Homogeneous core-shell structure stabilizes Mn^{4+} -doped fluoride red phosphors for high-performance warm-white LEDs

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One of the most important prerequisites for the development of phosphor materials for practical applications in lighting and displays is their long-term stability under ambient conditions [1,2]. Although manganese(IV)-doped narrow-band red-emitting fluoride phosphors with outstanding photoluminescence properties show great promise in white light-emitting diodes (LEDs) and wide-color-gamut LED backlight displays [3,4], their instability towards moisture remains the biggest challenge to be overcome [5–8]. Recently, as reported in *Angewandte Chemie International Edition*, a research group led by Xueyuan Chen demonstrated an effective and facile strategy to significantly improve the moisture resistance of the well-known efficient red phosphors $\text{K}_2\text{TiF}_6\text{:Mn}^{4+}$ (abbreviated as: KTF:Mn^{4+}) via homogeneous core-shell structure design [9]. This work enables the realization of simultaneous enhancement in moisture resistance and luminescence efficiency of core-shell-structured $\text{KTF:Mn}^{4+}\text{@KTF}$ red phosphors, thus paving the way for their commercial application in white LEDs.

For the first time, Chen and co-workers [9] used a facile reverse cation exchange reaction method to prepare the homogeneously coated $\text{KTF:Mn}^{4+}\text{@KTF}$ core-shell red phosphors (Fig. 1a). Notably, the reverse cation exchange process did not cause any changes in the morphology, particle size, and crystallographic structure of the KTF:Mn^{4+} red phosphors, which was beneficial for retaining the outstanding luminescence properties. Amazingly, the core-shell coating can protect the internal Mn^{4+} ions from oxidation in air at elevated temperatures, leading to better thermal quenching behavior in $\text{KTF:Mn}^{4+}\text{@KTF}$ sample. On the other hand, with regard to Mn^{4+} -doped fluoride red phosphors, owing to the weak parity-forbidden ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ absorption of Mn^{4+} ions, high

Mn^{4+} doping concentrations are generally required for ensuring sufficient absorption of the incident blue LED light; meanwhile the detrimental concentration quenching effect will inevitably take place and then cause reduced luminescence efficiency. Importantly, the $\text{KTF:Mn}^{4+}\text{@KTF}$ core-shell phosphors doped with 7 at% Mn^{4+} concentration had a much higher internal quantum efficiency (93%) than KTF:Mn^{4+} counterpart with the same Mn^{4+} concentration (75%), which could be attributed to that the KTF shell coating can cut off the path of energy migration to the surface defects and thus significantly mitigate the concentration quenching effect (Fig. 1a).

More importantly, Chen and co-workers achieved remarkable enhancement of moisture resistance in $\text{KTF:Mn}^{4+}\text{@KTF}$ core-shell red phosphors compared with KTF:Mn^{4+} (Fig. 1b–d). They found that after aging for 480 h under high temperature (85°C) and high humidity (85%) conditions, the color of $\text{KTF:Mn}^{4+}\text{@KTF}$ sample changed a little and its emission intensity slightly lost, while KTF:Mn^{4+} counterpart exhibited an obvious deep body color and its emission intensity reduced dramatically (Fig. 1e–g). Impressively, by using the $\text{KTF:Mn}^{4+}\text{@KTF}$ as red component, the authors fabricated a high-performance warm-white LED device (correlated color temperature = 3510 K, $R_a = 93$, $R_9 = 75$) with luminous efficacy as high as 162 lm/W under 60 mA drive current. And this LED device can keep 89% of its initial value of luminous efficacy after aging at 85°C and 85% humidity for 480 h (Fig. 1h).

Overall, the work presented by Chen and co-workers provides a powerful approach to overcome the moisture instability of Mn^{4+} -doped fluoride red phosphors. The finding that the homogeneous core-shell structure design

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Figure 1 Efficient and stable KTF:Mn⁴⁺@KTF core-shell red phosphors for white LEDs. (a) Fabrication of KTF:Mn⁴⁺@KTF core-shell phosphor via the reverse cation-exchange method. (b, c) Photographs of (b) KTF:Mn⁴⁺@KTF and (c) KTF:Mn⁴⁺ phosphors immersed in deionized water for various durations. (d) Integrated emission intensities of KTF:Mn⁴⁺ and KTF:Mn⁴⁺@KTF phosphors as a function of time in deionized water. (e, f) Photographs of KTF:Mn⁴⁺ and KTF:Mn⁴⁺@KTF phosphor flakes (e) before and (f) after aging under 85°C and 85% humidity conditions for 480 h. (g) Integrated emission intensities of KTF:Mn⁴⁺ and KTF:Mn⁴⁺@KTF phosphor flakes as a function of aging time. (h) Luminous efficacy of LED1 (KTF:Mn⁴⁺ + YAG:Ce³⁺) and LED2 (KTF:Mn⁴⁺@KTF + YAG:Ce³⁺) as a function of aging time under 60 mA driven current. Adapted by permission from Ref. [9]. Copyright 2019, Wiley.

could simultaneously improve the moisture resistance and luminescence efficiency in this work might be easily expanded to other Mn⁴⁺-doped fluoride systems, thus opening up a new perspective for the development of high-performance red phosphors towards both warm-white LEDs and wide-color-gamut LED backlights. There is no doubt that future research should speed up the commercialization of KTF:Mn⁴⁺@KTF red phosphors. Such important advances in Mn⁴⁺-activated narrow-band red-emitting LED phosphors hold great potential to deliver desirable artificial light sources with high color quality and high luminous efficacy but low production cost.

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- Huang X. New red phosphors enable white LEDs to show both high luminous efficacy and color rendering index. *Sci Bull*, 2019, 64: 879–880
- Huang X. Red phosphor converts white LEDs. *Nat Photon*, 2014, 8: 748–749

- Zhu H, Lin CC, Luo W, *et al*. Highly efficient non-rare-earth red emitting phosphor for warm white light-emitting diodes. *Nat Commun*, 2014, 5: 4312
- Lin H, Hu T, Huang Q, *et al*. Non-rare-earth K₂XF₇:Mn⁴⁺ (X = Ta, Nb): a highly-efficient narrow-band red phosphor enabling the application in wide-color-gamut LCD. *Laser Photonics Rev*, 2017, 11: 1700148
- Huang L, Liu Y, Yu J, *et al*. Highly stable K₂SiF₆:Mn⁴⁺@K₂SiF₆ composite phosphor with narrow red emission for white LEDs. *ACS Appl Mater Interfaces*, 2018, 10: 18082–18092
- Arun Kumar P, Kim YH, Kim HJ, *et al*. Hydrophobic organic skin as a protective shield for moisture-sensitive phosphor-based optoelectronic devices. *ACS Appl Mater Interfaces*, 2017, 9: 7232–7240
- Nguyen HD, Lin CC, Liu RS. Waterproof alkyl phosphate coated fluoride phosphors for optoelectronic materials. *Angew Chem Int Ed*, 2015, 54: 10862–10866
- Fang MH, Hsu CS, Su C, *et al*. Integrated surface modification to enhance the luminescence properties of K₂TiF₆:Mn⁴⁺ phosphor and its application in white-light-emitting diodes. *ACS Appl Mater Interfaces*, 2018, 10: 29233–29237
- Huang D, Zhu H, Deng Z, *et al*. Moisture-resistant Mn⁴⁺-doped core-shell-structured fluoride red phosphor exhibiting high luminous efficacy for warm white light-emitting diodes. *Angew Chem Int Ed*, 2019, 58: 3843–3847