



Original Article

Synthesis and Waterproofness Improvement of $K_3AlF_6:Mn^{4+}$ Phosphor for Warm White Light-emitting Diodes

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Abstract: In this study, we synthesized $K_3AlF_6:Mn^{4+}$ phosphor by co-precipitation method and investigated its crystal structure and photoluminescence properties. By surface modification of $K_3AlF_6:Mn^{4+}$ using K_3AlF_6 , the moisture resistance performance of the phosphor can be significantly improved. It was found that the luminescence performance of $K_3AlF_6:Mn^{4+}@K_3AlF_6$, which was dispersed in water for 2 h, was unchanged but the uncoated sample reduced dramatically. White light emitting diodes (WLEDs) based on the phosphor combined with commercial $YAG:Ce^{3+}$ coated on a blue LED showed significant improvement of performance with color correlated temperature (CCT) from 5307 K down to 3528 K and color rendering index (CRI) from 64 up to 87. The results exhibit the potential for the application of $K_3AlF_6:Mn^{4+}@K_3AlF_6$ as a red phosphor in warm WLEDs.

Keywords: $K_3AlF_6:Mn^{4+}$, phosphor, optical properties, surface modification, moisture resistance, warm WLED

1. Introduction

The commercialized WLEDs have based on combination of blue-emitting InGaN chip with a yellow phosphor ($YAG:Ce^{3+}$). The WLEDs have a good luminous efficiency but a poor CRI and a CCT because of the lack of red emission [1-3]. To improve the two color parameters of the WLED, red phosphors need to be combined to the WLED [4-6]. Among the various red phosphors, Eu^{2+} -doped nitrides have been reported as a good class of phosphors for WLEDs. However, the production cost is expensive due to the rigorous condition synthesis and high cost of the raw materials [7]. Recently, non-rare-earth ion

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activated phosphors have been an important material in developing WLED because these raw materials are cheaper than rare-earth doped nitride materials, and they can exhibit red light under the excitation of blue light. Red phosphors doped with transitional metal Mn^{4+} ions were widely studied for LED-based devices. Mn^{4+} -activated oxide-based red phosphors have broad absorption bands in the range of 300-500 nm and produce intense red emissions in the 600-700 nm wavelength range, and so, they have been more thermally stable and environmentally friendly [8-11]. The Mn^{4+} -activated oxide-based red phosphor has a low blue region absorption efficiency which is a drawback of the phosphor. Recently, Mn^{4+} -doped fluorides were widely developed for WLEDs due to their sharp red emissions around 630 nm under blue excitation, but they inherit poor moisture resistance due to their instability [8, 12]. To improve the stability of Mn^{4+} -doped fluorides, a coating layer on the phosphor surface for bettering the moisture resistance. Some authors reported a moisture-resistant Mn^{4+} -doped fluoride phosphor with host lattice material, alkyl phosphate, hydrophobic oleic acid, alkyl trimethoxy-silane, DL-mandelic acid, SiO_2 , Al_2O_3 , InO_2 , CaF_2 ,... [13-19]. K_3AlF_6 has been reported as a better thermal, chemical stability, melting point and lower water solubility than K_2SiF_6 [20-23]. Red emitting phosphor $K_3AlF_6:Mn^{4+}$ presented excellent luminescence performances [24, 25]. However, the phosphor suffers from luminescence degradation in high moisture environment. Thus, $K_3AlF_6:Mn^{4+}$ phosphor needs to be coated to enhance moisture resistance.

In this paper, we report on a red emitting $K_3AlF_6:Mn^{4+}$ phosphor synthesized by co-precipitation method. It is found that $K_3AlF_6:Mn^{4+}$ phosphor is extremely sensitive to humidity. The $K_3AlF_6:Mn^{4+}$ crystal surface treated by a The $K_3AlF_6:Mn^{4+}@K_3AlF_6$ proves an improved stability under water immersion. By employing the red phosphor, we fabricated warm WLEDs with a low CCT and a high CRI.

2. Experiment

2.1. Sample Preparation of $K_3AlF_6:Mn^{4+}$

K_2MnF_6 was synthesized according to the method described in the literature [26]. Specifically, 0.1 g $KMnO_4$ and 2 g KF were completely dissolved in 9 ml HF (40%) solution with a plastic beaker. The mixed solution was cooled to $-30\text{ }^\circ\text{C}$ for 48 h. Then H_2O_2 solution was added drop by drop until the solution turned yellow. The yellow powder of K_2MnF_6 sample was obtained by filtering, washing with acetone and drying at $60\text{ }^\circ\text{C}$ for 5 h.

K_3AlF_6 was synthesized via a room temperature coprecipitation method using DI water as the solvent. In a typical synthesis: First, 12 mmol of $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 55 mL H_2O and 222 mmol of KF was dissolved in 45 mL H_2O . The solutions were mixed together and stirred for 30 min to form uniform mixture. Then the solution was kept at $25\text{ }^\circ\text{C}$ for 24 h to form precipitate. Finally, the precipitate was collected by centrifugation, washed several times with absolute ethanol and deionized water and dried at $80\text{ }^\circ\text{C}$ for 4 h to get K_3AlF_6 powder.

For synthesis of $K_3AlF_6:Mn^{4+}$ red phosphor, in a typical synthesis of Mn^{4+} -doped sample, 0.6 mmol K_2MnF_6 was dissolved in 8 ml HF (40%) solution into a plastic beaker. 12 mmol of K_3AlF_6 was added into the beaker and completely dissolved with stirring. Then the reaction mixture was kept at various temperature from $-10\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$ for 2 h. The precipitate was collected by centrifugation, washed several times with absolute ethanol and deionized water to remove eventual soluble contaminants. Then the solution was dried at $80\text{ }^\circ\text{C}$ for 12 h to obtain the final productions.

2.2. Surface Passivation of $K_3AlF_6:Mn^{4+}$

The surface modification of $\text{K}_3\text{AlF}_6:\text{Mn}^{4+}$ was performed by using K_3AlF_6 solution. The $\text{K}_3\text{AlF}_6:\text{Mn}^{4+}$ powder was dispersed in the K_3AlF_6 solution and stirred for 30 min. The $\text{K}_3\text{AlF}_6:\text{Mn}^{4+}@\text{K}_3\text{AlF}_6$ was collected by centrifugation and dried at 80 °C for 5 h.

2.3. Analytical Methods

Crystal structure of $\text{K}_3\text{AlF}_6:\text{Mn}^{4+}$ sample was characterized by powder x-ray diffraction (XRD) on a Siemens D5005 diffractometer equipped with a $\text{CuK}\alpha$ radiation source ($\lambda = 1.5406\text{\AA}$). Morphology of the product was investigated by field emission scanning electron microscopy (FESEM, JSM-7600F, Jeol, Japan) at an acceleration voltage of 15 kV. Excitation and emission spectra were measured on a fluorescence spectrophotometer (NanoLog, Horiba, USA) equipped with a 450 W xenon discharge lamp as an excitation source at room temperature. The photoelectronic properties of the LED devices were recorded using an integrating sphere coupled to a spectrofluorometer (Gamma Scientific, USA).

3. Results and Discussion

Figure 1 shows the XRD patterns of the as-synthesized samples $\text{K}_3\text{AlF}_6:\text{Mn}^{4+}$. All the observed diffraction peaks well-indexed to $\alpha\text{-K}_3\text{AlF}_6$ with tetragonal superstructure (PDF#00-057-0227). The cell parameters of $\alpha\text{-K}_3\text{AlF}_6$ are $a = 18.8385(3)\text{\AA}$, $b = 18.8388(5)\text{\AA}$, $c = 33.9657(6)\text{\AA}$, $\gamma = 90^\circ$, $V = 12053.6(3)\text{\AA}^3$, and $Z = 80$. No impurity crystal phases are observed, which confirms that the phosphor sample is single phase.

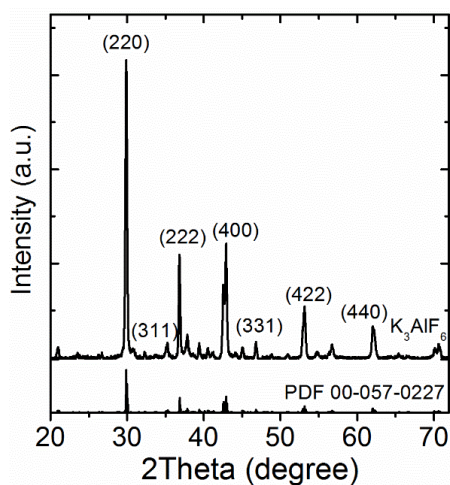


Figure 1. XRD patterns of $\text{K}_3\text{AlF}_6:\text{Mn}^{4+}$ synthesized by co-precipitation method.

The emission spectrum consists of several sharp emission peaks at around $\sim 626\text{ nm}$, corresponding to the spin-forbidden ${}^2\text{E}_g \rightarrow {}^4\text{A}_2$ transitions of Mn^{4+} . That is, emission peaks at 596, 605, 610, 618, 626.5, 630.5, and 643.5 nm are attributed to the anti-Stokes $\nu_3(t_{1u})$, $\nu_4(t_{1u})$, and $\nu_6(t_{2u})$, zero phonon line (ZPL), Stokes $\nu_6(t_{2u})$, $\nu_4(t_{1u})$, and $\nu_3(t_{1u})$ vibronic modes, respectively [24, 25]. In this work, the ZPL peak is stronger compared to previously observed Mn^{4+} activated fluoride such as $\text{K}_2(\text{Si,Ge,Ti})\text{F}_6$ due to the relatively lower symmetry of the substituted distorted octahedral Al^{3+} site in $\alpha\text{-K}_3\text{AlF}_6$ [27]. The excitation spectrum (monitored at 626 nm) contains two broad excitation bands centered at ~ 360 and $\sim 460\text{ nm}$, originating from the spin allowed ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions of Mn^{4+} , respectively. Notably, the blue excitation band ($\sim 460\text{ nm}$) is much stronger than the ultraviolet (UV) ($\sim 360\text{ nm}$) excitation band, and almost no spectral overlap can be observed between the emission spectrum of the

commercial yellow phosphor YAG:Ce³⁺ and the excitation spectrum of α -K₃AlF₆:Mn⁴⁺, indicating that the common problem of reabsorption can be resolved by using this present phosphor for the red light component.

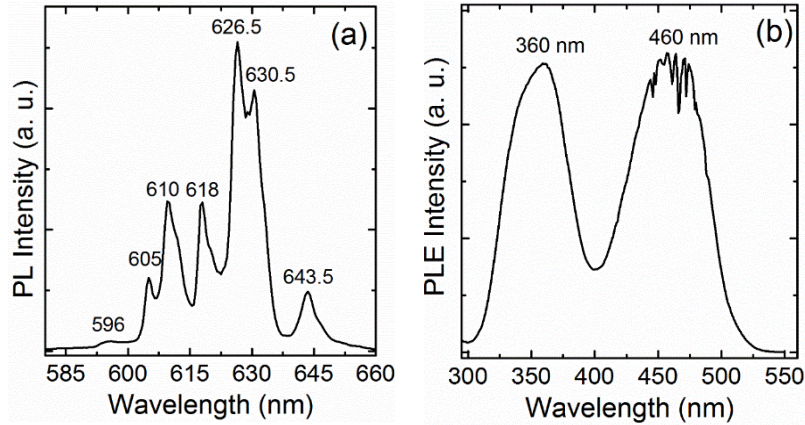


Figure 2. PLE (a) and PL (b) spectra of K₃AlF₆:Mn⁴⁺ phosphor measured at room temperature.

The influence of reaction temperature on luminescence intensity of K₃AlF₆:Mn⁴⁺ is described in Figure 3. The PL spectrum has the same shape and peak when reaction temperature changes from -10 °C to 80 °C. It is obvious that the emission intensity of the phosphor increases with the reaction temperature, until it reaches 30 °C, which is probably due to the improved crystallization. However, with the further increase in reaction temperature, the emission intensity decreases. This might be because Mn⁴⁺ tends to oxidize to non-emission Mn³⁺ at higher temperature. To confirm the moisture resistance of prepared K₃AlF₆:Mn⁴⁺ and K₃AlF₆:Mn⁴⁺@K₃AlF₆, the water immersion testing was performed for 2 h. It is clearly seen that there is no change in the shape of PL spectra of the phosphors. However, PL intensity of K₃AlF₆:Mn⁴⁺ reduces quickly to 8%, while K₃AlF₆:Mn⁴⁺@K₃AlF₆ maintains about 91% of initial intensity after 2 hours' water immersion. This result illustrates that the K₃AlF₆ shell is the main reason to improve the moisture resistance.

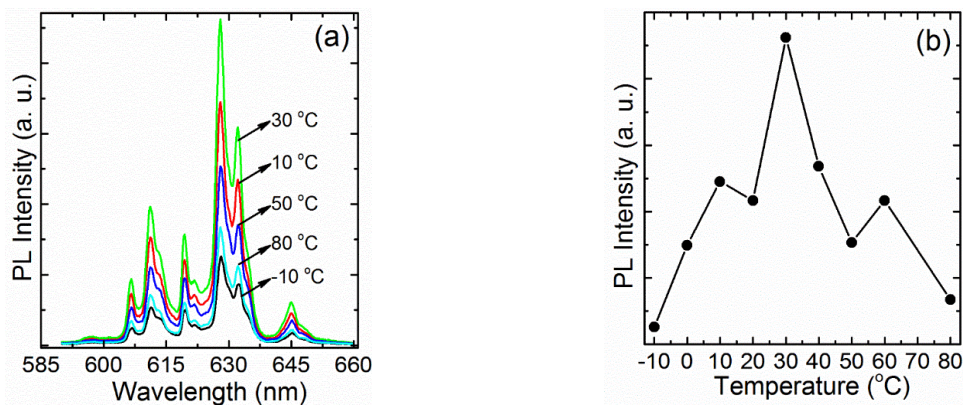


Figure 3. PL spectra (a) and PL intensity (b) of the phosphors were synthesized at various temperature.

Finally, the red phosphor is packed with yellow phosphor YAG:Ce³⁺ and blue chip to assess the performance of application in warm WLED devices. Figure 5a shows the electroluminescent (EL)

spectra of the devices based on blue chip LEDs coated YAG:Ce³⁺ and the red phosphor mixture under 150 mA current excitation. The peak at ~ 460 nm is attribute to the emission of LED chip and the broadband emission in yellow light peaking at around 550 nm is due to YAG:Ce³⁺ phosphor while the peaks at 626 nm are due to the emission of K₃AlF₆:Mn⁴⁺@K₃AlF₆ phosphor. As the amount of K₃AlF₆:Mn⁴⁺@K₃AlF₆ increases, the electroluminescence spectra of the WLEDs show an increased red component. The chromaticity coordinates of the five typical WLEDs were close to the black body radiation locus, as marked in Figure 5b.

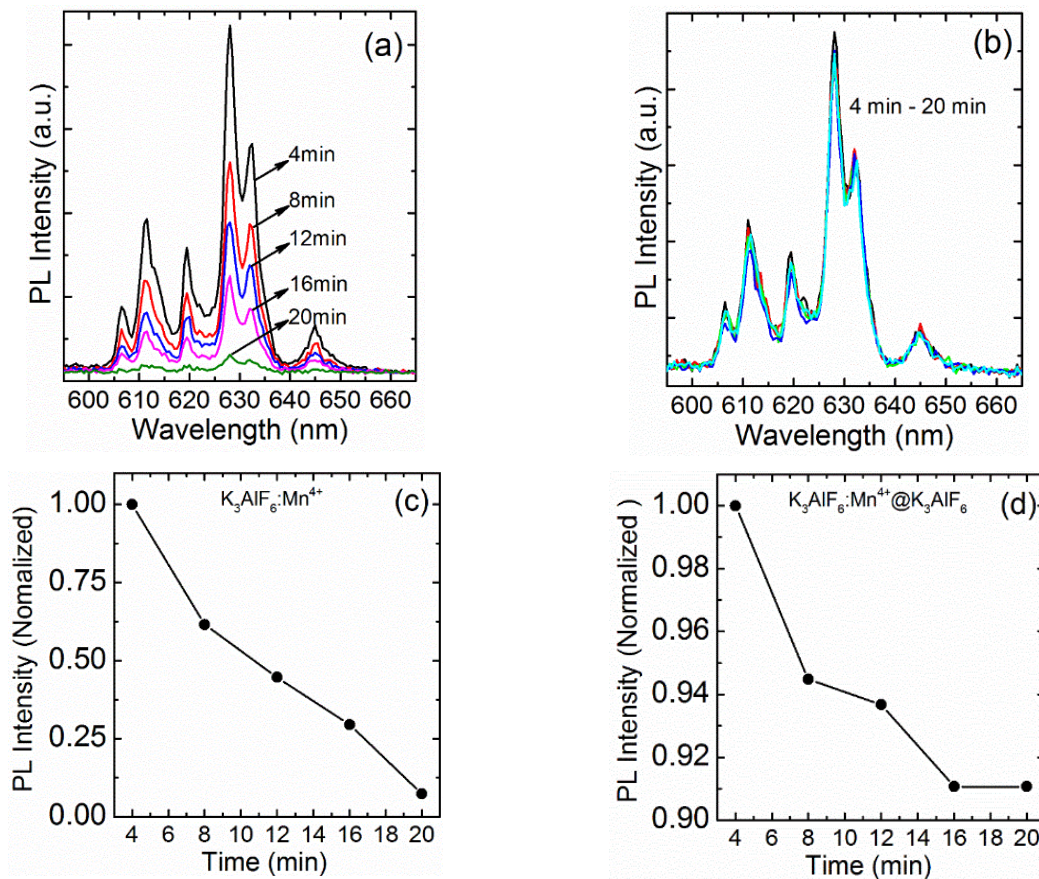


Figure 4. PL spectra of K₃AlF₆:Mn⁴⁺ (a), K₃AlF₆:Mn⁴⁺@K₃AlF₆ (b) and PL intensity as function of water immersing times of K₃AlF₆:Mn⁴⁺ (c), K₃AlF₆:Mn⁴⁺@K₃AlF₆ (d)

CCT of WLED reduces from 5307 to 3528 and CRI increases from 64 to 87 when mass ratio of YAG:Ce³⁺ and K₃AlF₆:Mn⁴⁺ changes from 1:1 to 1:4. To further evaluate the performance of the warm WLEDs, the device with the lowest CCT and highest CRI are chosen to record electroluminescence spectra under different drive currents between 50 and 350 mA and temperatures from 15 °C to 105 °C. It is observed that the shape of electroluminescence spectra is changed significantly with three contributed emission bands from the chip and the two typical phosphors. When the drive current and temperature of the device increase, the warm WLED only produces very small fluctuations in CCT and CRI. The above electroluminescent results demonstrate that K₃AlF₆:Mn⁴⁺@K₃AlF₆ may serve as a red emitting phosphor for warm WLEDs.

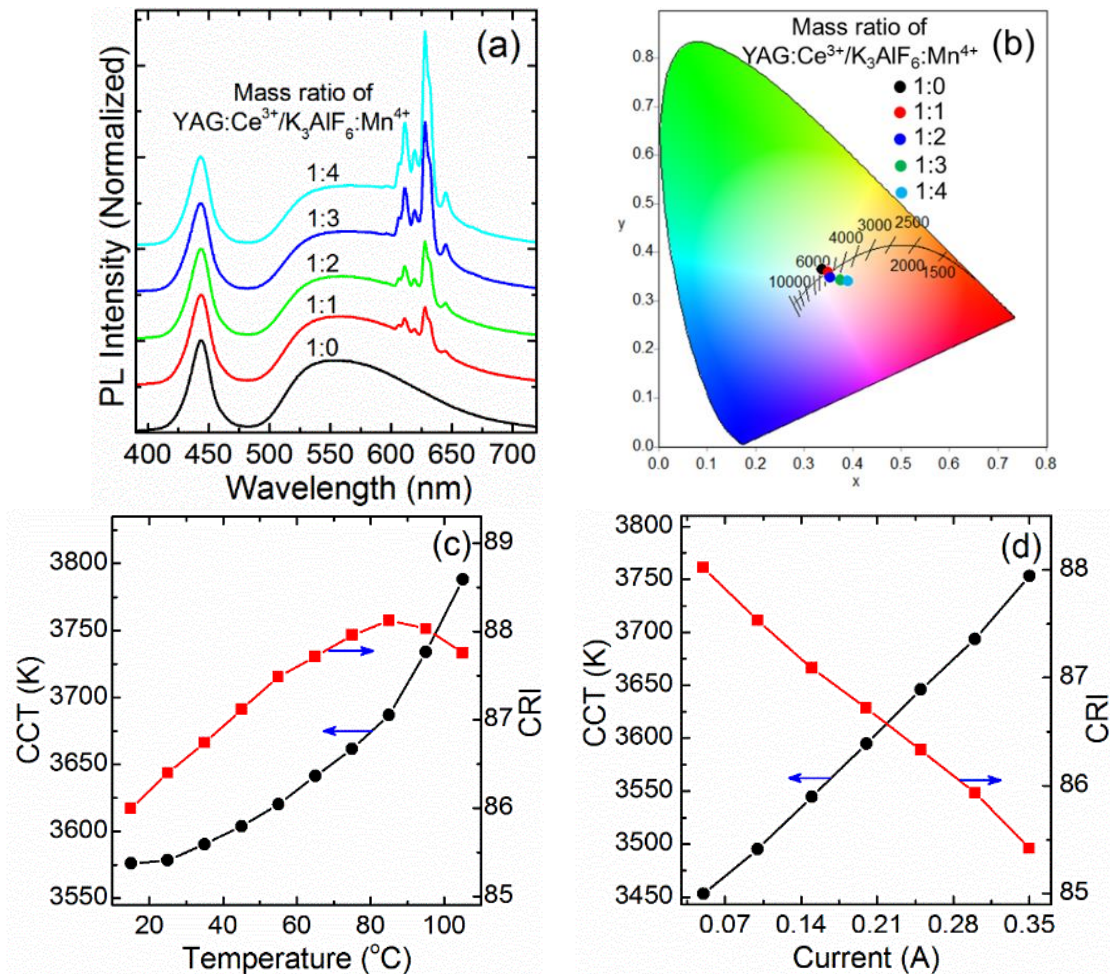


Figure 5. EL spectra (a), chromaticity coordinates (b) of the WLED with various mass ratio of YAG:Ce³⁺ and K₃AlF₆:Mn⁴⁺@K₃AlF₆, CCT and CRI of warm WLED as functions of temperature (c) and current (d)

4. Conclusion

In this study, K₃AlF₆:Mn⁴⁺ phosphor was prepared by co-precipitation method. The K₃AlF₆:Mn⁴⁺ phosphor emitted intense red light with sharp line in 590 – 650 nm region and presented broadband excitation in blue light, matching well with blue LED chips. By coating K₃AlF₆ on K₃AlF₆:Mn⁴⁺, the moisture resistance of the phosphor was improved. The warm WLED was fabricated by the combination of YAG:Ce³⁺ yellow, K₃AlF₆:Mn⁴⁺@K₃AlF₆ red phosphor and blue LED chip. The results indicate that the red phosphor may be promising red phosphor for warm WLED.

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References

- [1] H. D. Nguyen, C. C. Lin, M. H. Fang, R. S. Liu, Synthesis of $\text{Na}_2\text{SiF}_6: \text{Mn}^{4+}$ Red Phosphors for White LED Applications by Co-precipitation, *J. Mater. Chem. C*, Vol. 2, 2014, pp. 10268-10272, <https://doi.org/10.1039/C4TC02062F>.
- [2] Y. R. Shi, Y. H. Wang, Y. Wen, Z. Y. Zhao, B. Liu, Z. G. Yang, Tunable Luminescence $\text{Y}_3\text{Al}_5\text{O}_{12}: 0.06\text{Ce}^{3+}, x\text{Mn}^{2+}$ Phosphors with Different Charge Compensators for Warm White Light Emitting Diodes, *Opt. Express*, Vol. 20, 2012, pp. 21656-21664, <https://doi.org/10.1364/OE.20.021656>.
- [3] C. C. Lin, R. S. Liu, Advances in Phosphors for Light-emitting Diodes, *J. Phys. Chem. Lett*, Vol. 2, 2011, pp. 1268-1277, <https://doi.org/10.1021/jz2002452>.
- [4] Z. G. Xia, Z. H. Xu, M. Y. Chen, Q. L. Liu, Recent Developments in the New Inorganic Solid-state LED Phosphors, *Dalton Trans*, Vol. 45, 2016, pp. 11214-11232, <https://doi.org/10.1039/C6DT01230B>.
- [5] Q. Zhou, L. Dolgov, A. M. Srivastava, L. Zhou, Z. Wang, J. Shi, M. D. Dramićanin, M. G. Brik, M. Wu, Mn^{2+} and Mn^{4+} Red Phosphors: Synthesis, Luminescence and Applications in WLEDs. A Review, *J. Mater. Chem. C*, Vol. 6, 2018, pp. 2652-2671, <https://doi.org/10.1039/C8TC00251G>.
- [6] S. Liang, P. Dang, G. Li, Y. Wei, Y. Wei, H. Lian, J. Lin, New Insight for Luminescence Tuning Based on Interstitial Sites Occupation of Eu^{2+} in $\text{Sr}_3\text{Al}_{2-x}\text{Si}_x\text{O}_{5-x}\text{N}_x\text{Cl}_2$ ($x = 0-0.4$), *Adv. Opt. Mater*, Vol. 6, 2018, pp. 1800940.
- [7] H. M. Zhu, C. C. Lin, W. Q. Luo, S. T. Shu, Z. G. Liu, Y. S. Liu, J. T. Kong, E. Ma, Y. G. Cao, R. S. Liu, X. Y. Chen, Highly Efficient Non-rare-earth Red Emitting Phosphor for Warm White Light-emitting Diodes, *Nat. Commun*, Vol. 5, 2014, pp. 4312, <https://doi.org/10.1038/ncomms5312>.
- [8] S. Wang, Q. Sun, B. Devakumar, J. Liang, L. Sun, X. Huang, 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*, Vol. 9, 2019, pp. 3429-3435, <https://doi.org/10.1039/C8RA10158B>.
- [9] R. Cao, M. Peng, E. Song, J. Qiu, High Efficiency Mn^{4+} Doped $\text{Sr}_2\text{MgAl}_{12}\text{O}_{36}$ Red Emitting Phosphor for White LED, *ECS J. Solid State Sci. Technol*, Vol. 1, 2012, pp. R123-R126, <https://doi.org/10.1149/2.022204jss>.
- [10] J. Zhong, W. Xu, Q. Chen, S. Yuan, Z. Ji, D. Chen, $\text{Mn}^{4+}, \text{Li}^+$ Co-doped $\text{SrMgAl}_{10}\text{O}_{17}$ Phosphor-in-glass: Application in High-power Warm W-LEDs, *Dalton Trans*, Vol. 46, 2017, pp. 9959-9968, <https://doi.org/10.1039/C7DT02090B>.
- [11] L. Meng, L. Liang, Y. -X. Wen, Deep Red Phosphors $\text{SrMgAl}_{10}\text{O}_{17}:\text{Mn}^{4+}, \text{M}$ ($\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cl}^-$) for Warm White Light Emitting Diodes, *J. Mater. Sci. Mater. Electron*, Vol. 25, 2014, pp. 2676-2681, <https://doi.org/10.1007/s10854-014-1928-9>.
- [12] Y. Arai, S. Adachi, Optical Properties of Mn^{4+} -activated Na_2SnF_6 and Cs_2SnF_6 Red Phosphors, *J. Lumin*, Vol. 131, 2011, pp. 2652-2660, <https://doi.org/10.1016/j.jlumin.2011.06.042>.
- [13] H. D. Nguyen, C. C. Lin, R. S. Liu, Waterproof Alkyl Phosphate Coated Fluoride Phosphors for Optoelectronic Materials, *Angew. Chem. Int. Ed*, Vol. 54, 2015, pp. 10862-10866, <https://doi.org/10.1002/anie.201504791>.
- [14] P. Arunkumar, Y. H. Kim, H. J. Kim, S. Unithratil, W. B. Im, Hydrophobic Organic Skin as a Protective Shield for Moisture-sensitive Phosphor-based Optoelectronic Devices, *ACS Appl. Mater. Interfaces*, Vol. 9, 2017, pp. 7232-7240, <https://doi.org/10.1021/acsami.6b14012>.
- [15] M. H. Fang, C. S. Hsu, C. Su, W. Liu, Y. H. Wang, R. S. Liu, Integrated Surface Modification to Enhance the Luminescence Properties of $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$ Phosphor and Its Application in White-light-emitting Diodes, *ACS Appl. Mater. Interfaces*, Vol. 10, 2018, pp. 29233-29237, <https://doi.org/10.1021/acsami.8b12170>.
- [16] J. Kim, I. Jang, G. Y. Song, W. H. Kim, S. W. Jeon, J. P. Kim, Controlling Surface Property of $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ for Improvement of Lighting-emitting Diode Reliability, *J. Phys. Chem. Solids*, Vol. 116, 2018, pp. 118-125, <https://doi.org/10.1016/j.jpcs.2018.01.020>.
- [17] Q. Z. Dong, C. J. Guo, L. He, X. F. Lu, J. B. Yin, Improving the Moisture Resistance and Luminescent Properties of $\text{K}_2\text{TiF}_6:\text{Mn}^{4+}$ by Coating with CaF_2 , *Mater. Res. Bull*, Vol. 115, 2019, pp. 98-104, <https://doi.org/10.1016/j.materresbull.2019.03.020>.
- [18] L. Huang, Y. Liu, S. Si, M. G. Brik, C. Wang, J. Wang, A New Reductive DL-mandelic Acid Loading Approach for Moisture-stable Mn^{4+} Doped Fluorides, *Chem. Commun*, Vol. 54, 2018, pp. 11857-11860, <https://doi.org/10.1039/C8CC05850D>.

- [19] R. Verstraete, G. Rampelberg, H. Rijckaert, I. Van Driessche, E. Coetsee, M. M. Duvenhage, P. F. Smet, C. Detavernier, H. Swart, D. Poelman, Stabilizing Fluoride Phosphors: Surface Modification by Atomic Layer Deposition, *Chem. Mater.*, Vol. 31, No. 18, 2019, pp. 7192-7202, <https://doi.org/10.1021/acs.chemmater.9b01491>.
- [20] H. F. Sijbom, J. J. Joos, L. I. D. J. Martin, K. Van den Eeckhout, D. Poelman, 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.*, Vol. 5, No. 1, 2016, pp. R3040-R3048, <https://doi.org/10.1149/2.0051601jss>.
- [21] W. T. Thompson, D. G. W. Goad, Some Thermodynamic Properties of K_3AlF_6 - $KAlF_4$ Melts, *Can. J. Chem.*, Vol. 54, No. 21, 1976, pp.3342-3349, <https://doi.org/10.1139/v76-481>.
- [22] D. R. Lide, *Handbook of Chemistry and Physics*, 98th ed., CRC Press/Taylor & Francis, B^oCa Raton, 2017.
- [23] L. Lv, X. Jiang, S. Huang, X. Chen, Y. Pan, The Formation Mechanism, Improved Photoluminescence and LED Applications of Red Phosphor $K_2SiF_6:Mn^{4+}$, *J. Mater. Chem. C*, Vol. 2, No. 20, 2014, pp. 3879-3884, <https://doi.org/10.1039/C4TC00087K>.
- [24] E. Song, J. Wang, J. Shi, T. Deng, S. Ye, M. Peng, J. Wang, L. Wondraczek, Q. Zhang, Highly Efficient and Thermally Stable $K_3AlF_6:Mn^{4+}$ as a Red Phosphor for Ultra-high-performance Warm White Light-emitting Diodes, *ACS Appl. Mater. Interfaces*, Vol. 9, No. 10, 2017, pp. 8805-8812, <https://doi.org/10.1021/acsami.7b00749>.
- [25] T. Senden, R. G. Geitenbeek, A. Meijerink, Co-precipitation Synthesis and Optical Properties of Mn^{4+} -doped Hexafluoroaluminate W-LED Phosphors, *Materials*, Vol. 10, No. 11, 2017, pp. 1322, <https://doi.org/10.3390/ma10111322>.
- [26] H. J. H. Bode, F. Bandte, Über eine neue Darstellung des Kalium-hexafluoromanganats(IV), *Angew. Chem.*, Vol. 65, No. 11, 1953, pp. 304, <https://doi.org/10.1002/ange.19530651108>.
- [27] A. G. Paulusz, Efficient Mn (IV) Emission in Fluorine Coordination, *J. Electr^oChem. S^oC*, Vol. 120, No. 7, 1973, pp. 942, <https://doi.org/10.1149/1.2403605>.