Polskie Towarzystwo Materiałów Kompozytowych
Polish Society of Composite Materials

25: 1 (2025) 276–281

COMPOSITES THEORY AND PRACTICE

ISSN (online): 2299-128X

Tomasz Pawlik (0000-0002-0623-6319)

Silesian University of Technology, Faculty of Materials Engineering and Industrial Digitalisation, Department of Materials Technologies, Krasińskiego 8, 40-019 Katowice, POLAND
Correspondence: tomasz.pawlik@polsl.pl

Received (Otrzymano) 17.11.2025
Published on-line (Opublikowano) 31.12.2025

INFLUENCE OF MANUFACTURING PARAMETERS ON THE OPTICAL PROPERTIES OF LUMINESCENT GLAZES

https://doi.org/10.62753/ctp.2025.06.4.4

This article focuses on the glass-ceramic composite structure of glazes with photoluminescent properties. In this study the luminescent glaze is based on phosphor: $SrAl_2O_3$:Eu3$^+$, Dy^{3+} (called GS). The study investigated the effect of the phosphor concentration in the glaze within the range of 10-30 wt% and the effect of annealing time within the range of 0-60 minutes. Changes in phase composition were observed as a function of the process parameters (annealing time) and changes in the photoluminescent properties (excitation spectrum, emission spectrum, and quantum yield) to determine the optimal annealing time during glazing. The study found that with increasing glazing time, the luminescent properties deteriorated due to degradation of the crystalline structure.

Keywords: **glazes, photoluminescence, $SrAl_2O_3$:Eu3$^+$, Dy^{3+}, phase composition, glazing parameters**

INTRODUCTION

Luminescent glazes are an innovative group of materials used to create a protective layer on material surfaces, which are also required to possess photoluminescent properties. While there are few reports in the literature on this type of material, interest in them is growing, as evidenced by patents for this type of material [1]. These glazes combine the properties of traditional glazes (reducing the porosity of the substrate material and providing surface tightness, protecting against water absorption, hardening the surface, improving the mechanical properties, increasing abrasion resistance, ensuring appropriate smoothness, and adding aesthetic value) with the luminescent properties of the material surface. The photoluminescent glaze effect is most easily achieved by combining traditional glazes with a phosphor. The phenomenon of luminescence involves the emission of light (usually in the visible range) by a chemical substance, with the exception of light emitted by high temperature (incandescence). In luminescence, light emission occurs as a result of exciting a material (electrons to higher energy states) with various forms of energy. Therefore, we can speak of bioluminescence, chemiluminescence, radioluminescence, mechanoluminescence, and many others. In other words, luminescence involves the transfer of energy (of various types) into light energy. Photoluminophores (PL) are a special type of phosphor, where a material is excited to emit a different light (light of a different, usually shorter, wavelength) to emit light of a longer wavelength, i.e. lower energy. Currently, modern photoluminophores have a number of applications, including in medicine, television screens, LEDs, various types of fluorescent lamps, modern, energy-saving LED-based light sources, and even as a material in art [2]. Research is currently underway on the use of luminescent glazes as anti-counterfeiting protection [3]. The photoluminescence phenomenon is also employed in various types of warning and evacuation signs. Photoluminescence can have different time histories. In the case of fluorescence, light emission is immediate and ceases immediately after the material is no longer stimulated – the carrier lifetime is very short, lasting no longer than 10-8 s, whereas phosphorescence has a longer carrier lifetime, and light emission can last up to several days [4]. In the case of the investigated phosphor, $SrAl_2O_3$:Eu^{3+}, Dy^{3+}, each of its components performs a specific function. Strontium aluminate, which provides the structure, acts as a matrix containing Eu (activator) and Dy (coactivator), thus this phosphor exhibits prolonged luminescence [5]. The phenomenon of photoluminescence can be explained based on the so-called Jabłoński diagram, published in 1933 in the journal *Nature* [6], where the author presents a diagram of transitions between electron energy levels as a result of energy absorption (excitation). It also allows us to predict the type of light emission that will occur when an electron returns to its ground state, as the color (wavelength) of the emitted light depends primarily on the energy emitted by the electron upon transitioning to a lower level. Therefore, when assessing the luminescent properties of a given chemical substance, it is crucial to know the type of energy that can excite electrons to a higher energy state. In the case of photoluminophores, this will be energy (light of a specific wavelength). Therefore, it is necessary to conduct excitation spectrum studies, i.e. determine which wavelength is most effectively absorbed by the electron, causing it to be excited to higher energy states. After the electron is excited, it will remain in the excited state for a certain time and then begin to return to the ground state, shedding excess energy by emitting a quantum of light of a specific wavelength (depending on the difference in energy levels). As part of the emission spectrum study, the wavelength (wavelength distribution) of the emitted light can be determined. Knowing both parameters – the excitation wavelength and the emission range – allows us to determine the quantum yield and examine the luminescence (phosphorescence) time for optimized process parameters. As a result of intensive research in recent years, scientists have also developed modern multimode luminescent materials that emit more than one color of light, depending on the concentration of doped rare-earth ions. This allows progressive color emission and adjustable afterglow duration for multimode luminescence [3]. Due to the lack of clear information in the literature on the effect of glazing parameters on the photoluminescent properties of glazes, research in this area was undertaken.

EXPERIMENTAL PROCEDURE

A commercial phosphor $SrAl_2O_3$:Eu3^{+}, Dy^{3+} (called GS) was selected for the study, which was used to produce a luminescent glaze (product code: S-JN260, CHAOS TRADE, Poland). The base glaze was a commercial transparent glaze BSZ 210/TC 7910 manufactured by Steatyt, with an annealing temperature of 1020-1080°C. A suspension containing 2, 10, and 30 wt% of phosphor in the glaze was prepared. The given phosphor concentrations were selected based on previous studies. It was clearly established that as the phosphor content in the glaze increases, the glaze properties deteriorate at the expense of improved luminescence properties. Hence, for the purposes of this publication, a maximum glaze content of 30 wt% was adopted. The ingredients were homogenized in an aqueous suspension using a magnetic stirrer. The water-to-glaze mixture ratio was constant for every sample. The prepared glazes were applied by placing drops of constant volume (25 μl each) onto ceramic bases. The bases were made into pellets with a diameter of 12.5 mm and a height of 2 mm. The bases were made from an aluminosilicate ceramic mass and then sintered at 1050°C for 60 minutes. Commercial ceramic mass 23/WKFL from CARL JAEGER was utilized to produce the pellets using uniaxial pressing at a pressure of 160 MPa. After applying the glaze and drying to a constant mass, the bases were heated in a chamber furnace at 1050°C for 0; 2; 5; 10; 30; and 60 minutes in air, respectively. Once the desired holding time was reached, the samples were removed from the furnace chamber. A holding time of 0 minutes meant that the sample was removed from the furnace immediately after reaching a temperature of 1050°C. Studying the effect of heating time has a significant impact on the properties of photoluminescent glazes, as an inappropriate time or temperature during glazing can lead to degradation of the glaze properties [7]. For comparison, reference samples containing only phosphor (called GS raw or GS 100%: containing 100% phosphor) without the addition of glaze were also prepared and heated at this temperature for 0 and 60 minutes. Three samples were prepared for each experimental variant. The phase composition of the glazed samples was determined by means of XRD with a Philips PANalytical Empyrean equipped with a 1.5406A copper cathode and an automatic sample feeder. The studies were performed in the 10-70° 2Θ angle range with a 0.02° step. B The basic photoluminescent properties (excitation spectrum, emission spectrum) were studied on an Edinburgh Instruments spectrofluorometer FS5 equipped with a 150 W xenon lamp and an SC10 attachment. Based on qualitative excitation and emission spectral results, the optimal excitation wavelength was determined to achieve maximum emission. The phosphor used for the study was excited to emit light in the UV range, producing visible blue light. Quantitative quantum yield studies were then conducted using the determined optimal excitation and emission parameters employing an SC-30 device. All the optical property studies were conducted at room temperature.

RESULTS AND DISCUSSION

Preliminary tests of the luminescence properties in a UV chamber (for 366nm UV light) for the obtained samples confirmed the photoluminescent properties of the glazes with the GS addition and the clear effect of the luminophore concentration on the efficiency of this process. This was also confirmed by spectrofluorometric testing.

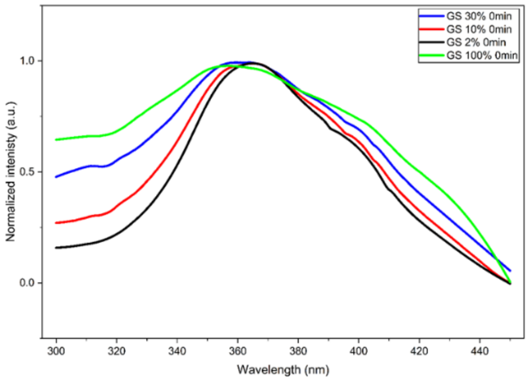

Fig 1. Excitation results for GS with phosphor concentrations of 2, 10, 30 and 100 wt% and hold time of 0 minutes

Analysis of the normalized excitation results revealed that the curves were not identical, but were similar in nature. Slight shifts in the excitation peak maximum were observed depending on the phosphor concentration in the glass. However, a clear difference in the shape of the curves was observed, with increasing phosphor concentration, resulting in broadening of the spectrum. The maximum width was recorded for the sample containing 100 wt% phosphor.

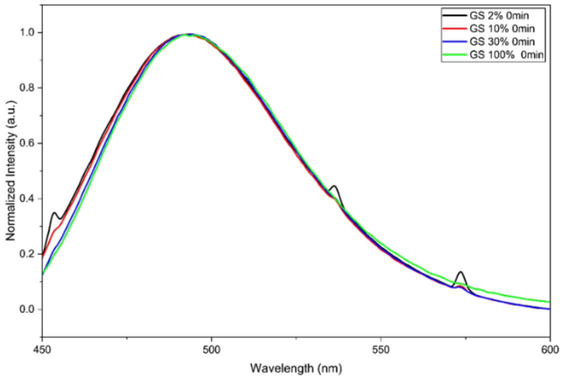

Fig. 2. Normalized emission results for GS with phosphor concentrations of 2, 10, 30 and 100 wt% and dwell time of 0 minutes

The emission spectral results (normalized) did not show any significant changes in the curves as a function of phosphor concentration. Nevertheless, the appearance of additional peaks around

453, 536, and 573 nm is noteworthy. This effect is suspected to be generated by the glass, as it was not observed in the sample containing only the luminophore (GS 100% 0 min), and the peak intensity grew with the increasing enamel content in the samples.

TABLE 2. **Positions of excitation and emission peak maxima for individual GS samples**

Sample	Ex position [nm]	Em position [nm]
GS 2% raw	368.8	490.8
GS 2% 0 min	366.0	493.8
GS 2% 60 min	370.0	453.2
GS 10% raw	360.4	493.0
GS 10% 0 min	365.0	492.8
GS 10% 60 min	367.0	453.0
GS 30% raw	367.6	496.2
GS 30% 0 min	357.0	494.8
GS 30% 60 min	362.6	493.4
GS ref (100%) raw	369.6	495.8
GS ref (100%) 0 min	357.6	495.6
GS ref (100%) 60 min	355.6	494.6

Therefore, based on PL studies, optimal excitation and emission wavelength parameters were determined, and quantum efficiency studies were conducted for these parameters, quantifying the efficiency of the energy conversion process as a function of annealing time. The studies were conducted for an excitation wavelength of 370 nm and an emission wavelength of 495 nm.

Based on the results presented in Figure 3, it was found that quantum efficiency strongly depends on the annealing (glazing) time. Quantum efficiency remains relatively similar or decreases slightly over an annealing time of approximately 10 minutes. For the GS30% sample, a sharp decline is observed after approximately 10 minutes of annealing, from approximately 20% to approximately 10% at 30 minutes, reaching a value close to 0 for an annealing time of 60 minutes. Nonetheless, the nature of the quantum efficiency decrease is not uniform across the sample series (phosphor content). Owing to the highest phosphor content in GS30%, the decrease is most pronounced after 10 minutes. For lower phosphor contents (2 and 10 wt%), the quantum yield declines practically from the outset. Thus, for samples with the lower glass content, any increase in hold time is associated with a drop in luminescent properties.

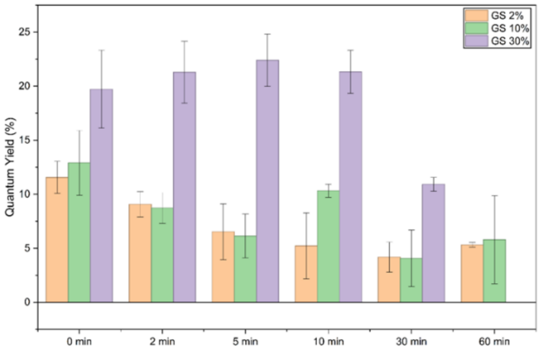

Fig. 3. Quantum efficiency results for samples with 2, 10 and 30% phosphor content at 0-60 minutes of exposure time

To explain the phenomenon, XRD phase composition analysis was performed. Studies of pure GS 100% phosphor, heated for up to 60 minutes, showed very high phase stability throughout the entire heating time range. Figure 4 presents the XRD phase composition results for the pure GF-ref phosphor sample without the addition of glaze, the GS 30% raw sample containing 30% phosphor without heat treatment, the GS 30% 0 min sample with a holding time of 0 minutes, and the 30% 60 min sample after heating for 60 minutes. The dashed line indicates the peaks originating from the $Sr_4Al_{14}O_{25}$ phase.

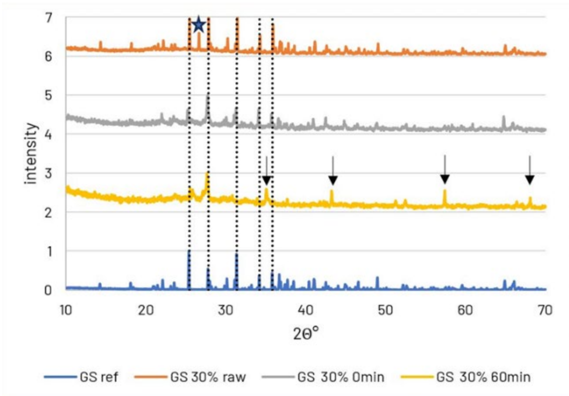

Fig. 4. XRD phase composition test results for different variants of GS 30% sample as a function of annealing time. Sr4Al14O25 phase is marked with dashed line

As a result of annealing, changes in the phase composition (disappearance and appearance of new phases) were observed as a function of annealing time. For the GS 30% 60 min sample containing 30 wt% phosphor, i.e. the one in which the quantum yield dropped to practically 0 after 60 minutes of annealing, these changes are most visible. Unlike the samples with the lower phosphor content (where a much larger amount of amorphous phase was observed), all the GS 30% samples were clearly crystallized (a low amorphous phase content), and in the all investigated samples, regardless of the annealing time, peaks originating from the $Sr_4Al_{14}O_{25}$ phase are clearly visible. For the GS 30% raw sample, an additional peak was observed at the position of approximately 26.6 (marked with a star in Fig. 4), which is not visible for other variants of the GS 30% samples. This phase is observed with varying intensity, but only in the raw samples – without heat treatment (GS 2% raw, GS 10% raw, and GS 30% raw). This is probably a peak of the phase originating from the glass components (raw powder components before vitrification), which transforms into the amorphous phase immediately after melting the glass (disappearance for post-melt materials). A trend can also be observed for all the GS30% samples: with increasing heating time, the background level in the 2-theta range below 20°C rises, indicating an increased amount of the glassy phase. The disappearance of certain peaks in this range is also clearly visible. These changes seem to progress with increasing heating time, and in the sample heated for 60 minutes, new, previously absent peaks (marked with a black arrow in Fig. 4) appear at positions 35.06; 43.23; 57.09; and 68.09. These peaks originate from the Al_2O_3 phase (98-003-0024). Its appearance in this sample is probably related to the dissolution of strontium aluminate in the liquid phase and subsequent crystallization of Al_2O_3. Given the increase in the amount of the amorphous phase, the gradual disappearance of certain phases, and the appearance of new ones (after 60 minutes of heating), it can be concluded that these phases dissolve in the glass (the glassy phase forming the amorphous phase) with increasing heating time, which is confirmed by the results of the quantum yield studies.

CONCLUSIONS

Creating a luminescent glaze by combining a classic glaze with a $SrAl_2O_3$:Eu^{3+}, Dy^{3+} phosphor using glazing technology enables the luminescent properties of the surface layer to be achieved. However, the technological parameters of the process have a significant impact on the quality of this luminescence. Extending the heating time beyond a certain time (0-10 minutes, depending on the sample) causes a decrease in luminescence, and in extreme cases, its disappearance. This does not result from the thermal instability of the phosphor itself, but rather from the presence of a glassy phase during the heating process and the probable dissolution of the phases responsible for luminescence from the liquid phase. Nevertheless, the course and dynamics of this process (maximum heating time after which luminescence decreases) vary depending on the phosphor concentration. Therefore, with the current state of knowledge, it is impossible to determine the optimal process conditions, as they depend on the glaze composition.

Acknowledgements

The author would like to thank to Kacper Komoniewski for the opportunity to use part of the results of his master's thesis, additionally for his research and editorial assistance, as well as Dr. Piotr Olesik from the Department of Materials Technology, Silesian University of Technology for his extensive support in creating this article, both during the research and editing stages.

The study was realized within the frames of Statutory Research Project nr 11/030/BK_25/1221 at the Silesian University of Technology, Poland.

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