

DEVELOPMENT OF GLAZE CONTAINING Eu^{3+} IONS FOR THE LUMINESCENT ARTWORK APPLICATION

Suebpong Powthai¹, Yotsakit Ruangtawee^{1,2,*}, Nawarut Jarucha^{1,2} and Jakrapong Kaewkhao^{1,2}

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Abstract

In this work, the luminescent properties of opaque glaze sample containing Eu^{3+} ions were investigated. The results revealed that the major chemical composition consisted of SiO_2 and Eu_2O_3 which corresponds to the XRD spectrum of glaze sample. The reflectance spectra exhibit photon absorbing of Eu^{3+} ions in the visible to near-infrared regions at 395, 465, 534, 2048, and 2191 nm. The luminescence spectra in the visible region, under the 395 nm excitation wavelength exhibited emissions at 578 nm ($5\text{D}_0 \rightarrow 7\text{F}_0$), 593 nm ($5\text{D}_0 \rightarrow 7\text{F}_1$), 611 nm ($5\text{D}_0 \rightarrow 7\text{F}_2$), 651 nm ($5\text{D}_0 \rightarrow 7\text{F}_3$) and 703 nm ($5\text{D}_0 \rightarrow 7\text{F}_4$). The decay time for the 7F_2 level of Eu^{3+} ions was also analyzed. Additionally, the CIE 1931 chromaticity diagram investigation found that the luminescence falls within the red-orange color region.

Keywords: Glaze; Luminescent Properties; Europium ions

Introduction

Over the last few decades, the potential applications of luminescent materials in the field of photonic devices, color display, and solid-state lasers have garnered significant attention due to their unique optical properties (Fuertes *et al.*, 2019). It is well known that rare earth ions (RE) have received particular attention as photoluminescent pigments associated with the 4f-4f and 4f-5d electron configuration which can exhibit a variety of excitation and emission over a broad spectral ultraviolet to the near-infrared region (Ichoja *et al.*, 2020; Jarucha *et al.*, 2022). Among RE ions, europium ions (Eu^{3+}) have been especially intriguing

and extensively researched due to their intense emission in the visible region with prominent orange and red emissions corresponding to $5\text{D}_0 \rightarrow 7\text{F}_1$ and $5\text{D}_0 \rightarrow 7\text{F}_2$ transitions, respectively. (Chen *et al.*, 2021; Szpikowska-Sroka *et al.*, 2021). Especially, $5\text{D}_0 \rightarrow 7\text{F}_2$ transition exhibits a strong red emission band with higher intensity compared to other ions that are suitable for various applications such as red laser, optical fibers, optical amplifiers, as well as scintillators (De *et al.*, 2020). Recently, there have been several reports of glass materials used as host composition for Eu^{3+} ions doping (Dalhatu *et al.*, 2016). Research and

¹ Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand.

² Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand.

* Corresponding author

development efforts focused on finding new materials as host matrix for RE ions doping. The opaque glaze is considered an attractive host for RE ions because its properties can enhance the absorption and emission efficiency of RE ions (Chen *et al.*, 2009). However, the luminescence properties of opaque glaze with RE ions have not many investigated in this field. In this work, the opaque glaze sample containing Eu^{3+} ions was intensively studied on optical properties such as absorption, luminescence and lifetime.

Experiment

In this work, the glaze sample (3Eu_g) were prepared by clear semi-matt glaze process. A powdered frit material from the ceramic industry and chemical Eu_2O_3 was utilized as a precursor to glaze preparation. In the preparation process, the mixture batches were ground to reduce the particle size by using an alumina ball mill for 6 hours. After that, the fine powder is mixed with water in a ratio 1:1 to produce a glaze slurry. The obtained glaze slurry was melted in an electric furnace at 1220°C for 6 hours before cooldown at room temperature. The optical absorption spectra were measured with a UV-vis and NIR spectrophotometer (Shimadzu UV-3600) in the wavelength range of 200-2500 nm. The emission color was evaluated using the chromaticity protocol designed by the Commission Internationale de l'Éclairage in 1931 (CIE 1931). The chemical compositions of sample by energy dispersive X-rays fluorescence (EDXRF) with standardless mode supplied by Philips model PW2400. The X-ray diffraction (XRD) was used to define the glaze ceramic structure by a diffractometer (SmartLab SE, Rigaku). The luminescence spectra were carried out using a Fluorescence Spectrophotometer (Cary Eclipse). Figure 1. on the left is a glaze sample under normal lighting. The Figure on the right is a glaze sample that was irradiated with UV excitation, causing the glaze sample to emit red light due to doped Eu_2O_3 .

Results and Discussion

X-ray fluorescence (EDXRF)

The chemical composition analysis of glaze samples using energy dispersive X-ray fluorescence (EDXRF) with standardless mode is presented in Table 1. The result indicates that the 3Eu_g was essentially composed of silicon oxide

(SiO_2) about 41.168 % by weight. The composition of europium oxide (Eu_2O_3) and calcium oxide (CaO) were 20.978 and 11.737 % by weight as 2nd and 3rd respectively. While the major composition of glaze sample without Eu_2O_3 (Blank) consisted of SiO_2 (39.664 %), ZnO (28.865 %) and CaO (14.655 %), respectively.

X-ray diffractometry (XRD)

The XRD patterns of Blank and 3Eu_g sample in the range $2\theta = 10^\circ$ - 80° using the Cu-K α radiation with wavelength $\lambda = 1.54056\text{\AA}$ are presented in Figure 2. It can be noticed the two prominent diffraction peaks appearing at $2\theta = 26.7^\circ$, 28° and the minor peaks which attributed to the SiO_2 phase (PDF# 00-013-0026). In addition, the XRD patterns of europium phase can be observed as main peaks around $2\theta = 26.7^\circ$, 27.5° , 28° and 29.5° which are assigned to the EuH_3O_3 form (PDF# 93-403-1477). However, the hydrogen atom in glaze structure may be caused by the infiltration of moisture. The appearance of these peaks confirms the silica and europium crystallinity in glaze structure, while the Blank sample showed SiO_2 phase in the range of approximately 28° .



Figure 1. The 3Eu_g glaze samples

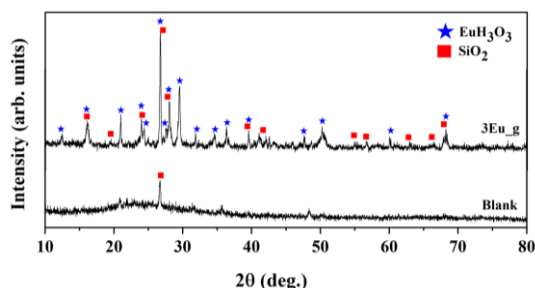


Figure 2. The XRD patterns

Table 1. Chemical composition analysis using XRF

Sample	% By weight							
	SiO ₂	Al ₂ O ₃	K ₂ O	CaO	ZnO	BaO	Eu ₂ O ₃	Fe ₂ O ₃
Blank	39.664	3.622	5.088	14.655	28.865	6.940	-	1.063
3Eu_g	41.168	6.856	2.160	11.737	10.113	6.987	20.978	0.356

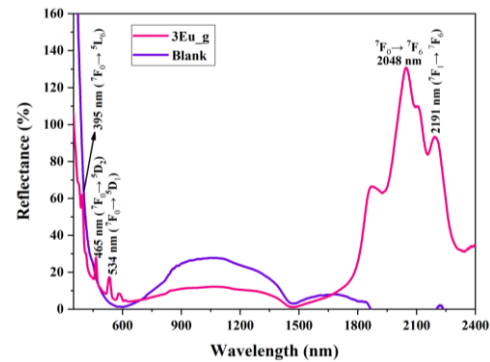
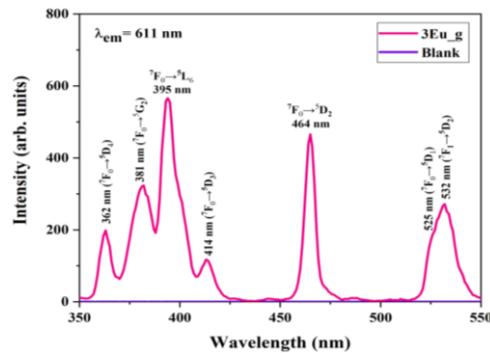
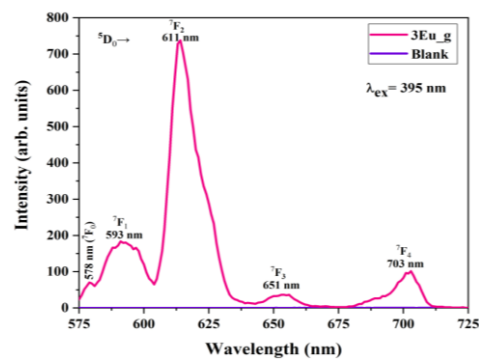
Reflectance spectra

Figure 3 displays the reflectance spectra of 3Eu_g sample in the wavelength range of 300–2,400 nm at room temperature. The 5 reflectance bands were observed at 395, 465, 525, 534, 2048, and 2191 nm associated with Eu³⁺ transitions of ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_1$, ${}^7F_0 \rightarrow {}^5D_2$, ${}^7F_1 \rightarrow {}^5D_1$, ${}^7F_0 \rightarrow {}^7F_6$, and ${}^7F_1 \rightarrow {}^7F_6$, respectively. It found the highest reflectance peak at 395 nm (${}^7F_0 \rightarrow {}^5L_6$) in visible region and 2048 nm (${}^7F_0 \rightarrow {}^7F_6$) in near-infrared region. In the transitions within 4f shell, electric dipole (ED) transitions are forbidden but magnetic dipole (MD) and electric quadrupole transitions are allowed by Laporte selection rule. The sharp and intense ${}^7F_0 \rightarrow {}^5L_6$ transition is forbidden by the ΔS and ΔL but allowed by the ΔJ selection rule. However, the band is sharp and intense among the UV-VIS absorption bands which might be a result of mixed parity states that mitigates the Laporte's rule. The absorption intensity comparison between ${}^7F_0 \rightarrow {}^5D_1$ induced MD and ${}^7F_0 \rightarrow {}^5D_2$ induced ED transitions shows that ED is stronger than MD which again violates the selection rule. This is possible when the crystal field is non-centrosymmetric and/or the atom is embedded in a non-centrosymmetric environment (Vijaya and Jayasankar, 2013; Aryal *et al.*, 2020). Meanwhile, the broad peak of Fe²⁺ ions was found at 1,050 nm, the intensity was decreased with the addition of Eu₂O₃ due to the effect of oxidation change between Eu₂O₃ and Fe₂O₃ as shown in Figure 3.

Excitation and emission spectra

The excitation spectra of 3Eu_g sample were observed under the emission wavelength at 611 nm, as illustrated in Figure 4. The result shows that multiple excitation bands of Eu³⁺ ions are located at 362, 381, 395, 414, 464, 525, and 532 nm. The transition of ${}^7F_0 \rightarrow {}^5L_6$ (395 nm) was found a prominent band for using emission spectra investigation. Figure 5 illustrates the emission spectra in the range of 250–800 nm under the excitation band at 395 nm. The emission spectra exhibited 5 emission bands corresponding to energy levels from 5D_0 to 7F_0 (578 nm, yellow), 7F_1 (593 nm, orange), 7F_2 (611 nm, red), 7F_3 (651 nm, red), and 7F_4 (703 nm, deep-red) transitions. Among emission bands, it was found that the intensity of red emission (${}^5D_0 \rightarrow {}^7F_2$) transition is

greater than the other transitions (Stanković *et al.*, 2020).

**Figure 3. The reflectance spectrum****Figure 4. Excitation spectrum under emission wavelength at 611 nm****Figure 5. The emission spectrum under excitation wavelength at 395 nm of 3Eu_g samples**

CIE 1931 chromaticity diagram was implemented to assess color emission contrast to assess glaze sample performance as illustrated in Figure 6. The color coordinates (x, y) for the 3Eu_g sample with 395 excitation wavelengths were found to be (0.61, 0.36), which is represented as a yellow star symbol on the reddish-orange region in the color diagram. The results indicate that the glaze sample emits light with a reddish-orange color and can be developed for phosphor material application (Sahu *et al.*, 2015).

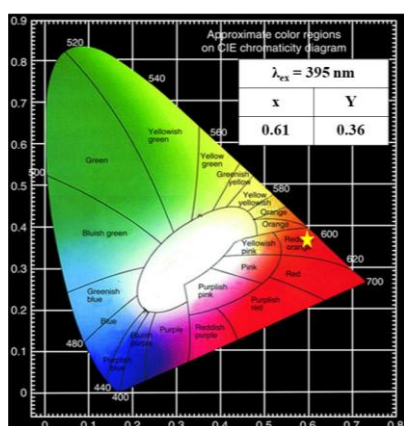


Figure 6. The CIE 1931 chromaticity diagram showing the emission of red color

Figure 7 depicts a lifetime of 3Eu_g sample at an $\lambda_{em} = 611 \text{ nm}$ and $\lambda_{ex} = 395 \text{ nm}$. The determination experimental lifetime (τ_{exp}) for the fluorescent $^5\text{D}_0$ level involves analyzing the non-exponential decay curves, where the average or effective lifetime is calculated using the formula

$$\tau = \frac{\int t I(t) dt}{\int I(t) dt} \quad (1)$$

where $I(t)$ represent the emission intensity at time 't'. The measured lifetime of the excited $^5\text{D}_0$ level has been obtained by calculating the first efolding times of decay curves. The $^5\text{D}_0$ level of effective decline time in the 3Eu_g sample was found to be 0.388 ms. The non-exponential decay of the $^5\text{D}_0$ level luminescence in Eu^{3+} singly doping phosphor has been linked to the cross-relaxation process Eu^{3+} ions.

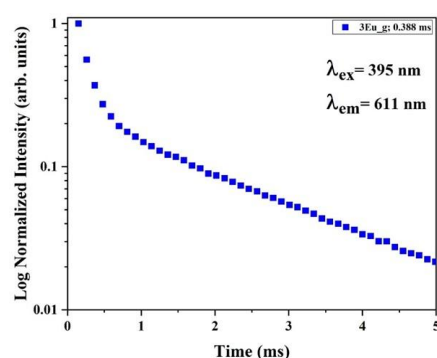


Figure 7. The lifetime of 3Eu_g glaze sample

Conclusions

The luminescent properties of glaze ceramics containing Eu^{3+} ions were investigated. The most abundant chemical SiO_2 composition of sample was observed using XRF. The XRD spectrum presented the two prominent of SiO_2 and EuH_3O_3 phases in glaze structure. The reflectance spectra in UV-visible to NIR regions are associated with the transition of Eu^{3+} ions. The emission spectra with a 395 nm excitation wavelength exhibit emission bands centered at 611 nm, with the highest intensity corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions. The CIE 1931 chromaticity analysis confirms the red-orange emission.

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