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 metrology1,2, 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 (LDLS)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 properties8–10, making them as the promising monochromatic bright emitters. However, toxicity and poor material stabilities of traditional lead perovskites impede their further commercialization11. Accordingly, lead-free halide double perovskites (DPs) have drawn increasing attention recently owing to their fascinating optical properties and excellent stabilities. In particular, lanthanide (Ln3+) 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 detecting12. The progresses leverage the opportunity to realize ultra-broadband emission using Ln3+-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 Cs2AgInCl6 DPs, by combining the self-trapped exciton (STE) and extra luminescence channel induced by Ln3+ doping13 (Fig. 1a). In particular, the Bi/Ln co-doped Cs2AgInCl6 (Bi/Ln (Ln = Nd, Yb, Er, Tm): Cs2AgInCl6) exhibit both visible STE and multiple NIR Ln3+ 4f-4f emissions under excitation14, which enables ultra-broadband emission (Fig. 1b). Energy transfer mechanism was proposed to explain the origin of the Ln3+ emission in Bi/Ln: Cs2AgInCl6 DPs. Notably, Bi3+ doping is critical to enabling Ln3+ emission, since Bi3+ 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 emission15. Moreover, two intense absorptions transitions of Bi3+ were observed, which were ascribed to the 1S0 → 1P1 and...
$^{1}S_{0} \rightarrow ^{3}P_{1}$ transition. The process effectively transfers energy to Ln$^{3+}$ dopants, to enable multiple emission of $4f-4f$ transitions that resulted in NIR emissions\textsuperscript{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\textsuperscript{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$_{2}$AgInCl$_{6}$, Yb:Er: Cs$_{2}$AgInCl$_{6}$ and Yb/Tm:Cs$_{2}$AgInCl$_{6}$ 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 200 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\textsuperscript{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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References
1. Xie, Z. W. et al. Ultra-broadband on-chip twisted light emitter for optical communications. Light. Sci. Appl. 7, 18001 (2018).
2. Tang, Z. B. et al. Eu$^{3+}$-doped ultra-broadband VIS-NIR emitting phosphor. Chem. Eng. J. 388, 124231 (2020).
3. Hou, C. C. et al. Near-infrared and mid-infrared semiconductor broadband light emitters. Light.: Sci. Appl. 7, 17170 (2018).
4. Joos, J. J. et al. Broadband infrared LEDs based on europium-to-erbium charge transfer luminescence. Nat. Commun. 11, 3647 (2020).
5. Kho, A. M. et al. Incoherent excess noise spectrally encodes broadband light sources. Light.: Sci. Appl. 9, 172 (2020).
6. Rajendran, V. et al. Super broadband near-infrared phosphors with high radiant flux as future light sources for spectroscopy applications. ACS Energy Lett. 3, 2679–2684 (2018).

7. Zhou, S. F. et al. Multifunctional bismuth-doped nanoporous silica glass: From blue-green, orange, red, and white light sources to ultra-broadband infrared amplifiers. Adv. Funct. Mater. 18, 1407–1413 (2008).

8. Koegel, A. A. et al. Correlating broadband photoluminescence with structural dynamics in layered hybrid halide perovskites. J. Am. Chem. Soc. 144, 1313–1322 (2022).

9. Zhang, L. et al. High-performance quasi-2D perovskite light-emitting diodes: From materials to devices. Light: Sci. Appl. 10, 61 (2021).

10. He, T. et al. Reduced-dimensional perovskite photovoltaics with homogeneous energy landscape. Nat. Commun. 11, 1672 (2020).

11. Jana, M. K. et al. Direct-bandgap 2D silver-bismuth iodide double perovskite: The structure-directing influence of an oligothiophene spacer cation. J. Am. Chem. Soc. 141, 6955–6964 (2019).

12. Tikhomirov, V. K. et al. Broadband telecommunication wavelength emission in Yb3+–Er3+–Tm3+ co-doped nano-glass-ceramics. Opt. Express 15, 9535–9540 (2007).

13. Jin, S. L. et al. Compact ultrabroadband light-emitting diodes based on lanthanide-doped lead-free double perovskites. Light: Sci. Appl. 11, 52 (2022).

14. Yu, J. C. et al. Broadband extrinsic self-trapped exciton emission in Sn-doped 2D lead-halide perovskites. Adv. Mater. 31, 1806385 (2019).

15. Arfin, H. et al. Bi3+–Er3+ and Bi3+–Yb3+ codoped Cs2AgInCl6 double perovskite near-infrared emitters. Angew. Chem. Int. Ed. 59, 11307–11311 (2020).

16. Awater, R. H. P. & Dorenbos, P. The Bi3+ 6s and 6p electron binding energies in relation to the chemical environment of inorganic compounds. J. Lumin. 184, 221–231 (2017).

17. Pan, Q. W. et al. Engineering tunable broadband near-infrared emission in transparent rare-earth doped nanocrystals-in-glass composites via a bottom-up strategy. Adv. Opt. Mater. 7, 1801482 (2019).