HIGHLIGHT

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Emerging substance class with narrow-band blue/green-emitting rare earth phosphors for backlight display application

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Solid state lighting (SSL) on the basis of phosphor-converted white light-emitting diodes (pc-wLEDs) is rapidly changing the lighting and display industry. New materials and concepts provide light sources and systems that have unmatched performance and/or functionality [1,2]. In addition to the well-known application of pc-wLEDs in home and office lighting, these efficient white light sources are also increasingly applied as alternative backlight units in liquid-crystal displays (LCDs), where there is a strong focus on improving resolution, wider color gamut, and decreased power consumption [3]. Especially, the improvement of color gamut is a hot issue as it enables more vivid colors that appeal to consumers. The color gamut is determined by the color coordinates of red, green, and blue (RGB) emissions from white LEDs that pass through the corresponding RGB color filters in the LCD. Compared to competing technologies for display backlights, such as individual RGB LED chips and multi-color quantum dot (QD) emitters, pc-wLEDs have the advantage of a higher color stability, being more robust, and are simpler in design [4–6].

The discovery of new rare earth (RE) phosphor materials is recognized as a key enabler for emerging applications in lighting and displays [7]. The development of narrow-band emitting phosphors in the RGB spectral region is a tremendous challenge. The operating conditions for phosphors in pc-wLEDs are extremely related to the high operating temperatures and photon fluxes. Nowadays, the commercial pc-wLEDs backlights combine a blue-emitting (In,Ga)N chip (λ=440–460 nm) with narrow-band green-emitting β-SiAlON:Eu^{2+} that has an emission band centered at ~540 nm with a full width at half maximum (FWHM) of ~55 nm and red-emitting K_2SiF_6:Mn^{4+} (KSF:Mn^{4+}) with sharp emission lines around 630 nm [5]. For example, the green phosphor β-SiAlON:Eu^{2+} still limits the maximum accessible color gamut and energy efficiency of LCDs. Moreover, the harsh synthesis condition of this oxynitride phosphor is a serious drawback. Accordingly, the discovery and development of alternative high efficiency narrow-emitting phosphors in the RGB spectral region is particularly important and a major challenge [8].

In this context, recent discoveries in the field of phosphor materials are worth to be highlighted. Based on the insight that famous nitridoaluminates like Ca[$LiAl_3N_4$] [9] and Sr[$LiAl_3N_4$] [2] crystallize in the Na[Li_3SiO_4] (Fig. 1a) and K[Li_3SiO_4] structure type, respectively, Prof. Hubert Huppertz and co-workers together with OSRAM Opto Semiconductors issued the patent WO 2018/029304 A1 on the alkali lithosilicate phosphors in Germany [10], where a number of additional narrow-band representatives for this material class are described, and then they also reported in *Angew. Chem. Int. Ed.* that alkali metal silicates such as Na[Li_3SiO_4] and K[Li_3SiO_4] can unexpectedly be doped with Eu^{2+} to yield highly efficient narrow band emission [11]. The fact that the substance class of alkali metal silicates only hosts monovalent cations makes it all the

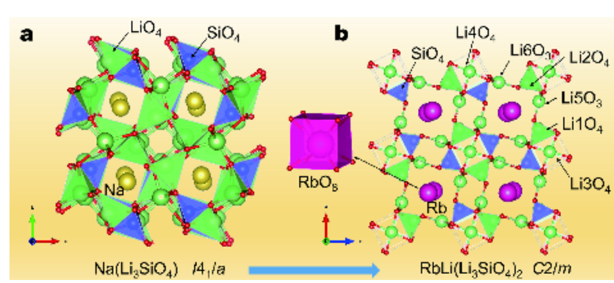

Figure 1 Mineral prototype inspired materials design from $NaLi_3SiO_4$ to $RbLi(Li_3SiO_4)_2$. (a) Crystal structure of $NaLi_3SiO_4$. (b) Crystal structure of $RbLi(Li_3SiO_4)_2$ and a distorted [RbO_8] cube.

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more astonishing. The group discovered three phosphors with the compositions $Na[Li_3SiO_4]:Eu^{2+}$, $K[Li_3SiO_4]:Eu^{2+}$, and $NaK_7[Li_3SiO_4]_8:Eu^{2+}$ from which the first compound possesses a narrow-band blue emission at 469 nm (FWHM = 32 nm).

Independently and at the same time, Prof. Zhiguo Xia and co-workers reported the discovery of a phosphor with the composition $RbNa_3(Li_3SiO_4)_4:Eu^{2+}$ ($Na[Li_3SiO_4]$ structure type) also exhibiting a narrow-band blue emission at 471 nm (FWHM=22.4 nm) in *Angew. Chem. Int. Ed.* [12] and a potential next-generation narrow-band green-emitting phosphor $RbLi(Li_3SiO_4)_2:Eu^{2+}$ (RLSO:Eu^{2+}) for backlight display application in *Adv. Mater.* [13]. In these works, the design principle proposed by their group, mineral-inspired phosphor design, is discussed as it has been successfully adopted to discover β-K_2SO_4-type, β-$Ca_3(PO_4)_2$-type, and now UCr_4C_4-type new compounds [14, 15]. It is argued, that learning from natural mineral structures to design new compounds is an efficient way to explore potential host lattices for applications in pc-wLEDs. Owing to the highly condensed network structure, a new narrow-band green-emitting phosphor, RLSO:Eu^{2+}, from the UCr_4C_4-type prototype structure, was discovered and reported. As shown in Fig. 1, $RbLi(Li_3SiO_4)_2$ originates from the above mentioned $NaLi_3SiO_4$, sharing the same UCr_4C_4-type structure basis, where the Na atom in $NaLi_3SiO_4$ is replaced by Rb and Li atoms. Interestingly, both compounds do not belong to isomorphic phases since $NaLi_3SiO_4$ has a tetragonal ($I4_1/a$) space group, whereas RLSO crystallizes in the monoclinic space group $C2/m$. Fig. 1b shows the crystal structure of RLSO, which has a highly condensed, rigid framework with a degree of condensation κ=1 ($Li_3Si:O_4$=1), and with Rb^+ ions coordinated by eight O^{2-} ions forming a distorted cube, which is the Rb^+ site for Eu^{2+} substitution.

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of RLSO:8%Eu^{2+} phosphor are shown in Fig. 2a. RLSO:Eu^{2+} shows a surprisingly narrow green emission band at 530 nm with a FWHM of only 42 nm under 460 nm excitation. The commercial β-SiAlON:Eu^{2+} was selected as a reference and has a narrow-band emission at 540 nm with FWHM of 54 nm under 460 nm excitation. Hence, the PL spectrum of RLSO:8%Eu^{2+} is narrower than that of β-SiAlON:Eu^{2+}. To demonstrate the potential application in display backlights, the authors fabricated white LED device combining the green phosphor RLSO:8%Eu^{2+}, the commercial red phosphor KSF:Mn^{4+} with a blue LED GaN chip (λ=460 nm). Fig. 2b shows the emission spectrum of the

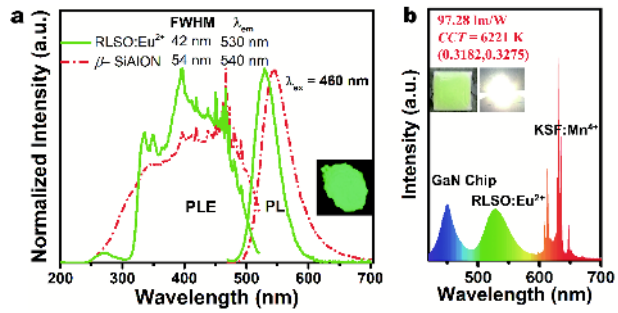

Figure 2 (a) PLE and PL spectra of RLSO:8%Eu^{2+} and the commercial β-SiAlON:Eu^{2+}. The inset is a digital photograph of green RLSO:8%Eu^{2+} phosphor under 365 nm UV lamp. (b) Emission spectrum of the LED device fabricated with the narrow-green phosphor RLSO:8%Eu^{2+} and the commercial red phosphor KSF:Mn^{4+} on a blue LED GaN chip (λ=460 nm) under a current of 20 mA. The inset shows the photographs of the as-fabricated and lightened white LED. Reproduced with permission from Ref. [13], Copyright 2018, Wiley.

fabricated white LED device under a current of 20 mA, and the obtained emission spectrum reveals that the CIE color coordinate is (0.3182, 0.3275) with a luminous efficacy of 97.3 lm W^{-1} and a white light correlated color temperature (CCT) of 6,221 K. The calculated color gamut of the fabricated white LED device defined in the CIE 1,931 color space is ~107% of NTSC, indicating that RLSO:Eu^{2+} is a promising narrow-band green phosphor for display backlight.

In conclusion, these recent inspiring breakthroughs in narrow-band blue and green phosphors represent important steps towards emerging new materials. It is remarkable that solid state chemistry inspired by the knowledge about mineral crystal structures is a promising concept for discovering new and totally unexpected narrow-emitting phosphors with versatile applications.

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