spin coating at 3000 rpm for 30 s with intermediate hot- plates at 300 °C; seven cycles yielded ~1 µm thickness. Lithium was introduced via two approaches: (i) solution-phase Li (Li-Sol) by adding LiClO4 to the mixed sol–gel solution and (ii) post-deposition Li (Li-Dep) by spin-coating a LiClO4 solution as a thin surface layer on the dried ACZTS precursor prior to annealing. Structural and optical characterizations included XRD (Cu Kα1), Raman (785 nm), SEM, AFM, and UV–Vis spectrophotometry.

Results and Discussion

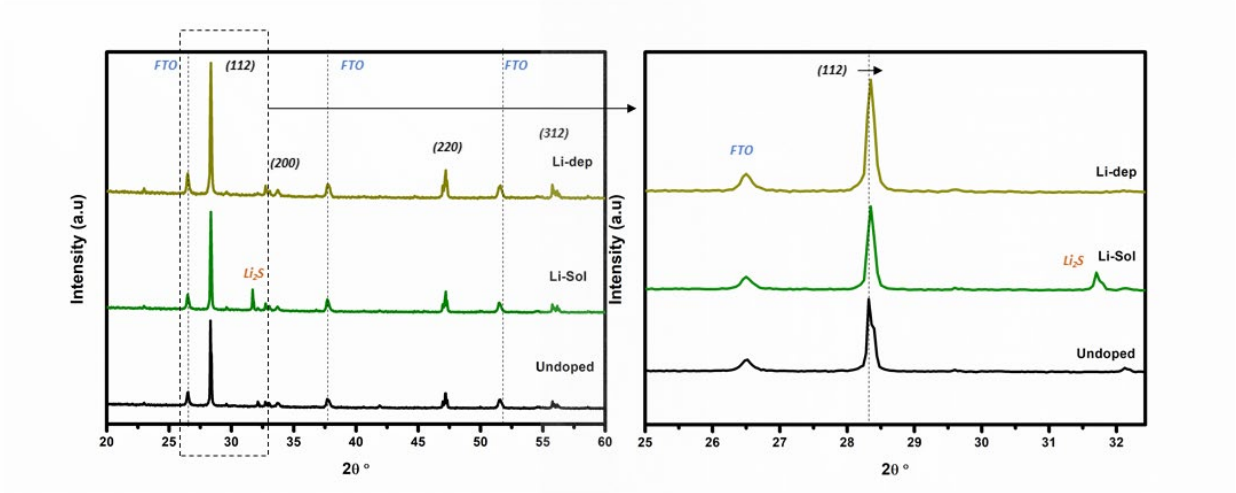

Figure 2: *XRD Patterns of Litium-Doped Li-Sol and Li-Dep Samples Compared with Undoped ACZTS*

The XRD patterns for the ACZTS samples doped with Li via both doping strategies and the undoped sample are shown in Figure 2. The peak intensities are greater for both Li-doped samples than for the undoped sample, indicating improved crystallinity with Li doping. This trend is consistent with previous reports that Li doping enhances the crystallinity of kesterite materials [15]

Materials Research Proceedings 64 (2026) 664-671 https://doi.org/10.21741/9781644904091-83

[16]. A comparison of the doping methods revealed that the Li-Dep sample doped via the proposed strategy and exhibited sharper and more intense peaks than did the Li-Sol sample. However, $LiClO_4$ was used for Li doping. $LiClO_4$, which is more thermally stable and has a higher decomposition temperature (420°C), remains in the films until the later stages of the annealing process. It then decomposes into LiCl, which eventually forms Li_2S [17]. This process is supported by additional peaks that may correspond to Li_2S observed in the XRD pattern of the Li-Sol sample. Note that these peaks can also be due to the presence of SnS2, as some of their XRD peaks overlapped. Previous studies on Li doped with $LiClO_4$, in which DMSO was used as a solvent and selenium was used in the annealing process, did not report that these Li_2S phases may be due to different interactions between sulfur or selenium and $LiClO_4$. In the Li-Dep sample, the $LiClO_4$ phase deposited on top of the precursor is in direct contact with the sulfur in the annealing atmosphere, facilitating the decomposition of $LiClO_4$ to LiCl and subsequently to Li_2S at lower temperatures. This interaction may enhance the growth of ACZTS materials. In addition, excess lithium can passivate grain boundaries and vacancies, leading to higher crystallinity and larger grains, as discussed in the next section. Overall, both Li-doped samples show improved crystallinity compared with that of the undoped sample. The issue of Li_2S formation can potentially be addressed by using LiCl instead of $LiClO_4$ or by optimizing the sulfurization temperature. The Raman spectra support these findings, with the Li-Dep sample exhibiting more intense peaks, indicating a more ordered structure. In contrast, the undoped and Li-Sol samples show comparable peak sharpness and intensity, potentially due to lower lithium incorporation and the presence of Li_2S, leading to a more disordered matrix [18]. The formation of Li_2S phase can be addressed using LiCl as a precursor for lithium doping instead of $LiClO_4$ and the optimization of the annealing conditions. Raman spectra shown in Figure 3 confirmed these findings. The Li-Dep sample exhibited the narrow and more intense peaks compared to that of the Li-Sol, indicating a more ordered matrix [18], where both Li-Sol and undoped samples present comparable peak intensities may be due to the presence of Li-S phases.

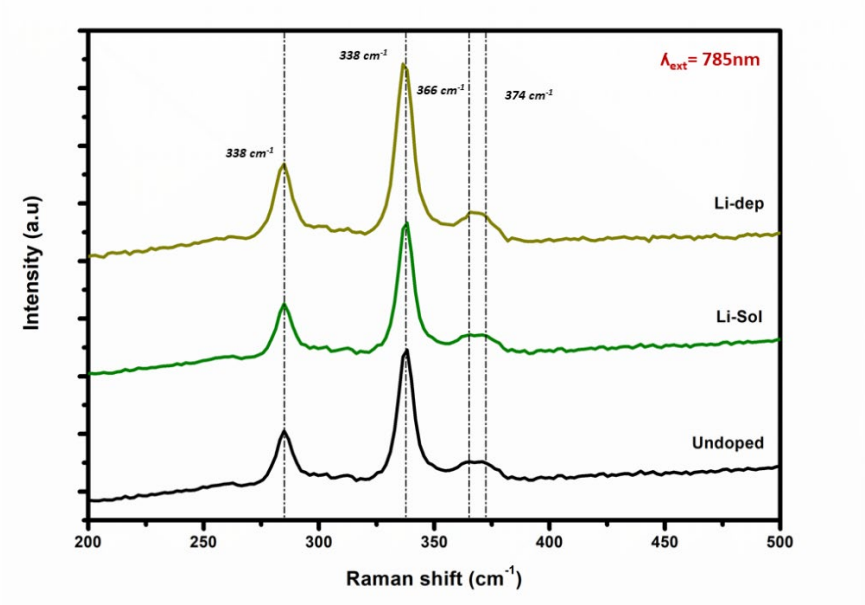

Figure 3: *Raman Spectra of Litium-Doped Li-Sol and Li-dep Samples Compared with Undoped ACZTS*

The SEM and AFM analysis of Li-Sol and Li-Dep have been used to evaluate the morphology of the surface, and the results are shown in Figure 4. an organized morphologies and larger grains have been shown by Li-Dep sample compared to the undoped sample, which reflect the reported effects of Li incorporation in kesterite materials [19]. Conversely, the Li-Dep sample (Li-Dep)

demonstrated a compacted and dense morphology with larger grain. In contrast, the sample doped during solution preparation (Li-Sol) displays a less compact morphology with smaller grains and a greater density of voids. These observations can be attributed to the lower solubility in the solvent and higher decomposition temperature of $LiClO_4$, which is distributed within the absorber in the Li-Sol sample. This can lead to the formation of some grains in some regions within the bulk of the absorber and complicate the formation of Li_2S. Similar results have been reported in [17]. Additionally, these results might be influenced by the amount of Li incorporated via each doping strategy (note that lithium cannot be detected via EDX analysis). From the EDX results (Table 1), both doped samples show greater amounts of Sn on the surface than the undoped sample does. However, the excess Tin in the Li-Sol sample may lead to the formation of SnS2, which has diffraction peaks similar to those of Li2S (JPCDS 23-0677).

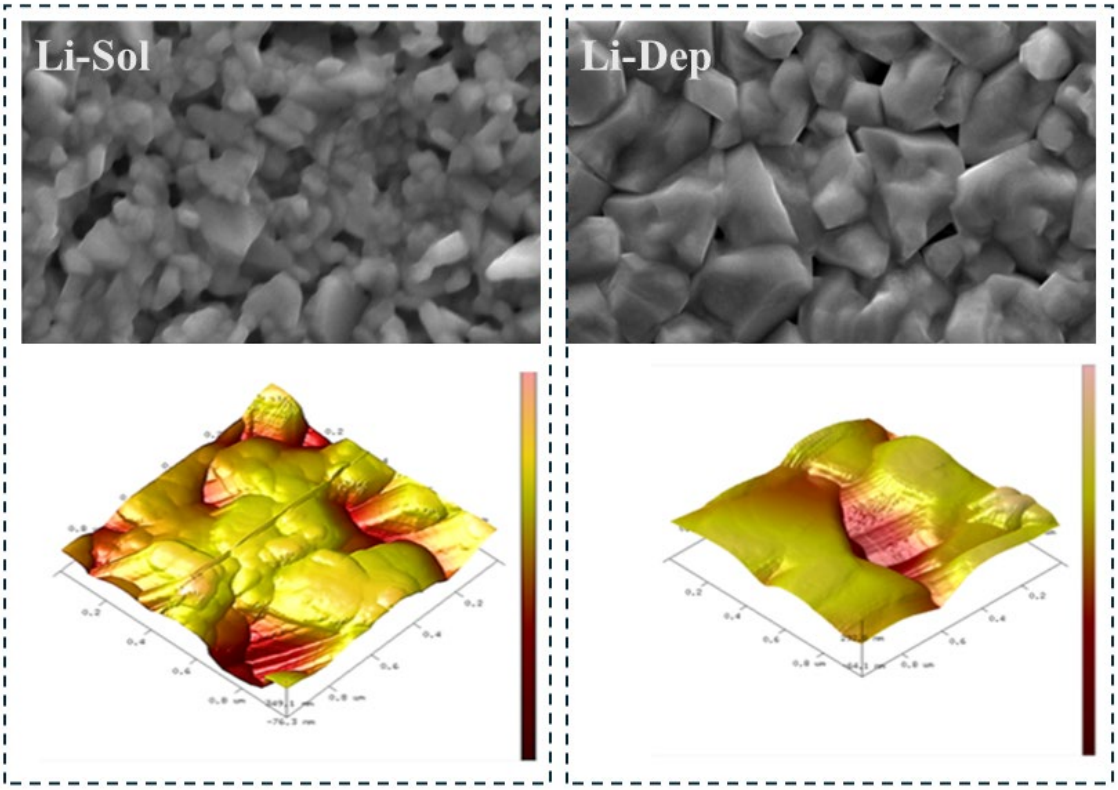

Figure 4: *Surface SEM images and 3D-AFM images of the lithium-doped Li-Sol and Li-Dep samples*

Table 1: *Cation ratios of the lithium-doped Li-Sol, Li-Dep C and Undoped samples from the EDS results*

Samples/Atom%	Cu	Sn	Zn	S	Li	Zn/Sn	Cu/(Zn + Sn)
Undoped	24.56	8.39	13.07	50.83	-----	1.55	1.14
Li-Sol	22.10	14.16	11.14	49.12	-----	0.78	0.87
Li-Dep	22.30	11.33	11.41	50.93	-----	1.01	0.98

The optical bandgap values for the Li-doped samples shown in Figure 5 are 1.63 eV for Li-Sol and 1.58 eV for Li-Dep. The bandgap of Li-Dep aligns with the expected bandgap for samples at the given silver concentration [20]. The higher bandgap observed for Li-Sol could be attributed to

off-stoichiometry or the presence of secondary phases, as confirmed by previous characterizations. The Urbach energy (Eu) for both samples, which indicates the extent of the band-tail states and defect density, is 426 and 403 meV for the Li-Sol and Li-Dep samples, respectively. This slight reduction in Eu for the Li-Dep sample compared with that of the Li-Sol sample confirms the decreased defect density and band-tailing in the sample doped via the precursor method. This improvement supports the effectiveness of the proposed doping strategy in enhancing the optoelectronic properties of kesterite materials.

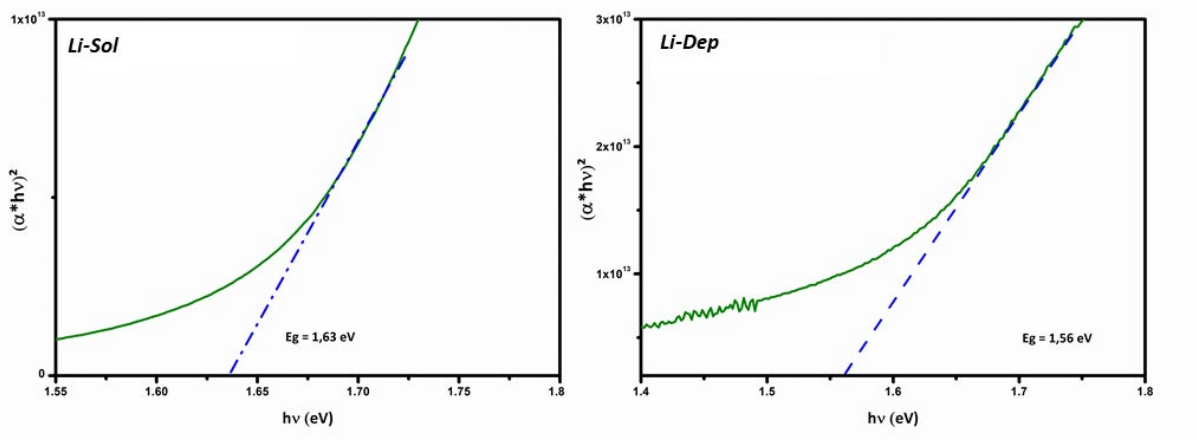

***Figure 5**: Energy band bandgap of the litium-doped Li-Sol and Li-Dep samples*

Summary

In this work we presented a simple strategy to incorporate Li into kesterite absorbers synthesized using sol-gel method. This approach of depositing a thin Li-contining layer on the top of kesterite precursor before the annealing process. Our results demonstrated enhanced films properties compared to the previously reported doping strategy. The post deposition approach results in higher crystallinity, larger grains, denser morphology, and lower Urbach energy. The approach proposed in this work can lead to more flexibility in doping kesterite materials with alkali metlas and can show a strong potential for developing highly efficient kesterite solar cells if carefully controlled similar to the reported doping strategies used in PVD-based kesterite thin films.

References

[1] N. Ali, M. Zubair, A. Khesro, R. Ahmed, S. Uddin, N. Shahzad, H. Alrobei, A. Kalam, A.G. Al-Sehemi, B. Ul Haq, A Study on Optoelectronic Properties of Copper Zinc Tin Sulfur Selenide: A Promising Thin-Film Material for Next Generation Solar Technology, Crystal Research and Technology 56 (2021) 2000159.

[2] A. Wang, J. Huang, J. Cong, X. Yuan, M. He, J. Li, C. Yan, X. Cui, N. Song, S. Zhou, M.A. Green, K. Sun, X. Hao, Cd-Free Pure Sulfide Kesterite Cu $_2$ ZnSnS $_4$ Solar Cell with Over 800 mV Open-Circuit Voltage Enabled by Phase Evolution Intervention, Advanced Materials 36 (2024) 2307733. https://doi.org/10.1002/adma.202307733.

[3] N. Ali, A. Hussain, R. Ahmed, M.K. Wang, C. Zhao, B.U. Haq, Y.Q. Fu, Advances in nanostructured thin film materials for solar cell applications, Renewable and Sustainable Energy Reviews 59 (2016) 726–737. https://doi.org/10.1016/j.rser.2015.12.268.

[4] Y.E. Romanyuk, S.G. Haass, S. Giraldo, M. Placidi, D. Tiwari, D.J. Fermin, X. Hao, H. Xin, T. Schnabel, M. Kauk-Kuusik, P. Pistor, S. Lie, L.H. Wong, Doping and alloying of kesterites, J. Phys. Energy 1 (2019) 044004. https://doi.org/10.1088/2515-7655/ab23bc.

[5] A. Mule, B. Vermang, M. Sylvester, G. Brammertz, S. Ranjbar, T. Schnabel, N. Gampa, M. Meuris, J. Poortmans, Effect of different alkali (Li, Na, K, Rb, Cs) metals on Cu 2 ZnSnSe 4 solar cells, Thin Solid Films 633 (2017) 156–161. https://doi.org/10.1016/j.tsf.2016.11.027.

[6] Y. Gong, A. Jimenez-Arguijo, A.G. Medaille, S. Moser, A. Basak, R. Scaffidi, R. Carron, D. Flandre, B. Vermang, S. Giraldo, H. Xin, A. Perez-Rodriguez, E. Saucedo, Li-Doping and Ag-Alloying Interplay Shows the Pathway for Kesterite Solar Cells with Efficiency Over 14%, Adv Funct Materials (2024) 2404669. https://doi.org/10.1002/adfm.202404669.

[7] N. Bansal, B.C. Mohanty, K. Singh, Diffusional investigation of alkali ions from composition tuned glass substrates to Mo-thin film for solar cell application, Surfaces and Interfaces 24 (2021) 101060. https://doi.org/10.1016/j.surfin.2021.101060.

[8] Q. Zhao, H. Shen, K. Gao, Y. Xu, X. Wang, Y. Li, Effect of sodium doping on crystal growth and band matching of the heterojunction in flexible CZTS solar cells, J. Mater. Chem. C 9 (2021) 17531–17541. https://doi.org/10.1039/D1TC03957A.

[9] M. He, X. Zhang, J. Huang, J. Li, C. Yan, J. Kim, Y. Chen, L. Yang, J.M. Cairney, Y. Zhang, S. Chen, J. Kim, M.A. Green, X. Hao, High Efficiency $Cu_2ZnSn(S,Se)_4$ Solar Cells with Shallow Li_{Zn} Acceptor Defects Enabled by Solution-Based Li Post-Deposition Treatment, Advanced Energy Materials 11 (2021) 2003783. https://doi.org/10.1002/aenm.202003783.

[10] Z. Laghfour, S. Aazou, M. Taibi, G. Schmerber, A. Ulyashin, A. Dinia, A. Slaoui, M. Abd-Lefdil, Z. Sekkat, Sodium doping mechanism on sol-gel processed kesterite Cu2ZnSnS4 thin films, Superlattices and Microstructures 120 (2018) 747–752. https://doi.org/10.1016/j.spmi.2018.05.018.

[11] G. Tseberlidis, V. Trifiletti, A. Le Donne, L. Frioni, M. Acciarri, S. Binetti, Kesterite solar-cells by drop-casting of inorganic sol–gel inks, Solar Energy 208 (2020) 532–538. https://doi.org/10.1016/j.solener.2020.07.093.

[12] H. Xin, S.M. Vorpahl, A.D. Collord, I.L. Braly, A.R. Uhl, B.W. Krueger, D.S. Ginger, H.W. Hillhouse, Lithium-doping inverts the nanoscale electric field at the grain boundaries in $Cu_2ZnSn(S,Se)_4$ and increases photovoltaic efficiency, Phys. Chem. Chem. Phys. 17 (2015) 23859–23866. https://doi.org/10.1039/C5CP04707B.

[13] J. Xu, S. Shang, J. Yang, J. Liu, S. Jiang, Effect of sodium-doping on the performance of CZTS absorb layer: Single and bifacial sodium-incorporation method, Solar Energy 221 (2021) 476–482. https://doi.org/10.1016/j.solener.2021.04.063.

[14] A. Ruiz-Perona, M. Guc, Y. Sánchez, T. Kodalle, J.M. Merino, M. León, R. Caballero, Wide band gap Cu2ZnGe(S,Se)4 thin films and solar cells: Influence of Na content and incorporation method, Solar Energy 226 (2021) 251–259. https://doi.org/10.1016/j.solener.2021.08.032.

[15] M. Mohamad, B.U. Haq, R. Ahmed, A. Shaari, N. Ali, R. Hussain, A density functional study of structural, electronic and optical properties of titanium dioxide: Characterization of rutile, anatase and brookite polymorphs, Materials Science in Semiconductor Processing 31 (2015) 405–414. https://doi.org/10.1016/j.mssp.2014.12.027.

[16] D.S. Dhawale, A. Ali, A.C. Lokhande, Impact of various dopant elements on the properties of kesterite compounds for solar cell applications: a status review, Sustainable Energy Fuels 3 (2019) 1365–1383. https://doi.org/10.1039/C9SE00040B.

[17] Y. Gong, A. Jimenez-Arguijo, A.G. Medaille, S. Moser, A. Basak, R. Scaffidi, R. Carron, D. Flandre, B. Vermang, S. Giraldo, H. Xin, A. Perez-Rodriguez, E. Saucedo, Li-Doping and Ag-

Alloying Interplay Shows the Pathway for Kesterite Solar Cells with Efficiency Over 14%, Adv Funct Materials (2024) 2404669. https://doi.org/10.1002/adfm.202404669.

[18] Z. Shen, S. Wang, Y. Liu, Y. Sun, J. Wu, H. Guo, K. Zhang, S. Zhang, F. Liu, Y. Zhang, Li2S doping into CZTSe drives the large improvement of VOC of solar cell, Journal of Energy Chemistry 62 (2021) 637–644. https://doi.org/10.1016/j.jechem.2021.04.018.

[19] Y. Mao, J. Guo, C. Cao, J. Ao, F. Liu, Y. Zhang, Eliminating cracking morphology of solution-processed CZTSSe absorbers by Sn-rich composition engineering, Materials Science in Semiconductor Processing 159 (2023) 107388. https://doi.org/10.1016/j.mssp.2023.107388.

[20] J. Kumar, S. Ingole, Structural and optical properties of (AgxCu1-x)2ZnSnS4 thin films synthesised via solution route, Journal of Alloys and Compounds 727 (2017) 1089–1094. https://doi.org/10.1016/j.jallcom.2017.08.222.