Increasing the effective absorption of Eu^{3+}-doped luminescent materials towards practical light emitting diodes for illumination applications

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Increasing the effective absorption of Eu^{3+}-doped luminescent materials towards practical light emitting diodes for illumination applications

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White light emitting diodes (LEDs) composed of a blue LED and a green/yellow downconverter material (phosphor) can be very efficient, but the color is often not considered very pleasant. Although the color rendering can be improved by adding a second, red-emitting phosphor, this generally results in significantly reduced efficacy of the device due to the broad emission of available conventional red-emitting phosphors. Trivalent europium is well-known for its characteristic narrow-band emission in the red region, with little radiation outside the eye sensitivity area, making it an ideal candidate for enabling high color quality as well as a high lumen equivalent of radiation from a spectrum point of view. However, a thorough study of the practical potential and challenges of Eu^{3+} as a red emitter for white LEDs has remained elusive so far due to the low excitation probability in the blue spectral range which is often even considered a fundamental limitation. Here, we show that the absorption in the blue region can be brought into an interesting regime for white LEDs and show that it is possible to increase both the color rendering and efficacy simultaneously using Eu^{3+} as a red emitter, compared to warm white LEDs comprising conventional materials. *Published by AIP Publishing.* https://doi.org/10.1063/1.5016948

Over the last decade, light emitting diode (LED) technology has realized its promise of a revolution in lighting technology for signaling, automotive, display, and illumination applications, providing more reliable and compact lighting solutions for a mere fraction of the operational energy consumption of traditional lighting technologies.[1–3] As LEDs continue to penetrate the general lighting market, the desire for high color quality (i.e., color rendering) is in increasing demand.[4] Indeed, the most low-cost approaches (e.g., blue-emitting LED chips coupled with a single yellow-emitting phosphor) do not deliver a full spectrum and are not adequate for many lighting applications,[5] recently engendering significant negative end-user feedback which could portend a threat to widespread adoption of LED technology along with its substantially beneficial energy savings and lower environmental impact.[6] While higher color quality LEDs are indeed available (e.g., by adding a red-emitting phosphor to the LED device), the widely available solution, $M\mathrm{AlSiN_3}:\mathrm{Eu^{2+}}$ (M = alkaline earth metals such as Ca, Ba, and Sr), presents a very broad-emitting—full-width at half-maximum (FWHM) of ~100 nm—class of phosphors[7] that produce much of their radiation in the infrared (non-visible) wavelength regime (see Fig. 1) and are moreover quite expensive to synthesize compared to more common phosphor materials based on oxides, e.g., $\mathrm{Y_3Al_5O_{12}}:\mathrm{Ce^{3+}}$ ("YAG")[8] and $(\mathrm{Ba,Sr})\mathrm{SiO_4}:\mathrm{Eu^{2+}}$. The higher costs and lower efficacy mean that for any given lighting application, a high color rendering solution today requires more, and more expensive, LEDs with less energy saving potential compared to low-color-rendering solutions.

Not lost on industry, the search for a "narrow red" emitter solution has been going on for quite some time, and some progress has been made. General Electric has recently demonstrated a narrow line-emitter at $\lambda \sim 631$ nm, $\mathrm{K_2SiF_6}:\mathrm{Mn^{4+}}$,[9] which has achieved commercial penetration in the display market but limited penetration in the general lighting market due to the availability and possibly the tendency of the fairly long-decay ($\tau \sim 8$ ms) phosphor to exhibit photo-saturation at power levels achievable in high-power LEDs.[10] Semiconductor nanoparticles ("quantum dots") also present a potential solution, but the only demonstration of on-chip LED performance[11] has been from Cd-containing quantum dots that are not compliant with the European Commission's Restriction of Hazardous Substances (RoHS) protocol.

An alternative narrow-band emitter is trivalent europium in a suitable host lattice, which is well-known for its

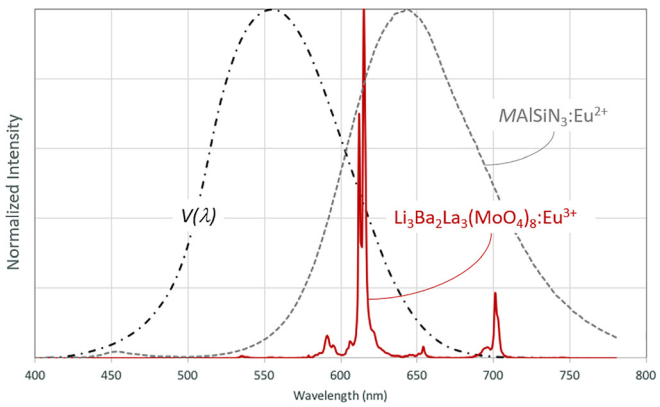

FIG. 1. Measured emission spectra of the conventional red phosphor $M\mathrm{AlSiN_3}:\mathrm{Eu^{2+}}$ (grey, dotted line) and $\mathrm{Li_3Ba_2La_3(MoO_4)_8}:\mathrm{Eu^{3+}}$ (red, solid line), exhibiting the well-known emissions from the sharp $\mathrm{Eu^{3+}}$ $^5D_0$-$^7F_{1,2}$ transitions, as well as the eye sensitivity curve V (black, dashed-dotted line).

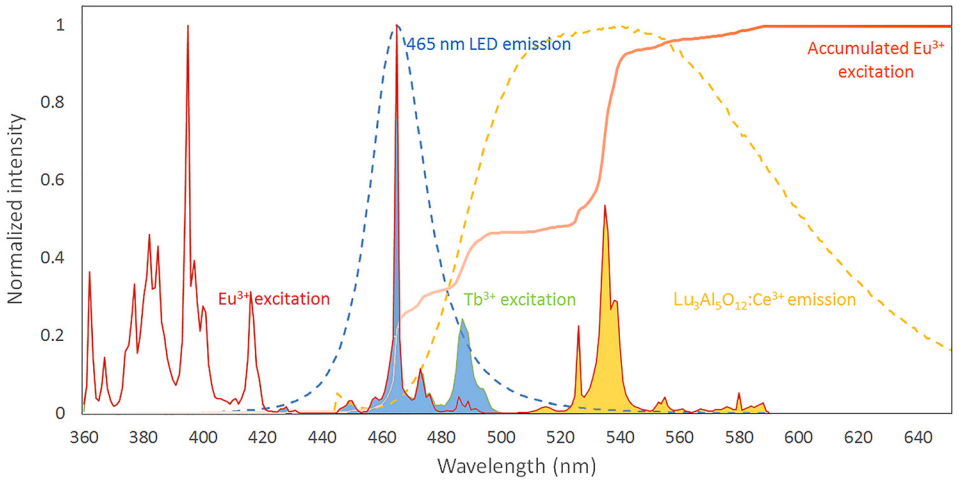

FIG. 2. Illustration of excitation mechanisms for Eu^{3+} in a warm white LED (correlated color temperature ~3000 K). The Eu^{3+} and Tb^{3+} excitation spectra are plotted as red and green solid lines, respectively, together with the emission of a 465 nm peak wavelength LED (blue dotted line) and the emission of the commonly used garnet $Lu_3Al_5O_{12}:Ce^{3+}$ (yellow dotted line). The solid orange line represents the accumulated excitation of Eu^{3+}. The shaded areas are guides to the eye to distinguish between Eu^{3+} excitation originating from absorption of blue LED light (blue region) or re-absorption of garnet emission (yellow region). In this illustration, Eu^{3+} and Tb^{3+} are both embedded in $Li_3Ba_2La_3(MoO_4)_8$ in a 4:1 molar ratio, respectively. We assume a 1:1 peak ratio of the blue to garnet light emission available for absorption by Eu^{3+}/Tb^{3+}.

extremely stable $^5D_0$–$^7F_{1,2}$ transitions resulting in sharp emission lines in the 590–630 nm spectral range, with little emission outside the eye sensitivity range (see Fig. 1). The narrow band red emission together with the typical high quantum yield of this emission (in some materials approaching 100%)[12] due to the efficient shielding of the 4f-shell suggests that Eu^{3+} could be an ideal candidate for enabling both high color quality and a high lumen equivalent of radiation (LER) for solid state lighting applications.

Eu^{3+}-doped materials, such as $Y_2O_3:Eu^{3+}$, have been used in fluorescent lighting applications for decades.[13] However, a directed and thorough study of the practical potential and challenges of Eu^{3+} as a red emitter for white LEDs has not been undertaken so far. The reason is the challenge of exciting Eu^{3+} in the blue/violet spectral range, which is, unlike the case for Hg-discharge based fluorescent lighting, a requirement for successful exploitation in LEDs. Due to quantum mechanical selection rules related to forbidden transitions, this excitation probability is extremely low and is often considered even a fundamental limitation.

Taken alone, the typically low excitation probability for Eu^{3+} around $\lambda = 450$ nm (a "pump" wavelength commonly used for white LEDs) would indeed result in required down-converter material thicknesses much too large for practical LEDs. Here, we show that this issue can be minimized, and the overall absorption can be brought into an interesting regime by engineering the effective Eu^{3+} excitation in the *combined* phosphor system. Moreover, we demonstrate a warm white Eu^{3+} composite ceramic LED device, enabling us to investigate the color properties of the resulting highly structured spectrum and confirm its high luminous efficacy.

We chose $Li_3Ba_2La_3(MoO_4)_8$ as a host lattice for Eu^{3+}. This host lattice has a small unit cell size and can be highly doped with Eu^{3+} before concentration quenching reduces the quantum efficiency.[14,15] In this material, Eu^{3+} also shows a relatively high $^7F_0 \rightarrow {}^5D_2$ transition strength and thus a high excitation probability at $\lambda = 465$ nm.[14,15] Furthermore, it is well-known that Eu^{3+} can be sensitized via Tb^{3+}, which has a $^7F_6 \rightarrow {}^5D_4$ transition around $\lambda = 490$ nm and effectively increases the Eu^{3+} excitation probability via energy transfer.[15] Due to these properties, this material has been mentioned before to be interesting for LED applications,[14–16] but a practical realization of a white LED based on it has never been demonstrated.

$Li_3Ba_2La_3(MoO_4)_8:Eu^{3+},Tb^{3+}$ was synthesized using a solid state reaction. 0.7894 g (4.000 mmol) $BaCO_3$ (Merck, 99%–101% pure), 2.3030 g (16.000 mmol) MoO_3 (Merck, 99.5% pure), and 0.2217 g (3.000 mmol) Li_2CO_3 (Merck, >99% pure) were ground together in a mortar together with Eu_2O_3 (Treibacher, 99.99% pure), Tb_4O_7 (Treibacher, 99.99% pure), and/or La_2O_3 (Heraeus, 99.99% pure) in amounts depending on the targeted doping level. Acetone was used as a grinding aid. The obtained powder was dried, transferred to a porcelain crucible, and calcinated in air at 800 °C for 12 h with a 200 K/h heating rate and ground. The phase purity of the materials was confirmed using energy dispersive X-ray spectroscopy (EDX), and the morphology was investigated using scanning electron microscopy (SEM), revealing a d_{50} particle size of about 50 μm (see supplementary material, Figs. S1 and S2, respectively).

First, the optimum Eu^{3+}/Tb^{3+} doping ratio was found by first determining the maximum Eu^{3+} doping level that could be used without suffering from concentration quenching, followed by gradually increasing the Tb^{3+} doping level until concentration quenching and/or charge transfer quenching was observed. For the $Li_3Ba_2La_3(MoO_4)_8$ host lattice, we found an optimum $Eu^{3+}:Tb^{3+}$ doping ratio of 80:20, where the La^{3+} is completely substituted, which is in agreement with Ref. 15. Figure 2 shows the relative excitation strength for this optimized material, together with the emission spectrum of commercial $Lu_3Al_5O_{12}:Ce^{3+}$ (TL-0033 from Tailorlux) and a commercially available 465 nm LED (Luxeon Z LXZ1-PR01). It can be seen from this figure that co-doping with Tb^{3+} gives rise to an additional excitation peak around 487 nm, resulting in a factor of ~1.5 increase in absorption.

Interestingly, in the case of a white LED, not only the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} at 465 nm but also the $^7F_6$

$\rightarrow {}^5D_4$ transition of Tb^{3+} at 490 nm can be used to effectively excite Eu^{3+}. Since the red-emitting material is combined with a relatively broad yellow/green-emitter such as the conventionally used garnet $(Lu,Y)_3Al_5O_{12}:Ce^{3+}$, additional Eu^{3+} excitation via the ${}^7F_0 \rightarrow {}^5D_1$ transition around 535 nm via reabsorption of the emitted light from the second phosphor occurs. This effect enhances the absorption by an additional factor in the order of 2–3, depending on the targeted color point and the choice of garnet.

In order to increase the Eu^{3+} excitation probability further, a 465 nm peak-wavelength excitation LED could be used instead of the conventionally used 450 nm LED. This excitation wavelength shift of only 15 nm more than doubles the excitation probability. However, in order to compare more directly with standard warm white LEDs based on Ce^{3+}-doped garnets and red emitters from the $CaAlSiN_3:Eu^{2+}$ family of phosphors and to ensure high color rendering properties, 450 nm was chosen as the pump wavelength for the LEDs characterized in this study.

Geometrical considerations can be brought to view in order to increase the effective excitation further. We increased the density of the material by employing a ceramic form factor, which provides typically 3–4 times more density than for powder phosphors. Conventionally, luminescent ceramics consist of a single material, for example, $(Lu,Y)_3Al_5O_{12}:Ce^{3+}$ of a singular composition. In this work, an innovative concept of producing advanced composite ceramics was applied containing both red and green emitting materials, which provides a strong ionic interaction as well as a high optical density for increased absorptivity.[17]

A mixture of low melting $Li_3Ba_2(Eu_{0.2}Tb_{0.8})_3(MoO_4)_8$ material and $Lu_3Al_5O_{12}:Ce^{3+}$ (Tailorlux TL-033) in the ratio desired for a certain color point was thoroughly ground in an agate laboratory ball mill until a medium particle size of approx. $d_{50} = 6.5\,\mu m$ was achieved. The homogeneously mixed and fine ground phosphor powder composition was mixed with a polyvinylpyrrolidone binder as a pressing additive, densified, and formed into pellets of 13 mm diameter by axial pressing at approx. 225 MPa. The thus obtained ceramic green bodies were placed on a corundum firing shelve and heated up to 850 °C in air with a heating rate of 5 K/min and a dwell time of 2 h at maximum temperature. After natural cooling to room temperature, the ceramic wafers were ground and polished. Using this method, in principle any (warm) white color point can be obtained by controlling the ceramic thickness, ratio of the two phosphors, and doping levels of the active ions. Figure 3 shows a comparison of two ceramic samples from a pure $(Lu_{0.9935},Ce_{0.0065})_3Al_5O_{12}:Ce^{3+}$ ceramic, 90:10 vol. % and 99:1 $Li_3Ba_2(Tb_{0.2}Eu_{0.8})_3(MoO_4)_8$–$(Lu_{0.99935},Ce_{0.00065})_3Al_5O_{12}$ vol. % composite ceramics. Microstructural analysis was carried out by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) (see supplementary material Figs. S3–S5 and S6, respectively). $Lu_3Al_5O_{12}:Ce^{3+}$ filler particles can homogeneously be dispersed and embedded in the low melting Eu^{3+}-containing and red emitting matrix. No indications of chemical reactions between filler particles and the matrix could be found by means of X-ray diffraction analysis (see supplementary material Figs. S3–S5). Homogeneous compaction of the composite ceramics yielded densities of >97% of the theoretical density after sintering.

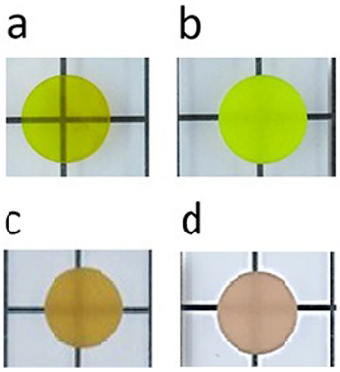

FIG. 3. Transmitted light image of ceramic wafers from (a) and (b) pure $(Lu_{0.9935},Ce_{0.0065})_3Al_5O_{12}$ with different porosity and transparency or translucency and of composite ceramics comprising (c) 90 vol. % $Li_3Ba_2(Tb_{0.2}Eu_{0.8})_3(MoO_4)_8$ and 10 vol. % $(Lu_{0.99935},Ce_{0.00065})_3Al_5O_{12}$ and (d) 99 vol. % $Li_3Ba_2(Tb_{0.2}Eu_{0.8})_3(MoO_4)_8$ and 1 vol.% $(Lu_{0.99935},Ce_{0.00065})_3Al_5O_{12}$.

The obtained composite ceramics were applied to a commercially available LED (Luxeon Z LXZ1-PR01). In order to compare more directly with conventional white LEDs, the "pump" LED was chosen with the peak emission wavelength at ~450 nm. The combined emission of the fully operating warm white LED was collected in an integrating sphere and compared to the spectral characteristics of commercially available ~3000 K LED based using $(Lu,Y)_3Al_5O_{12}:Ce^{3+}$ and $MAlSiN_3:Eu^{2+}$ phosphors.

Figure 4 shows the measured warm white spectrum of the composite-ceramic down-conversion LED. Clearly, the Eu^{3+}-containing spectrum looks quite different from a conventional LED spectrum (also shown in Fig. 4). The interaction between the different emitters in both materials is clearly observed, resulting in a highly structured spectrum. The dip at ~535 nm originates from Eu^{3+} absorption, thereby effectively increasing the height of the Eu^{3+} emission intensity at 614 nm. Despite the sharp dips and peaks in the spectrum, a color rendering index (CRI) > 90 is achieved along with a luminous efficacy of radiation (LER) of 351 lm/W_{opt}. Conventional LEDs appear to suffer most in the color rendering of blue-green and purplish test colors, which could be attributed to the poor balance in radiation in the blue-

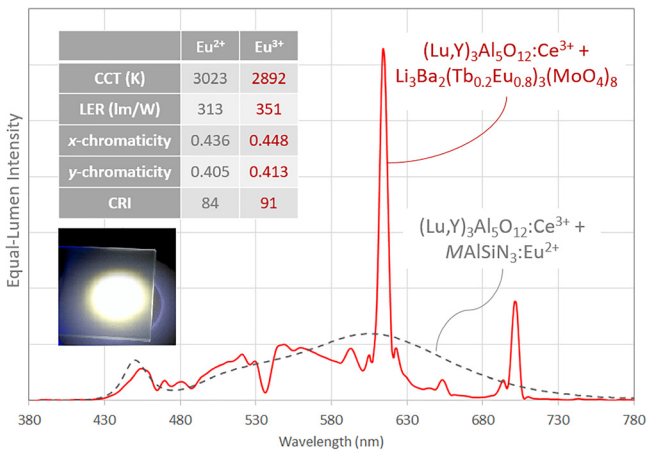

FIG. 4. Measured warm white $Li_3Ba_2(Tb_{0.2}Eu_{0.8})_3(MoO_4)_8/Lu_3Al_5O_{12}:Ce^{3+}$ composite ceramic spectrum together with a conventional $Y_3Al_5O_{12}:Ce^{3+}$/$CaAlSiN_3:Eu^{2+}$LED spectrum. The inset shows a photograph of the warm white emission.

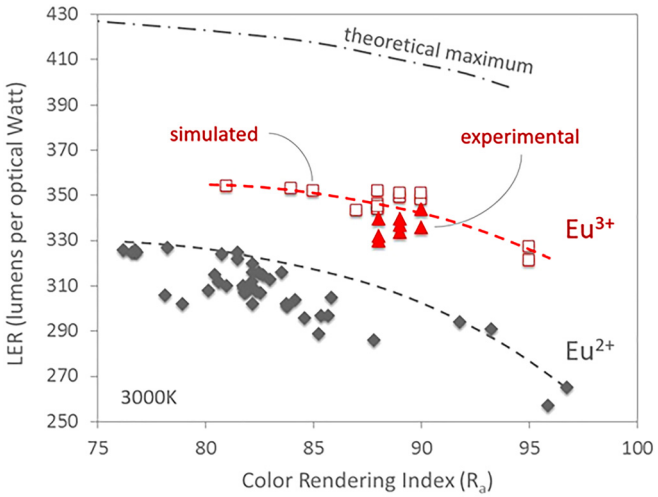

FIG. 5. Typical LER/CRI values for commercially available 3000 K white LEDs (grey diamonds) together with values for Eu^{3+}-containing white LEDs, both simulated (white squares) and measured (red triangles).

green versus red wavelength regimes for conventional LEDs. The color rendering of the Eu^{3+} containing spectrum is suppressed by the dips in the green, but the high CRI can be explained by compensation due to a better balance of the overall spectrum.

Next, we compare the LERs of various measured Eu^{3+}-containing white spectra to those of state of the art warm white LEDs (correlated color temperature (CCT) ~3000 K). In addition to the experimental measurements, simulations were employed to survey a broader landscape in terms of the color rendering index. Both the measured and simulated results are shown in Fig. 5 and compared to conventional LEDs. As shown, the Eu^{3+} based solution shows significant improvement in efficacy for all color rendering indices, with a gain of ~10% to ~20% in LER for CRIs from 80 to 95, respectively, significantly closing the gap between existing solutions and the theoretically maximally obtainable LER, based on the extreme case of multiple laser lines.[18]

In conclusion, we show that harnessing Eu^{3+} for LED based lighting applications, commonly believed not possible due to the low excitation probability in the blue region, can in fact be brought into an interesting regime through proper engineering of several factors. The Eu^{3+} excitation probability was effectively increased more than an order of magnitude by (1) proper host-lattice selection, (2) increased sensitization by co-doping, (3) optical interaction with other down-converters for increased excitation at wavelengths outside the blue regime, and (4) geometrical factors. A warm white (~3000 K) LED employing a composite luminescent ceramic was demonstrated, and an LER of 351 lm/W_{opt} and a CRI of 91 were achieved, compared to ~300 lm/W_{opt} for conventional LEDs employing MAlSiN$_3$:Eu^{2+} as a red emitter for a similar CRI. Given that many known Eu^{3+} hosts are oxides with fairly simple synthesis routes and demonstrated upscaling potential, the work here showcases a potential path forward for RoHS-compliant high quality LED lighting for general illumination with higher luminous efficacies and color rendering properties, and for lower costs, than achieved by today's conventional materials.

See supplementary material for SEM, EDX, and XRD data on the synthesized materials and composite ceramics.

[1]R. Haitz and J. Y. Tsao, "Solid-state lighting: 'The case' 10 years after and future prospects," Phys. Status Solidi A **208**, 17–29 (2011).
[2]M. R. Krames, O. B. Shchekin, R. Mueller-Mach, G. O. Mueller, L. Zhou, G. Harbers, and M. George Craford, "Status and future of high-power light-emitting diodes for solid-state lighting," IEEE J. Disp. Technol. **3**(2), 160–175 (2007).
[3]DOE SSL Program, https://energy.gov/sites/prod/files/2016/10/f33/energysavingsforecast16_0.pdf for Energy Savings Forecast of Solid-State Lighting in General Illumination Applications; accessed September 2016.
[4]B. C. Wang, Y. G. Liu, Z. H. Huang, and M. Fang, "Energy transfer and thermal stability of Ce^{3+}, Tb^{3+} co-doped $Ca_3Si_2O_4N_2$ phosphors for white light-emitting diodes," Chem. Phys. Lett. **690**, 31–37 (2017).
[5]B. Wang, Y. G. Liu, Z. Huang, M. Fang, and X. Wu, "Discovery of novel solid solution $Ca_3Si_{3-x}O_{3+x}N_{4-2x}$:$Eu^{2+}$ phosphors: Structural evolution and photoluminescence tuning," Sci. Rep. **7**, 18103 (2017).
[6]M. R. Krames, http://http://arkesso.com/2017/04 for "Rome needs red," Arkesso (blog); accessed 26 April 2017.
[7]K. Uheda, N. Hirosaki, Y. Yamamoto, A. Naito, T. Nakajima, and H. Yamamoto, "Luminescence properties of a red phosphor, $CaAlSiN_3$:Eu^{2+}, for white light-emitting diodes," Electrochem. Solid-State Lett. **9**(4), H22–H25 (2006).
[8]G. Blasse and A. Bril, "A new phosphor for flying-spot cathode ray tubes for color television: Yellow-emitting $Y_3Al_5O_{12}$-Ce^{3+}," Appl. Phys. Lett. **11**(2), 53–55 (1967).
[9]A. A. Setlur, F. Garcia-Santamaria, J. E. Murphy, and S. P. Sista, "Comparing the properties and performance of GE TriGain™ phosphors versus typical K_2SiF_6: Mn^{4+} phosphors," Phosphorus Safari, Niigata, Japan (2015).
[10]H. F. Sijbom, J. J. Joos, L. I. D. J. Martin, K. Van den Eeckhout, D. Poelman, and P. F. Smet, "Luminescent behavior of the K_2SiF_6:Mn^{4+} red phosphor at high fluxes and at the microscopic level," ECS J. Solid State Sci. Technol. **5**(1), R3040–R3048 (2016).
[11]K. T. Shimizu, M. Böhmer, D. Estrada, S. Gangwal, S. Grabowski, H. Bechtel, E. Kang, K. J. Vampola, D. Chamberlin, O. B. Shchekin, and J. Bhardwaj, "Toward commercial realization of quantum dot based white light-emitting diodes for general illumination," Photonics Res. **5**(2), A1–A6 (2017).
[12]K. Shinozaki, T. Honma, and T. Komatsu, "High quantum yield and low concentration quenching of Eu^{3+}emission in oxyfluoride glass with high BaF_2 and Al_2O_3 contents," Opt. Mater. **36**, 1384–1389 (2014).
[13]C. Feldmann, T. Juestel, C. R. Ronda, and P. J. Schmidt, "Inorganic luminescent materials: 100 years of research and application," Adv. Funct. Mater. **13**(7), 511–516 (2003).
[14]A. Katelnikovas, J. Plewa, S. Sakirzanovas, D. Dutczak, D. Enseling, F. Baur, H. Winkler, A. Kareivab, and T. Jüstel, "Synthesis and optical properties of $Li_3Ba_2La_3(MoO_4)_8$:Eu^{3+} powders and ceramics for pcLEDs," J. Mater. Chem. **22**, 22126–22134 (2012).
[15]D. Böhnisch, F. Baur, and T. Jüstel, "Photoluminescence and energy transfer behavior of narrow band red light emitting $Li_3Ba_2Tb_3(MoO_4)_8$:Eu^{3+}," Dalton Trans. **47**, 1520 (2018).
[16]C. Guoa, F. Gaoa, L. Liangb, B. Chun Choic, and J.-H. Jeongc, "Synthesis, characterization and luminescent properties of novel red emitting phosphor $Li_3Ba_2Ln_3(MoO_4)_8$:Eu^{3+} (Ln = La, Gd and Y) for white light-emitting diodes," J. Alloys Compd. **479**, 607–612 (2009).
[17]T. Juestel, S. Moeller, F. Baur, N. Kratz, J. Werner, M. Demirtas, J. Honold, and T. Hilgerink, PCT patent application WO2016207380 (29 December 2016)
[18]J. M. Phillips, M. E. Coltrin, M. H. Crawford, J. Fischer, M. R. Krames, R. Mueller-Mach, G. O. Mueller, Y. Ohno, L. E. S. Rohwer, J. A. Simmons, and J. Y. Tsao, "Research challenges to ultra-efficient inorganic solid-state lighting," Laser Photonics Rev. 1(**4**), 307–333 (2007).