Tuning the bandgap of double perovskites

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With great achievements in efficiency, stability, and large-scale preparation of perovskite solar cells (PSCs), the commercialization of PSC is ongoing, but there is still an issue on lead toxicity. Although lead content in the device is low, the water solubility of lead salts leads to potential environmental pollution. At present, the non-lead perovskites studied include: divalent metal perovskite (e.g., Sn^{2+}, Ge^{2+}, Cu^{2+}), trivalent metal perovskite (e.g., Bi^{3+}, Sb^{3+}, In^{3+}), tetravalent metal double perovskite (e.g., Sn^{4+}, Pd^{4+}, Ti^{4+}, Pt^{4+}) and mono-trivalent mixed double perovskite (e.g., Ag^+ and Bi^{3+}, Ag^+ and In^{3+}, Ag^+ and Sb^{3+}). Their properties are summarized in Table 1. Since the first report on non-lead double perovskite $Cs_2AgBiBr_6$ in 2016[1], this material has caused extensive research in optoelectronic devices because of its long carrier lifetime[1] and good stability[2]. However, owing to its wide and indirect bandgap (E_g) (~2.0 eV), its light absorption range is narrow, which limits its application in photovoltaics. At present, the power conversion efficiency (PCE) of $Cs_2AgBiBr_6$ device is ~3%[3]. To enhance PCE, the E_g needs to be narrowed. The efforts in this area focus on adjusting chemical composition and physical structure (Fig. 1) to tune E_g.

A common attempt to tune the E_g of double perovskite is to adjust the chemical composition of compound $A_2B(I)B(III)X_6$.

A-site. Doping alkali metal ions like Rb^+, K^+, and Na^+ made little effect on E_g[4]. Chen *et al.*[5] introduced Rb^+ into $Cs_2AgBiBr_6$ to form $(Cs_{1-x}Rb_x)_2AgBiBr_6$ and effectively passivated the defects of double perovskite, thus increasing PCE to 1.5%. But this doping could not significantly change the E_g. When doping A-site to change the dimension of perovskite from 3D to 2D, the E_g and electronic structure can be tuned. In 2019, Mitzi *et al.*[6] reported that a stable 2D double perovskite $[AE2T]_2AgBiI_8$ was formed by using multifunctional organic molecules with a direct E_g of 2.01 eV.

X-site. For lead-based perovskites, the E_g decreases with the increasing of halogen atom radius, and similar results are also observed in double perovskites. The introduction of Cl^- can greatly increase E_g, while I^- doping can significantly reduce E_g, which is 2.77 eV (X = Cl), 1.95 eV (X = Br), and 1.75 eV (X = I) for Cs_2AgBiX_6[7]. When X site is I, the stability for double perovskite decreases. It is difficult to prepare

Cs_2AgBiI_6 experimentally, because the formation energy of $Cs_3Bi_2I_9$ is lower. As reported by Ma *et al.*[8], the E_g of Cs_2NaBiI_6 was relatively narrow (1.66 eV), but it can easily decompose into $Cs_3Bi_2I_9$, yielding a 0.42% PCE.

B-site. The structure of double perovskite consists of $B(I)X_6$ and $B(III)X_6$ with alternating octahedrons connected by vertices. Substituting B-site elements can tune E_g. Karunadasa *et al.*[9] found that doping low content of toxic Tl (Tl^+, Tl^{3+}) into $Cs_2AgBiBr_6$ to form $Cs_2(Ag_{1-a}Bi_{1-b})Tl_xBr_6$ (0.003 < x = a + b < 0.075) can significantly reduce its E_g to 1.40 eV for $Cs_2(Ag_{1-a}Bi_{1-b})Tl_{0.075}Br_6$. Replacing Ag^+ and Bi^{3+} by Tl^+/Tl^{3+} yielded defects, leading to band-edge reconstruction. Using unstable Sn^{2+} (can be oxidized to Sn^{4+}) to replace both Ag^+ and Bi^{3+} can also reduce E_g to 1.71 eV (indirect) and 1.48 eV (direct)[10]. These results indicate that the band-edge reconstruction caused by the lattice distortion due to B-site ion doping can tune the E_g of double perovskite. Mitzi *et al.*[11] reported that the use of trivalent metal In^{3+} or Sb^{3+} can also significantly tune E_g, which could be increased to 2.4 eV by replacing 75% of Bi^{3+} with In^{3+}. While replacing 37.5% Bi^{3+} with Sb^{3+} could reduce E_g to 1.86 eV. When using In^+ to replace Ag^+, it was predicted that the E_g of $Cs_2InBiCl_6$ (1.02 eV) and $Cs_2InSbCl_6$ (0.91 eV) would be very suitable for photovoltaics[12]. However, In^+ is extremely unstable and can be easily oxidized into In^{3+}[13].

When using Cu^+/Cu^{2+} to replace part of Ag^+ in $Cs_2AgBiBr_6$, there is no obvious effect on E_g[14]. Cu^+ (ionic radius 77 pm, hereafter omit) and Cu^{2+} (73 pm) are much smaller than Ag^+ (115 pm). They can cause lattice defects, and the absorption tail extends from 610 to 860 nm. This was due to the absorption of the defect intermediate state. Similarly, Fe^{3+} (65 pm) was used to replace part of Bi^{3+} (103 pm)[15]. Since the size of Fe^{3+} is quite different from Bi^{3+}, it can easily cause lattice distortion and defects. The lattice constant was reduced from 11.27 to 11.25 Å, and $Cs_2AgBi_{0.886}Fe_{0.114}Br_6$ was obtained as a black crystal. Though E_g did not change obviously, the light absorption was greatly increased by defects. Recently, Gao *et al.*[16] demonstrated that Fe^{3+} could replace diamagnetic In^{3+} to yield $Cs_2AgIn_{1-x}Fe_xCl_6$ and form $[FeCl_6]^{3-}$-$[AgCl_6]^{5-}$ domains, and the connection of larger $[FeCl_6]^{3-}$-$[AgCl_6]^{5-}$ domains leads to segregated Fe^{3+}-rich phases. The E_g of $Cs_2AgInCl_6$ was tuned from 2.8 to 1.6 eV *via* Fe^{3+}-alloying.

The second approach to tune E_g of double perovskite is to adjust the physical structure. First-principles calculations indicated that changing the order of Ag^+ and Bi^{3+} in space can significantly reduce E_g. When the arrangement of Ag^+ and

Table 1.　Properties of lead-free perovskites.

Structure formula	Representative	Advantage	Disadvantage
$AB(II)X_3$	$FASnI_3$	High absorption, high mobility	Unstable
$A_2B(IV)X_6$	Cs_2SnI_6	Stable, suitable E_g	Defect
$A_3B(III)_2X_9$	$Cs_3Bi_2I_9$	Stable	Wide E_g, defect
$A_2B(I)B(III)X_6$	$Cs_2AgBiBr_6$	Stable	Wide E_g
$A_aB(III)_bX_{a+3b}$	Ag_3BiI_6	High absorption	Phase separation, defect

Table 2.　Tuning E_g of double perovskites.

Precursor	Method	Product	E_g (eV)	Feature	Ref.
$Cs_2AgBiBr_6$	A	$Cs_2(Ag_{1-a}Bi_{1-b})Tl_xBr_6$ ($x = a+b$)	1.40–1.95	Toxicity of Tl	[9]
$Cs_2AgBiBr_6$	A	$Cs_2(Ag_{1-(2a+b)}Sn_a(II))(Bi_{1-b}Sn_b(IV))Br_6$	1.48 (i) and 1.71 (d)	Unstable Sn^{2+}	[10]
$Cs_2AgBiBr_6$	A	$Cs_2Ag(Bi_{1-x}M_x)Br_6$(M:In,Sb)	1.86 ($Sb_{0.375}$) −2.28 ($In_{0.75}$)	Sb^{3+} decreases while In^{3+} increases E_g	[11]
$Cs_2AgBiBr_6$	A	$Cs_2(Ag:Cu^+/Cu^{2+})BiBr_6$	Tailing to 860 nm	Defect absorption	[14]
$Cs_2AgBiBr_6$	A	$Cs_2Ag(BiFe)Br_6$	Tailing to 800 nm	Defect absorption	[15]
$Cs_2AgInCl_6$	A	$Cs_2AgIn_{1-x}Fe_xCl_6$	1.6–2.8	For single crystal	[16]
$Cs_2AgBiBr_6$	B (temperature)	$Cs_2AgBiBr_6$	Reversible		[18]
$Cs_2AgBiBr_6$	B (temperature)	$Cs_2AgBiBr_6$	1.72–1.98	For single crystal	[19]
$Cs_2AgBiBr_6$	B (pressure)	$Cs_2AgBiBr_6$	1.70 @15 GPa	Partially retainable	[20]

A: Chemical composition. B: Physical structure.
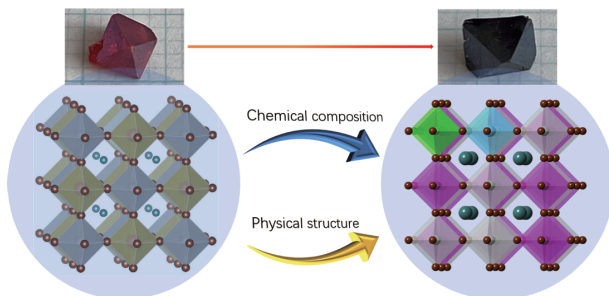
Fig. 1. (Color online) Tuning E_g of double perovskites.

Bi^{3+} was completely disordered, the E_g could be reduced to 0.44 eV[17]. Gao *et al*.[18] reported that through thermally-induced defects, as the temperature increased, the color of $Cs_2AgBiBr_6$ single crystal and film can change from red to black, the E_g decreased, but the original color of the film recovered after cooling. The finite-temperature molecular dynamics simulations indicated the synergistic effect of the incongruous bond lengths (R_{Ag-Br} and R_{Bi-Br}) fluctuations and the related electron-phonon coupling, as well as the special spin-orbit coupling effect, were the cause for the thermochromism. Gao *et al*.[19] increased the disorder degree of [Ag-Br_6] and [$BiBr_6$] octahedral by adjusting the crystallization speed of $Cs_2AgBiBr_6$. As the temperature increases, the disorder degree gradually increases, the lattice shrinks, initially leading to the formation of isolated defect states in the forbidden band, and finally a series of defect states, and reduced E_g (60 °C, 1.98 eV; 150 °C, 1.72 eV). And this reduced E_g can keep stable at room temperature. Zou *et al*.[20] found that high pressure can also significantly reduce E_g of $Cs_2AgBiBr_6$ single crystal. Under 15 GPa pressure, the E_g was reduced from 2.2 to 1.7 eV. When the pressure was released, the E_g was relatively lower than that at atmospheric pressure.

In summary, for double perovskite $Cs_2AgBiBr_6$, the effect of A-site doping on E_g is not obvious, the stability of X-site doping is intractable, and only B-site doping can significantly tune E_g. Changing the order of Ag^+ and Bi^{3+} in space is much effective for reducing E_g (Table 2). We need further study E_g-narrowing mechanism of double perovskites and find effective methods to realize it.

Acknowledgments

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