

# INVESTIGATING THE OPTICAL PROPERTIES OF GLAZE DOPED WITH Nd<sub>2</sub>O<sub>3</sub>

Suebpong Powthai<sup>1</sup>, Watcharin Rachniyom<sup>1,2,\*</sup>, Yotsakit Ruangtaweep<sup>1,2</sup>, Nawarut Jarucha<sup>1,2</sup> and Jakrapong Kaewkhao<sup>1,2</sup>

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## Abstract

In this work, the sample was prepared by mixing a frit powder with Nd<sub>2</sub>O<sub>3</sub> as a glaze (3Nd\_g). The glaze sample was prepared using a single sintering process at 1,220°C in an electric furnace. the chemical composition and crystalline structure of the glaze sample was measured with energy dispersive X-ray fluorescence (EDXRF) and X-ray diffractometry (XRD). The results indicated that the main composition comprised SiO<sub>2</sub>, Nd<sub>2</sub>O<sub>3</sub>, and CaO, respectively. Furthermore, the main crystalline structure consisted of SiO<sub>2</sub> and H<sub>3</sub>NdO<sub>3</sub>. The optical reflectance spectra of the glaze sample were investigated using a UV-vis and NIR spectrophotometer, revealing nine central peaks at 880, 812, 752, 685, 629, 584, 529, 477, and 433 nm. The luminescence properties of Nd<sup>3+</sup> ions were investigated by exciting at 808 nm, resulting in emission bands observed around 943, 1067, and 1338 nm.

**Keywords:** Glaze; Luminescence Spectra; Nd<sup>3+</sup> Ions

## Introduction

Glaze is a glassy coating that creates a thin layer on the surface of ceramic body. This layer is formed by changing the physicochemical reaction of the coating, such as high temperature melting and crystallization (Xu *et al.*, 2023) which has the effect to closed porosity in the ceramic body, increasing the strength, decorating the surface beautifully, and prolonging the service life of ceramics with glazing and single sintering process (Pradell *et al.*, 2020). The productions of ceramic color glaze are chemical process which always produce creative and attractive results. Basically, The colors of

glazes are derived from coordination number (two, three, four, ...) and geometrical arrangement (tetrahedral, octahedral, ...) of the given atom transition metal element (Colomban, 2021). The oxidizing or reducing conditions are caused by firing processes. The color is a specific characteristic of light absorption wavelengths by a given transition metal ion.

Currently, there are many research studies on the properties and color of glazes, which are obtained by additives with transition metal elements. In addition, there are also studies on the

<sup>1</sup> Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand. E-mail: watcharin@webmail.npru.ac.th

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

\* Corresponding author

addition of new substances such as rare earth (RE) elements. Rare earths have good properties in refractory, non-volatile, and non-toxic, so are good candidates for use as glaze materials. The RE elements leads to a distinctive range of colors compared to common transition metals. This could potentially pave the way for innovations in improving ceramic products for aesthetic enhancement, diverging from conventional products available in the market.

In this work, the glaze sample was prepared with frit and Neodymium oxide (Nd<sub>2</sub>O<sub>3</sub>). the Nd<sub>2</sub>O<sub>3</sub> is not excessively expensive when compared to other RE element. Furthermore, it has high density properties, low thermal expansion coefficient. Therefore, it may improve the properties of ceramics mixed with this substance in various aspects. In this experiment, the glaze doped with Nd<sub>2</sub>O<sub>3</sub> were prepared by sintering method, and investigated the optical properties such as absorption, and luminescence.

## Experiments

In this work, the Nd<sub>2</sub>O<sub>3</sub> glaze samples were obtained by transparent semi matt technique. The raw materials were prepared frit industrial grade and chemical Nd<sub>2</sub>O<sub>3</sub> commercial grade was introduced to obtain the target glaze. The mixture was homogenized by alumina ball milling for 6 h. After that, the mixture was mixed with water in a 1:1 ratio into a glaze slurry. The glaze slurry was contained in bath and melted in an electrical furnace at 1,220 °C for 6 hours, then allowed to cooldown at room temperature. The properties of glaze sample were reported in chemical composition, crystalline structure, and optical spectra. The energy dispersive X-rays fluorescence (EDXRF) was used to determine the chemical compositions in sample by Philips PW2400. The crystalline structures of sample were examined with X-ray diffraction (XRD). XRD patterns were collected using a Shimadzu XRD-6100 diffractometer (Cu-K $\alpha$  radiation,  $\lambda$  = 1.5406 Å). The Reflectance spectrum was measured in range of 200-2,500 nm by a UV-vis and NIR spectrophotometer (Shimadzu UV-3600)

## Results and Discussion

### Energy dispersive X-ray fluorescence (EDXRF)

The oxide composition of glaze and 3Nd\_g expressed in weight % is presented in Table 1. The main oxide compositions of glaze are SiO<sub>2</sub>, CaO and ZnO with weight percentages of 58.664, 17.655 and 11.865, respectively. The dominant oxide compositions of 3Nd\_g included SiO<sub>2</sub>, Nd<sub>2</sub>O<sub>3</sub>, and CaO. SiO<sub>2</sub> is the largest composition, about 48.655 % by weight. Nd<sub>2</sub>O<sub>3</sub> and CaO are the second and third components at 15.095 and 14.775% by weight, respectively. The result of EDXRF can confirm that Nd<sub>2</sub>O<sub>3</sub> is completely melted in the glaze sample after melting process.

### X-ray diffraction (XRD)

The XRD pattern of glaze and 3Nd\_g is shown in Figure 1. The structure of glaze is amorphous structure. However, the structure of 3Nd\_g is different in XRD pattern of SiO<sub>2</sub> and H<sub>3</sub>NdO<sub>3</sub> (JCPDS #96-210-6883) (Beall *et al.*, 1976) as the main phase. In the XRD pattern, a major peak of the SiO<sub>2</sub> is observed at position of angular 2 $\theta$  around 20.88°, 23.89°, 26.65°, 39.47°, 42.43°, 54.87° and 68.16°. While the high peaks indicated as H<sub>3</sub>NdO<sub>3</sub> occurred at angular 2 $\theta$  around 15.59°, 27.93°, 29.44°, 36.24°, 40.43°, 50.15° and 59.96°. These results are in good agreement with the chemical composition of the 3Nd\_g sample as reported by EDXRF. The amount of SiO<sub>2</sub> is highest, followed by Nd<sub>2</sub>O<sub>3</sub>.

### FTIR Spectra

FTIR spectroscopy was applied to identified and determination of analogous to Nd<sub>3</sub>\_g in the range of 2000-400 cm<sup>-1</sup>. FTIR spectra of Nd<sub>3</sub>\_g (Figure 2) revealed that the main quartz phase (Si-O) could be also easily identified in the FTIR spectrum of 1084, 1000, 774, 692 and 530 cm<sup>-1</sup> (Sevaitiene *et al.*, 2007). The absorption bands at 1434 and 874 cm<sup>-1</sup> were ascribed the presence of C-O stretching vibration of carbonate molecules (calcite phase) (Kashyap *et al.*, 2021). However, additionally the characteristic of M-O (Metal-Oxides) vibrations at 647, 585, and 413 cm<sup>-1</sup> could be also determined. It is possible that interaction between Nd - O was showed at wavenumber of 647 and 413 cm<sup>-1</sup> (Lembang *et al.*, 2018).

**Table 1.** XRF analysis of chemical composition of glaze sample

| Sample | % By weight      |                  |        |        |       |                                |
|--------|------------------|------------------|--------|--------|-------|--------------------------------|
|        | SiO <sub>2</sub> | K <sub>2</sub> O | CaO    | ZnO    | BaO   | Nd <sub>2</sub> O <sub>3</sub> |
| glaze  | 58.664           | 5.088            | 17.655 | 11.865 | 6.940 | -                              |
| 3Nd_g  | 48.655           | 2.677            | 14.775 | 9.950  | 8.849 | 15.095                         |

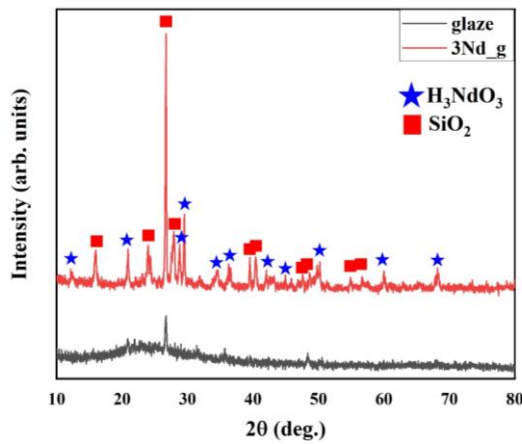


Figure 1. X-ray diffraction spectra of glaze and glaze doped with  $\text{Nd}_2\text{O}_3$  (3Nd\_g) sample

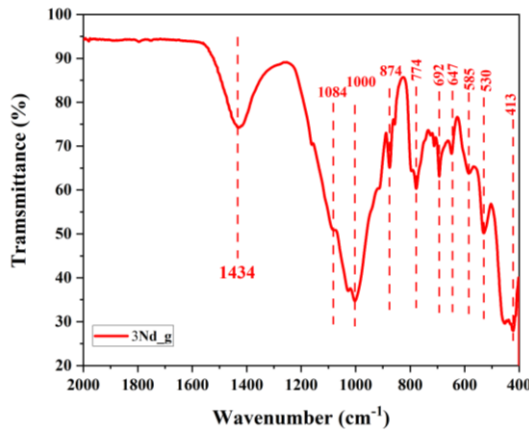


Figure 2. FTIR spectra of glaze doped with  $\text{Nd}_2\text{O}_3$  (3Nd\_g) samples

### Reflectance Spectra

The spectral reflectance of glaze and 3Nd\_g samples is shown in Figure 3. The 3Nd\_g sample can be observed nine reflection peaks in the wavelength range from 400-1,000 nm. The characteristic of reflection peaks observed are compared with previous works (Mhareb *et al.*, 2014; Pugliese *et al.*, 2020; Jose *et al.*, 2022). The center of these peaks appeared at 880, 812, 752, 685, 629, 584, 529, 477, and 433 nm. The reflection peaks were corresponding to the transitions from the ground state of  $^4\text{I}_{9/2}$  to various higher energy levels  $^4\text{F}_{3/2}$ ,  $^4\text{F}_{5/2} + ^2\text{H}_{9/2}$ ,  $^4\text{F}_{7/2} + ^4\text{S}_{3/2}$ ,  $^4\text{F}_{9/2}$ ,  $^2\text{H}_{11/2}$ ,  $^4\text{G}_{5/2} + ^2\text{G}_{7/2}$ ,  $^4\text{G}_{7/2} + ^4\text{G}_{9/2}$ ,  $^2\text{G}_{9/2} + ^2\text{D}_{3/2} + ^2\text{K}_{15/2}$  and  $^2\text{P}_{1/2}$ , respectively. This result, it is certain that the observed effect of 3Nd\_g was caused by Nd ions. The position of reflection peaks slight variation when compared to various glasses doped with

$\text{Nd}_2\text{O}_3$ . However, the reflectance spectra of 3Nd\_g are in the same pattern of  $\text{RE}^{3+}$  ions. Therefore, it can be confirmed that the reflectance spectra of glaze sample originated from the  $\text{RE}^{3+}$  ions. Figure 4 shows the color of Nd3\_g sample (Figure 4b) compared to the glaze without  $\text{Nd}_2\text{O}_3$  (Figure 4a) in sunlight. The Nd3\_g sample shows purple shade when illuminated by sunlight. It demonstrates that  $\text{Nd}_2\text{O}_3$  can be beneficial as an additive in the glazing process to impart color to the surface of the target material.

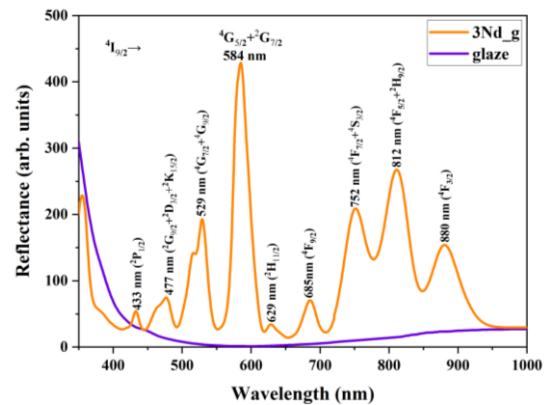


Figure 3. Reflectance spectra of glaze and glaze doped with  $\text{Nd}_2\text{O}_3$  (3Nd\_g) samples

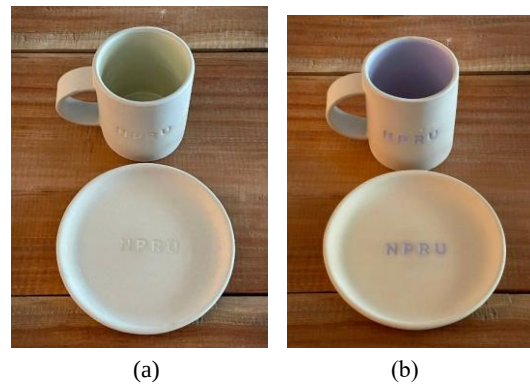
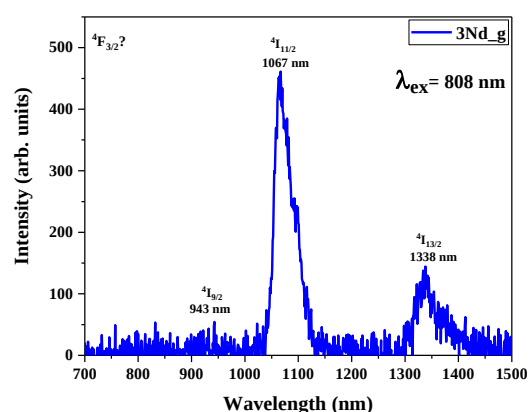


Figure 4. The color of glaze sample under sunlight compared between (a) glaze without  $\text{Nd}_2\text{O}_3$  and (b) glaze doped with  $\text{Nd}_2\text{O}_3$

### Photoluminescence properties

Although, the results of reflectance spectra of 3Nd\_g showed the highest absorption spectra at 584 nm that associate with the  $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2} + ^2\text{G}_{7/2}$  transition. In this work, the 808 nm wavelength associated with the  $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$  transition has been selected for exciting the emission band. Because

808 nm laser diodes are cheap and widely used as excitation sources (Trejgis *et al.*, 2020). The emission spectrum of the 3Nd\_g sample has been shown in Figure 5. three emission spectra occurred in the NIR range around 943, 1067, and 1338 nm. The  $^4F_{3/2} \rightarrow ^4I_{11/2}$  transition is the strongly emission band at 1067 nm. The emission spectra confirmed the presence of a distribution of Nd<sup>3+</sup> in glazed sample, which is the same emission of the glassy and amorphous nature material (Yang *et al.*, 2013; Shanmugavelu *et al.*, 2014).



**Figure 5.** The emission spectrum under excitation wavelength at 808 nm of glaze doped with Nd<sub>2</sub>O<sub>3</sub> (3Nd\_g) sample

## Conclusions

The glazing process successfully doped Nd<sub>2</sub>O<sub>3</sub> through a single sintering process. The main chemical constituents are SiO<sub>2</sub>, Nd<sub>2</sub>O<sub>3</sub>, and CaO, respectively. These are present within the crystalline structure of SiO<sub>2</sub> and H<sub>3</sub>NdO<sub>3</sub>. The optical properties of reflectance spectra in UV-visible and NIR regions as a result of the presence of Nd<sup>3+</sup> ions. The emission spectra under an excitation wavelength of 808 nm exhibit emission bands in NIR region, with the highest peak centered at 1067 nm. These optical properties are similar to the effect of doping Nd<sub>2</sub>O<sub>3</sub> into glass materials. The obtained results contribute to understanding the luminescent behavior of rare earth elements in glaze materials and can be valuable for the development of novel ceramic glazes with enhanced optical properties.

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