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Lanthanide doped lead-free double perovskites as the promising next generation ultra-broadband light sources

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Abstract
Efficient ultra-broadband emitter is realized by using lanthanide ion doping coupled with "DPs-in-glass composite" (DiG) structure. The synergy of self-trapped exciton together with the energy transition induce this ultra-broadband emission emerge.

Ultra-broadband emitter is critical to advancing the applications of light sensing, spectrum analysis, and life sciences imaging, et al. With the development of high-capacity optical data communications and ultra-precision metrology[1,2], efficient ultra-bandgap emission becomes particularly important. Traditional ultra-broadband light sources generally include halogen tungsten lamps (HTLs)[3], super-luminescent diodes (SLDs)[4], ultra-broadband semiconductor lasers (UBSLs)[5], laser-driven light sources (LDLSs)[6], super-continuum light sources (SCLSs)[7], etc. However, many shortcomings still exist, such as spectral instability, high electrical consumption, short lifetime, substantial heat generation, and non-compactness. Hence, alternative ultra-broadband light sources with outstanding optical and structural properties are highly demanded.

Metal halide perovskites have attracted widespread attention due to their outstanding optoelectronic properties[8–10], making them as the promising monochromatic bright emitters. However, toxicity and poor material stabilities of traditional lead perovskites impede their further commercialization[11]. Accordingly, lead-free halide double perovskites (DPs) have drawn increasing attention recently owing to their fascinating optical properties and excellent stabilities. In particular, lanthanide (Ln^{3+}) ion doping to tailor the optical or electrical properties of DPs has been well documented, aiming for their applications in white LED, NIR-LED, scintillator, anti-counterfeiting, and X-ray detecting[12]. The progresses leverage the opportunity to realize ultra-broadband emission using Ln^{3+}-doped DPs, which has never been explored.

Chen's group here reported the pioneer work to realize ultra-broadband continuous emission from visible to near-infrared spectral region (400–2000 nm) in $Cs_2AgInCl_6$ DPs, by combining the self-trapped exciton (STE) and extra luminescence channel induced by Ln^{3+} doping[13] (Fig. 1a). In particular, the Bi/Ln co-doped $Cs_2AgInCl_6$ (Bi/Ln (Ln = Nd, Yb, Er, Tm): $Cs_2AgInCl_6$) exhibit both visible STE and multiple NIR Ln^{3+} 4f-4f emissions under excitation[14], which enables ultra-broadband emission (Fig. 1b). Energy transfer mechanism was proposed to explain the origin of the Ln^{3+} emission in Bi/Ln: $Cs_2AgInCl_6$ DPs. Notably, Bi^{3+} doping is critical to enabling Ln^{3+} emission, since Bi^{3+} doping can modulate the density of states at the band edge, break parity forbidden transition of STE states and promote exciton localization, giving rise to new optical channels at a lower energy level and promoting efficiency of STE emission[15]. Moreover, two intense absorptions transitions of Bi^{3+} were observed, which were ascribed to the $^1S_0 \rightarrow {}^1P_1$ and

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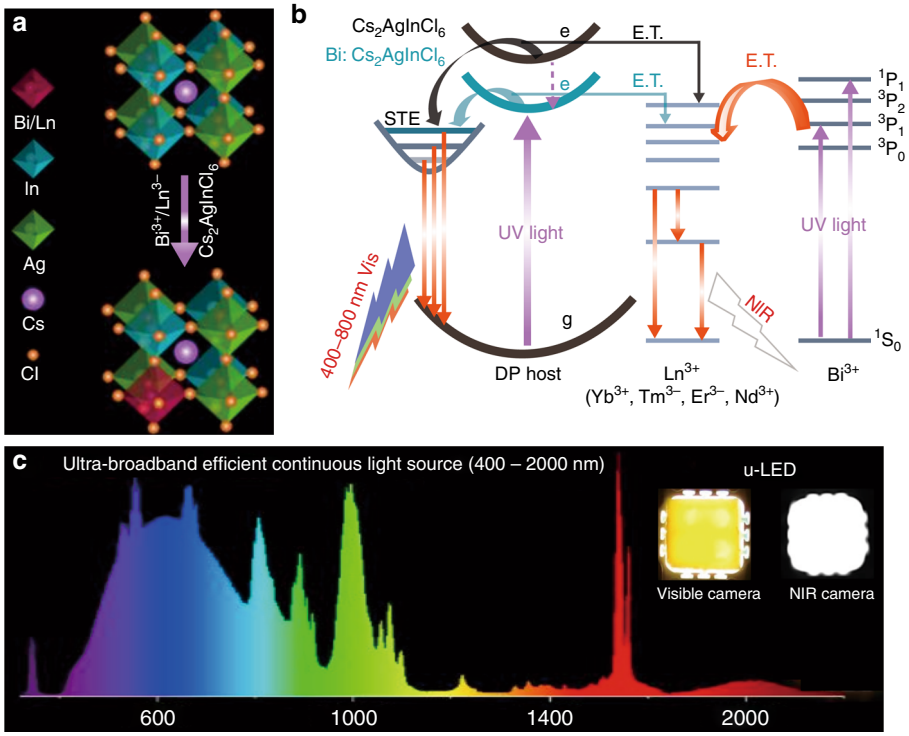

Fig. 1 *u*-LED relying on the synergy of (STE) recombination and Ln^{3+} dopants' 4f-4f transitions of the multi-Ln^{3+}-DiG. a Structure diagram of Bi/Ln:$Cs_2AgInCl_6$ DPs. **b** The ultra-broadband emission mechanisms in Bi/Ln:$Cs_2AgInCl_6$ DPs. **c** PL spectrum of the u-LED device. The inset is the photographs of the multi-Ln^{3+}-DiG u-LED by visible camera (yellow) and NIR camera (white)

$^1S_0 \rightarrow {}^3P_1$ transition. The process effectively transfers energy to Ln^{3+} dopants, to enable multiple emission of 4f–4f transitions that resulted in NIR emissions[16].

The synergy of STE broadband emission (400–800 nm) and narrowband NIR emissions from Ln^{3+} (Yb^{3+}, Tm^{3+}, Er^{3+}, and Nd^{3+}) thus induce ultra-broadband continuous luminescence. As shown in Fig. 1, multiple Ln^{3+} activators need to be doped into DPs host, but the energy transfer and cross-relaxation processes among them typically led to the energy loss via non-radiative relaxation, resulting in quenched Ln^{3+} emissions in the multi-doped DPs[17]. To solve the problem, they constructed a unique DPs-in-glass (DiG) monolithic composite to confine different Ln^{3+} dopants and avoid their interaction. Specifically, Nd: $Cs_2AgInCl_6$, Yb/Er: $Cs_2AgInCl_6$ and Yb/Tm:$Cs_2AgInCl_6$ DPs were dispersed into an inorganic glass matrix by low temperature co-sintering. The above bottom-up strategy endows the prepared Ln^{3+}-doped DiG with an improved PLQY of 40% and superior long-term stability.

The DiG was then coupled with commercial 350 nm UV chip to fabricate lighting devices, representing the record ultra-broadband light source covering spectral region from 400 to 2000 nm with full width at half maxima (FWHM) of ~365 nm (Fig. 1c). Furthermore, Chen et al. showcase the compact ultra-broadband LED's (u-LED's) applications in nondestructive spectroscopic analysis and multifunctional lighting[13].

The brand-new strategy conceived by Chen et al. thus provides a powerful toolbox to tailoring multi-Ln^{3+}-doped DPs to realize efficient ultra-broadband emitters. The strategy certainly will attract widespread attention from the whole community, and facilitate their application in various fields such as multi-functional lighting, optical communication, and nondestructive spectral analysis. The lanthanide-doped lead-free DPs thus represent a promising candidate for next generation ultra-broadband light sources.

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