

MODIFICATION OF GLAZE FOR LUMINESCENCE ART

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Received: December 20, 2021; Revised: June 02, 2022; Accepted: June 21, 2022

Abstract

In this work, the glazed ceramic doped with Ho^{3+} ions were introduced to understand luminescence artwork. The glaze samples were separated to three conditions consist of raw glaze material (GR), glaze mixing with Ho_2O_3 before melting (GHO), and glaze mixing with Ho_2O_3 after melting (GHO-M). The samples were analyzed by X-ray fluorescence (XRF), X-ray diffractometry (XRD), scanning electron microscopy (SEM), optical and luminescence spectral properties. The absorption spectra in the visible and near-infrared region were being identified at 361, 419, 453, 486, 539, 646, 900, 1,157, and 1,963 nm. For luminescence spectra, the result showed a strong emission peak at 543 nm via $^5\text{F}_4\text{-}^5\text{I}_8$ transition of Ho^{3+} under excitation at 398 nm. Moreover, the SEM images revealed homogeneous dispersion of glazed sample with Ho^{3+} ions. The glazed ceramic containing Ho^{3+} ions can be considered as luminescence artwork for ceramic materials.

Keywords: Absorption; glaze; luminescence; rare earth ions

Introduction

A glaze is a thin layer coating formed on the ceramic surface by using glass materials and processing it by firing at high temperatures (Hennicke and Hesse, 1991; Olupot *et al.*, 2006; Li and Ren, 2011). With features as high chemical stability, a glaze is widely applied to produce ceramic arts and crafts such as interior decoration because of beautiful pattern, no discoloring and unfading. In addition, glazed ceramics have been also attracted for potential applications in the field of electrical porcelain,

refractories, tableware, and engineering ceramics. There has been carried investigation on new functional glazed ceramic products. Especially, it is aimed to enhance and obtain better chemical resistance, antibacterial ability, photocatalytic activity, self-cleaning properties, and photoluminescence properties (Casasola *et al.*, 2012; Karasu *et al.*, 2020).

Photoluminescence is an optical phenomenon that materials give light emissions by stimulating

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with incident light. The excited electrons generated by optical excitation reach high energy levels and return to the ground state, accompanied by emitting photons (Wang *et al.*, 2019). Photoluminescent in glazes are obtained by adding photoluminescent pigments to the glaze matrix. Rare earth ions are received special attention as photoluminescent pigments because they have high emission efficiencies. These emissions related to the 4f-4f and 4f-5d electronic transition which 4f shell is shielded by the outer 5s and 5p orbital (Meejitpaisan *et al.*, 2016). Among of rare earth ions, Holmium ions is an important active ion for many applications, due to high luminescence intensity of green and red emission (Kesavulu *et al.*, 2017). In addition to the applications, the glaze containing Ho^{3+} ions can be applied to the variety of artwork products, give visible light emissions and color change with different light source, consequently adding value to the end products.

The aim of this present work is to analyze the luminescence properties of glaze containing Ho^{3+} with different conditions for the investigation of structural transformation. Therefore, it is important to understand the effect of Ho^{3+} on glaze properties and the possibility of glaze modification for luminescence art.

Materials and Methods

In this work, the glazed samples were separated into three conditions for physical and optical property investigations; (1) raw glaze material (GR), (2) glaze mixing with Ho_2O_3 before melting (GHo), and (3) glaze mixing with Ho_2O_3 after melting (GHoM). In this process, the glaze samples were prepared by a clear semi-matt glaze process. The raw materials used for the preparation of the glaze samples are the mixture of frit (composition of SiO_2 , Al_2O_3 , BaO) and chemical Ho_2O_3 commercial grade. The mixture batches were milled by using an alumina ball mill for 6 h. After this procedure, they dried and water was mixed in the ratio of 1:1 to produce a glaze slurry. The obtained glaze slurry was placed in porcelain crucibles and then melted in an electric furnace at $1,220^\circ\text{C}$ for 6 h before cooldown at room temperature. The X-ray diffraction (XRD) technique was used to define the glaze ceramic structure by

a diffractometer (Shimadzu, XRD-6100) PXRD (Bruker D2 diffractometer with $\text{Cu-K}\alpha$ radiation). The optical absorption spectra of samples are measured with a UV-Vis and NIR spectrophotometer (Shimadzu UV-3600) in the range between 200-2,500 nm. The emission color was evaluated using the chromaticity protocol designed by the Commission Internationale de l'Eclairage in 1931 (CIE 1931). The chemical compositions of the sample by energy dispersive X-rays fluorescence (EDXRF) with standardless mode supplied by Philips model PW2400. The luminescence spectra were carried out using Fluorescence Spectrophotometer (Cary Eclipse) with 351 nm exciting radiation from a Xenon compact arc lamp.

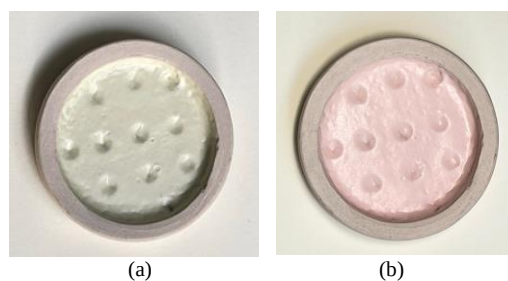


Figure 1. (a) The glaze sample under daylight
(b) The glaze sample under incandescent light

Results and Discussion

The glaze samples were obtained under daylight and incandescent light sources, as shown in Figures 1(a-b). The photograph shows the difference between different illumination sources of light for the viewer to understand the changes observed with various sources. The incident daylight and incandescent light sources react with Ho^{3+} ions with different wavelength range. As a result, the glaze sample display the different colors.

X-ray Fluorescence (XRF)

The quantification of chemical compositions of all samples were measured by X-ray fluorescence as shown in Table 1. The result shows that the most of composition of GR sample was a quantity of

Table 1. Chemical composition of all glaze samples using XRF

Sample	% By weight								
	SiO_2	Al_2O_3	K_2O	CaO	Na_2O	ZrO_2	MgO	Fe_2O_3	Ho_2O_3
GR	52.826	17.767	3.352	13.552	-	7.716	4.231	0.526	-
GHo	43.068	15.503	2.407	9.246	2.089	5.390	-	-	22.295
GHoM	42.744	19.590	2.443	7.298	2.396	5.276	-	0.409	19.843

silicon oxide (SiO_2) about 52.826% by weight. The composition of aluminum oxide (Al_2O_3) and calcium oxide (CaO) were 17.767% and 13.552% by weight as 2nd and 3rd, respectively. For GHo and GHoM samples, SiO_2 was the largest composition of these samples with 43.068 and 42.744 % by weight, respectively. The composition of Al_2O_3 and Ho_2O_3 which ranked second and third, respectively. Al_2O_3 were 15.503% and 19.590% by weight and Ho_2O_3 were 22.295% and 19.843% by weight, respectively.

X-ray Diffraction (XRD)

The XRD pattern of glaze samples clearly exhibits two prominent peaks at $2\theta = 20.9^\circ$ and 26.6° . Figure 2 displays indexed diffraction pattern of GHo exhibiting all the Bragg reflections in the range $2\theta = 0^\circ$ - 90° , which corresponds to the body-centered cubic (bcc) structure with C-type holmium sesquioxide of lattice parameter $a = 10.6 \text{ \AA}$, belonging to Ia-3 space group. Various Bragg reflections of Ho_2O_3 , its located the main peaks at $2\theta = 20.9^\circ$, 26.6° , 29.5° , 32.6° , 43.5° , 48.5° , and 57.7° , corresponding to (211), (222), (400), (411), (134), (440), and (622) crystal planes, respectively. While the (134), (440), and (622) peaks disappeared in GHoM because of the homogeneous glaze after melting process, which corresponds to the data file of the Joint Committee on Powder Diffraction Standard (JCPDS) data file no. 65-3177. Figure 4 shows the XRD pattern of GHoM, wherein all the peaks of Ho_2O_3 have appeared the diffraction pattern of the GR has exhibited the same (222) crystal plane of Ho_2O_3 as the preferential orientation. This indicates the crystalline nature of the glaze (Abdusalyamova *et al.*, 2014; Megha *et al.*, 2017; Manjunatha *et al.*, 2019).

Reflectance Spectra

The reflectance spectra of GHoM sample in UV-visible and NIR regions are shown in Figure 3. The reflectance spectra consist of totally nine bands at 361, 419, 453, 486, 539, 646, 900, 1,157, and 1,963 nm and are attributed to the transition from $5I_8$ ground level to the different excited energy levels such as 3H_6 , 5G_5 , $^5F_1+^5G_6$, 5F_3 , $^5F_4+^5S_2$, 5F_5 , 5I_5 , 5I_6 , and 5I_7 transitions of the Ho^{3+} ions, respectively. The GHo also showed that the Ho^{3+} reflectance peaks at the same locations with lower intensity because of its homogeneity. While the GR was not detected in the reflectance spectra (Srinivasa Rao *et al.*, 2012; Bhargavi *et al.*, 2014; Venkateswarlu *et al.*, 2015).

Photoluminescence Properties

The observed excitation and emission spectra of the GHoM as shown in Figures 4 and 5.

The excitation spectra were obtained by monitoring with a strong emission at 543 nm in the wavelength region of 300-500 nm. The excitation spectra of the glaze sample exhibit five peaks located at 320, 344, 398, 413, and 479 nm, which are mainly attributed from the ground state 5I_8 to 5G_2 , 3L_9 , 5G_4 , 5G_1 , and 5F_2 , respectively of Ho^{3+} ions. According to the excitation spectra, the $^5I_8 \rightarrow ^5G_2$ transition observed at 398 nm has been the highest intensity and was selected to investigate the emission spectra. The emission spectra using 398 nm excited wavelength show the emission bands centered at 543 and 630

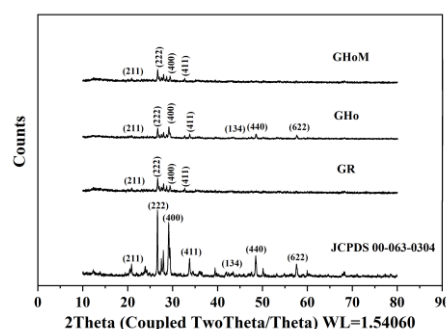


Figure 2. X-ray diffraction spectra of all glaze samples

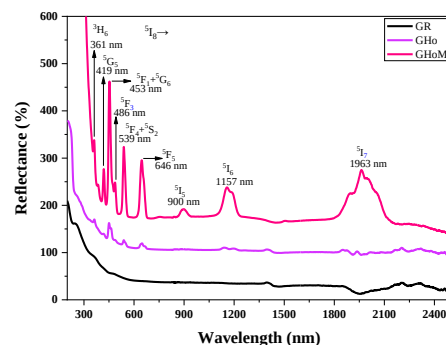


Figure 3. Reflectance spectra of all glaze samples

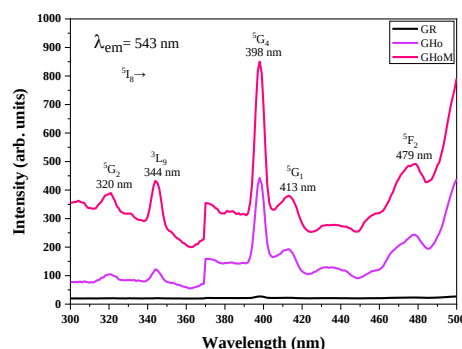


Figure 4. Excitation spectra under emission wavelength at 543 nm of all glaze samples

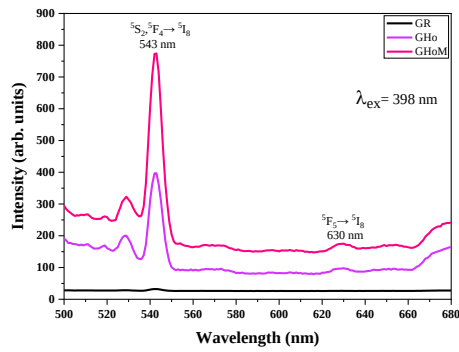


Figure 5. The emission spectra under excitation wavelength at 398 nm of all glaze samples

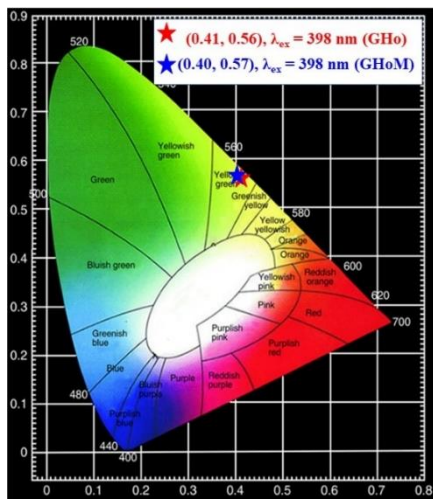


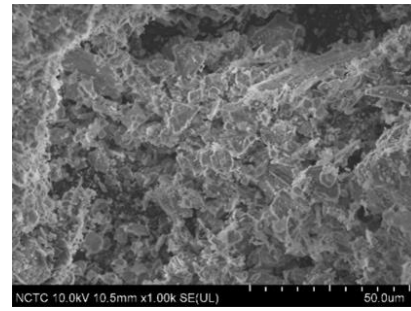
Figure 6. The CIE 1931 chromaticity diagram showing the emission colors of glaze sample

nm which is due to the $^5S_2, ^5F_4 \rightarrow ^5I_8$, and $^5F_5 \rightarrow ^5I_8$ transitions, respectively. Among the two transitions, the intense band at 543 nm is very dominant in the green region compared to the red emission at 630 nm. Moreover, the excitation and emission peaks of the GHoM displays the same locations within different intensities. While the glaze was not found the excitation and emission peaks (Suhasini *et al.*, 2012).

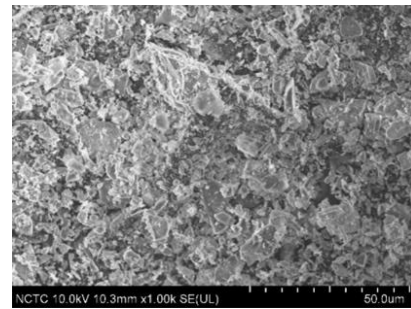
The CIE 1931 chromaticity values of glaze samples were calculated from the emission spectra with 543 nm for the color of light emitting estimation. The color coordinate in X-Y axis of glaze A (0.41, 0.56) and glaze B (0.40, 0.57) which located in the yellow-green region of diagram, as shown in Figure 6.

SEM Image

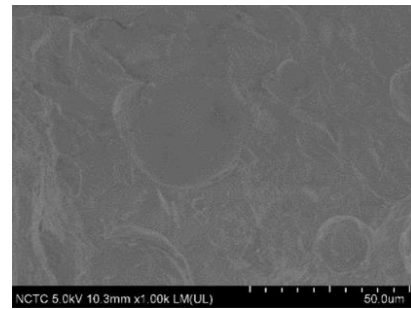
The images of SEM of glaze samples as shown in Figures 7(a-c). The particles of GR and GH



(a)



(b)



(c)

Figure 7. The SEM image (a) GR sample (b) GHo sample (c) GHoM sample

samples are of many different sizes and shapes, the average size of the sample is estimated to be about 2-180 μm and evenly distributed. While the GHM sample has a smoother texture more than the other because it arises from agglomeration of particles to form a homogeneous mixture with proper condition satisfying to agglomerate into spherical shape after melting at 1,220 °C.

Conclusions

The glaze samples with three conditions were prepared for physical and optical properties investigation in order to modify the luminescence glaze art. The most abundant chemical SiO_2 composition found in these samples were observed using by XRF. The XRD pattern has exhibited its crystalline main peaks of Ho^{3+} ions. The reflectance

spectra in UV-visible and NIR regions are attributed to the transition of Ho^{3+} ions. The emission spectra under 398 nm excitation wavelength show the emission bands centered at 543 with the highest intensity corresponding to $^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_8$ transitions which confirm they emit yellow-green color and useful for yellow-green light-emitting glazed ceramic dishes which can be used in the darkroom with UV light illuminated on it. The CIE 1931 chromaticity analysis confirms the yellow-green emission. While the SEM image shows that the GHM sample arises from agglomerating the particles to a homogeneous conditions with spherical shape.

Acknowledgement

J. Kaewkhao would like to thanks National Research Council of Thailand (NRCT) for supported this project. Thanks are also due to Thailand Science Research and Innovation (TSRI) for partially supporting this research.

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