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Tuning the optoelectronic properties of emerging solar absorbers through cation disorder engineering

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Chalcogenide solar absorbers, such as AgBiS_2 and kesterites, have gained a resurgence of interest recently, owing to their high stability compared to metal–halide compounds, as well as their rising efficiencies in photovoltaic devices. Although their optical and electronic properties are conventionally tuned through the composition and structure, cation disorder has increased in prominence as another important parameter that influences these properties. In this minireview, we define cation disorder as the occupation of a cation crystallographic site with different species, and the homogeneity of this cation disorder as how regular the alternation of species in this site is. We show that cation disorder is not necessarily detrimental, and can lead to increases in absorption coefficient and reductions in bandgap, enabling the development of ultrathin solar absorbers for lightweight photovoltaics. Focusing on kesterites and ABZ_2 materials (where A = monovalent cation, B = divalent cation, and Z is a chalcogenide anion), we discuss how the degree and homogeneity of cation disorder influences the optical properties, charge-carrier transport and photovoltaic performance of these materials, as well as how cation disorder could be tuned and quantified. We finish with our perspectives on the important questions moving forward in making use of cation disorder engineering as a route to achieve more efficient solar absorbers.

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Fig. 1 Cation disorder in different materials. (a) Unit cells of ordered (left) and disordered (right) $\text{Cu}_2\text{ZnSnS}_4$. During the order–disorder transition, the Wyckoff positions of $\text{Cu}_2\text{ZnSnS}_4$ will be changed from $2c$ and $2d$ to position $4d$. The space group will also change from $I\bar{4}$ to $I\bar{4}2m$. Reprinted with permission from ref. 39. Copyright 2017 Elsevier. (b) Schematic of AgBiS_2 crystal structures with different degrees of cation disorder. In the homogeneous cation disorder configuration, Ag^+ and Bi^{3+} cations can randomly occupy the same lattice sites. Reprinted with permission under the CC-BY-4.0 license from ref. 32. (c) The change on the planar-averaged local electronic density of states (DOS) for AgBiS_2 when changing from inhomogeneously (left) to homogeneously cation-disordered. The color bar refers to the normalized $\sqrt{\text{DOS}}$. Reprinted with permission from ref. 31. Copyright 2022, Springer Nature.

Since the bandgap reduction in these cation-disordered materials has been attributed to band-edge broadening, it is intuitive to assume an enlarged Urbach energy E_U in a more disordered phase. Although some works did report a larger E_U in a more cation-disordered $\text{Cu}_2\text{ZnSnS}_4$ film,⁴¹ other works have also reported the opposite trend.⁴² Additionally, AgBiS_2 has exhibited a significant reduction in E_U from 173 meV to 26 meV when cation disorder became more homogeneous (*i.e.*, closer to an arrangement where completely random Ag^+ and Bi^{3+} cations are distributed in the octahedral holes in the rock-salt structure). On the one hand, a more disordered structure

could cause bandgap or band edge fluctuations, raising the possibility of band tailing. But on the other side, the spread of the band-edge DOS might be decreased when the structure approaches the homogeneously cation-disordered phase, as displayed in Fig. 1(c). We hence note that the correlation between E_U values and cation disorder is not as straightforward as expected.

If the upper valence band (VB) and lower conduction band (CB) of a cation-disordered material are mainly composed of the orbitals from a specific species, then the band edge DOS of such a material will be significantly influenced by the





Fig. 2 Impact of cation disorder on optoelectronic properties. (a) The change in the bandgap of $\text{Cu}_2\text{ZnSnS}_4$ with different degrees of cation disorder (controlled by different annealing temperatures). The inset shows the Tauc plots of $\text{Cu}_2\text{ZnSnS}_4$ annealed at different temperatures. Reprinted with permission from ref. 33. Copyright 2014, AIP Publishing. (b) Absorption coefficient spectra of AgBiS_2 nanocrystals (NCs) annealed at different temperatures. Reprinted with permission from ref. 31. Copyright 2022, Springer Nature. (c) The Tauc plots and photoluminescence (PL) spectra of $\text{Cu}_2\text{ZnSnS}_4$ with different degrees of cation disorder. Reprinted with permission from ref. 41. Copyright 2017, John Wiley and Sons. (d) Charge density isosurfaces of a relaxed electron-hole pair in a cation-disordered NaBiS_2 supercell. Na, Bi, and S atoms are colored pink, blue and yellow, respectively. The translucent yellow and blue isosurfaces represent electron and hole densities, respectively. Reprinted under the CC-BY-4.0 license from ref. 45. (e) The normalized kinetics of NaBiS_2 NCs acquired from the short-time transient absorption (TA) and optical-pump-terahertz-probe (OPTP) measurements. Reprinted under the CC-BY-4.0 license from ref. 45. (f) Photoconductivity transients ($\Delta\sigma$) of $\text{Cu}_2\text{ZnSnSe}_4$ in different cation ordering configurations. Reprinted with permission from ref. 48. Copyright 2018, Elsevier.

degree of cation disorder. As an example, the band edge DOS of disordered rocksalt AgBiS_2 is shown in Fig. 1(c), where we can see that both the Ag-dominated VB maximum (VBM) and

Bi-dominated CB minimum (CBM) are homogenized following an increase in the uniformity of the $\text{Ag}^+ - \text{Bi}^{3+}$ distribution. The more homogeneous band-edge DOS then leads to enhanced



such a localized DOS will lead to a reduced dimensionality in the electronic structure of AgBiS_2 despite its 3D crystal structure, which can potentially limit the charge-carrier transport. In addition, according to Holstein-Anderson theory, even minimal disorder can also lead to the formation of small polarons.^{46,47} As a result, significant charge-carrier localization could be still present in cation-disordered AgBiS_2 .

Interestingly, for kesterite materials, such as $\text{Cu}_2\text{ZnSnSe}_4$, the degree of cation disorder barely affects the sum mobilities or carrier kinetics,⁴⁸ as shown in Fig. 2(e). A possible explanation can be seen from the electronic structure of $\text{Cu}_2\text{ZnSnSe}_4$, for which the upper VB and lower CB primarily consist of Cu d orbitals and Sn s-S p orbitals, respectively. Since calculations have predicted the Cu-Zn antisites to be the most favourable defects in $\text{Cu}_2\text{ZnSnSe}_4$, cation disorder in this material is expected to primarily affect the VB states and hole transport. Nevertheless, due to the fluctuating VB,⁴⁹ the hole mobility of $\text{Cu}_2\text{ZnSnSe}_4$ is lower than its electron mobility by over an order of magnitude, and therefore, the cation disorder will not significantly limit the charge-carrier transport, which is dominated by the much more mobile electrons, of this material. In terms of $\text{Cu}_2\text{ZnSnS}_4$, although direct experimental evidence is currently lacking, calculations have shown no signs of either small electron or hole polaron formation in its disordered phase.⁵⁰

2.3 PV performance

Given the significant impact of cation disorder on the optoelectronic properties of materials, it is not surprising to see different PV performance in solar cells fabricated based on materials with different degrees of cation disorder. It has been shown that AgBiS₂ nanocrystals (NCs) with more homogeneous cation disorder can exhibit stronger absorption and hence a higher spectroscopic limited maximum efficiency (SLME), as displayed in Fig. 3(a). Therefore, improving the homogeneity of cation disorder was critical for AgBiS₂ solar cells to reach its current certified record power conversion efficiency (PCE) of 8.85%, which is one of the highest values among all bismuth-based solar absorbers.

More studies on the role of cation disorder in kesterite solar cells have been reported. Earlier work used to regard cation disorder as the main cause of the large open-circuit voltage (V_{OC}) deficit^{42,51–53} (*i.e.*, difference between the experimental V_{OC} values and theoretical V_{OC} values, usually >380 meV), which was believed to be the culprit limiting the PCEs of kesterite solar cells. However, more recent studies have indicated that the V_{OC} deficit of kesterite solar cells was in fact not directly related to the degree of cation disorder in kesterites.⁵³ As shown in Fig. 3(b), the minimum V_{OC} deficit that could be achieved in $\text{Cu}_2\text{ZnSnSe}_4$ solar cells with different degrees of cation disorder was almost unchanged. Such a lack of a dependence of the V_{OC} on cation disorder has been rationalized by the shallow levels of $\text{Cu}_{\text{Zn}}/\text{Zn}_{\text{Cu}}$ antisite defects, as well as the limited effect of these defects on the band edges.^{50,54} However, it has been computationally predicted that the formation energies for deep-level Sn_{Zn} antisite defects



Fig. 3 Impact of cation disorder on photovoltaic performance. (a) The spectroscopic limited maximum efficiencies (SLMEs) of AgBiS₂ NC films as a function of thickness and annealing temperature, which changes the degree of cation disorder. Reprinted with permission from ref. 31. Copyright 2022, Springer Nature. (b) Open-circuit voltage deficit (V_{OC}^{def}) of solar cells fabricated based on Cu₂ZnSnSe₄ with different degree of cation disorder and hence different bandgaps E_g . Reprinted with permission from ref. 53. Copyright 2016, Elsevier. (c) A set of short-circuit current density (J_{SC})-open-circuit voltage (V_{OC}) data points acquired from the same batch of Cu₂ZnSnSe₄ solar cells. PD and PO refer to highly cation disordered and relatively cation ordered Cu₂ZnSnSe₄, respectively. Reprinted with permission from ref. 42. Copyright 2016, John Wiley and Sons. (d) Current density-voltage curves of Cu₂ZnSnS₄ devices with different degrees of cation disorder. LT-PDA and HT-PDA refer to the post deposition annealing at low (160 °C) and high temperatures (300 °C), respectively. LT-PDA could lead to a higher degree of cation order, while HT-PDA tended to lower the degree of cation order. "dx" in the brackets refers to the xth day after device fabrication. Reprinted with permission from ref. 41. Copyright 2017, John Wiley and Sons.

and their defect complexes can be lowered when cation disorder is present, even at a relatively low degrees.⁵⁰ Since a fully ordered configuration can never be achieved at room temperature, the V_{OC} deficit in kesterite solar cells is most likely caused by the inevitable non-radiative recombination resulting from deep-level defects. Based on the Shockley-Read-Hall recombination model with these disorder-facilitated defects taken into account, the maximum PCE for Cu₂ZnSnS₄ solar cells has been estimated to drop from 25% to 14%,⁵⁰ which is close to the present record value.

At the same time, we can expect the V_{OC} values to increase in solar cells fabricated with more ordered kesterites, not necessarily because of reduced V_{OC} deficits, but rather the wider bandgaps compared to their disordered counterparts, which can lead to larger quasi-Fermi level splitting. However, this V_{OC} increase is usually accompanied by a decrease in short-circuit current density (J_{SC}) (Fig. 3(c)) because of the reduced absorption range. As a result, improved and reduced PCEs/external quantum efficiencies (EQEs) in solar cells with a more ordered configuration have been reported simultaneously in literature.^{41,55} Therefore, compared to AgBiS₂

solar cells, it is still too early to conclude if cation disorder has a similarly positive impact on kesterite solar cells.

Apart from the main characteristics discussed above, some additional considerations that could affect the performance of kesterite solar cells were also reported recently. For the conventional Cu₂ZnSnS₄ solar cell architecture (glass/MoS₂/Cu₂ZnSnS₄/CdS/ZnO/ITO), a parasitic diode at the MoS₂/Cu₂ZnSnS₄ interface may block hole transport and lead to "S-shaped" J - V curves with very low fill factors (FFs), as displayed in Fig. 2(d). It has been shown that with more disordered Cu₂ZnSnS₄, such an S-shaped feature could be removed, leading to smoother J - V curves with improved FFs. The proposed explanation is that this phenomenon is caused by the shallower VBM in more disordered Cu₂ZnSnS₄, which could make a better energy level alignment between MoS₂/Cu₂ZnSnS₄ interface and Cu₂ZnSnS₄. Consequently, both the hole transport and FF were improved.⁴¹ In addition, from capacitance-voltage (C - V) measurements, a smaller charge-carrier density was observed in more ordered Cu₂ZnSnS_xSe_{1-x} solar cells, which could result in a wider space charge region and enhance charge-carrier collection efficiency.⁴² However,



found to lead to different degrees of cation disorder. As shown in Fig. 4(c), using lower cooling rates seemed to further mitigate the cation disorder in $\text{Cu}_2\text{ZnSnS}_4$ powders, leading to blue shifts of the bandgaps and corresponding PL peak positions.⁶¹

On the other hand, post-synthesis annealing treatment has been widely adopted in kesterites and ABZ_2 materials since it is the most convenient strategy to tune cation disorder in thin film samples, which could be potentially applied in PV devices. As indicated in Section 2.1 and Fig. 2(a), post-synthesis annealing could lead to a continuous transition of $\text{Cu}_2\text{ZnSnS}_4$ from a more ordered phase to a completely disordered phase when passing through the critical temperature T_C .³³ It should be noted that although most post-synthesis annealing treatments only required around 1 h to achieve the final disordered phases, a longer time (>20 h) was usually needed for the transformation into (relatively) ordered phases at temperatures below 150 °C. Such a long treatment time can then allow the slow diffusion process of cations to fully complete, and also enable the structure to reach thermal equilibrium. Similar phase transitions through a critical temperature T_C were also observed in AgBiS_2 and AgBiSe_2 ,^{62,63} which exhibited a sudden drop in conductivity and thermopower (*i.e.*, thermoelectric voltage divided by the temperature difference across the material) when a homogeneous disordered configuration was reached in these materials. Since the T_C for these ABZ_2 materials was usually above 300 °C, we might expect post-synthesis annealing at temperatures below 300 °C should mitigate the cation disorder of these materials, as observed in kesterites. However, the latest experimental results showed that for AgBiS_2 NC films, even post-synthesis annealing at temperatures below 150 °C seemed to be sufficient to increase the degree of cation disorder.^{31,32} This clear difference between AgBiS_2 and kesterites is not yet explained until now.

Finally, apart from thermal energy discussed above, light energy or an applied electric field might also change the cation disorder of materials. Valakh *et al.* have shown that when a $\text{Cu}_2\text{ZnSnS}_4$ particle was excited by a high-power 514.5 nm wavelength laser, its Raman peaks shifted and broadened, indicating an increased degree of cation disorder.⁶⁴ In terms of the impact of an applied electric field on cation disorder, although a direct investigation has not yet been reported, significant ion migration has been observed in AgBiS_2 and NaBiS_2 devices under bias,^{65,66} suggesting that the cations may be mobile. Nevertheless, more quantitative investigations will be needed to verify the effectiveness and reproducibility of these light- or electric field-induced changes in cation disorder.

4. Quantifying and comparing cation disorder

The most common technique for characterizing cation disorder is Raman spectroscopy.^{67–69} As shown in Fig. 5(a), disordered $\text{Cu}_2\text{ZnSnS}_4$ powders (VF) showed clearly broadened

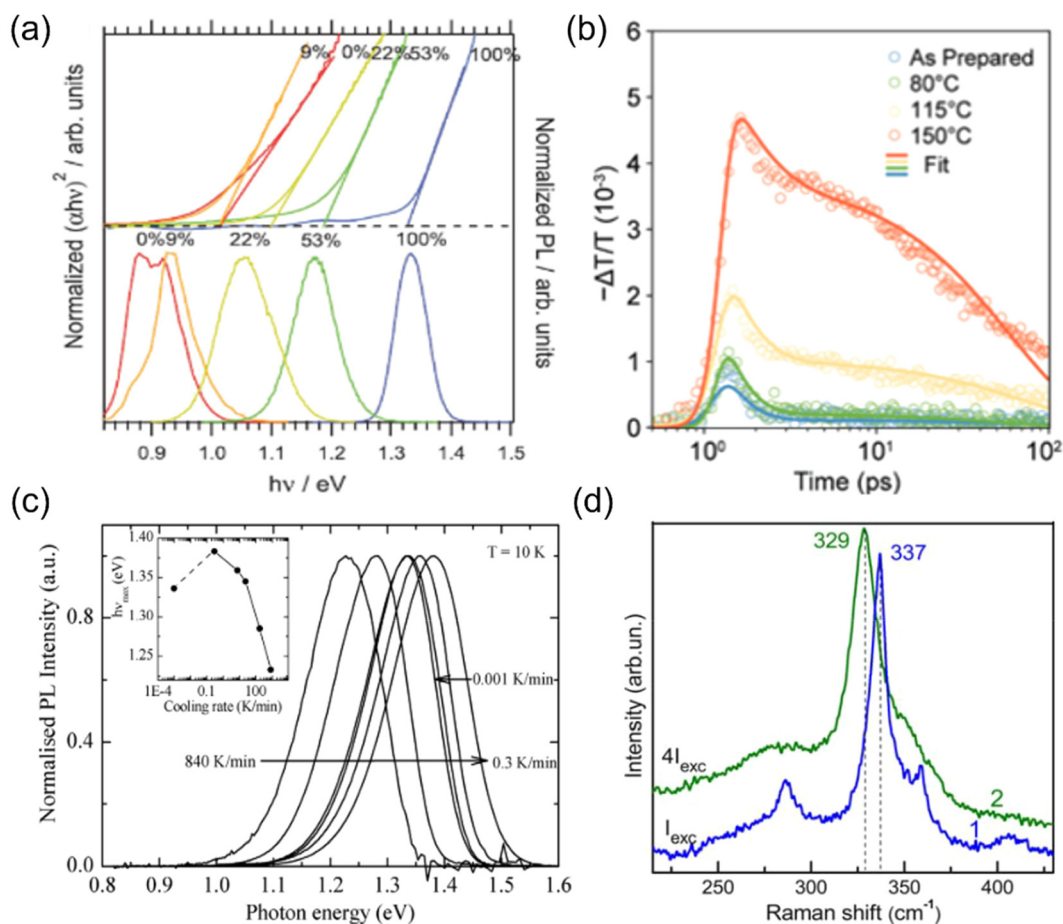


Fig. 4 Strategies to tune cation disorder. (a) Normalized Tauc plots (top) and normalized PL spectra (bottom) of $(\text{Cu,Ag})_2\text{ZnSnSe}_4$. The labelled ratios correspond to Ag/(Ag + Cu) values. α and $h\nu$ represent the absorption coefficient and photon energy, respectively. Reprinted with permission from ref. 58. Copyright 2016, John Wiley and Sons. (b) Photoconductivity (proportional to $-\Delta T/T$) kinetics of AgBiS₂ NC films annealed (post-synthesis) at different temperatures for 10 min. Higher post-synthesis annealing temperatures can lead to higher degrees of cation disorder in AgBiS₂. Reprinted under the CC-BY-4.0 license from ref. 32. (c) Low-temperature (10 K) PL spectra of Cu₂ZnSnS₄ powders quenched from 573 K to 473 K at different cooling rates. The inset shows the PL peak positions ($h\nu_{\text{max}}$) for the samples quenched at different cooling rates. Reprinted with permission from ref. 61. Copyright 2014, Elsevier. (d) Raman spectra of a Cu-rich Cu₂ZnSnS₄ sample excited by a 514.5 nm wavelength laser at a low (blue line) and high (green line) power. Reprinted with permission ref. 64. Copyright 2013, John Wiley and Sons.

Raman peaks compared to relatively ordered ones (VS) owing to a distribution of vibrational modes caused by different cation configurations.⁶⁷ The difference between the ordered and disordered samples can be further enhanced if resonance Raman spectroscopy is used^{67,68} (lower part of Fig. 5(a), which used a 785 nm wavelength laser excitation). Scragg *et al.* also proposed that the order parameter S of a specific sample can be quantified by its “ Q value”, which is defined as the ratio of the characteristic Raman m_{2A} peak to m_{3A} peak intensity.⁶⁷ The former peak corresponds to the main A -symmetry mode, while the latter is believed to highly associate with the Cu–Zn distribution. Both peaks have been found to be highly sensitive to cation disorder. Fig. 5(b) presents the Q values and full-width-at-half-maximum (FWHM) values of the main m_{1A} peaks for a series of Cu₂ZnSnS₄ films annealed at different temperatures, where we can deduce a critical temperature T_C for the order-disorder transition.

Additionally, different cation configurations can also slightly change the bond lengths and hence the corresponding X-ray diffraction (XRD) patterns. An example can be seen in AgBiS₂ NC films annealed at higher temperatures (Fig. 5(c)), which tended to have shorter Ag–S bonds when cation disorder became more homogeneous, causing a shift of the XRD peaks towards larger angles.³¹ Furthermore, if single-crystalline materials can be synthesized, single-crystal XRD can serve as another powerful tool for characterizing the degree of cation disorder since it can provide information on lattice parameters and cation occupancies at specific lattice sites.^{70,71} Unfortunately, this technique cannot apply to the kesterites discussed in this review, due to the identical electron densities of Cu⁺ and Zn²⁺ cations. In this respect, neutron scattering measurements can be more suitable for studying cation disorder in kesterites because the neutron scattering length of Cu⁺ and Zn²⁺ cations is very different. By fitting the average





Fig. 5 Characterization techniques for understanding and quantifying cation disorder. (a) Normalized Raman spectra with peak fitting for disordered (VF) and relatively ordered (VS) $\text{Cu}_2\text{ZnSnS}_4$ powders. The spectra taken under 532 nm (non-resonance) and 785 nm (resonance) laser excitations were recorded for comparison. Reprinted with permission from ref. 67. (b) Variation in the Q value, which is defined as the ratio of the Raman peak intensity on m_{2A} to m_{3A} modes (part Fig. (a)), for $\text{Cu}_2\text{ZnSnS}_4$ films annealed at different temperatures for 1 h (blue circles) and 24 h (red squares). The full-width-at-half-maximum (FWHM) values of the Raman peak on the m_{1A} mode for these samples are also displayed. The shaded area indicates the probable region of the critical temperature T_c for order-disorder transition. Reprinted under the terms of the CC-BY-4.0 license from ref. 67. (c) X-ray diffraction (XRD) patterns of pristine and AgBiS_2 NC films annealed at different temperatures. Reprinted with permission from ref. 31. Copyright 2022, Springer Nature. (d) Fitted average neutron scattering lengths in the $\text{Cu}_2\text{ZnSnS}_4$ powders using different structural models. Closed and open symbols refer to the disordered and relatively ordered samples, respectively. The two solid lines indicate the neutron scattering length for Cu^+ and Zn^{2+} cations, and the dotted line refers to the average neutron scattering length of Cu^+ and Zn^{2+} cations. Reprinted with permission from ref. 72. Copyright 2011, Elsevier. (e) Extended X-ray absorption fine structure (EXAFS) spectra of a AgBiS_2 NC film (open circles) along with the simulated curves (solid lines) based on 4 structures: acanthite (AcB), matildite (Mat), matildite with random cation occupation (MaR), and schapbachite (Sch). Reprinted under the terms of the CC-BY-4.0 license from ref. 73. (f) Solid-state nuclear magnetic resonance (NMR) spectra of ^{119}Sn , ^{67}Zn , and ^{65}Cu for $\text{Cu}_2\text{ZnSnS}_4$ powders cooled down at different rates. The VF and VS samples are as indicated in Fig. (a). The unit of the horizontal axis (chemical shift) is in ppm. Reprinted with permission from ref. 74. Copyright 1999, Royal Society of Chemistry.

Conflicts of interest

The authors declare no conflicts of interest.

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