



Preparation of Persisted Luminescence Pigment and Investigation in Glaze Compatibility

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ABSTRACT

In this paper, preparation of SrAl₂O₄:Eu,Dy luminescent pigment has been investigated. Coprecipitation as a low cost and facile method was selected. X-ray diffraction patterns indicated the formation of SrAl₂O₄ phase through calcinations process above 800 °C. Moreover, adding a few amount of silica to rawmaterials caused the structural transformation to Aluminosilicate phase during the calcination. Transparent glaze which consist of a few amount of luminescent pigment was obtained at 600 °C under different atmosphere conditions. The photoluminescence properties of luminescence glaze revealed that the firing atmosphere has significant effect on luminescence features of glaze. Although, the luminescence decay of glaze was completely eliminated in oxide atmosphere, but the green afterglow of obtained sample was remained in argon atmosphere. Prog. Color Colorants Coat. 5(2012), 55-63. © Institute for Color Science and Technology.

1. Introduction

Phosphors are especial powders that emit emission of visible radiation for significant periods of time following the removal of the excitation source. [1]. These materials are kind of energy storage materials, which can absorb both ultraviolet (UV) and visible lights from the sunlight and gradually release the energy in the darkness at a certain wavelength [1, 2].

Most of inorganic phosphors consist of a crystalline material called host which contains two kinds of specific dopants called activator and auxiliary activator. Basically, activators are responsible for the formation of the luminescence mechanism. Other one is necessary for trapping the released hole or electron. Both activators and auxiliary activators are incorporated in the structure

of the crystal at high temperatures during firing [1, 2].

In 1996, T. Matsuzawa et al. reported a new type of long-persistent phosphor SrAl₂O₄: Eu²⁺, Dy³⁺ with a strong emission at 520 nm (green). The persistence time of SrAl₂O₄: Eu²⁺, Dy³⁺ is longer than 16 hours. This phosphor drew considerable attentions from many researchers because a value of 16 hours persistent time could bring the phosphorescence over a whole night [3]. Compared with sulfide phosphorescent phosphors, Sr₄Al₁₄O₂₅: Eu²⁺, Dy³⁺ phosphor possesses safe, chemically stable, very bright and long-lasting photoluminescence in addition to no radiation [4], which results in wide field of applications, such as emergency signs, luminous paints in highway, airport, building and

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ceramics, textile printing, textile fibers, dial plate of glowing watch, warning signs and escaping route way [5,6].

Despite developing many new phosphors during the last decade, only some of them are able to be excited under natural visible light. The others required UV or deep UV excitation to trap electrons. The issue whether the long persistence can be obtained by natural light excitation, is very important and actually it sometimes limits the application of long lasting phosphors [7].

Recently, Yan et. al. reported the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ luminescent glaze with high brightness and long afterglow. Sintering of glaze in air atmosphere was investigated; however the change of luminescence properties due to calcinations under inert atmosphere has not been evaluated [8]. Also, Coating the phosphor pigment could be enhancing its luminescent intensity in oxygen atmosphere during the luminescent glaze firing.

In this paper, luminous phosphor of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ was mixed with transparent glaze, coated onto ceramic surface and then heat-treated in different conditions. The silica coating on the phosphor pigment was also investigated as one of the luminescent enhancing parameters. For this purpose, TEOS (tetraethylsilane) was applied as silica precursor during the luminescent pigment synthesis to investigate whether silica is formed on the surface of the particle or not. Microstructure, photoluminescence and after glow properties were characterized in details. The morphology, structure and luminescent properties of these powder samples were investigated by a scanning electron microscopy (SEM), X-ray diffraction (XRD) and fluorescent spectrophotometer.

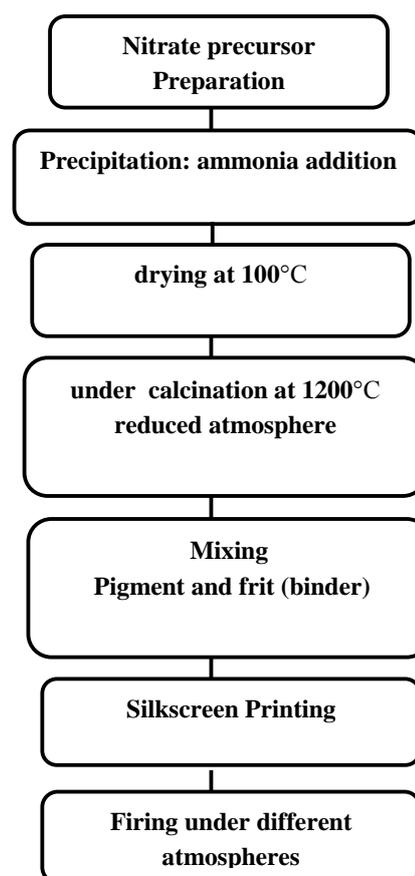
2. Experimental

2.1. Materials

High purity raw materials including Strontium nitrate, aluminum nitrate, Dy_2O_3 , Eu_2O_3 , ammonia and nitric acid solutions for the synthesis of luminescent pigment were selected. TEOS 99%, absolute ethanol (EtOH), ammonia 28% ($\text{NH}_3\cdot\text{H}_2\text{O}$) were used for coating the silica on the luminescent particles. All the reagents were supplied from Merck company. The transparent frit (LA-1039 Loab Iran Company) was formulated for this purpose.

2.2. Preparation of luminescent pigment and glaze

The schematic process for synthesis of luminescent glaze is described in Scheme 1. The precipitation method was applied to synthesis the luminescent pigment. stoichiometric amounts of Dy_2O_3 (0.248 g) and Eu_2O_3 (0.1176 g) were dissolved in nitric acid to form $\text{Dy}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ solution, respectively. In another vessel, SrN_2O_5 (3.4 g), $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (21.88 g) were dissolved in distilled water. Then, all solutions were mixed together and diluted ammonia (5%) was gradually added to change the pH value of final solution. The color of the solution became opaque and finally converted to a white gel. The obtained gel was dried in 100°C for 24 hours. Then the powder was calcinated in N_2 atmosphere at 1200°C following the firing program which is shown in Figure 1. The sample obtained by calcinations at 800 , 1000 , 1200 and 1300°C were named as SrAl800, SrAl1000, SrAl1200 and SRA1300, respectively.



Scheme 1: Flowchart of luminescent tile production.

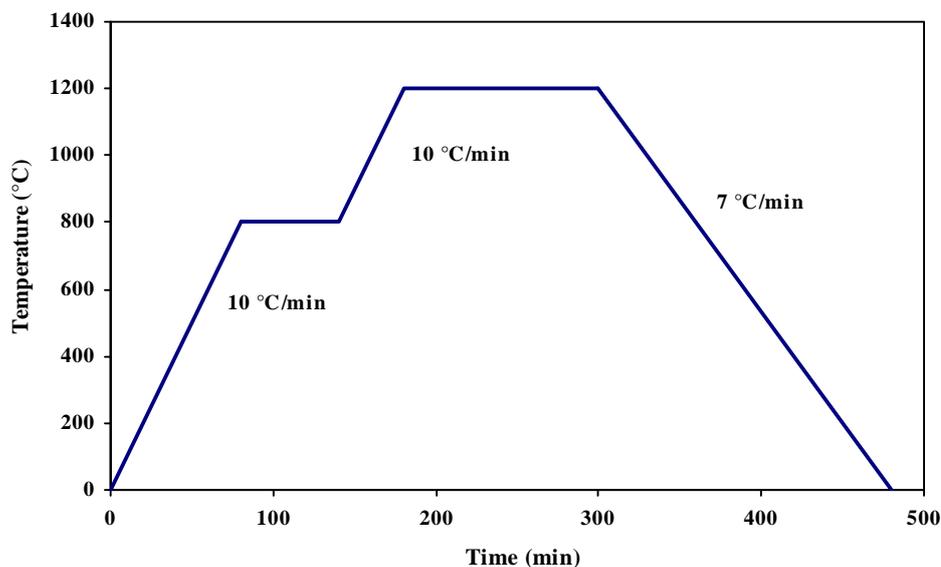


Figure 1: Firing program of calcination.

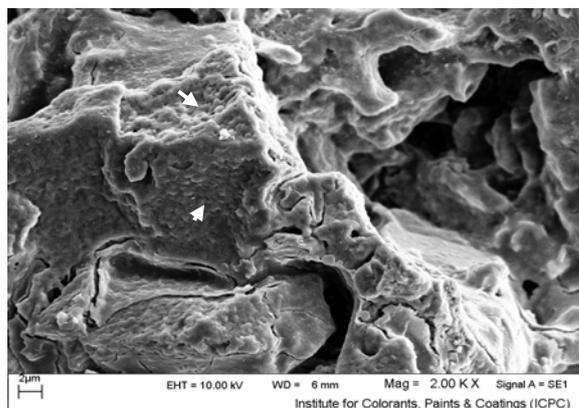


Figure 2: SEM image of the synthesized phosphor at 1300°C (arrows show the nanoscale feature of agglomerate).

For investigating the effect of silica, TEOS (1mL for 20 mL of nitrate solution), ammonia (same amount of TEOS) and water (4 mL for 20 mL nitrate solution) were mixed in a vessel and then quickly added to nitrate solution. Then the process mentioned in the schematic 1 was applied to synthesis luminescent glaze.

The luminous glaze was prepared by mixing the synthesized phosphor with transparent glazes in distilled water. Then it was vigorously grinded in a mortar for 10 min. The amount of phosphor in the luminous glazes was adjusted in the range of 10-30 weight percentages. The

luminous glazes were then coated onto the surface of a tile by silk screen printing. Finally, the tiles were heated in different atmospheres at 900 °C for 30 minutes.

3. Characterization

Structural studies of synthesized samples play an important role to characterize the SrAl_2O_4 : Eu, Dy phase. Because, there are various Sr_2O_3 - Al_2O_3 systems. The crystal structure of samples was studied by means of X-rays diffraction (XRD, AD500 instrument, Siemens, DE)

using Cu K_{α} radiation working with 30 kV accelerating voltage, 25mA current and 2° 2θ /min. The morphology of luminescent particles was observed by scanning electron microscopy using a LEO 1450 VP SEM instrument (LEO Electron Microscopy Ltd., UK). Photoluminescence properties of obtained sample was studied by UV-Visible cabin (UV-Betrachter of camag company). The emission and excitation spectra of $SrAl_2O_4: Eu, Dy$ phosphor particles was carefully determined by a Perkin Elmer LS 5 spectrophotometer.

3.1. Studies of microstructure

SEM images (Figure 2) of luminescent pigments which were calcinated at $1300^{\circ}C$ show that particles were completely consolidated due to liquid phase sintering. However, nanoscale feature of calcinated sample was obviously detected in the agglomerates (as shown by arrows). The liquid phase improves distribution of dopants so uniformly on whole of the host material during the sintering [9].

3.2. Structural studies

Evaluation of phase transformation during calcination processes plays an important role to investigate the luminescence properties [10]. The XRD patterns of SrAl, SrAl800, SrAl1000, SrAl1200 and SrAl1300 are illustrated in Figure 3. The SrAl sample shows the pattern consists of nitrate phases of ammonium and strontium [11]. Probably, preparation of ammonium nitrate phase is due to exceed amount of ammonia which was added to complete the precipitation. Calcination temperature above $800^{\circ}C$ was selected due to entire decomposition of nitrate compound. The amorphous structure of SrAl800 confirms the destruction of nitrate phases. Furthermore, increase of calcination temperature in SrAl1000-1300 samples causes the formation of strontium aluminum oxide structure ($Sr_4Al_{14}O_{25}$ JCPDS No. 01-074-1810). Although, the structure of these samples shows a close similarity, the crystallinity degree of $Sr_4Al_{14}O_{25}$ phase increases significantly with calcination temperature.

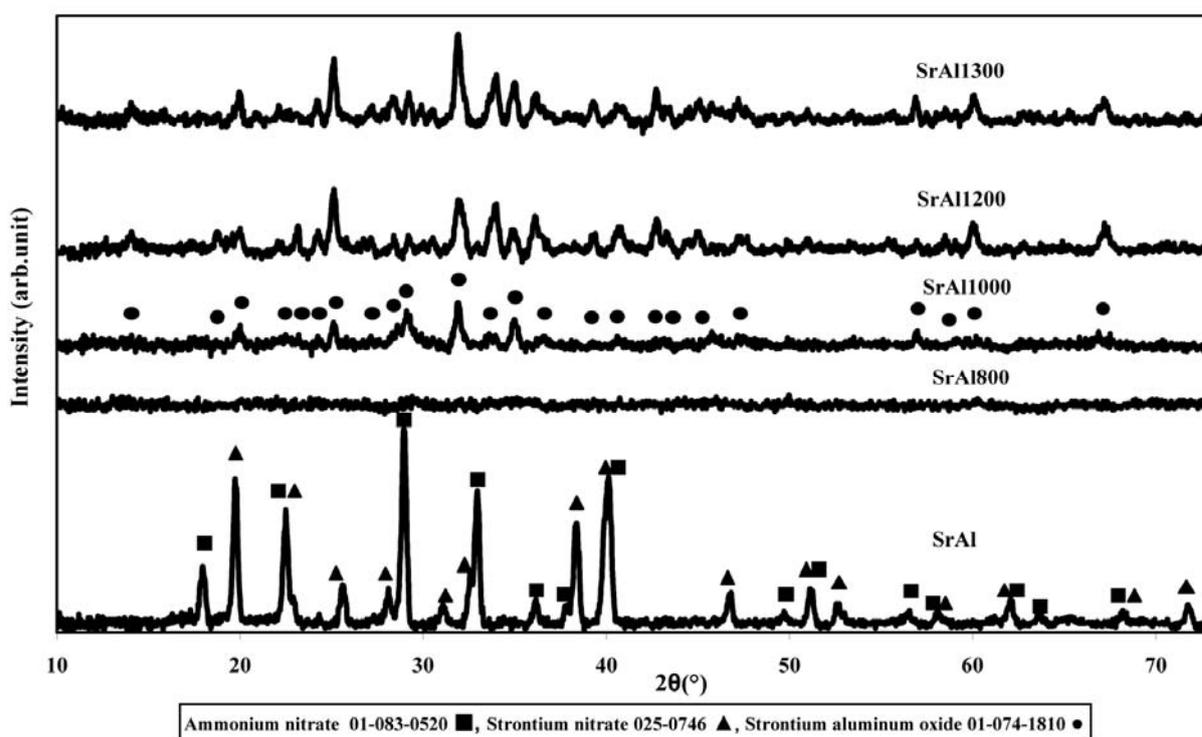


Figure 3: XRD patterns of SrAl, SrAl800, SrAl1000, SrAl1200, and SrAl1300.

The final structure of calcinated samples have good compatibility with calculated stoichiometry. Consequently, the accurate determination of chemical composition in SrO-Al₂O₃ structure is possible via coprecipitation method.

Structural changes in the presence of TEOS as silica

precursor is also investigated. The XRD patterns of SrAl1300 and TEOS-added SrAl1300 are shown in Figure 4. It is indicated that the structure is entirely changed to strontium aluminum silicate phase (Sr₆Al₁₈Si₂O₃₇ JCPDS No. 010-0025) via the reaction of strontium aluminate phase by obtained amorphous silica.

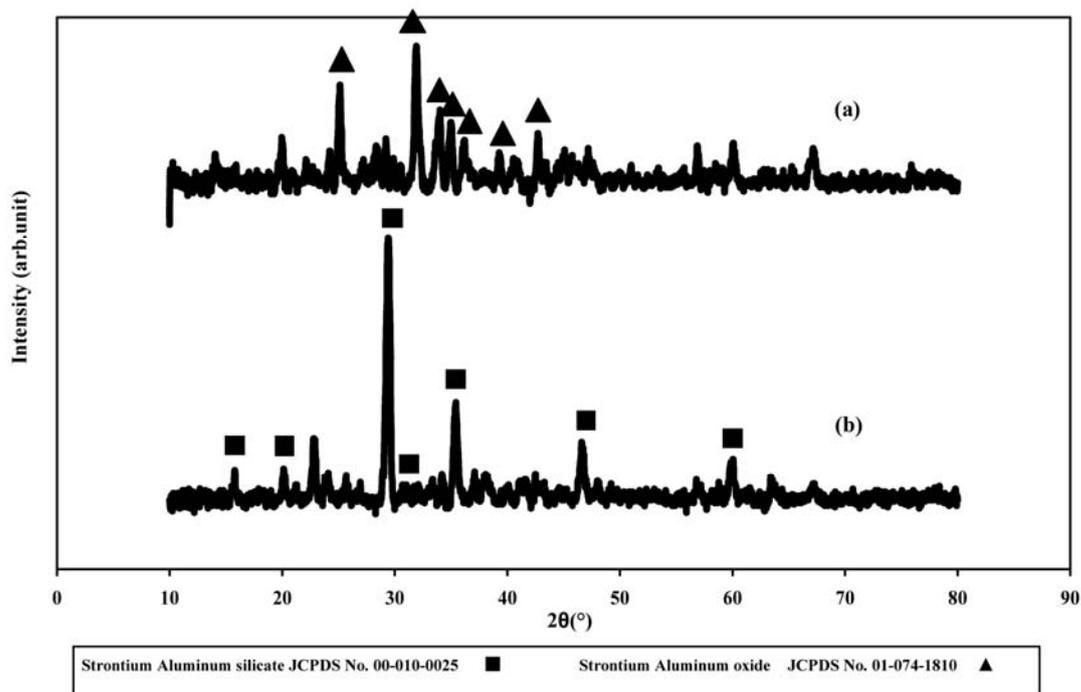


Figure 4: XRD patterns of (a) SrAl1300 (b) TEOS added-SrAl1300.

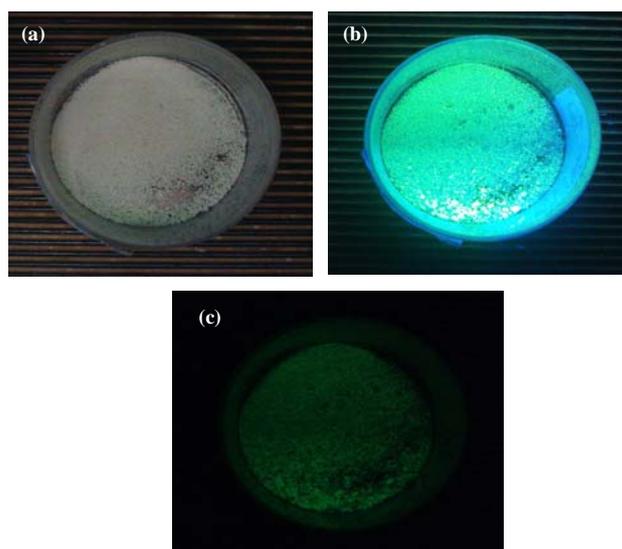


Figure 5: Macro images of SrAl1300 phosphor under UV exposure (366 nm), (a) before excitation, (b) during excitation (c) 30 min after removing the excitation source.

3.3. Photoluminescence studies

3.3.1. Luminescent pigment

As shown in Figure 5, SrAl₁₃O₃ luminescent pigment glows green under exposure of UV lamp. After removing the UV source, the afterglow emission

of the pigment continued for several hours.

Nevertheless, the alumina silicate structure of the sample obtained in the presence of a few amount of silica leads to blue emission (Figure 6).

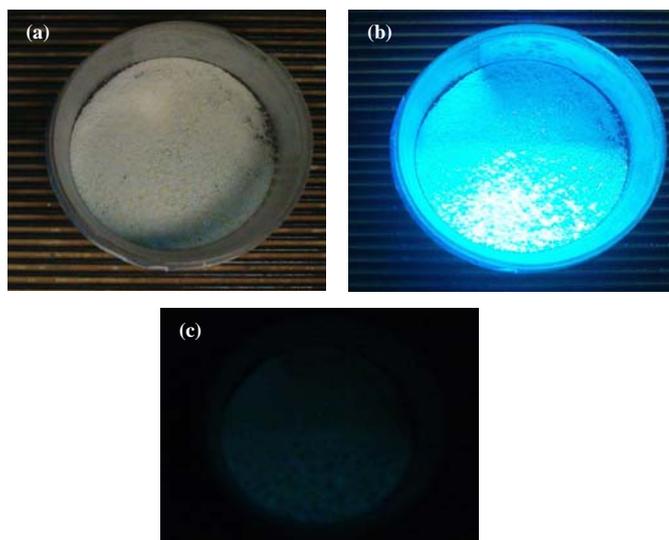


Figure 6: The images of Sr₆Al₁₈Si₂O₃:Eu,Dy phosphor in UV cabin, (a) before excitation, (b) during excitation and (c) 5 min after removing the excitation source.

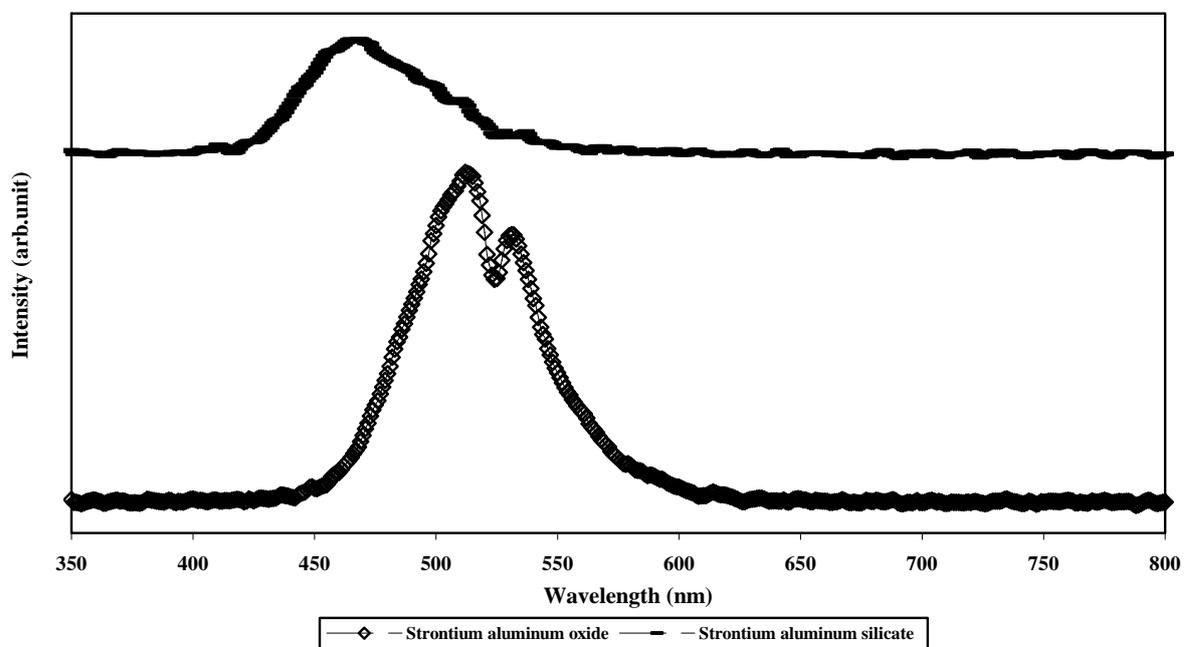


Figure 7: Emission spectra of SrAl₂O₄:Eu,Dy (below) and Sr₆Al₁₈Si₂O₃:Eu,Dy under 325 nm excitation.

Moreover, this structure shows shorter afterglow in comparison with SrAl1300 sample. Figure 7 shows the emission spectra of SrAl1300 and Aluminosilicate samples. The emission spectra of SrAl1300 sample consist of two broad green peaks. The emission of strontium aluminum oxide at 515-535 nm is due to characteristic emission of $4f^65d^1 \rightarrow 4f^7$ transition in Eu^{2+} at 520 nm [12]. However, the emission spectra of Aluminosilicate sample show intense blue shift probably due to the changing the phase. The broad blue-green

emission of this sample is observed around 460 nm.

3.3.2. Photoluminescence properties of glaze

One of the main problems in the production of a luminescence glaze is the oxidizing atmosphere of the glaze and the oxide nature of glaze components. Decreasing the sintering temperature and soaking time improve the luminescence intensity and decay time [8]. The emission of luminescence glazes under UV exposure (366 nm excitation) is illustrated in Figure 8.

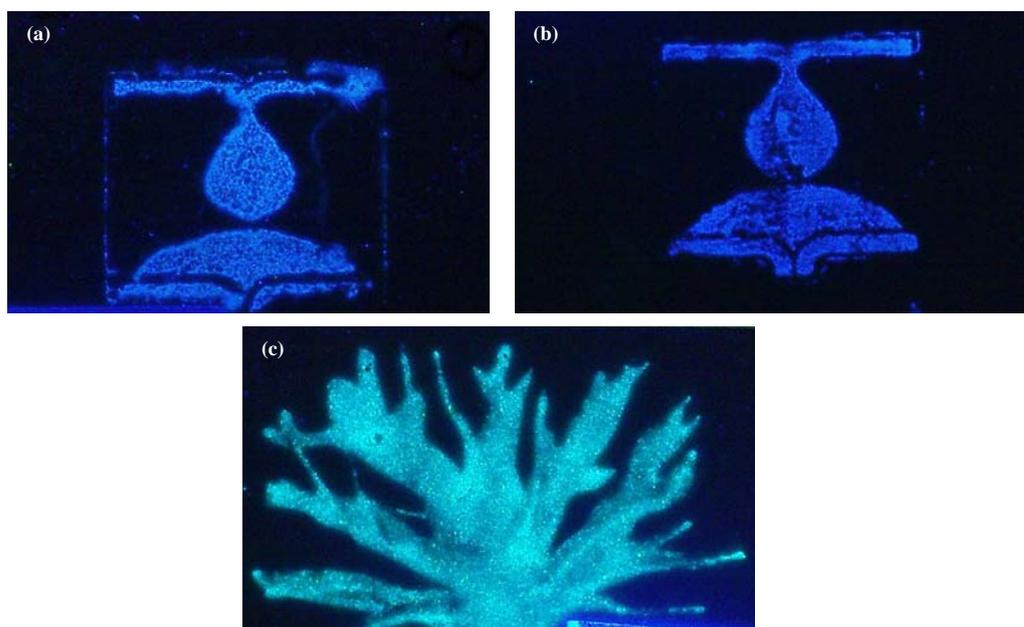
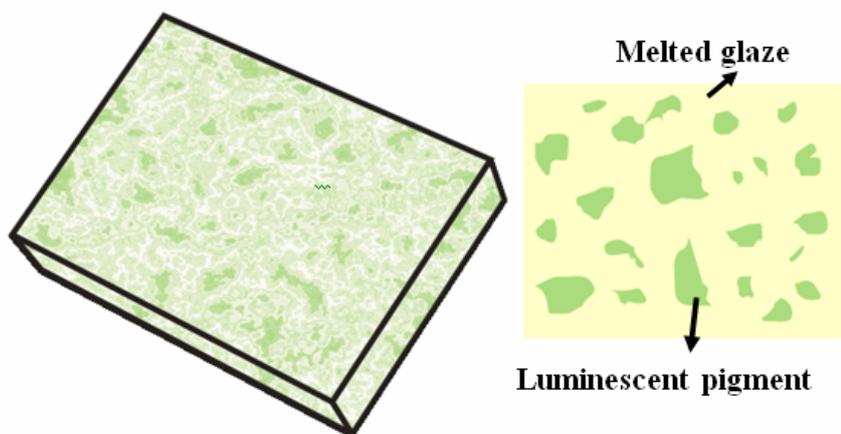


Figure 8: Macro images of emission under UV exposure (366 nm excitation) (a) on glaze, (b) under glaze fired at 900°C in Argon atmosphere (c) over glaze fired at 900°C in air atmosphere.



Scheme 2: Suggested model for luminescence glaze in different magnitude.

The emission color of luminescence glaze is hardly sensitized to firing atmosphere. Moreover, all phosphorescent pigments are converted to fluorescent ones which could be due to intense oxidizing state of melted glaze during the firing step. Schematic model during the firing of glaze is suggested in Scheme 2. Although, the samples obtained in different atmospheres show fluorescent properties, but the emission color depends intensely on the firing

atmosphere.

Figure 9 shows the emission spectra of luminescent glazes. It is clear that the emission of samples is affected by firing atmosphere. The sample which is treated in Argon atmosphere shows blue-green emission (420 nm) and green (520 nm). The later is characteristic peak of Eu^{2+} in the strontium aluminate system [4,13]. However, the green emission of the obtained sample in air has been completely eliminated.

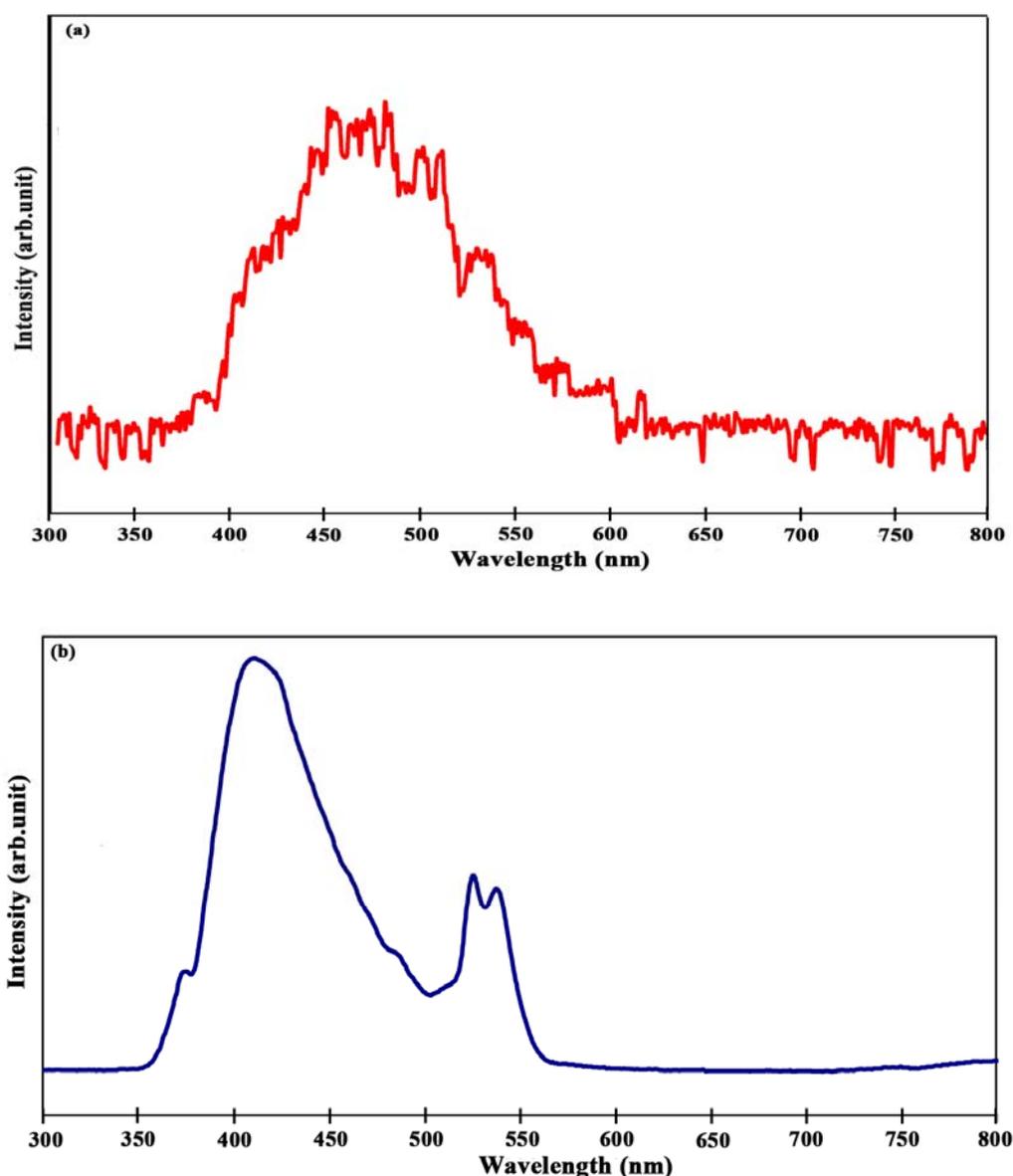


Figure 9: The photoluminescence spectra of glazes fired (a) at air and (b) Argon atmosphere.

4. Conclusions

In this study, SrAl₂O₄:Eu,Dy luminescent pigments are synthesized successfully by co-precipitation method as a simple and controllable technique. The results showed that the synthesized phosphor has strontium aluminate structure. Silica alters the host structure and the obtained powder glows blue and its decay time decreases drastically.

The synthesized powders are used to produce luminescent glaze. The luminescent properties of obtained glaze are sensitive to firing atmosphere. The oxidizing atmosphere completely degrades the decay time in all samples. The emission color of the luminescence glaze shifted from green to blue regions by changing the firing atmosphere.

5. References

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