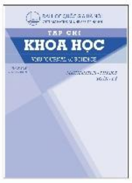
VNU Journal of Science: Mathematics – Physics, Vol. 40, No. 2 (2024) 49-55

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP



Original Article

# Comparing the Luminescence and Moisture Resistance of $K_3AlF_6$:$Mn^{4+}$ Phosphor to Commercial Phosphors

Nguyen Thi Kim Lien, Nguyen Duy Hung*

*School of Materials Science and Engineering, Hanoi University of Science and Technology,*
*1 Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam*

Received 10 November 2023
Revised 29 March 2024; Accepted 15 May 2024

**Abstract:** Nowadays, red-emitting phosphors based on $Mn^{4+}$ doped fluorides with a high color purity and a relatively short decay time can improve the optical performance of WLED. However, they are easily oxidized in humid environment and elevated temperatures. This is the reason why both the brightness and luminous efficiency of WLED quikly decreased. To solve this problem, KF was added throughout the $K_3AlF_6$:$Mn^{4+}$ phosphor synthesis process (KKAFM). This work is focused on aging evaluation of the phosphors and comparing its performance with commercial phosphors (YAG:$Ce^{3+}$, $Sr_2Si_5N_8$:$Eu^{2+}$). Thus, EL spectra of blue LED chips coated with the phosphors were investigated over time in an environment of 85 % RH and 85 °C. The results of EL spectra showed the improvement in the the reduction of the emission intensity of KKAFM. Aging tests of WLEDs using KKAFM and $Sr_2Si_5N_8$:$Eu^{2+}$ indicated that KKAFM phosphors exhibited a good stability, thus they can be used as a potential replacement for commercial red-emitting phosphors in WLEDs fabrication.

*Keywords*: $K_3AlF_6$:$Mn^{4+}$, red-emitting phosphor, WLED, moisture resistance.

## 1. Introduction

In recent years, white light-emitting diodes (WLEDs) play an important role in daily life because of their low energy consumption and environmental friendliness [1-4]. Up to now, the advanced commercial WLEDs which have been widely used are typically composed of a blue-emitting LED chip (InGaN) with a yellow phosphor (YAG:$Ce^{3+}$). However, they still have a low color rendering index (CRI) and a high correlated color temperature (CCT) because of the lack of the red-light component.

---

[*] Corresponding author.
*E-mail address:* hung.nguyenduy@hust.edu.vn

https//doi.org/10.25073/2588-1124/vnumap.4893

Thus, many efforts have been developed for producing WLEDs with larger CRI and lower CCT, f.i. by incorporation of red-emitting phosphors.

Among red-emitting phosphors, $Mn^{4+}$-doped fluoride materials have gained significant attention due to their exceptional optical properties. $Mn^{4+}$-doped fluoride phosphors offer advantages such as efficient absorption of a broad range of blue light, emission of narrow-band light within the spectral sensitivity of the human eye, high quantum yield, thermal stability, and excellent CRI. However, the practical applications of these fluoride phosphors have been limited due to their sensitivity to atmospheric moisture. Prolonged exposure to high temperatures and humidity under LED operating conditions causes hydrolysis of the phosphors, resulting in the formation of hydrated $MnO_2$ and a noticeable decrease in brightness and luminous efficiency. The way for the advancements in moisture-resistant fluoride phosphors for WLEDs have recently focused on coating the moisture-sensitive phosphors with hydrophobic materials to improve their durability under operating conditions of the devices. This coating acts as a protective layer, preventing the intrusion of moisture and enhancing the life-span of WLEDs [5-8].

Among $Mn^{4+}$-doped fluoride phosphors, $K_3AlF_6$:$Mn^{4+}$ garnered significant attention due to its desirable properties, including a high melting point, high decomposition temperature, and low water solubility [9-11]. Previous research groups have synthesized the phosphors using co-precipitation and low-heating state reaction methods and evaluated their performance. To enhance its moisture resistance, $K_3AlF_6$:$Mn^{4+}$ has been coated with oleic acid and reduced graphene oxide [14, 15]. However, there is an urgent need to improve the emission intensity and moisture resistance to meet various application requirements. $Mn^{4+}$ ions are introduced as a replacement for $Al^{3+}$ ions in $K_3AlF_6$ to create positive charge defects [15-17]. However, this is not only reduction of the luminescence intensity but also making the $Mn^{4+}$ ions susceptible to oxidation, resulting in the formation of $MnO_2$. To mitigate these defects for enhancing the luminescence and increasing the durability of the phosphor powder in humid environment, KF has been embedded in during the synthesis process [18].

In this work, the phosphors were coated on blue LED chips, and their moisture resistance were evaluated under high-temperature and high-humidity environments. The moisture resistance of the phosphors was also compared to that of commercial yellow and red phosphors.

## 2. Experimental

### 2.1. Materials

The KKAFM phosphor was synthesized by the co-precipitation method which has been reported in [18].

All commercial products such as blue LED chips, yellow phosphor (YAG:$Ce^{3+}$ - Epoch) and red phosphor ($Sr_2Si_5N_8$:$Eu^{2+}$ - Epoch) were used for the comparison characterization.

### 2.2. Fabrication of LED Devices

Step 1: The KKAFM, YAG:$Ce^{3+}$, and $Sr_2Si_5N_8$:$Eu^{2+}$ phosphor or a mixture of YAG:$Ce^{3+}$ with KKAFM, YAG:$Ce^{3+}$ with $Sr_2Si_5N_8$:$Eu^{2+}$ were weighed according to the calculated mass ratio of 1:10:2 with silicon and a curing agent.

Step 2: Each phosphor or a mixture was blended with silicon and a curing agent using a Kurabo Mazerustar KK-V300SS mixer for a duration of 5 min. Next, the obtained mixture was coated onto the surface of the blue LED chips using an NSW Automation i-DR S320A CE Desktop Dispensing System. The coating process ensured that the phosphors were evenly distributed on the surface of the blue LED chips. After coating, the devices were dried at 70 ºC for 2 hours, followed by additional annealing at 150 ºC for 2 hours. This treatment process helped solidify the coating and ensure its stability.

Finally, the packaged LEDs were placed in an aging chamber under conditions of 85 °C and 85% relative humidity (RH). This aging chamber provided a controlled environment to simulate long-term usage conditions and evaluate the performance of the devices over time.

Fluorescence spectra of the phosphors were recorded using a Horiba NanoLog spectrofluorophotometer equipped with a 450 W Xenon lamp. The photoelectronic properties of the devices were recorded using an integrating sphere connected to a Gamma Scientific spectrofluorometer.

## 3. Results and Discussion

### 3.1. Luminescence of the Phosphors

The fluorescence characteristics of the phosphors were evaluated at room temperature before coating to the blue LED chips. Figure 1a illustrates the fluorescence spectra of the phosphors when excited by a 460 nm wavelength. The KKAFM phosphor shows sharp emission peaks at 596 nm, 605 nm, 608 nm, 610 nm, 627 nm, 631 nm, and 644 nm. These emission peaks are attributed to different vibration modes, including anti-Stokes ($v_3(t_{1u})$, $v_4(t_{1u})$), $v_6(t_{1u})$), zero phonon line, and Stokes ($v_6(t_{2u})$), ($v_4(t_{2u})$, $v_3(t_{2u})$) [12-15, 18]. On the other hand, YAG:$Ce^{3+}$ and $Sr_2Si_5N_8$:$Eu^{2+}$ phosphors exhibit broad spectra with peaks at 530 nm and 620 nm, respectively. The emission peak at 530 nm of YAG:$Ce^{3+}$ arises from transitions between the lowest Stark level of the 5d excited state and the two Stark levels ($2F_{5/2}$ and $2F_{7/2}$) of the 4f ground state of $Ce^{3+}$ [19]. During that the emission peak at 620 nm of $Sr_2Si_5N_8$:$Eu^{2+}$ phosphor is assigned to the $4f^65d^1 \rightarrow 4f^7$ (5d-4f) transition of $Eu^{2+}$ [20]. In terms of intensity, the KKAFM phosphor exhibits higher intensity compared to commercial phosphors. The excitation fluorescence spectrum of the KKAFM phosphor was measured at the emission peak of 627 nm showing an absorption band that extends from the ultraviolet (UV) to 525 nm. The absorption spectrum of this phosphor powder shows two absorption peaks at 360 nm and 460 nm, corresponding to electronic transitions from the $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ levels, respectively. Similarly, the YAG:$Ce^{3+}$ phosphor powder, measured at 540 nm, presents two absorption peaks at 340 nm and 457 nm, attributed to 4f5d transitions of the $Ce^{3+}$ ions. The $Sr_2Si_5N_8$:$Eu^{2+}$ phosphor exhibits a broad absorption band from UV to 600 nm. From the emission spectrum of YAG:$Ce^{3+}$ and the excitation spectrum of $Sr_2Si_5N_8$:$Eu^{2+}$, it is evident that the $Sr_2Si_5N_8$:$Eu^{2+}$ phosphor absorbs the emission light of YAG:$Ce^{3+}$. This reabsorption of the red-emitting $Sr_2Si_5N_8$:$Eu^{2+}$ phosphor reduces the efficiency of the WLED when the phosphor is combined with YAG:$Ce^{3+}$.

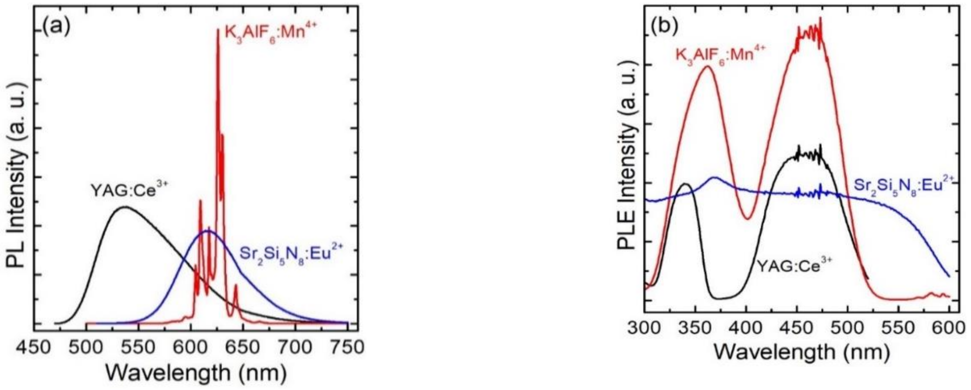


Figure 1. PL (a) and PLE (b) spectra of KKAFM, YAG:$Ce^{3+}$, and $Sr_2Si_5N_8$:$Eu^{2+}$ phosphors.

In comparison of the red-emitting phosphors, their color purities were calculated from the PL spectra. The chromaticity coordinates of KKAFM are (0.686, 0.319) and $Sr_2Si_5N_8:Eu^{2+}$ are (0.631, 0.368). The color purities of the KKAFM and $Sr_2Si_5N_8:Eu^{2+}$ were determined using Eq. (1):

$$Cp = \frac{\sqrt{(x-x_i)^2+(y-y_i)^2}}{\sqrt{(x_d-x_i)^2+(y_d-y_i)^2}} \times 100\% \tag{1}$$

where ($x$, $y$) are the color coordinates of the red-emitting phosphors, ($x_i$, $y_i$) are the CIE of an equivalent white light with a value of (0.333, 0.333), and ($x_d$, $y_d$) are the chromaticity coordinates corresponding to the dominant wavelength of the light source. The color purities of the three samples were determined to be of 96.49%, 69.56% for the KKAFM and $Sr_2Si_5N_8:Eu^{2+}$, respectively. These results indicate that the color purity of KKAFM is close to 100% and is larger than that of $Sr_2Si_5N_8:Eu^{2+}$.

### *3.2. Aging Testing of the Phosphor with LED Chip*

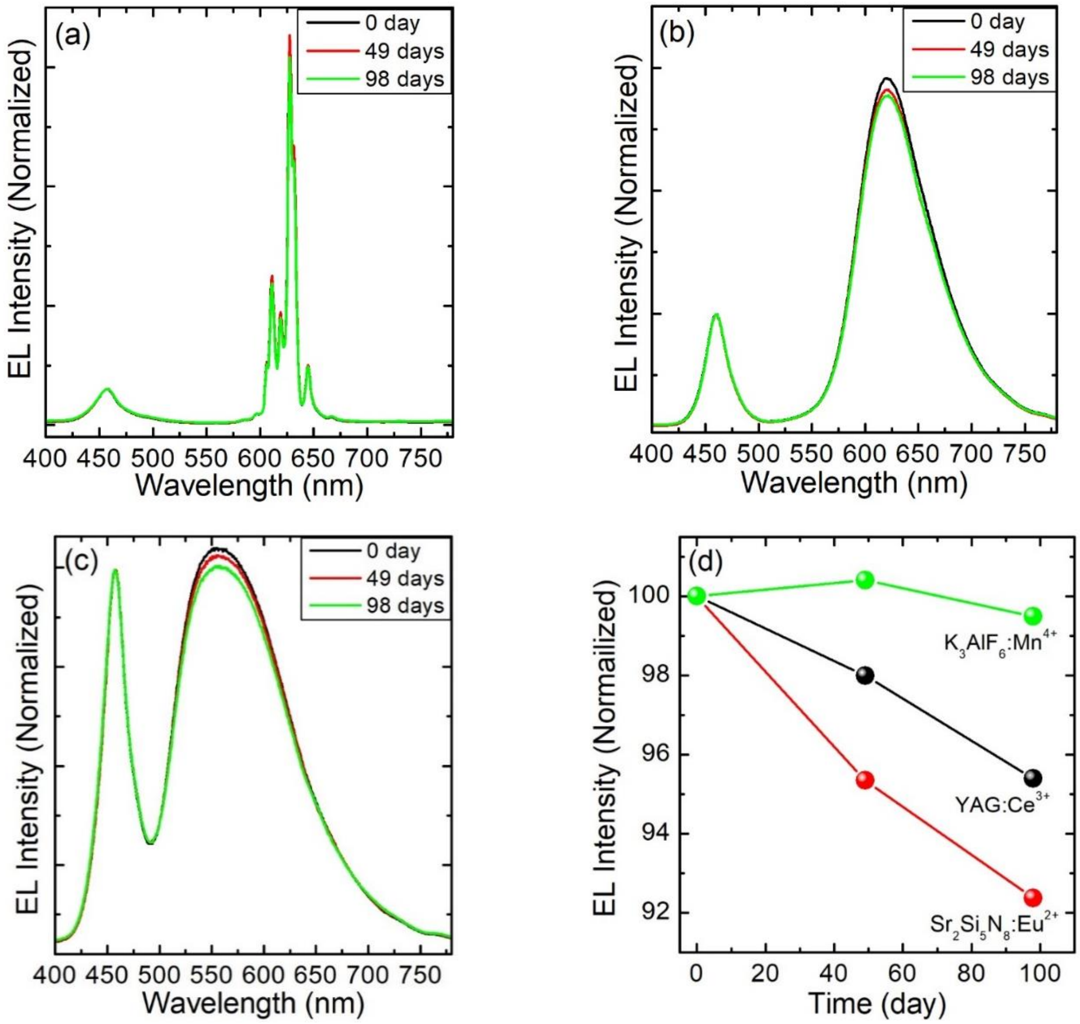


Figure 2. EL spectra of blue LED coated by KKAFM (a), $Sr_2Si_5N_8:Eu^{2+}$ (b), $YAG:Ce^{3+}$ (c), and EL intensity of the phosphors (d) which were measured at various times.

The devices packaged with individual phosphors were incubated in a climate chamber set at a temperature of 85 °C and a humidity of 85%. The optoelectronic characterization of these components was performed for 98 days. The EL spectra of the LED chips coated with each type of fluorescent powder include spectral regions with peaks at 460 nm (blue LED chip) and 627 nm (KKAFM), 530 nm (YAG:$Ce^{3+}$), 620 nm ($Sr_2Si_5N_8$:$Eu^{2+}$). To compare the degradation between the phosphors, the EL spectra of the devices were normalized at the peak of LED chip (460 nm). It has been observed that the spectral sharps of the phosphors are unchanged.

However, their fluorescence intensities decrease over time. The degradation of the devices is attributed to LED chips, phosphors, and other components [21-23]. From the EL spectra, it has been observed that the intensity emission reduction of the KKAFM is slower than that of YAG:$Ce^{3+}$ and $Sr_2Si_5N_8$:$Eu^{2+}$ phosphors for 98 days (Fig. 3). This indicates that all three phosphors have experienced comparable degradation in terms of fluorescence intensity under the given conditions.

### *3.3. Aging Testing of WLEDs*

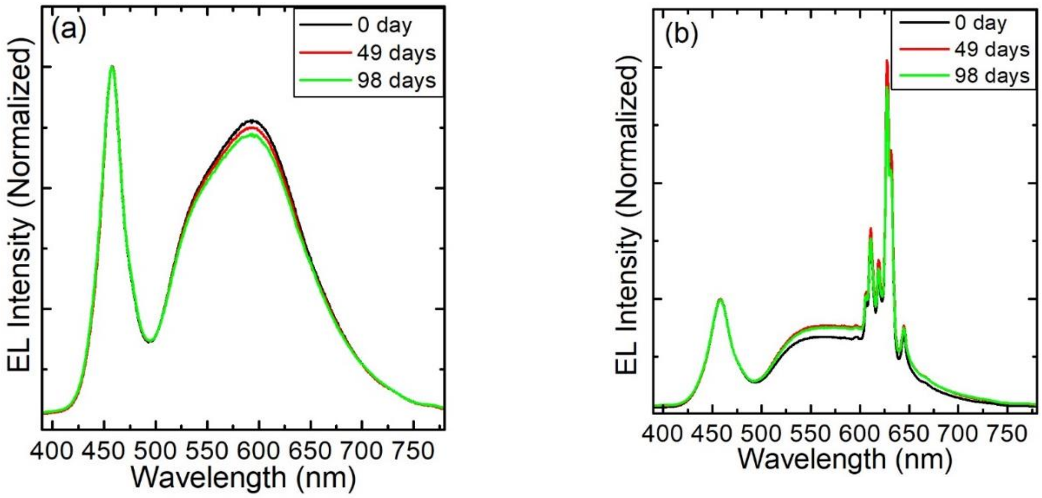


Figure 3. EL spectra of WLED which were coated by the combination of YAG:$Ce^{3+}$ with $Sr_2Si_5N_8$:$Eu^{2+}$ (a) and YAG:$Ce^{3+}$ with KKAFM (b) measured at various times.

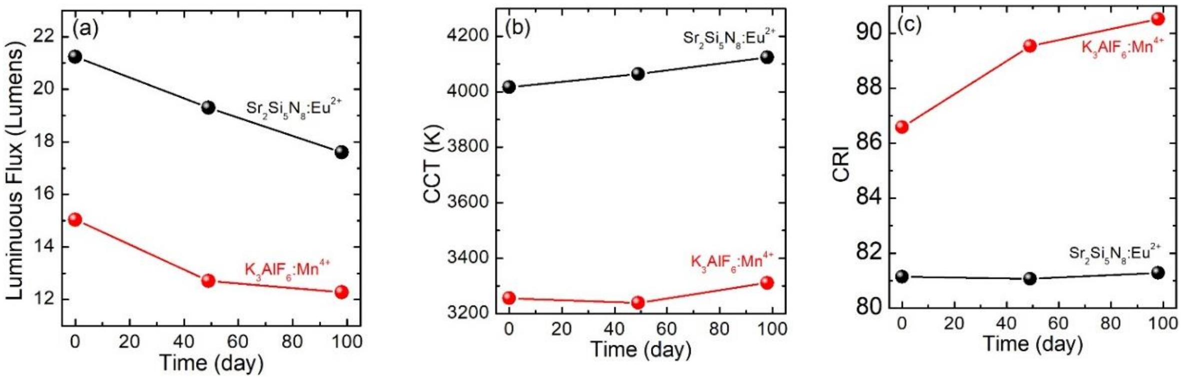


Figure 4. Luminous flux (a), CCT (b), and CRI (c) of the WLEDs used $Sr_2Si_5N_8$:$Eu^{2+}$ and KKAFM phosphors.

In the characterization of the KKAFM phosphor degradation in WLEDs, a test was conducted on a set of WLEDs. The devices were packaged by blue LED chip with $YAG:Ce^{3+}$ and KKAFM phosphors, and another blue LED chip with $YAG:Ce^{3+}$ and $Sr_2Si_5N_8:Eu^{2+}$ phosphors. Figure 4a shows the luminescence flux of the WLEDs plotted against degradation time. It can be observed that the luminescence flux decreases as a function of degradation time, indicating a reduction in the overall light output of the WLEDs. Specifically, the luminous flux of a WLED utilizing $Sr_2Si_5N_8:Eu^{2+}$ phosphor is reported to remain at 82.8% of its initial value after degradation. On the other hand, the WLED using KKAFM phosphor retains 81.6% of its initial luminous flux after degradation.

## 4. Conclusion

The investigation conducted on the moisture resistance of KKAFM phosphor by coating it on a blue LED chip has yielded positive results. After subjecting the phosphor to aging at 85 $^{o}$C and 85% RH for 98 days, the luminescence intensity of the phosphor reduced to 99% of its original intensity. The luminescence intensity reduction can be compared with the one of commercial phosphors. The KKAFM phosphors combined with $YAG:Ce^{3+}$ phosphors were coated on blue chip LEDs to get WLEDs. Aging tests on the WLEDs showed that KKAFM phosphors have a good moisture resistance. The obtained result indicated that KKAFM phosphors may replace the commercial red-emitting phosphors for fabricating WLEDs with improved performance parameters.

## Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.03-2019.45.

## References

[1] S. Adachi, H. Abe, R. Kasa, T. Arai, Synthesis and Properties of Hetero-Dialkalinehexa Fluorosilicate Red Phosphor $KNaSiF_6:Mn^{4+}$, J. Electrochem. Soc., Vol. 159, No. 2, 2011, pp. J34-J37, https://doi.org/10.1149/2.064202jes.

[2] H. D. Nguyen, R. S. Liu, Narrow-band Red-emitting $Mn^{4+}$-doped Hexafluoride Phosphors: Synthesis, Optoelectronic Properties, and Applications in White Light-Emitting Diodes, J. Mater. Chem. C, Vol. 4, No. 46, 2016, pp. 10759-10775, https://doi.org/10.1039/C6TC03292C.

[3] H. F. Sijbom, R. Verstraete, J. J. Joos, D. Poelman, P. F. Smet, $K_2SiF_6:Mn^{4+}$ as a Red Phosphor for Displays and Warm-White Leds: A Review of Properties And Perspectives, Opt. Mater. Express, Vol. 7, No. 9, 2017, pp. 3332-3365, https://doi.org/10.1364/OME.7.003332.

[4] 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, No. 11, 2018, pp. 2652-2671, https://doi.org/10.1039/C8TC00251G.

[5] Q. Z. Dong, C. J. Guo, L. He, X. F. Lu, J. B. Yin, Improving the Moisture Resistance and Luminescent Properties of $K_2TiF_6:Mn^{4+}$ by Coating with $CaF_2$, Mater. Res. Bull., Vol. 115, 2019, pp. 98-104, https://doi.org/10.1016/j.materresbull.2019.03.020.

[6] D. C. Huang, H. M. Zhu, Z. H. Deng, Q. L. Zou, H. Y. Lu, X. D. Yi, W. Guo, C. Z. Lu, X. Y. Chen, Moisture-Resistant $Mn^{4+}$-doped Core-shell-Structured Fluoride Red Phosphor Exhibiting High Luminous Efficacy for Warm White Light-emitting Diodes, Angew. Chem. Int. Ed., Vol. 58, 2019, pp. 3843-3847, https://doi.org/10.1002/anie.201813363.

[7] O. M. T. Kate, Y. J. Zhao, K. M. B. Jansen, J. R. V. Ommen, H. T. Hintzen, Effects of Surface Modification on Optical Properties and Thermal Stability of $K_2SiF_6:Mn^{4+}$ Red Phosphors by Deposition of An Ultrathin $Al_2O_3$ Layer

Using Gas-Phase Deposition in A Fluidized Bed Reactor, ECS J. Solid State Sci. Technol., Vol. 8, 2019, pp. R88-R96, https://doi.org/10.1149/2.0281906jss.

[8] T. C. Lang, T. Han, S. Q. Fang, J. Y. Wang, S. X. Cao, L. L. Peng, B. T. Liu, V. I. Korepanov, A. N. Yakovlev, Improved Phase Stability of the Metastable $K_2GeF_6:Mn^{4+}$ Phosphors with High Thermal Stability and Water-Proof Property by Cation Substitution, Chem. Eng. J., Vol. 380, 2020, pp. 122429 (1-7), https://doi.org/10.1016/j.cej.2019.122429.

[9] V. Danielik, J. Gabčová, Phase Diagram of the System NaF-KF-$AlF_3$. J. Therm. Anal. Cal., Vol. 76, 2004, pp. 763-773, https://doi.org/10.1023/B:JTAN.0000032261.54207.1e.

[10] H. F. Sijbom, J. J. Joos, L. I. D. J. Martin, K. V. D. 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 Solid State Sci. Technol., Vol. 5, No. 1, 2016, pp. R3040-R3048, https://doi.org/10.1149/2.0051601jss.

[11] S. D. Kirik, Y. N. Zaitseva, D. Y. Leshok, A. S. Samoilo, P. S. Dubinin, I. S. Yakimov, D. A. Simakov, A. O. Gusev, NaF–KF–$AlF_3$ System: Phase Transition in $K_2NaAl_3F_{12}$ Ternary Fluoride, Inorg. Chem., Vol. 54, No. 12, 2015, pp. 5960-5969, https://doi.org/10.1021/acs.inorgchem.5b00772.

[12] 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.

[13] Y. Liu, T. Wang, X. Zhang, C. Cao, L. Yang, Y. Huang, S. Liao, H. Zhang, Synthesis, Luminescence Properties and Nephelauxetic Effect of Nano Stick Phosphors $K_3AlF_6:Mn^{4+}$ for Warm White LED, J Mater Sci: Mater Electron, Vol. 30, 2019, pp. 1870-1877, https://doi.org/10.1007/s10854-018-0459-1.

[14] L. Q. Dat, N. T. Lan, N. T. K. Lien, N. V. Quang, C. V. Anh, N. H. Tinh, N. T. Duyen, V. T. K. Thoa, N. T. Hanh, P. T. L. Huong, N. Tu, D. H. Nguyen, Excellent Hydrophobic Property of $K_3AlF_6:Mn^{4+}$ Phosphor by Coating with Reduction Graphene Oxide on the Surface of Materials, Opt. Mater., Vol. 129, 2022, pp. 112552, https://doi.org/10.1016/j.optmat.2022.112552.

[15] D. Peng, S. He, Y. Zhang, L. Yao, W. Nie, Z. Liao, W. Cai, X. Ye, Blue Light-Induced Rare-Earth Free Phosphors for the Highly Sensitive and Selective Imaging of Latent Fingerprints Based on Enhanced Hydrophobic Interaction. J. Mater., Vol. 8, No. 1, 2022, pp. 229-238, https://doi.org/10.1016/j.jmat.2021.03.005.

[16] H. Ming, J. Zhang, L. Liu, J. Peng, F. Du, X. Ye, Luminescent Properties of a $Cs_3AlF_6:Mn^{4+}$ Red Phosphor for Warm White Light-Emitting Diodes, ECS J. Solid State Sci. Technol., Vol. 7, 2018, pp. R149-R155. https://doi.org/10.1149/2.064202jes.

[17] F. A. Kröger, H. J. Vink, Relations Between the Concentrations of Imperfections in Crystalline Solids, Solid State Phys., Vol. 3, 1956, pp. 307-435, https://doi.org/10.1016/S0081-1947(08)60135-6.

[18] D. H. Nguyen, V. L. Pham, V. H. Tran, T. K. L. Nguyen, V. T. Pham, T. K. Pham, X. V. Dao, T. Nguyen, T. H. Pham, Enhanced Quantum Efficiency and Moisture-Resistant Red-Emitting $K_3alf_6$: $Mn^{4+}$ Phosphor for High Color Rendering Index WLED, Optical Materials, Vol. 145, 2023, pp. 114511, https://doi.org/10.1016/j.optmat.2023.114511.

[19] S. Agarwal, M. S. Haseman, A. Khamehchi, P. Saadatkia, D. J. Winarski, F. A. Selim, Physical and Optical Properties of Ce:YAG Nanophosphors and Transparent Ceramics and Observation of Novel Luminescence Phenomenon, Opt. Mater. Express, Vol. 7, 2017, pp. 1055-1065, https://doi.org/10.1364/ome.7.001055.

[20] H. L. Li, R. J. Xie, N. Hirosaki, Y. Yajima, Synthesis and Photoluminescence Properties of $Sr_2Si_5N8:Eu^{2+}$ Red Phosphor by A Gas-Reduction and Nitridation Method, J. Electrochem. Soc., Vol. 155, 2008, pp. J378-J381, https://doi.org/10.1149/1.2999278.

[21] G. Meneghesso, M. Meneghini, E. Zanoni, Recent Results on the Degradation of White LEDs for Lighting, J. Phys. D: Appl. Phys., Vol. 43, 2010, pp. 354007 (1-11), https://doi.org/10.1177/1477153515603757.

[22] S. Hariyani, J. Brgoch, F. Garcia-Santamaria, S. P. Sista; J. E. Murphy, A. A. Setlur, from Lab to Lamp: Understanding Downconverter Degradation in LED Packages, J. Appl. Phys., Vol. 132, 2022, pp. 190901(1-14), https://doi.org/10.1063/5.0122735.

[23] M. A. Hoque, R. K. Bradley, J. Fan, X. Fan, Effects of Humidity and Phosphor on Silicone/Phosphor Composite in White Light-Emitting Diode Package, J. Mater. Sci.: Mater. Elec., Vol. 30, 2019, pp. 20471-20478, https://doi.org/10.1007/s10854-019-02393-8.