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Glass and Ceramics with Phosphorescent Ability

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Selvin Yeşilay Kaya and Bekir Karasu detail their research

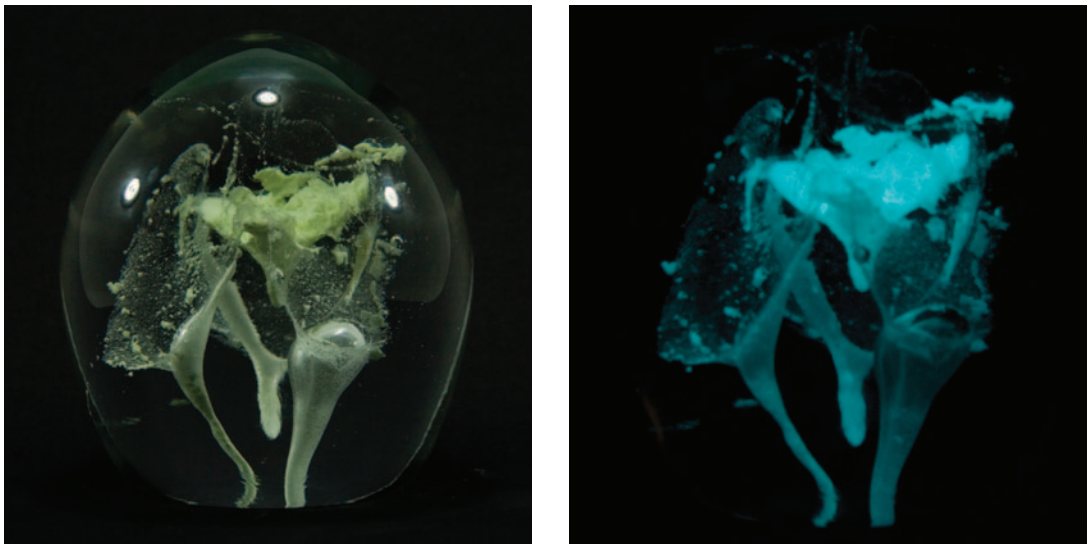


Figure 8. *The studies conducted by hot glass fusion methods.*

PHOSPHORS HAVE GREAT POTENTIAL IN SEVERAL applications for devices and luminous paints and have been widely studied. They are a kind of energy storing material that can absorb both ultraviolet (UV) and visible lights from the sunlight and gradually release the energy in the dark at a certain wavelength. A phosphorescent material, such as the ZnS matrix, has been well known as a long lasting phosphor but did not show sufficient brightness and long phosphorescent behaviour.[1–2] As is known, strontium aluminates doped with divalent europium ions possess high quantum efficiency, long phosphorescence persistence and good stability, indicating their good practical prospects. For specific dark vision applications involving signage, blackouts, emergency rescue guidance systems and luminous watches, the phosphor with appreciable brightness and a long persistence duration for more than five hours is strongly requested.[3] The photo luminescent particles preferably consist of non-radioactive photo luminescent pigments. Suitable pigments are formed from rare earth materials. They are characterised by low toxicity, short excitation time, high brightness and long glow life.[4]

The usage of such pigments in artistic glass and ceramics is not so common. There are extremely limited studies conducted on phosphorescent ceramic bodies and glazes, therefore, only a few relevant publications were made.[4–6]

Frits are essentially a fragmentary form of glass and constitute the main component of glazes. They are produced by mixing various raw materials in powdered form and introducing them into special frit kilns where they decompose, interact and are transformed into viscous liquid masses.[7]

The reason for making frit is to form a water insoluble and homogeneous material for preparing glaze formulations. Many ceramic tile manufacturers produce their own frits, so they have their own glaze formulations to allow independence from frit suppliers. Commercial frits can be produced in either a continuous or rotary type furnace. Frit kilns of a continuous type are generally used for frit production and are rectangular in construction, with raw materials fed in at one end and the frit melt discharged from the other end.[8]

To develop highly transparent decoration frit, further understanding of the mechanisms of interaction between materials and light is required. Transparency is achieved when materials are able to transmit large fractions of incident electromagnetic radiation, while opaque materials reflect higher fractions of incident light. Homogeneous glasses tend to present high transparency because they allow light to be transmitted inside

them without offering barriers for the development of this phenomenon. Heterogeneous glasses may, however, contain barriers to light transmission and, through refractive and reflective phenomena, increase the reflected fractions of incident light, especially when they contain phases with different refractive indices.[9]

Considering the nature of ceramic frits and the process used in the manufacture of ceramic wall tiles, the possible sources of heterogeneity that can potentially generate loss of transparency in frits are:[9]

- porosity (air bubbles)
- devitrification (formation of crystalline phases during firing)
- separation of vitreous phases

For a given chemical composition, using frits has certain advantages compared to using unfritted raw materials, such as:

- Insolubility of certain chemical elements
- Lower toxicity; owing to its size and structure, the frit tends to form less ambient dust than the original raw materials, thus reducing the hazard associated with raw materials toxicity.
- Wider glaze working temperature range, as they have no defined melting points.

Silica is the main acidic constituent of the more usual glaze frits and, with boric oxide acting in a subsidiary role, is the main glass network-forming oxide. In frit melting, silica is heated with 'fluxes', the most common of which are compounds of the alkali metals, sodium and potassium. These together with compounds of the alkaline earth metals calcium and magnesium are network modifiers. Barium, zinc and strontium compounds are used to some extent to replace some, or all, of the more widely used lime and magnesia. The fluxing property of the available basic frit ingredients (in decreasing order of effectiveness) is:

LiO_2 Na_2O K_2O BaO CaO SrO MgO ZnO

The desired glost temperature and the possibility of cation release from the glaze affects the degree of usefulness of lead oxide as a flux. The product of the heating process is a homogeneous glass, which is almost insoluble in water, thereby providing the source of a major proportion of the flux needed for bringing glaze-maturing temperatures to practical levels.[10]

In this study, firstly, yellowish-green and bluish-green phosphorescent pigments were synthesized and produced under laboratory working conditions. A new transparent frit recipe was developed for glazed wall-tiles decoration. The produced frit has a low maturation temperature and low thermal expansion coefficient. Finally, decorative and functional products were produced by using phosphorescence pigments in wall tile decorations and hot and cold artistic glass applications.

Experimental Studies

Samples of Eu and Dy-doped strontium aluminates were prepared by a solid state reaction. In such a procedure, B_2O_3 was used as a fluxing agent and the starting materials were $SrCO_3$, H_3AlO_3, Eu_2O_3, Dy_2O_3, Y_2O_3, Nd_2O_3 and H_3BO_3. Before sintering, the mixtures were preciously weighed and were ball mixed for 2–4 hours with a certain amount of isopropyl alcohol. In Table 1, the mole values of the oxides are given that were used for each recipe.

Table 1. The recipes of yellowish-green and bluish-green pigments

Oxide	Amount (moles)	
Al_2O_3	0.3-0.8	7-13
B_2O_3	0.001-0.01	0.1-0.2
Eu_2O_3	0.001-0.01	0.01-0.06
Dy_2O_3	0.001-0.01	0.01-0.06
Nd_2O_3	-	1.001-0.003
Y_2O_3	0.001-0.003	-
SrO	0.06	-

After drying at 120ºC for one day the mixtures were calcined at desired temperatures with a heating rate of 10ºC/minute under reducing atmosphere of 95-98.5 percent N_2 + 5–1.5 percent H_2. The calcined powders were re-milled using an agate mortar.

The second part of this study involves production of a new transparent frit recipe for decoration of glazed wall tiles. Raw materials used in frit production provided by Vitra Karo San ve Tic A Ş located in Eskişehir, Türkiye. Chemical analysis of the raw materials used in the study are presented in Table 2.

Table 2. Chemical analysis of raw materials.

Raw Materials	Oxides-Weight (%)											
KNO_3	Na_2O	MgO	SiO_2	ZnO	SrO	K_2O	PbO	CaO	Al_2O_3	BaO	Fe_2O_3	L.O.I.*
	0.11	-	0.04	-	-	40.86	-	0.09	-	0.22	0.02	58.66
ZnO	-	0,01	0.04	99.67	-	0.14	0.10	-	-	-	0.04	-
$BaCO_3$	0.77	-	0.05	-	0.13	-	-	0.05	-	77.67	-	21.33
Al_2O_3	0.44	-	-	-	-	0.04	-	0.03	97.79	-	0.04	1.66
Quartz	0.09	0,06	98.29	-	-	-	-	0.07	0.64	-	0.05	0.8
Wollastonite	0.26	0.40	51.60	-	-	0.18	-	45.9	1.01	-	-	0.65

*Loss on Ignition.

Initially $CaCO_3$ was used as CaO resource but using this raw material at higher amounts caused the foaming of the frit batch. Therefore this oxide was provided from wollastonite raw material. A small amount of Li_2O was used to facilitate melting and reduce the viscosity. K_2O was added to the final recipe to increase strength to both the water and the chemical solutions. To modify the thermal expansion coefficient, the amount of boric oxide (B_2O_3) was increased. Boric acid accelerates glass formation, gives a smooth surface, high mechanical strength and scratch resistance. The firing temperature of the frit increases by adding silica (SiO_2). But this also gives high mechanical and chemical strength to the glaze. The amount of SiO_2 was high in the GF coded frit recipe and then it was decreased gradually. Furthermore, to decrease the thermal expansion coefficient of the starting frit composition, the amount of Na_2O was decreased. Produced frits were applied on the glazed wall-tiles, then fired in the industrial kiln. According to obtained products, the frit coded F15 gives better results. It was selected as a main composition and coded as S1B.

The thermal expansion coefficients values and curves of GF coded commercial and S1B frits at 400°C are given in Table 3 and Figure 1.

Table 3. Thermal expansion values of GF and S1B coded frits (400ºC).

Frit	The Coefficient of Thermal Expansion (x 10^{-7} 1/ºC)
GF	100.5
S1B	64.86

According to obtained results, GF frit has a higher thermal expansion coefficient (100.5) than S1B frit (64.86). The S1B frit is more compatible with wall-tile glazes.

In the last stage of the study the pigments produced were used in the wall tile decorations and hot and cold artistic glass applications. From the wall tile glazes decoration point of view, certain amounts of phosphorescent pigments were added into the vetrosa frits for receiving the suitable, matured, frit-based decors with phosphorescence ability. Afterwards, with suitable pigment added frits three firings (decoration firings) of wall tile glaze decors were conducted in the fast firing furnaces of both VitrA Karo Co and Termal Seramik Co factories. For this purpose, some

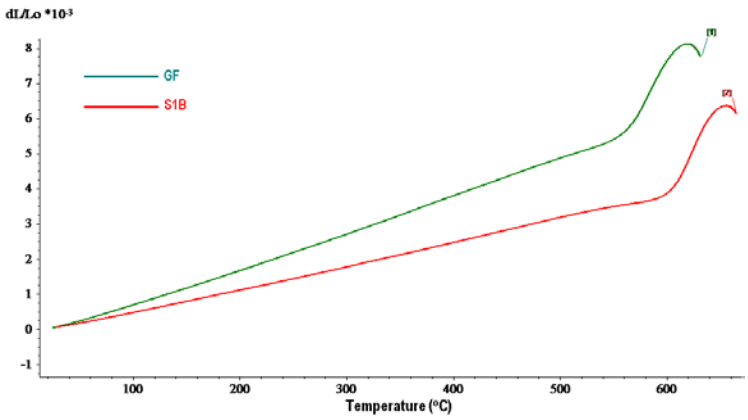


Figure 1. Dilatometer curves of GF (1) and S1B (2) coded frits.

experiments were made in order to determine the most suitable firing temperature and time by adding different amounts of phosphorescent pigments to the several vetrosa frits recipes. Moreover, the effects of vetrosa frits thickness used on wall tile glazes, particle size and composition on phosphorescent characteristics were studied.

In the case of glass works first, the objects were produced with the hot glass blowing method. In order to maintain homogeneity, phosphorescent pigments were sprinkled by sieving on the vesicle surface removed from the glass melting furnace. Later, the vesicle was shaped with blowing, putting one more layer on the glass surface. For the fusion technique it is applied on sheet glass, first the surface of the glass was covered with a one-sided protective band to achieve the desired design. Then, a certain depth was achieved by means of sandblasting the parts containing the figures. Next, a frit whose thermal expansion coefficient was compatible with sheet glass and phosphorescent pigments was combined, the parts with figures were then filled with such mixtures.

The protective bands were removed before the object was placed in the furnace. The purpose of using frit is to lead pigments to interact with frit at fusion treatment temperature and to disperse. The effects of the phosphorescent pigment level, application and mixing methods on the luminescence characteristic in the dark and on the decorative appearance were analysed. The phosphorescent pigments obtained in the study were used on the glass produced with the hot glass blowing method and on those produced with fusion method and the results were discussed. In Figure 2 the patterns of glass that are covered with the protective band and the fusion furnace are given.





Left and right: ***Figures 2.*** *The photos of sheet glass on which phosphorescent decors were applied, produced by the fusion technique.*

In the cold glass applications, phosphorescent yellowish-green and bluish-green pigments were mixed with epoxy resin composed of thermoset polymers. The phosphorescent pigments whose average particle sizes were ~10μm were added into epoxy resin and mixed for 10 minutes with an automatic mixer in order to avoid agglomeration. Decorative applications were performed on the ordinary and artistic glass objects and the sheet glasses by Anadolu University, Fine Arts Faculty, Glass Department staffs and students.

After the phosphorescent pigments were homogeneously distributed in the resin and 17 wt percent hardener was incorporated into the mixture. In order to make the phosphorescent pigment/resin combination a little bit harder and reduce the fluidity of it mixture was held for 10

min. In the studies done with especially the objects having upright surfaces, the resin needed to obtain a little hardness in order to cover the glass surface without streaming from it.

As for the studies of decoration on sheet glass, firstly, as in the fusion method, the design desired was formed by cutting the sandblasting band (sticky silver foil). Later, the sandblasting band with one-sided stick was pasted on the sheet glass and figured parts were left uncovered in order to make up the desired figures by sandblasting. The sandblasted parts were filled with phosphorescent pigment-epoxy resin combination and kept at room temperature for achieving sufficient hardness. After the combination had completely frozen, some decorative and functional glasses with phosphorescent ability in the dark were obtained.

Results

XRD patterns of yellowish-green and bluish-green pigments produced under laboratory working conditions are given in Figure 3.

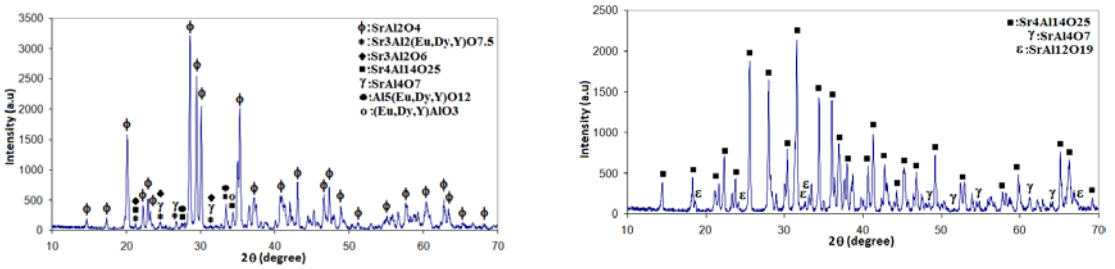


Figure 3. *XRD analysis of (a [left]) yellowish-green and (b [right]) bluish-green phosphorescent pigments.*

In the XRD analysis of the yellowish-green phosphorescent pigment, $SrAl_2O_4$ phase making emission in the green region (~520 nm) is seen; in the case of the bluish-green pigment, $Sr_4Al_{14}O_{25}$ phase giving emission in the blue region (~490 nm) is observed. The emission graphics of the pigments can be followed from Figure 4.

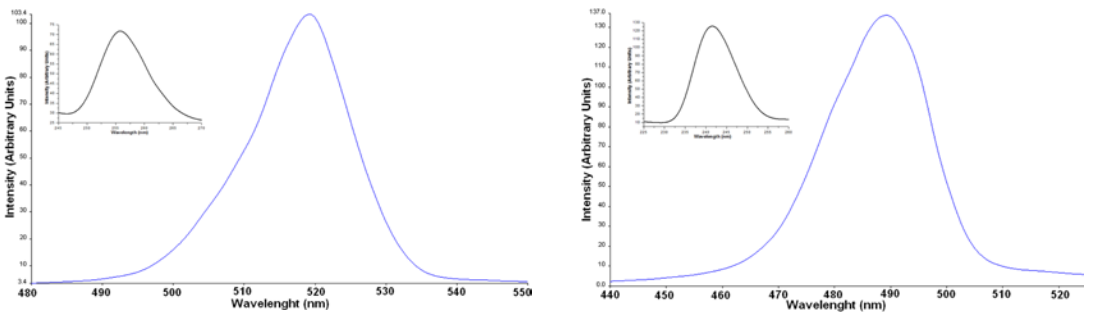


Figure 4. Emission graphs of (a [left])yellowish-green and (b [right]) bluish-green pigments.

The photos of the decorated wall tile glazes obtained at 920ºC after a total firing time of 40 min in the studies are presented in Figures 5-7.



Left: ***Figure 5.*** *The photos of decorated wall tiles with phosphorescent ability (a [left]) in the daylight (b [right]) in the dark.*

Right: ***Figure 6.*** *The photos of decorated wall tiles with phosphorescent ability (a [left]) in the daylight (b [right]) in the dark.*

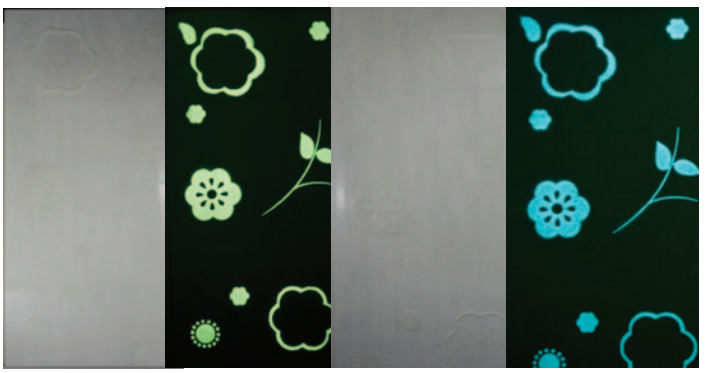




Figure 7. *The photos of decorated wall tiles with phosphorescent ability (a) in the daylight (b) in the dark.*



Figure 8. *The studies conducted by hot glass fusion methods. The studies conducted by the hot glass blowing method are pictured on page 94.*

As it is obvious from Figures 5-7, the bordures (Fig. 5) and the wall tile glazes on which the S1B frit with phosphorescent pigment was applied (Figs. 6 and 7) have the phosphorescent characteristic in the dark. The transparent frit took on the shape of the desired figure.

In Figure 8, the phosphorescent glass applications made with the hot glass blowing and the fusion methods are displayed. As seen from the hot glass blowing studies (Fig. 7) performed with the vesicles taken from the hot glass furnace working at about 1500ºC, the yellowish-green and the bluish-green pigments produced keep their phosphorescent characteristic even after their usage at high temperatures. As to the fusion practice, the desired design was obtained as a result of melting frit incorporated pigments at fusion temperature. The critical and important point is the compatibility of thermal expansion coefficient values of the low temperature frit and sheet glass.

With this study it is proved that usage of phosphorescent pigments in artistic glasses and ceramics supplies can provide attractive decorations and functionality to the final products

Footnotes

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