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Designing Multifunctional Electron-Trapping Materials with Tunable Afterglow

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Abstract: Persistent luminescence or photostimulated luminescence, as a unique energy storage-releasing phenomenon, holds great promise for versatile applications. In this preview, we highlight an excellent example of designing a new class of X-ray-activated electron-trapping materials, wherein tunable persistent luminescence and photostimulated luminescence can be achieved simultaneously through trap distribution engineering.

Energy storage and conversion materials can effectively promote energy utilization.[1] Among these materials, electron-trapping materials (ETMs), exhibiting persistent luminescence (PersL) or photostimulated luminescence (PSL), have attracted intense research interest for their striking energy-trapping property.[2] Since Matsuzawa *et al.* reported the green afterglow phosphors of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} in 1996,[3] tremendous investigations have been devoted to this fascinating field to develop various ETMs for diverse applications in biological imaging, flexible X-ray detectors, and optical information storage.[4-6] Nevertheless, the studies of ETMs are almost focused on a single mode of PersL or PSL. It is a formidable challenge to design multifunctional ETMs with both multicolor PersL and PSL for emerging applications.

ETMs are usually composed of host lattices, emitting centers, and trap centers. Theoretically, the stored energy in shallow traps would be released gradually at room temperature to achieve PersL, whereas the stored energy in deep traps can be activated by optical stimulation to produce PSL. Thus, appropriate trap distribution is critical for PersL and PSL performance.[7,8] Such traps are often associated with defects in the host like intrinsic vacancies or introduced dopants, which means that introducing dopants can be a valid strategy for trap distribution modulation in ETMs.[9] Hence, clarifying the role of different dopants in traps is a crucial and essential prerequisite in guiding the rational design of new ETMs.

In a recent study, Chen *et al.* reported an ingenious strategy to develop a new class of X-ray-activated multicolor PersL and PSL phosphors based on lanthanide (Ln^{3+})-doped Cs_2NaGdF_6, in which the origin of traps and the effect of doped Ln^{3+} on afterglow were systematically investigated (Figure 1A).[10] In the host of Cs_2NaGdF_6, the heavy Cs^+ ions possess a strong X-ray absorption capability, which makes Cs_2NaGdF_6 superior to conventional fluoride counterparts as X-ray-activated phosphors. More importantly, the electron and hole trap distribution can be elaborately manipulated by introducing different Ln^{3+} dopants, rendering both multicolor PersL of more than one week and tunable PSL with a broad response from ultraviolet (UV) to near-infrared (NIR). Furthermore, their intriguing PersL/PSL/thermal-stimulated luminescence inspired the authors to fabricate flexible composite films containing the proposed $Cs_2NaGdF_6:Ln^{3+}$ phosphors, which can be utilized for triple-modal anti-counterfeiting applications.

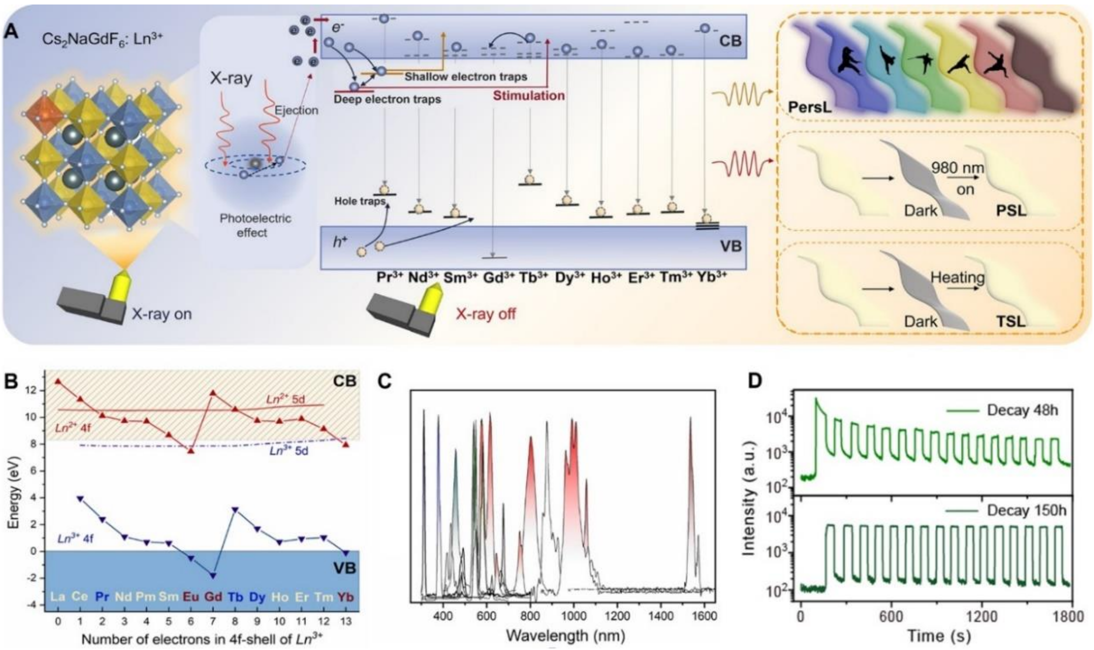

Figure 1. Multicolor PersL and PSL phosphors via trap distribution engineering.

(A) Schematic illustration of X-ray-charged Cs_2NaGdF_6 phosphors with multicolor PersL and PSL via trap distribution engineering.

(B) VRBE diagram of Ln^{2+}/Ln^{3+} in the Cs_2NaGdF_6 host.

(C) Sum of the normalized PersL spectra of $Cs_2NaGdF_6:Ln^{3+}$ (Ln = Tb, Dy, Sm, Pr, Nd, Ho, Er, Tm, Yb) phosphors after cessation of X-ray for 5 min.

(D) PSL decay curves (monitored at 550 nm) with 980 nm laser stimulation after cessation of X-rays for 48-150 h.

Ln^{3+} ions are widely employed as dopants owing to their unique *4f* electronic configurations and abundant energy level structure, making them ideal for a wide spectral range from UV to NIR. In this work, the Ln^{3+} dopants in Cs_2NaGdF_6 played a key role in engineering the trap distribution. Through analyzing the results of thermoluminescence characterization and density functional theory calculations, the origin of traps was elucidated. It was revealed that Ln^{3+} dopants acted as hole trap centers while fluorine vacancies (V_F) were conducted as electron traps. By determining the different energy level locations of Ln^{3+} in Cs_2NaGdF_6 phosphors based on the calculated vacuum referred binding energy (VRBE) diagram (Figure 1B), it was further clarified that the ground states of most Ln^{3+} dopants are located at the top of the valence band (VB), ensuring the hole capture for PersL or PSL. However, several Ln^{3+} ions (*e.g.*, Eu^{3+} and Gd^{3+}) whose 4f ground states are inside VB cannot trap the holes under irradiation, making them inappropriate as hole trap centers.

Benefiting from the manipulation of the depth and density of electron and hole traps via selecting different Ln^{3+} dopants in Cs_2NaGdF_6 phosphors, tunable PersL with emissions was achieved ranging from 311 nm to 1536 nm, which covered the UV, visible, and NIR regions (Figure 1C). In addition, multicolor PSL upon NIR light stimulation was readily gained as well. Notably, after ceasing the excitation for more than 150 h, stable and intense PSL signals can still be gained, indicating the great optical storage capability of $Cs_2NaGdF_6:Ln^{3+}$ phosphors (Figure 1D). Such excellent optical properties impart significant advantages of $Cs_2NaGdF_6:Ln^{3+}$ phosphors toward various applications.

In summary, this work provides a universal strategy to engineer the trap distribution for designing novel multifunctional ETMs with both tunable PersL and PSL. These fundamental insights into the trap manipulation of ETMs may open a promising avenue for their burgeoning applications such as high-resolution radiography, complex anti-counterfeiting, and multidimensional information storage, to name a few.

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