High-throughput DFT screening enables the discovery of a super-broadband white-emitting phosphor for high-CRI white LEDs

Xiaoyong Huang

Nowadays, solid-state white lighting technology based on phosphors-converted white light-emitting diodes (LEDs) has deeply penetrated in our daily life as next-generation light sources due to the benefit of energy saving and equipment miniaturization [1–3]. The development of new high-performance phosphor materials will promote the advance of white LEDs and thus further extend the impact of solid-state lighting technology in lighting, displays and other applications. Currently, the white LEDs fabricated by using blue LED chips and YAG:Ce³⁺ yellow phosphors suffer from low color-rendering index (CRI < 80) and high correlated color temperature (CCT ≈ 6494 K) owing to the cyan gap and lack of the red-light component [4,5], whereas the alternative white LED devices based on the combination of ultraviolet (UV) LED chips with tricolor (red, green, and blue) phosphors encounter serious problems such as inevitable energy re-absorption and color variation [6–9]. Accordingly, it is urgent and challenging to discover new high-quality single-phased white-light-emitting materials with full-visible-spectrum emission to construct high-CRI white LEDs. Traditionally, researchers use the time-consuming and expensive trial-and-error approach to explore new materials for white LEDs. Just recently, reporting in *Chemistry of Materials*, Li and co-workers [10] demonstrated an inexpensive and easy way to find the first-known Eu²⁺-activated full-visible-spectrum phosphor of Sr₂AlSi₂O₆N:Eu²⁺, based upon combining data mining of high-throughput density functional theory (DFT) calculations and experimental validation. Impressively, the reported Sr₂AlSi₂O₆N:Eu²⁺ white-emitting phosphors showed a super-broadband emission with a bandwidth up to 230 nm, and the fabricated prototype UV-pumped white LED by employing only Sr₂AlSi₂O₆N:Eu²⁺ phosphor exhibited superior color quality (Ra = 97, R9 = 91, CCT =

3892 K), which was greater than that of commercial tri-color phosphor-converted LEDs. This work opens up new perspectives on finding desirable LED phosphor materials for high-color-quality solid-state lighting.

In their recent work, Li and co-workers used the DFT prediction and following experimental validation to discover the single-phased Eu²⁺-activated white-emitting LED phosphors. At first, the authors chose the relatively unexplored Sr–Al–Si–O–N quinary chemistry as the target, and then they carried out high-throughput screening (Fig. 1a). Using a data-mined ionic substitution algorithm on all prototype structures in ICSD-2017, Li and co-workers generated a total of 496 new phosphor candidates containing these Sr–Al–Si–O–N elements and performed further DFT calculations to predict which would perform well as a phosphor. Finally, the Sr₂AlSi₂O₆N compound emerged as the most promising candidate for Eu²⁺-activated broadband-emitting phosphors because of its phase stability, large host band gap, and high Debye temperature. Subsequently, Li and co-workers successfully prepared pure-phased Sr₂AlSi₂O₆N:Eu²⁺ phosphors by using conventional high-temperature solid-state reaction method. Amazingly, they found that the as-prepared Sr₂AlSi₂O₆N:Eu²⁺ phosphors had a broadband absorption in the near-UV range (Fig. 1b), and under UV excitation these phosphors created a super-broadband white emission light in the 400–850 nm wavelength range with peak at 600 nm and bandwidth of 230 nm (Fig. 1c), which can be attributed to the multiple luminescent centers for Eu²⁺ activators. Importantly, the white-emitting Sr₂AlSi₂O₆N:Eu²⁺ phosphors exhibited high resistance to the thermal quenching (only 12% emission intensity loss at 150°C, see Fig. 1d), which was beneficial for practical LED applications. Notably, the authors fabricated a prototype white LED device by

College of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan 030024, China
Email: huangxy04@126.com

Figure 1 (a) Computational high-throughput screening workflow for identifying promising broadband emitters. E_g is the host band gap calculated with both Perdew-Burke-Ernzerhof (PBE) functional and Heyd-Scuseria-Ernzerhof (HSE) functional. Θ_D is the calculated Debye temperature. (b) Room-temperature excitation and (c) emission spectra of white-emitting $\text{Sr}_2\text{AlSi}_2\text{O}_6\text{N}:\text{Eu}^{2+}$ phosphors. (d) Temperature dependence of the peak emission intensity of $\text{Sr}_2\text{AlSi}_2\text{O}_6\text{N}:\text{Eu}^{2+}$ phosphors. (e) Emission spectrum of the fabricated white LED device with $\text{Sr}_2\text{AlSi}_2\text{O}_6\text{N}:\text{Eu}^{2+}$ white-emitting phosphor and an UV LED chip ($\lambda_{\text{em}} = 375\text{--}380\text{ nm}$) under 350 mA driven current. Adapted by permission from Ref. [10]. Copyright 2019, American Chemical Society.

coating the single $\text{Sr}_2\text{AlSi}_2\text{O}_6\text{N}:\text{Eu}^{2+}$ phosphors on an UV LED chip, and upon 350 mA driven current the device produced warm-white light with excellent CRI ($R_a = 97$, $R_9 = 91$) and low CCT of 3892 K (Fig. 1e). Moreover, the LED device exhibited good color stability at different driven currents. Unfortunately, the developed fascinating full-visible-spectrum emitting $\text{Sr}_2\text{AlSi}_2\text{O}_6\text{N}:\text{Eu}^{2+}$ phosphors possessed relatively modest quantum efficiency of 7.9%, but Li and co-workers improved the quantum efficiency up to 19.1% through chemical substitution strategy. Further research is still needed to optimize the material to achieve better quantum efficiency.

Overall, for the first time, with the help of data mining technique, Li and co-workers successfully discovered a new super-broadband white-emitting $\text{Sr}_2\text{AlSi}_2\text{O}_6\text{N}:\text{Eu}^{2+}$ phosphor to make LEDs with excellent color quality. This work opens a door to using high-throughput DFT calculations for the computational design and optimization of phosphor materials for lighting and displays applications. There is no doubt that more research efforts should be devoted to this field, and it is anticipated that more and more novel interesting phosphor materials with new luminescence properties will be identified *via* this proposed high-throughput computational approach.

Received 10 October 2019; accepted 21 October 2019;
published online 30 October 2019

- Pan M, Liao WM, Yin SY, *et al.* Single-phase white-light-emitting and photoluminescent color-tuning coordination assemblies. *Chem Rev*, 2018, 118: 8889–8935
- Huang X. Red phosphor converts white LEDs. *Nat Photon*, 2014, 8: 748–749
- Pust P, Schmidt PJ, Schnick W. A revolution in lighting. *Nat Mater*, 2015, 14: 454–458
- Zhao M, Liao H, Molokeev MS, *et al.* Emerging ultra-narrow-band cyan-emitting phosphor for white LEDs with enhanced color rendition. *Light Sci Appl*, 2019, 8: 38
- Wang S, Sun Q, Devakumar B, *et al.* Mn^{4+} -activated $\text{Li}_3\text{Mg}_2\text{SbO}_6$ as an ultrabright fluoride-free red-emitting phosphor for warm white light-emitting diodes. *RSC Adv*, 2019, 9: 3429–3435
- Leng Z, Li R, Li L, *et al.* Preferential neighboring substitution-triggered full visible spectrum emission in single-phased $\text{Ca}_{10.5-x}\text{Mg}_x(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphors for high color-rendering white LEDs. *ACS Appl Mater Interfaces*, 2018, 10: 33322–33334
- Liu S, Liang Y, Zhu Y, *et al.* Full visible spectra emission introduced by crystal-site engineering in $\beta\text{-Ca}_3(\text{PO}_4)_2$ -type solid solution phosphors for high quality white light emitting diodes application. *Chem Eng J*, 2019, 375: 121976
- Dai PP, Li C, Zhang XT, *et al.* A single Eu^{2+} -activated high-color-rendering oxychloride white-light phosphor for white-light-emitting diodes. *Light Sci Appl*, 2016, 5: e16024
- Cui M, Wang J, Shang M, *et al.* Full visible light emission in Eu^{2+} , Mn^{2+} -doped $\text{Ca}_9\text{LiY}_{0.667}(\text{PO}_4)_7$ phosphors based on multiple crystal lattice substitution and energy transfer for warm white LEDs with high colour-rendering. *J Mater Chem C*, 2019, 7: 3644–3655
- Li S, Xia Y, Amachraa M, *et al.* Data-driven discovery of full-visible-spectrum phosphor. *Chem Mater*, 2019, 31: 6286–6294