

Investigation on the Luminescent Behaviour of Er³⁺ Doped SrO-Al₂O₃-SiO₂-Based Glass-Ceramic Coatings

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Abstract

Glass-ceramic (GC) coatings which possesses luminescence properties are excellent candidates for coating surfaces that are in direct contact with external conditions such as architectural panels, traffic and advertising signs, thanks to their mechanical strength, chemical resistance and aesthetic properties. The aim of the study is to develop a luminescent glass-ceramic (LGC) system based on SrO-Al₂O₃-SiO₂ and integrate it into a glass-ceramic coating applied onto a metal substrate by 3-coat-2 firing method. The LGC was produced by doping Er³⁺ into the SrO-Al₂O₃-SiO₂-based glass matrix, melting at 1100-1400 °C and subsequent quenching. The produced LGCs were incorporated into the GC coating formulation as a mill additive in the amounts of 20-40 wt.%. The LGC-added GC coating formulation was applied on a low carbon steel substrate via the wet spraying method as the final coat layer and crystallized at 820 °C for 4 min. A spectrofluorometer was used to evaluate the luminescence characteristics of the final coatings by measuring the emission spectrum and excitation spectra. XRF, XRD, and SEM-EDS analyses were conducted to examine the chemical composition, crystalline structure, microstructure and surface morphology of coatings, respectively.

Er³⁺ Katkılı SrO-Al₂O₃-SiO₂ Esaslı Cam-Seramik Kaplamaların Lüminesans Davranışlarının İncelenmesi

Özet

Lüminesans özellik kazandırılan cam-seramik kaplamalar, mekanik mukavemeti, kimyasal direnç ve estetik özelliklerinden dolayı mimari paneller, trafik ve reklam tabelaları gibi dış koşullarla doğrudan temas halinde olan yüzeylerin kaplanması için mükemmel adaylardır. Çalışmanın amacı, SrO-Al₂O₃-SiO₂ esaslı bir lüminesans cam-seramik (LGC) sistemi geliştirmek ve bunu 3 kat-2 pişirim metodu ile metal bir alt tabakaya uygulanan cam-seramik kaplamaya entegre etmektir. LGC, Er³⁺'in SrO-Al₂O₃-SiO₂ esaslı cam matrisine katılması, 1100-1400°C'de egrilmesi ve ardından su verilmesiyle üretildi. Üretilen LGC, GC kaplama formülasyonuna değirmen katkı maddesi olarak ağırlıkça %20-40 olarak eklendi. LGC katkılı GC kaplama formülasyonu, son kaplama tabakası olarak ıslak püskürtme yöntemiyle düşük karbonlu bir çelik altlık üzerine uygulandı ve 4 dakika boyunca 820 °C'de kristallendirildi. Yayınım ve uyarma spektrumlarını ölçerek nihai kaplamaların lüminesans karakterini değerlendirmek için bir spektrofotometre kullanıldı. Kaplamaların sırasıyla kimyasal bileşimini, kristal yapısını, mikro yapısını ve yüzey morfolojisini incelemek için XRF, XRD ve SEM-EDS analizleri yapılmıştır.

1. INTRODUCTION

The quality of human life beings has improved visibly after finding lighting and many things have changed afterwards. This development, which started with wood fire and continued with candles and gas lamps, was accelerated significantly with the invention of electricity. Thanks to the incredible development in lighting technologies that started with the invention of incandescent lamps, fluorescent and led technologies have been developed, and these events have significantly affected our both working and daily life.

The luminescence phenomenon, which occurs when excited atoms or molecules return to their basic energy level by making electromagnetic radiation, varies according to the external stimulating effect. If the excitation energy is obtained from a chemical reaction, it is called chemiluminescence, if it is obtained from the electrode reaction, it is called electroluminescence, if it is provided by heating, it is called thermoluminescence, and if it is provided by the absorption of photons, it is called photoluminescence. Photoluminescence is a special case of electromagnetic radiation and is divided into two main groups as fluorescence and phosphorescence. Fluorescent materials absorb energy as a result of the excitation of an electron in the ground state and move to another level. By emitting the energy it has absorbed, it returns to its basic energy level and radiates at the same time. In fluorescence, the energy transfer does not cause a change in the spin of the electron, which causes the radiation lifetime to be very short. Phosphorescence, on the other hand, differs from fluorescence in that it does not return the energy it absorbs in a short time.¹⁻³

With the use of luminescent materials in fluorescent and LEDs, studies in this field have intensified. Phosphorus studies, which started with the calcination of barium sulfate, continued with zinc sulfide and other alkaline earth sulfides, but their chemical instability caused them to be replaced by Sr₂Al₂O₄ phosphorus in the following years.³ Although aluminates have important advantages such as better chemical and thermal stability, higher luminous intensity and a much longer luminescence time than conventional phosphors, their inability to remain stable in contact with water is disadvantageous. Therefore, silicate-based phosphors have attracted great attention thanks to their high chemical stability, color variety and water resistance.⁴

The use of GC coatings, according to many historians, dates back to the A.D. 5th century. These coatings, which were initially used to color sculptures, adjust color tones by jewelers, and for painting, were used in many areas such as boiling water tanks, kitchen tools and utensils, traffic and advertising signs and architectural coatings with the industrial revolution.⁵ They were obtained by controlled crystallization and nucleation of glass and were have properties such as superior mechanical robustness, thermal durability, chemical inertness, thanks to the certain crystal phases that form them.⁶ Different metal substrates such as steel, cast iron, aluminum, and copper can be coated with them.

Frit, which is the main component of glass-ceramic coating, is obtained by homogeneously dispersing quartz, borax, feldspar and metal oxides in a molten state and by quenching. Then, it is applied onto the metal substrate surface with the wet or powder application method after grinding to the micron level with various mill additives. It is fired in the range of 710-850°C, allowing crystallization and nucleation at the glass

transition temperature. It is then left to cool at room temperature.⁷

GC coatings are a type of coating with improved physical properties such as colour, glossiness, surface smoothness, and light transmittance values. In addition to covering all the defects on the metal substrate surface, they allow the opacity to be adjusted by incorporating TiO₂, which is an opacifier, into the main glass structure.⁸ In order to adjust the opacity, the elements that provide the adhesion mechanism to the metal substrate cannot be included, so that the coloring elements are not allowed to enter the main glass structure. For this reason, the ground layer coating on the metal substrate ensures that the top layer coatings adhere to the metal substrate. Under the transparent topcoat with LGC added, a white intermediate coat is applied to make this luminescent effect glow more clearly. The upper layer is the layer where the luminescence mechanism takes place. This 3-layer 2-firing method allows the use of luminescent pigments in glass-ceramic coatings.

In the study of Rossi et al.⁹, an LGC pigment of uncertain composition was obtained, and they coated the metal substrate surface with 3 layers 2 firing method by ground layer, white intermediate layer and top layer that containing 50%LGC pigment. Zhang et al.¹⁰, on the other hand, worked with SrAl₂O₄: Eu²⁺, Dy³⁺ doped GC systems with the same method. Wie et al.¹¹, on the other hand, chose the SrO-Al₂O₃-SiO₂ GC system due to its features such as high crystallinity, high thermal resistance and mechanical robustness.

In this study, the luminescence behavior of SrAl₂Si₂O₈: Er³⁺, Dy³⁺ glass-ceramic system was selected as a LGC pigment in GC coatings applied on metal substrates and investigated. The primer coat and the white intermediate coat applied onto the metal substrate surface are in the traditional glass-ceramic composition. The LGC pigment embedded in the transparent glass-ceramic system applied to the topcoat was added in two different ratios, 20% and 40%, and subjected to various analyzes.

2. METHODS

2.1. Materials

Initially, the frit composition in the SrO-Al₂O₃-SiO₂ -based LGC system, ground and intermediate glass-ceramic system layers and all application devices were supplied by Akcoat Advanced Chemical Coating Materials (Sakarya, Turkey).

2.2. Preparation of Samples

Raw materials weighed and homogeneously mixed in accordance with 45SiO₂-31SrO-15Al₂O₃-4,5Li₂O-3.5B₂O₃-0.5Na₂O-0.5TiO₂-(0-0.5)Er₂O₃-(0-0.5)Dy₂O₃ mass stoichiometry were put in an alumina-zircon-silicate crucible and melted with an electric furnace. After holding in the molten phase for 1 hour, it was poured into water to obtain an LGC pigment in a frit form.

All frits were ground in mills with alumina-zircon balls. The frit mixtures were prepared for the ground, intermediate and topcoat, whose chemical compositions are given in Tables 1, 2 and 3, were ground for 12 min. Then, the flotation agents and mill additives (clay, boric acid, and sodium nitrite⁶) were added and the grinding process is carried out for 3 more min. Powders are sieved through a 60-mesh (250

µm) sieve. The LGC pigment was ground in a mill with alumina-zirconia balls for 10 min and then sieved through a 200-mesh (50 µm) sieve. 40-50% of the water of the total volume was added to the powders and homogenized in the mill for 2 min. The same processes were applied to the upper layer by adding LGC pigment at the rates given in Table 4.

Table 1. Chemical composition of ground coat (%).

Oxide Group	Amount (%)
R ₂ O (Na ₂ O, K ₂ O, Li ₂ O)	16.09
RO (CaO, MgO, BaO, NiO, CoO, CuO, MnO)	8.07
RO ₂ (SiO ₂ , TiO ₂)	51.87
R ₂ O ₃ (Fe ₂ O ₃ , B ₂ O ₃ , Al ₂ O ₃)	21.76
Others (P ₂ O ₅ , F ₂)	2.21

Table 2. Chemical composition of intermediate coat (%).

Oxide Group	Amount (%)
R ₂ O (Na ₂ O, K ₂ O, Li ₂ O)	15.02
RO (CaO, MgO, CoO)	1.36
RO ₂ (SiO ₂ , TiO ₂)	60.82
R ₂ O ₃ (Fe ₂ O ₃ , B ₂ O ₃ , Al ₂ O ₃)	18.18
Others (P ₂ O ₅ , F ₂)	4.62

Table 3. Chemical composition of topcoat (%).

Oxide Group	Amount (%)
R ₂ O (Na ₂ O, K ₂ O)	17.65
RO (CaO, BaO, ZnO)	12.98
RO ₂ (SiO ₂ , TiO ₂)	52.71
R ₂ O ₃ (Fe ₂ O ₃ , B ₂ O ₃ , Al ₂ O ₃)	14.18
F ₂	2.47

Table 4. LGC ratios added to the transparent top coat (%)

Samples	Amount (%)
LUM 1	20
LUM 2	40

2.3. Coating Process

The surface cleaning process was applied to the metal substrate of 10cmx10cm size selected in accordance with EN 10209 standard before coating. The ground coat, which was applied to the prepared metal substrate by the wet spray method, was kept in an oven at 110°C and the water in it was evaporated. Then an intermediate layer was applied, and the water was evaporated by keeping it in the oven again. The coated sample was firstly sintered in a pre-heated oven at 550°C for 4 min. and then fired in a box oven at 820°C for 4 min for controlled crystallization. A transparent topcoat glass-ceramic coating with luminescence additive was applied on the coated sample, again by wet spray method, and it was kept in an oven and after the water inside was evaporated, it was baked in a pre-heated oven at 550°C for 4 min and in a box oven at 820°C for 4 min for controlled crystallization. After firing at all steps, coated samples were cooled down to room temperature.

2.3. Characterization

The chemical composition of the designed LGC pigment was analyzed using the Bruker S8 Tiger X-ray fluorescent (XRF) device. The oxide percentages of the frit were observed to confirm that it was produced in the correct chemical composition and ratio and to make correct interpretations. X-Ray Diffraction (XRD) analysis with Cu-K_α radiation in the 2θ scanning range of 10°–80° was performed using the Bruker D8 Advanced device to examine the successful production of the luminescent frit and to examine whether the Sr-celsian (SrAl₂Si₂O₈) glass-ceramic matrix desired to be achieved after controlled crystallization was formed. The cross-section of the coating applied on the sample was examined by Jeol JSM-6060LV scanning electron microscopy (SEM) equipped with EDS. An acceleration voltage of 20 kV was used at working distances of 9.5 and 10 mm for SEM analysis. To analyze the emission, emission colour, excitation, spectrophotometer and UV/Vis/NIR spectrofluorometer analysis were performed on the GC coated state by using Perkin Elmer Lambda 950 and Edinburgh Instruments FS5 devices, respectively.

3. RESULTS AND DISCUSSION

3.1. Chemical Structure

Results from XRF analysis are shown in Table 5. According to XRF analysis, LGC pigment was obtained with high accuracy. The XRD analysis of the LGC pigment before firing is shown in Fig.1. As seen in the XRD analysis, the frit was successfully obtained in fully amorphous state. According to the XRD analysis of the LGC pigment after firing, it was observed that the structure was completed in the Sr-celsian phase.

Table 5. Chemical composition of LGC pigment (%).

Oxide Group	Composition (%)
SiO ₂	45.4
SrO	30.50
Al ₂ O ₃	14.4
Li ₂ O	4.2
B ₂ O ₃	3.4
Na ₂ O	0.4
TiO ₂	0.4
Er ₂ O ₃	0.5-1.00
Dy ₂ O ₃	0.5-1.00
Total	100

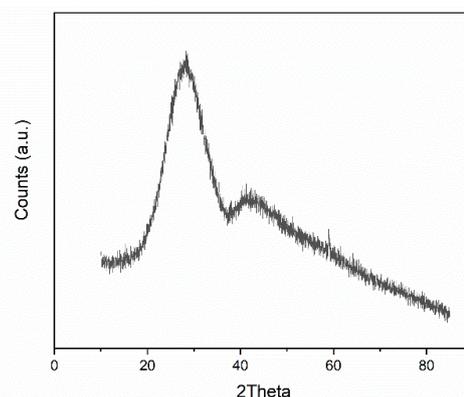


Figure 1. XRD analysis of the LGC pigment before firing.

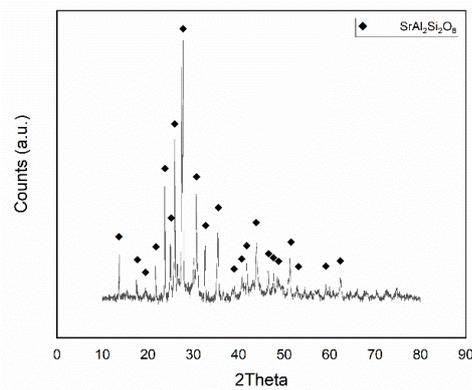


Figure 2. XRD analysis of the LGC pigment after firing.

3.2. Microstructural Analysis

SEM analysis was performed to examine the morphology of the studied samples. The bright layer seen at the bottom shows the metal substrate. Contrast turns up in each layer upwards from the metal substrate. This shows that there is a ground coat which is the black layer at the bottom, an intermediate coat in the middle, and a transparent coat at the top. It is clearly seen in Fig.3 and Fig.5 that the luminescent pigment was successfully embedded in the upper transparent layer and remained intact in the structure. As shown in the EDS analysis in Fig.4 and Fig.6, the particles embedded in the glass-ceramic structure are the LGC pigment we designed.

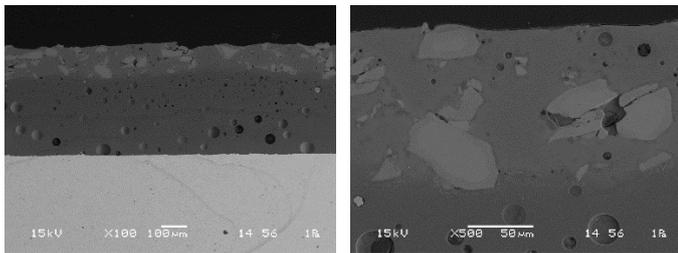


Figure 3. SEM images analysis of the LUM 1 which contains 20% LGC pigment on the top layer.

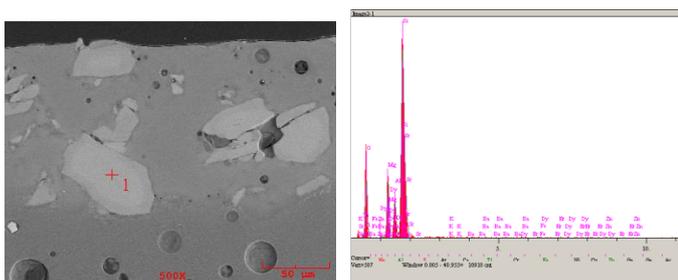


Figure 4. EDS analysis of the LUM 1 which contains 20% LGC pigment on the top layer.

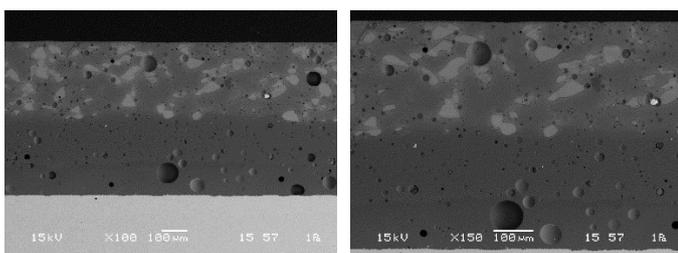


Figure 5. SEM images analysis of the Lum 2 which contains 40% LGC pigment on the top layer.

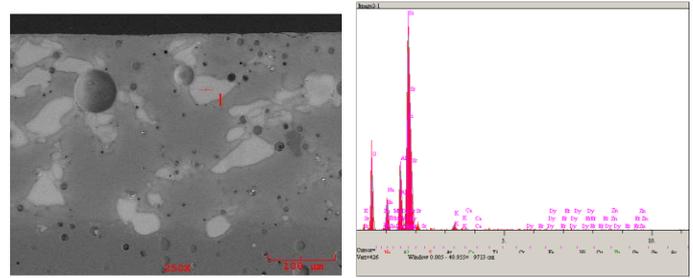


Figure 6. EDS analysis of the Lum 2 which contains 40% LGC pigment on the top layer.

As can be seen in Fig.5, an increase was observed in the number of pigments per unit area in the transparent topcoat coating of LGC pigment in the Lum 2 sample.

3.3. Luminescent Properties

UV/VIS/NIR and spectrophotometer analyzes were performed to measure the luminescence in (Fig.7 and Fig.8). The strongest excitation value shown at 325nm does not change in both samples. Even though the ratio of LGC pigment in Lum1 and Lum 2 samples changed, the excitation intensity did not change, showing that the SAS glass-ceramic system allowed maximum absorbance.

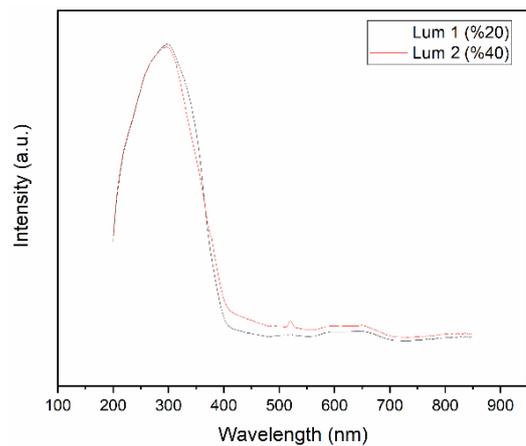


Figure 7. Excitation spectra of Lum 1 and Lum 2 samples.

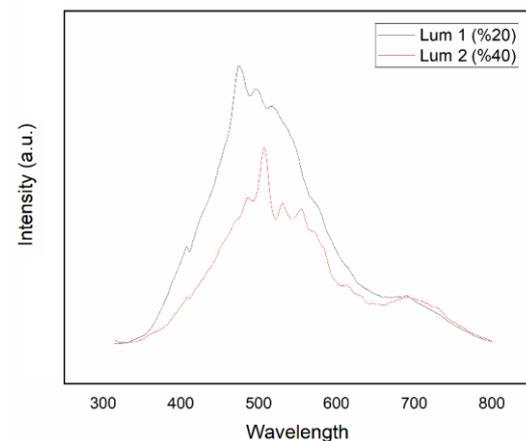


Figure 8. Emission spectra of Lum 1 and Lum 2 samples.

As can be seen in Fig.6, it emits around 450-600nm. The Lum 1 sample emits its strongest at around 480nm, while the Lum 2 sample emits its strongest at around 525nm. However, the resulting graphics are very

similar to each other. When we examine the excitation graph, the absorbance value does not change as the number of luminescent pigment increases, but when we examine the emission graph, the emission intensity decreases as the wt% ratio of the luminescent pigment increases. The reason for this is that the glass-ceramic matrix has reached the saturation level.

Since the Lum 1 sample emits around 480 nm wavelength, it is at the border of the blue region on the color scale, while the Lum 2 sample is at the green region border as it emits at 525 nm wavelength. This difference is clearly seen in Fig.9.

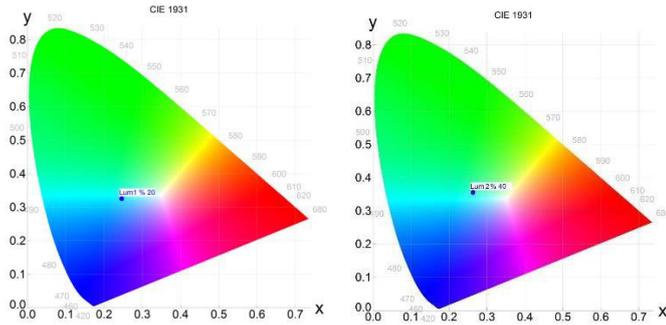


Figure 9. Color coordinate of Lum 1 and Lum 2 samples which are left and right side, respectively.

4. CONCLUSIONS

In this study, the LGC pigment was designed and its luminescence behaviour in glass-ceramic coatings was investigated. Er^{3+} ions and Dy^{3+} ions embedded in the SAS-based glass matrix acted as radiation centres and trapped atoms, respectively. This LGC pigment, which was created, was added to the transparent top layer GC coating at the rates of 20% and 40% and added into the GC coating, and its luminescence behaviour was investigated. The LGC pigment embedded in the GC showed luminescent properties. It has been observed that the $SrO-Al_2O_3-SiO_2$ glass-ceramic system supports the luminescence phenomenon. However, as the LGC pigment per unit area in the GC increases, it is clearly demonstrated by the graph that there is a decrease in the emission value.

The excitation and emission values obtained as a result of the analyzes are promising. For this reason, the subject will continue to be examined in more depth.

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