TẠP CHÍ KHOA HỌC VÀ CÔNG NGHỆ ĐẠI HỌC DUY TÂN
DTU Journal of Science and Technology 05(78) (226) 28-34
ĐẠI HỌC DUY TÂN
DUYTAN UNIVERSITY

Valence State and Luminescence Properties of Eu in Al_2O_3-SiO_2-Eu_2O_3 Glasses Prepared by Sol-gel Method

Trạng thái hóa trị và tính chất quang của Eu trong thủy tinh Al_2O_3-SiO_2-Eu_2O_3 chế tạo bằng phương pháp sol-gel

Ho Van Tuyen[a*, b], Nguyen Thi Thai An[a, b], Le Van Khoa Bao[a, b], Ho Ngoc Cuong[c], Nguyen Thi Phuong Thao[a, b], Tran Ngo[a, b]
Hồ Văn Tuyến[a*, b], Nguyễn Thị Thái An[a, b], Lê Văn Khoa Bảo[a, b], Hồ Ngọc Cường[c], Nguyễn Thị Phương Thảo[a, b], Trần Ngọ[a, b]

[a]*Institute of Research and Development, Duy Tan University, Da Nang, 550000, Vietnam*
[a]*Viện Nghiên cứu và Phát triển Công nghệ cao, Đại học Duy Tân, Đà Nẵng, 550000, Việt Nam*
[b]*Faculty of Environment and Natural Sciences, School of Engineering and Technology, Duy Tan University, Da Nang, 550000, Vietnam*
[b]*Khoa Môi trường và Khoa học Tự nhiên, Trường Công nghệ và Kỹ thuật, Đại học Duy Tân, Đà Nẵng, 550000, Việt Nam*
[c]*Le Quy Don Specialized High School - Dong Hai, Khanh Hoa, Vietnam*
[c]*Trường Trung học phổ thông chuyên Lê Quý Đôn - Đông Hải, Khánh Hòa, Việt Nam*

(Date of receiving article: 07/09/2026, date of completion of review: 01/10/2026, date of acceptance for posting: 12/10/2026)

Abstract

Eu-doped aluminosilicate glasses with a composition of $5Al_2O_3$–$95SiO_2$ were successfully prepared using the sol–gel method, followed by annealing in air and under a 100% H_2 atmosphere. X-ray diffraction and scanning electron microscopy confirmed the amorphous and homogeneous nature of the prepared glasses, while energy dispersive X-ray spectroscopy (EDS) analysis verified the incorporation of Eu ions. Photoluminescence (PL) and photoluminescence excitation (PLE) measurements revealed the coexistence of Eu^{2+} and Eu^{3+} emissions in the as-prepared glass, indicating that partial reduction of Eu^{3+} to Eu^{2+} occurs even under air atmosphere. This behavior is attributed to the low optical basicity of the prepared $5Al_2O_3$–$95SiO_2$: Eu glass. H_2 annealing significantly enhanced the reduction of Eu^{3+} to Eu^{2+}, resulting in stronger Eu^{2+} emissions. Moreover, the Eu^{2+} emission maximum shifted from 434 to 447 nm after H_2 annealing, which is attributed to the increased crystal-field strength surrounding the Eu^{2+} ions. These results demonstrate that the valence state and luminescence properties of Eu ions can be effectively controlled by adjusting the glass composition and annealing atmosphere, providing a promising approach for developing tunable Eu^{2+}/Eu^{3+} dual-emission luminescent glasses.

Keywords: glass, Eu^{3+}, luminescence, reduction

Tóm tắt

Thủy tinh aluminosilicate $5Al_2O_3$–$95SiO_2$ pha tạp Eu đã được chế tạo thành công bằng phương pháp sol-gel, sau đó được ủ trong không khí và trong môi trường khí khử H_2 100%. Kết quả nhiễu xạ tia X và hiển vi điện tử quét (SEM) đã xác nhận cấu trúc vô định hình và tính đồng nhất của các mẫu, trong khi đó phổ EDS cho thấy sự hiện diện của các ion

[*]*Corresponding author:* Ho Van Tuyen
Email: hovantuyen@gmail.com

Eu trong thủy tinh sau khi chế tạo. Các phép phân tích quang phát quang (PL) và kích thích quang phát quang (PLE) cho thấy sự tồn tại đồng thời của các bức xạ Eu^{2+} và Eu^{3+} trong mẫu thủy tinh sau khi chế tạo; điều này chứng tỏ một phần Eu^{3+} đã được khử thành Eu^{2+} ngay cả khi chế tạo trong môi trường không khí. Hiện tượng này được lý giải là do tính bazơ quang học thấp của thủy tinh $5Al_2O_3$–$95SiO_2$:Eu. Quá trình ủ trong môi trường khí khử 100% H_2 đã thúc đẩy mạnh mẽ quá trình khử từ Eu^{3+} về Eu^{2+}, dẫn đến cường độ phát xạ của Eu^{2+} tăng lên; đồng thời, cực đại phát xạ của Eu^{2+} dịch chuyển từ 434 nm sang 447 nm do sự gia tăng cường độ trường tinh thể xung quanh vị trí ion Eu^{2+}. Những kết quả này chứng minh rằng trạng thái hóa trị và tính chất phát quang của các ion Eu có thể được kiểm soát hiệu quả thông qua việc điều chỉnh thành phần thủy tinh và môi trường ủ, mở ra hướng đi đầy hứa hẹn cho việc phát triển các loại thủy tinh phát quang có khả năng điều chỉnh được sự phát xạ kép Eu^{2+}/Eu^{3+}.

Từ khóa: vật liệu thủy tinh, Eu^{3+}, tính chất quang, quá trình khử

1. Introduction

Aluminosilicate (Al_2O_3–SiO_2: AS) glasses doped with Eu^{3+}/Eu^{2+} ions have been widely investigated for applications in optical solid-state lasers and luminescent materials owing to their excellent thermal stability, high chemical durability, large rare-earth solubility, and superior optical transparency [1-3]. Because Eu^{3+} and Eu^{2+} exhibit significantly different optical properties, controlling the valence state of europium is of great importance for the development of luminescent materials. Eu^{3+} typically exhibits sharp emission lines arising from the forbidden 4f → 4f transitions, which are relatively insensitive to the surrounding crystal field. The red emission of Eu^{3+} can enhance the color rendering index (CRI) of white LEDs and display devices [4, 5]. In contrast, Eu^{2+} exhibits broad-band emission resulting from the allowed 5d → 4f transition. Because the 5d → 4f transition is strongly affected by the crystal field, the emission peak position of Eu^{2+} ions can vary over a wide wavelength range depending on the host material. In addition, because the 5d → 4f transition is an allowed electric-dipole transition, Eu^{2+} luminescent centers generally exhibit high absorption and emission intensities, making them suitable for UV-excited LED applications [6, 7]. The generation of dual Eu^{2+}/Eu^{3+} emission from a single material has attracted considerable attention for applications in optical security and solid-state lighting [8-10]. In a 2024 study [8], Gupta et al. reported that Eu^{2+}/Eu^{3+} dual-emitting glasses could be used for anti-counterfeiting and optical thermometry. In a 2025 study [9], Eu^{2+}/Eu^{3+} dual emission was investigated for potential applications in optical security. Therefore, controlling the relative Eu^{2+}/Eu^{3+} emission intensity provides an effective strategy for tuning the emission color and luminescence efficiency. In this work, Al_2O_3–SiO_2:Eu_2O_3 glasses were synthesized using the sol–gel method, and the Eu^{2+}/Eu^{3+} dual emission was controlled by adjusting the reducing conditions. The structural and luminescent properties of the prepared glasses were systematically investigated.

2. Experimental

In this study, aluminosilicate glasses with a composition of $5Al_2O_3$–$95SiO_2$ doped with 1.0 wt% Eu_2O_3 were prepared using the sol–gel method. The precursors were calculated according to the desired composition and subjected to a hydrolysis process to obtain gel solutions, as shown in Figure 1a. The gel was naturally dried for one month to obtain a dry gel, as illustrated in Figure 1b. Subsequently, the dry gel was annealed at 700°C for 4 h to form the glass. The prepared glass is noted as 5AEu sample. To investigate the reduction of Eu^{3+} ions to Eu^{2+} under a reducing atmosphere, the as-prepared glass sample was subsequently annealed in a 100% H_2 atmosphere at 700 °C for 5 h. The annealed H_2 glass sample was labeled 5AEu-H2. Figure 1c and 1d present photographs of the 5AEu-H2 sample under natural light and 254 nm UV illumination.

The structural properties of the synthesized glass samples were investigated by X-ray diffraction (XRD) using a D8-Advance diffractometer equipped with Cu-Kα radiation (λ = 1.54056 Å; Bruker, Germany). The surface morphology of the samples was examined using a JEOL 6490 scanning electron microscope equipped with a JED2300 system (Japan). The excitation and emission spectra were recorded using an FL322 fluorescence spectrometer (Horiba Jobin-Yvon) with a 450 W Xe lamp as the excitation source.

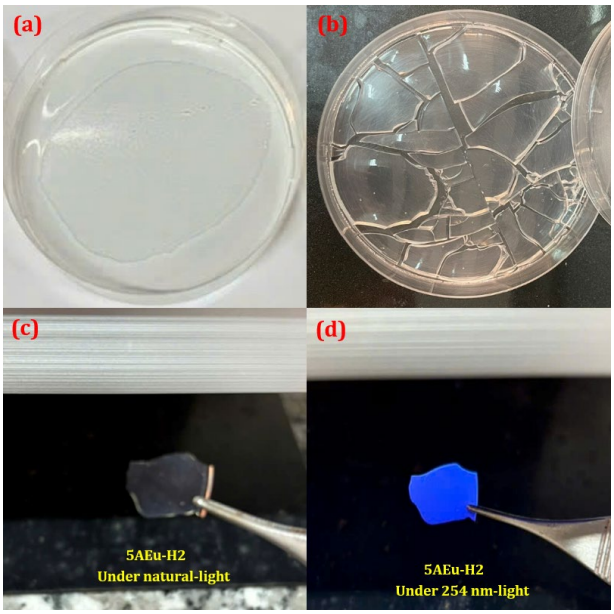


Fig. 1. (a) Sol-gel after hydrolysis process (b) a dense xerogel after one month in air, 5AEu-H2 glass sample under (c) natural light and (d) 254 nm-light.

3. Results and discussion

Figure 2 shows the XRD pattern of the as-prepared 5AEu glass. The XRD pattern exhibits only a broad diffraction band centered at 2θ ≈ 22°. This broad feature is characteristic of the amorphous nature of the aluminosilicate glass network, confirming the absence of long-range structural order. Such an amorphous diffraction profile is commonly observed in silicate-based glass systems containing Al_2O_3.

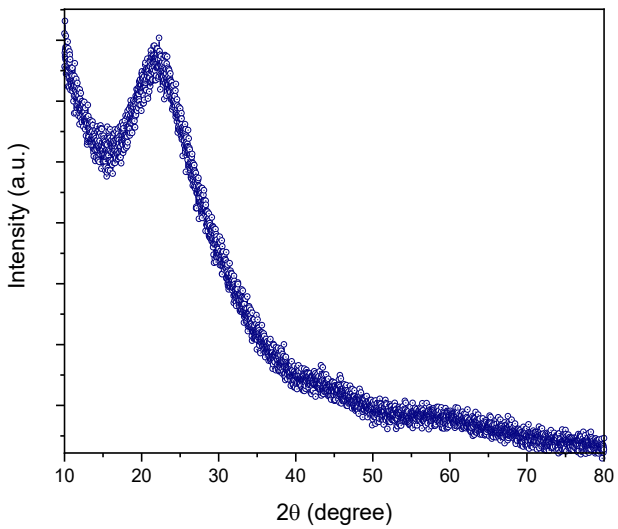


Fig. 2. XRD pattern of the 5AEu prepared glass.

Figure 3 presents the SEM image and EDS spectrum of the 5AEu glass sample. The SEM image shows no evidence of crystal growth, indicating the high homogeneity of the prepared glass. The EDS spectrum in Fig. 3 clearly confirms the presence of the chemical composition in the sample and indicates that Eu ions were successfully incorporated into the glass matrix.

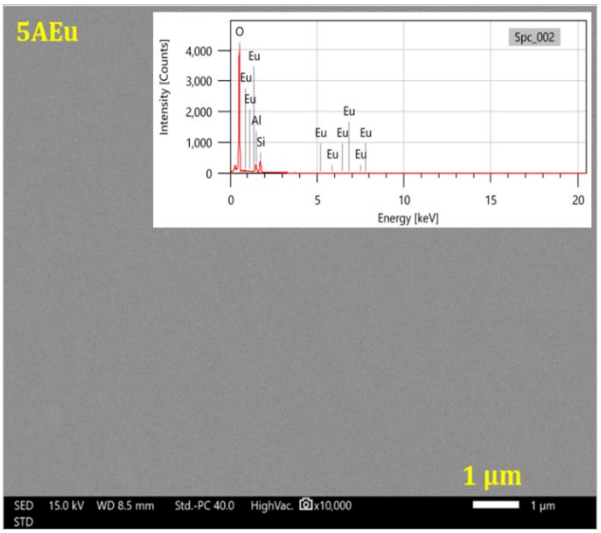


Fig. 3. SEM image and EDS spectrum of the prepared 5AEu glass.

The photoluminescence (PL) spectra of the two samples (5AEu and 5AEu-H2) before and after annealing in a 100% H_2 gas atmosphere are presented in Fig. 4. The PL spectra of the 5AEu and 5AEu-H2 samples under excitation at a wavelength of 360 nm, measured at room temperature, are shown in Fig. 4(a). The PL spectra of both samples exhibit a broad band emission, which is attributed to the 5d-4f electronic transitions of Eu^{2+} ions in the host lattice. However, the emission intensity of the 5AEu-H2 sample is higher than that of the 5AEu sample, and emission maximum position of the 5AEu-H2 sample is shifted toward a longer wavelength. These results indicate that Eu^{3+} ions can be reduced to Eu^{2+} in both the air atmosphere (5AEu sample) and the reducing H_2 atmosphere (5AEu-H2 sample). In addition, the PL spectra reveal that the reduction process is more efficient in the H_2 atmosphere and modifies the crystal field surrounding the Eu^{2+} ions. Fig. 4(b) presents the PL spectra of two samples under excitation at wavelength of the 393 nm, which was selected as the excitation wavelength for Eu^{3+} emission corresponding to the most excited transition ($^7F_0$-$^5L_6$ transition). The PL spectra include several sharp emission peaks in the 550-725 nm region, which are assigned to the 4f-4f electronic transitions of Eu^{3+} ions. Among these, the emission peak at 612 nm, corresponding to the $^5D_0$-$^7F_2$ transition, exhibits the highest intensity and contributes predominantly to the red emission of Eu^{3+} in the 5AEu sample. Several weaker peaks are observed at 577, 591, 654, and 702 nm, which are attributed to the $^5D_0$-^7F_J transitions (J=0, 1, 3, and 4) of Eu^{3+} ions. As shown in Fig. 4(b), the emission intensity at 612 nm for the 5AEu-H2 sample is significantly lower than that of the 5AEu sample, indicating that the Eu^{3+} ions are well reduced to Eu^{2+} ions during annealing in the H_2 annealing.

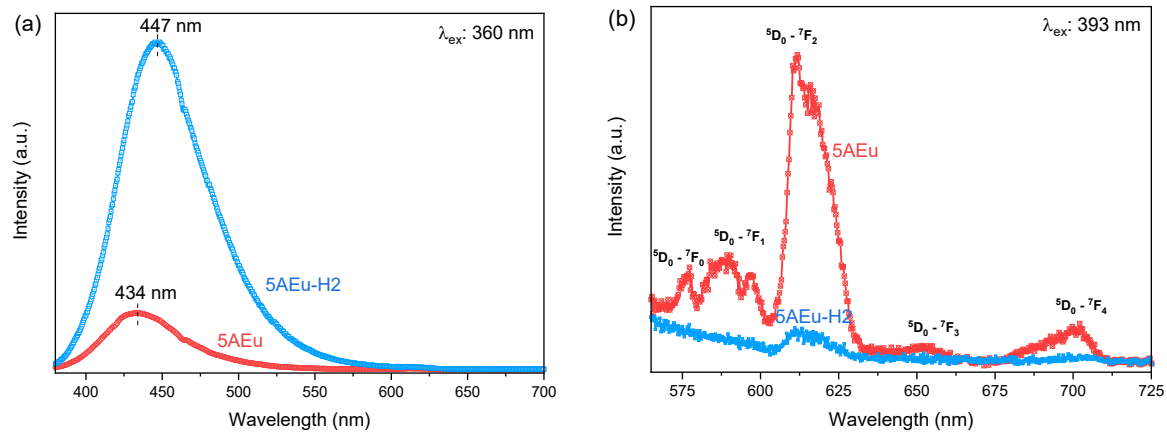


Fig. 4. PL spectra of the 5AEu and 5AEu-H2 glass samples under excitation wavelength of (a) 360 nm and (b) 393 nm.

The reduction of Eu^{3+} ions to Eu^{2+} ions in the air condition is an interesting observation because rare-earth ions (Eu^{3+} and Sm^{3+}) are usually reduced by annealing in the strong reducing environments such as H_2/N_2 [11, 12] or through interaction with X-rays [12, 13] or lasers [14]. Hence, the observed reduction of Eu^{3+} ions in the air condition in this work enables dual emission Eu^{3+}/Eu^{2+} in the glass sample without the need for a reducing atmosphere. This reduction process in the air environment of the 5AEu glass can be explained through the optical basicity model proposed by Duffy and Ingram [15]. In this model, the optical basicity for a glass is expressed as $\Lambda = \sum X_i \Lambda_i$, where X_i is the equivalent oxygen fraction of the i^{th} oxide component relative to the overall glass, and Λ_i is the optical basicity of oxide component. With the Λ_i known values of SiO_2 and Al_2O_3 are 0.48 and 0.6, respectively, the Λ calculated value for the 5AEu glass sample is 0.488, which is less than the critical value of 0.585. According to this theory, glasses with lower optical basicity possess a greater ability to form a lower valence state. Consequently, a part of the Eu^{3+} ions in the 5AEu glass can be reduced to lower state of Eu^{2+}, resulting in Eu^{2+} emission from the sample prepared in air (5AEu), as shown in the Fig. 4(a).

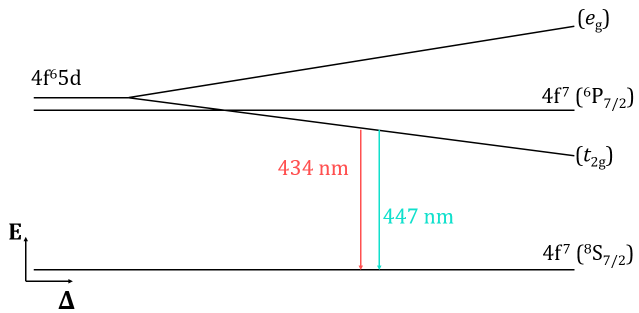


Fig. 5. Crystal field splitting of Eu^{2+} in the 5AEu and 5AEu-H2 glasses.

Furthermore, the results in Fig. 4(a) reveal a red shift in the emission maximum of the H_2-annealed sample (5AEu-H2 sample) compared with that of the air-prepared sample (5AEu sample). This result indicates that the crystal field surrounding the Eu^{2+} ions in the 5AEu-H2 sample is stronger [16, 17]. The red shift is more clearly demonstrated in Fig. 5, which shows the different Eu^{2+} emission maximum positions at 434 and 447 nm for two glasses. It is well known

that the lowest 5d level (e_g) of Eu^{2+} shifts to lower energy under a strong crystal field [16, 17]. Therefore, the 5d-4f emission band of Eu^{2+} will shift toward the red wavelength when Eu^{2+} ions are in a stronger crystal field.

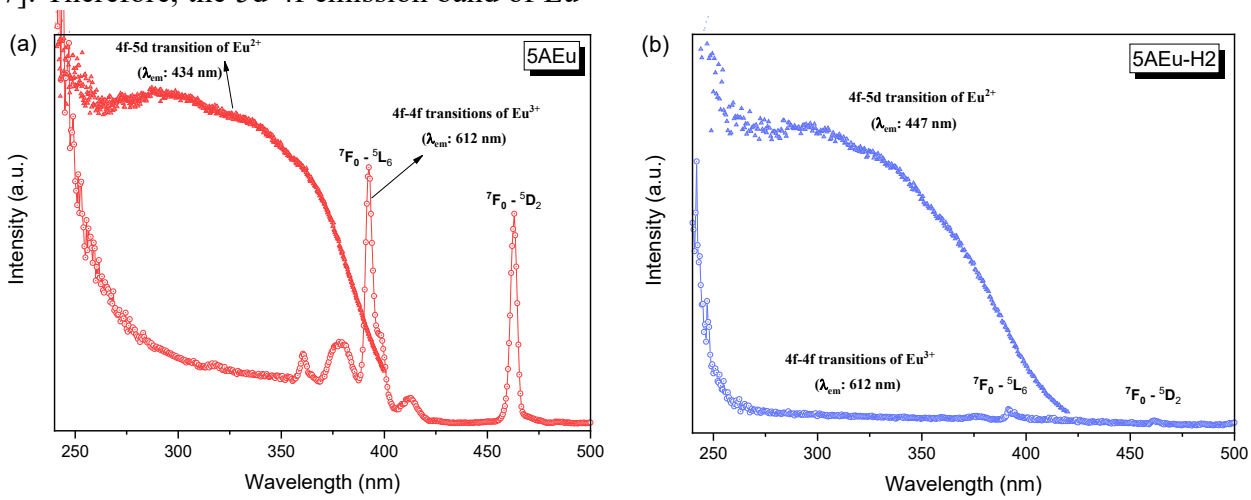


Fig. 6. PLE spectra of the (a) 5AEu and (b) 5AEu-H2 glass samples.

Figure 6 shows the photoluminescence excitation (PLE) spectra of the (a) 5AEu and (b) 5AEu-H2 glass samples. For the 5AEu sample, the PLE spectrum monitored at 434 nm (Eu^{2+} emission) exhibits a broad excitation band in the UV region, which is attributed to the allowed 4f–5d transitions of Eu^{2+} ions. In addition, several sharp excitation peaks are observed in the 350–400 nm region, corresponding to the characteristic 4f–4f transitions of Eu^{3+} ions when monitored at 612 nm (Eu^{3+} emission). The excitation peak near 393 nm is assigned to the $^7F_0$-$^5L_6$ transition of Eu^{3+}. For the 5AEu-H2 sample, a broad excitation band is also observed when monitoring the emission at 447 nm of Eu^{2+}, confirming the presence of Eu^{2+} ions. Compared with the 5AEu sample, the Eu^{2+} excitation band extends over the UV–visible region and is associated with the 4f–5d transitions of Eu^{2+}. The sharp Eu^{3+}-related excitation peaks are strongly suppressed compared with the 5AEu sample, particularly the peak near 393 nm monitored at 612 nm. This result further confirms that annealing in a 100% H_2 atmosphere promotes the reduction of Eu^{3+} to Eu^{2+}, resulting in enhanced Eu^{2+} emission and significantly weakened Eu^{3+} emission.

4. Conclusion

In this work, homogeneous amorphous $5Al_2O_3$–$95SiO_2$ glasses doped with 1.0 wt% Eu_2O_3 were successfully prepared by the sol–gel method. PL results revealed the coexistence of Eu^{2+} and Eu^{3+} emissions in the as-prepared glass, indicating that partial reduction of Eu^{3+} to Eu^{2+} can occur even in air atmosphere due to the low optical basicity of the glass. Annealing in 100% H_2 significantly enhanced the $Eu^{3+} \rightarrow Eu^{2+}$ reduction and increased the Eu2+ emission intensity. The red shift of the Eu^{2+} emission from 434 to 447 nm after H_2 annealing was attributed to the strong crystal field surrounding the Eu^{2+} ions. These results demonstrate that the luminescence properties and Eu ion valence states can be effectively tuned by controlling the glass composition and annealing atmosphere.

Acknowledgements

This research is funded by Vietnam National Foundation for Science and Technology

Development (NAFOSTED) under grant number 103.03–2025.30.

References

[1] G.A. Rosales-Sosa, A. Masuno, Y. Higo, H. Inoue. (2016). "Crack-resistant Al_2O_3-SiO_2 glasses". *Sci Rep* (6), 23620.

[2] L. Liu, X. Shao, Z. Zhang, J. Liu, Y. Hu, C. Zhu. (2023). "Spectral properties and self-reduction of Eu^{3+} to Eu^{2+} in aluminosilicate oxyfluoride glass". *RSC Advances* (13), 23708-23715.

[3] Y. Ma, M. Fei, W. Zhang, L. Teng, F. Hu, R. Wei, H. Guo. (2020). "Energy transfer and tunable luminescent properties in Eu^{2+}/Tb^{3+}/Eu^{3+} co-doped oxyfluoride aluminosilicate glass". *Journal of Luminescence* (219), 116966.

[4] Y. Hua, S.K. Hussain, J.S. Yu. (2019). "Eu^{3+}-activated double perovskite Sr_3MoO_6 phosphors with excellent color purity for high CRI WLEDs and flexible display film". *Ceramics International* (45), 18604-18613.

[5] Y. Wang, Z. Liang, K. Jiang, Y. Lin, D. He, J. Liu, W. Wang, J. Wang, B. Deng, D. Zhan, R. Yu. (2023). "$SrLaNaTeO_6$:Eu^{3+} red-emitting phosphors with high luminescence efficiency and high thermal stability for high CRI white LEDs". *Ceramics International* (49), 579-590.

[6] Y. Chen, H. Zhang, Y.-Y. Sun. (2025). "Eu^{2+} doped $Ba_2Sc_2B_4O_{11}$ phosphor for UV-violet-excited white LEDs". *Journal of Luminescence* (285), 121315.

[7] Z. Xu, B. Devakumar, N. Ma, W. Li, X. Huang. (2022). "High-brightness cyan-emitting Eu^{2+}-activated orthophosphate phosphors for near-UV-pumped white LEDs". *Journal of Luminescence* (243), 118640.

[8] S.K. Gupta, P.S. Ghosh, A. Arya, V. Natarajan. (2024). "Origin of blue emission in ThO_2 Nanorods: Exploring it as a host for photoluminescence of Eu^{3+}, Tb^{3+} and Dy^{3+}". *RSC Advances* (4), 51244-51255.

[9] C. Sun, T. Zhu, Y. Yue, X. Wang. (2025). "Tunable emission properties and energy transfer of Tb^{3+}/Eu^{3+} co-activated glasses for anti-counterfeiting". *Journal of Alloys and Compounds* (1040), 183516.

[10] S.B. Mallur, T.C. Khoo, S. Rijal, O.R. Huff, P.K. Babu. (2021). "Peak stimulated emission cross sections and quantum efficiencies of Sm^{3+} and Sm^{3+}-Eu^{3+} co-doped bismuth boro-tellurite glasses". *Materials Chemistry and Physics* (258), 123886.

[11] N.T.Q. Lien, L.X. Hung, N.T.P. Thao, T.T. Hong, T.N. Dat, N.N. Trac, P.V. Do, H.V. Tuyen. (2025). "Reduction process and energy transfer from Eu^{3+}/Sm^{3+} co-doped $Sr_2MgSi_2O_7$ phosphors by heat treatment in 100% H_2 gas environment". *Journal of Physics and Chemistry of Solids* (200), 112591.

[12] Y. Huang, K. Jang, W. Zhao, E. Cho, H.S. Lee, X. Wang, D. Qin, Y. Zhang, C. Jiang, H.J. Seo. (2007). "Irradiation-induced reduction and luminescence properties of Sm^{2+} doped in $BaBPO_5$". *Journal of Solid State Chemistry* (180), 3325-3332.

[13] G. Okada, N. Ikenaga, Y. Koguchi, T. Yanagida, S. Kasap, H. Nanto. (2023). "X-ray induced reduction of Sm^{3+} into Sm^{2+} in Li_2CaSiO_4 and its potential for radiation measurement applications". *Materials Research Bulletin* (159), 112107.

[14] G.J. Park, T. Hayakawa, M. Nogami. (2003). "Formation of Sm^{2+} ions in femtosecond laser excited Al_2O_3 – SiO_2 glasses". *Journal of Physics: Condensed Matter* (15), 1259.

[15] J.A. Duffy, M.D. Ingram. (1976). "An interpretation of glass chemistry in terms of the optical basicity concept". *Journal of Non-Crystalline Solids* (21), 373-410.

[16] Y. Jia, A. Miglio, S. Poncé, M. Mikami, a.X. Gonze. (2017). "First-principles study of the luminescence of Eu^{2+}-doped phosphors". *Physical Review B* (96), 089902.

[17] H. Li, R. Li, C. Chang. (2022). "Red-shift and improved afterglow of Sr_3Al_2-$xB_xO_5Cl_2$:Eu^{2+}, Dy^{3+} phosphors via a cation substitution strategy". *Ceramics International* (48), 1814-1819.