Production of Violet-blue Emitting Phosphors via Solid State Reaction and Their Uses in Outdoor Glass Fountain

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Abstract: The rare earth metal ions-doped calcium aluminate phosphors have been studied in depth and widely used thanks to their high quantum efficiency, anomalous long phosphorescence and good stability. In this study, violet-blue phosphors in the $CaAl_2O_4$:Eu^{2+}, Nd^{3+} and Dy^{3+} systems were produced through a solid-state reaction. The optimum concentrations of Nd and Dy rare earths were investigated. The phosphor powders were further searched by X-ray diffractometer (XRD), scanning electron microscopy (SEM) attached with EDX and photoluminescence excitation and emission spectra (PL). It is thought that Nd^{3+} and Dy^{3+} ions doping in the phosphor generate deep traps resulting in long afterglow phosphorescence. Final long-lasting, violet-blue emitting phosphors were evaluated on the outdoor glass fountain.
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1. Introduction

Long after glow phosphor is a kind of pigment that absorbs energy and then releases it in the form of light after being excited. The released luminescent light can last several or even dozens of hours [1]. The aluminates with spinel structure are well known phosphorous materials in visible region when doped with suitable activator ions. During last two decades a new generation of luminescent phosphors, Eu^{2+}-doped alkaline-earth aluminates, MAl_2O_4:Eu^{2+} (M ¼ Ca, Ba, Sr), have been studied and developed. Compared to sulfide based phosphors, Sr, Ba and Ca-based aluminate phosphors possess safer, chemically stable, very bright and long-lasting photoluminescence without any harmful radiation [2].

The effects of europium doping in several phosphorescent pigment systems have recently been studied [2-13]. The emission of Eu^{2+} is very strongly dependent upon the host lattice and can occur from ultraviolet to the red region of the electro-magnetic spectrum. The valence state of the activator ion is determined by the effective electron-phonon interactions of the surrounding basic matrices [14]. Neodymium oxide (Nd_2O_3) is widely chosen in various applications such as luminescent materials, catalyst for automotive industry, UV absorbent, glass-polishing material and protective coatings. Rare earth sesquoxides exist in three different structural types depending on the ionic radii of the rare earth ion. Those with larger cations form hexagonal (A-type) with seven coordinated polyhedron while those with smaller cations form cubic lattice (C-type) with both seven and six coordinated polyhedron in the ratio of 2:1 [15]. In addition, considerable attention has recently been devoted to the conversion of near-infrared radiation to visible light from erbium- and ytterbium-doped materials and similarly, conversion of yellow into the violet from neodymium-doped optical materials for a wide range of applications including color displays, optical data storage, sensors and optical communications. Especially, neodymium is a unique element as an emission center for the construction of a laser system because the four-level energy structure of neodymium is ideal for laser transition. That is to say, the 4fn electronic level structures of these ions provide many long-lasting intermediate levels and these could be populated with infrared radiation with also some meta-stable higher lying levels causing such strong visible emissions [16].

In this study, violet-blue phosphors in the $CaAl_2O_4$:Eu^{2+}, Nd^{3+} and $CaAl_2O_4$:Eu^{2+}, Dy^{3+} systems were produced through a solid-state reaction. The optimum concentrations of Nd and Dy rare earths were investigated. The phosphor powders were further searched by X-ray diffractometer (XRD), SEM attached with EDX and photoluminescence excitation and emission spectra (PL).

2. Experimental

The starting materials were $CaCO_3$, Al_2O_3, Eu_2O_3, Dy_2O_3, Nd_2O_3 and H_3BO_3. The polycrystalline $CaAl_2O_4:Eu^{2+}$, Nd^{3+} and $CaAl_2O_4:Eu^{2+}$, Dy^{3+} materials were prepared with a solid state reaction. In both system the nominal concentration of the Eu^{2+} ions was 0.29 mole % of the calcium amount, while Nd_2O_3 and Dy_2O_3 being in the range of 0.005-0.02 mole %. In each system 3 different pigment compositions were studied and coded as N1-3 and D1-3. Exact chemical compositions of the recipes are not presented here due to the possibility of their commercial productions. The starting materials were ground to a homogeneous mixture in a ball mill. The mixtures were initially sintered under reducing atmosphere at the temperatures of 1250-1600 ° C for 1-5 h. The particles size of each sample was analyzed by the Malvern Instruments Mastersizer Hydro 2000G laser particle size analysis instrument. Phase identifications were made by XRD at 40 kV and 30 mA with Rigaku Rint 2000 using Cu-Kα radiation. The morphology and element analysis of sintered powders were designated by Zeiss EVO 55 SEM fitted with an EDX. The photoluminescence (PL) emission spectra were taken on Perkin Elmer LS55 luminescence spectrometer.

The particle size analysis results of the phosphorescence samples coded N1 with 0.02 mole Nd_2O_3 and D1 with 0.02 mole Dy_2O_3, which were found to give the highest luminescence, are given in Fig. 1. Before moving the sintering stage, we were sure of the fact that the most of the powders were sieved below 90 µm.

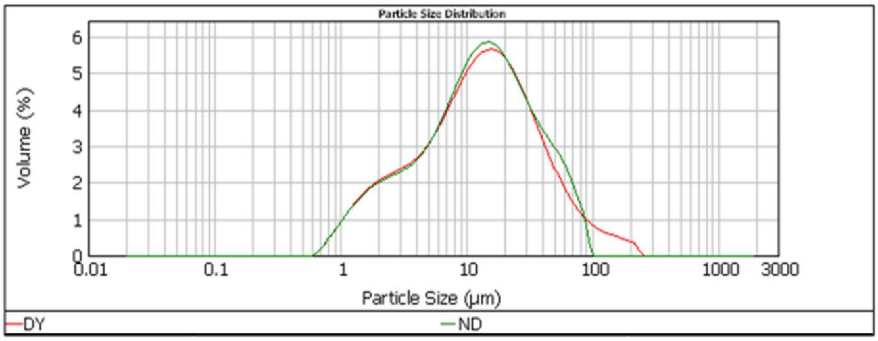

Figure 1. Particle size analysis results of N1 and D1 phosphors with Nd_2O_3 and Dy_2O_3 respectively.

The XRD patterns of violet-blue emitting phosphor samples synthesized under laboratory conditions are shown in Fig. 2. As clearly seen from the peaks, the major crystal phase was determined as $CaAl_2O_4$ in both systems.

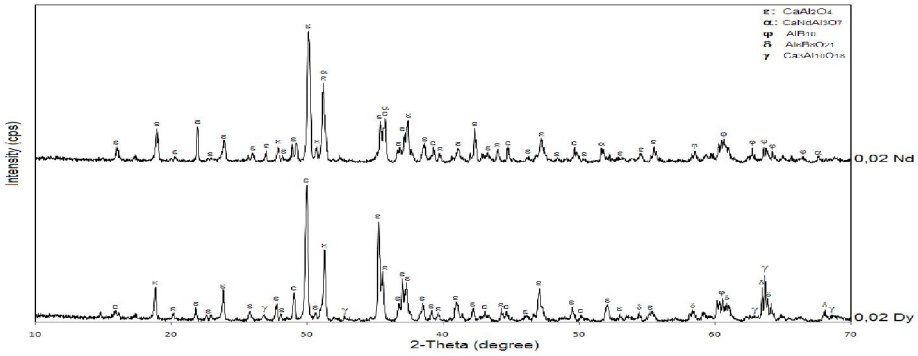

Figure 2. X-ray diffraction patterns of the powder samples in the $CaAl_2O_4:Eu^{2+}$, Nd^{3+} and $CaAl_2O_4:Eu^{2+}$, Dy^{3+} systems.

The morphology (by SEM) and EDX analysis results of the phosphorescent powders sintered are presented in Fig. 3 (a-d).

The excitation and emission spectra of powders were recorded by means of a fluorescence spectrophotometer (Perkin Elmer LS55). Emission spectra of $CaAl_2O_4:Eu^{2+}$, Nd^{3+} and $CaAl_2O_4:Eu^{2+}$, Dy^{3+} system phosphors (N1 and D1) fired at 1250-1600 ºC for 1-5 hours can be seen in Fig. 4. When compared to Nd ions, Dy ones seem to be more efficient on the luminescence effects in the $CaAl_2O_4:Eu^{2+}$ system.

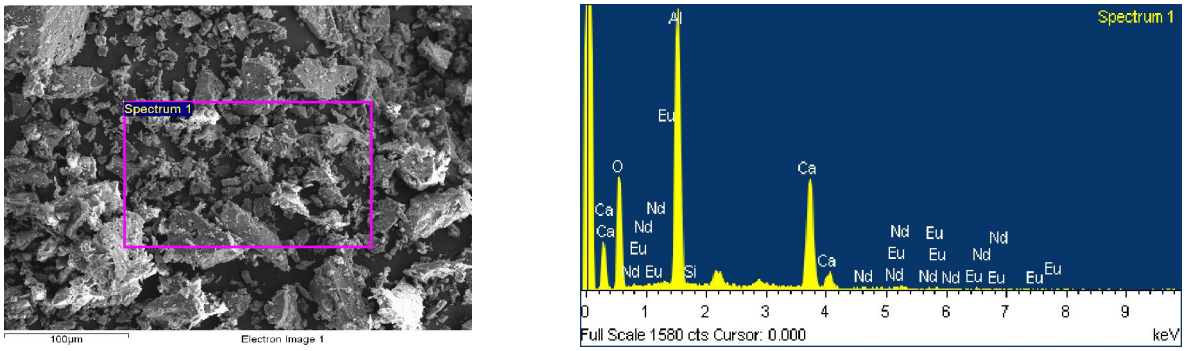

Figure 3. SEM photographs and EDX analysis results of the phosphorescence samples containing Nd_2O_3 (N1) **(a-b)** and Dy_2O_3 (D1) **(c-d)** beside Eu_2O_3.

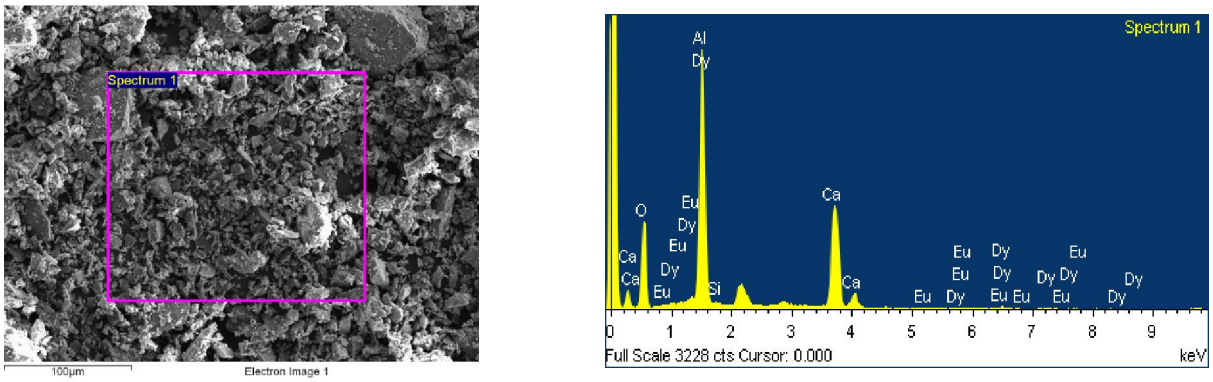

Figure 4. Excitation **(a)** and emission **(b)** spectra of $CaAl_2O_4:Eu^{2+}$, Nd^{3+} and $CaAl_2O_4:Eu^{2+}$, Dy^{3+} system phosphors

3. Artistic Glass Applications

First of all, phosphorescent pigments with violet-blue (D1) and yellowish-green luminescence ability were applied onto flat glass surfaces and fired in a fusion furnace at 810 ^{o} C for 15 min in order to see whether they may indicate any application capability or not. After receiving positive effects (Figure 5), a glass fountain was designed as three layers. 6 mm thick base windows glass one with the dimensions of 50x70 cm was black colored as a result of the fusion firing at 800 ^{o}C for 15 min followed by fast cooling down to 600 ^{o} C and hold at between the temperatures of 540-480 ^{o} C

for 360 min to complete the annealing stage. Since the production of a three layer glass fountain was desired, for second and third layers each piece was separately cut and decorated. Then, for phosphorescent pigment applications ordinary transparent window glass was crushed in a mortar and sieved below 90 µ. Afterwards, glass powders were equally mixed with either violet-blue luminescence emitting pigment or yellowish-green luminescence given one. At this stage, the most critical point is to be careful about the thermal expansion coefficient values of powder and pigments which must be close to each other. When ideal mixture was achieved, it was applied onto the desired parts of the decoration. The second and third layer's decorated parts with the thickness of 4 mm were placed onto the pre-fired base black glass layer as two separate layers and the whole fountain was fusion-fired at 820 ^{o}C for 15 min followed by fast cooling down to 600 ^{o}C and remained between the temperatures of 540-480 ^{o}C for 480 min to complete the annealing stage (Figures 6-8).

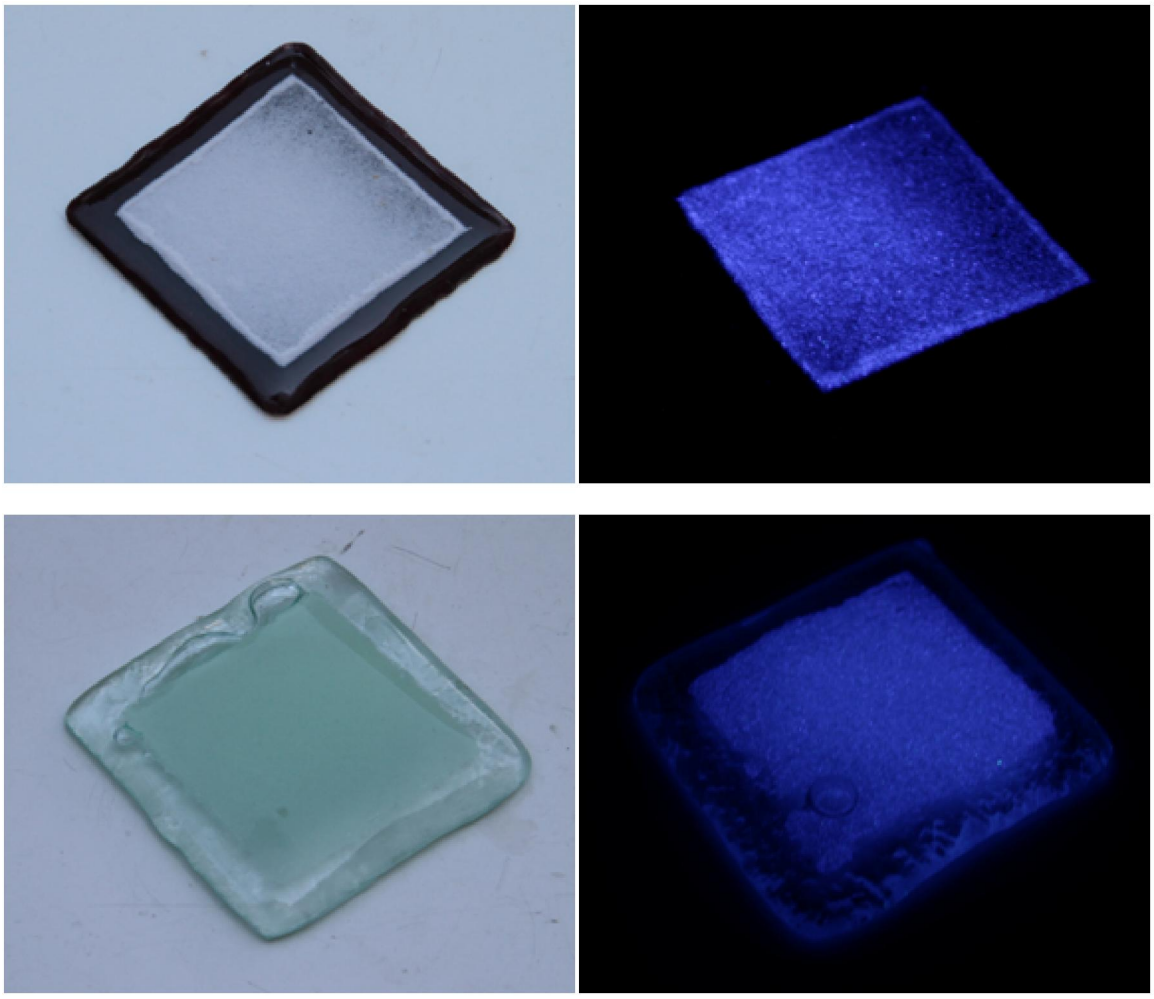

Figure 5.Violet-blue phosphorescent pigment applications made on the flat glass surfaces and their appearances in the day light (left) and in the dark (right).

Figure 6. The overall view of the decorated three-layered fountain

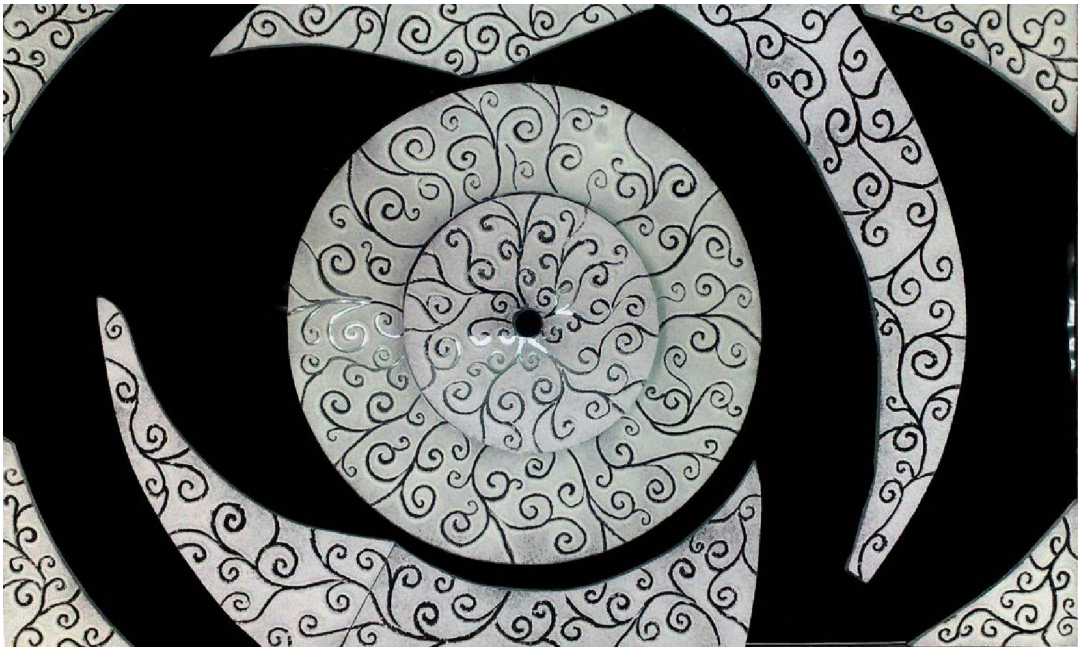

Figure 7. The middle part's pigmented decoration of the fountain which was fusion-fired in an electrically heated furnace.

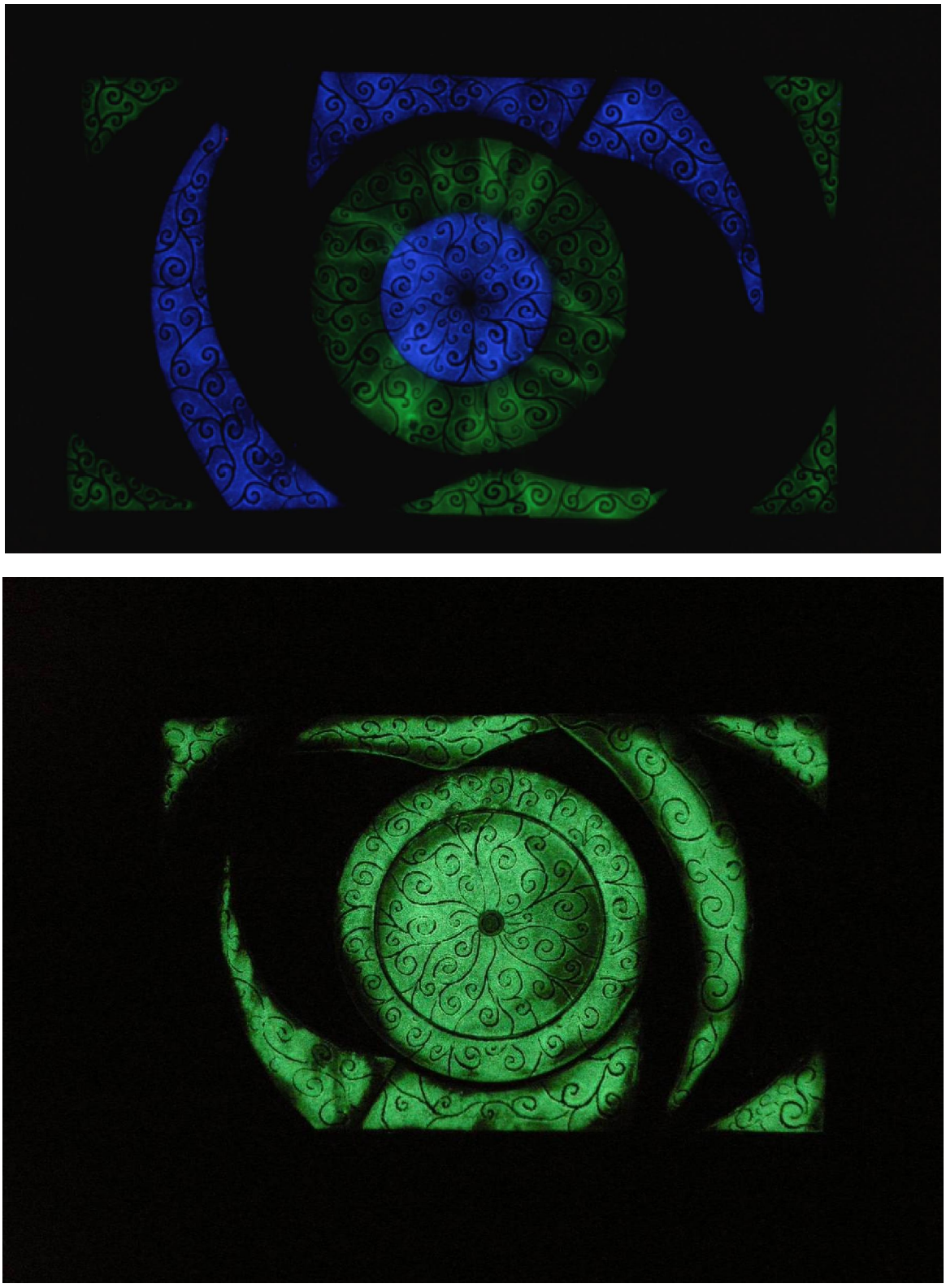

Figure 8. The views from the middle part of decorated and painted fountain in the dark

4. Conclusion

Violet-blue color emitting long-lasting phosphorescent pigments in the $CaAl_2O_4:Eu^{2+}$, Dy^{3+}, Nd^{3+} systems have been successfully synthesized and produced. The trivalent rare-earth ion, Dy^{3+}co-doping would effectively enhance the persistent luminescence intensity considering the phosphor with Nd^{3+} ions. By using either violet-blue or yellowish-green luminescence given phosphorescent pigments an artistic three layered glass fountain with an attractive appearance was successfully achieved.

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