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Process parameters determination of phosphorescent pigment added, frit-based wall tiles vetrosa decorations

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Abstract

In this study bluish-green (BG) and yellowish-green (YG) phosphorescent pigments were synthesized and produced under laboratory conditions and the best ones in terms of higher phosphorescence intensity and longer duration were, afterwards, added into wall tile transparent vetrosa frits to obtain new, functional and decorative products. Their uses under industrial working conditions were also examined. Throughout the study the optimum process parameters were determined.

Keywords: Phosphorescent pigments; Production; Process parameters; Transparent vetrosa frit; Glazed wall tile

1. Introduction

The Eu^{2+}-activated alkaline earth aluminates became an important class of phosphorescent materials for their quantum efficiency in the visible region. They were considered as a new generation of long afterglow phosphors for their high brightness, long life time, good chemical stability and non-radioactivity [1,2].

Phosphorescence, also called afterglow, refers to a luminescence with delayed radiative return that is caused by trapping of photo-generated electrons and/or holes at intrinsic or extrinsic defect sites of the material. When freed by thermal energy, these trapped charge carriers recombine at the ionized luminescent centers. The amount of thermal energy needed for freeing the charge carriers depends on the trap depth, E_T. Thus, phosphorescence is a thermo-activated physical phenomenon, in which charge carriers are released at well-defined temperatures characteristic of the trap depths. In other words, phosphorescence is a thermo-luminescence with de-trapping at room temperature [3].

It is known that the persistent luminescence life time and intensities of phosphors can be enhanced by co-doping them with other rare earth ions. The phosphorescence from the aluminates is believed to be caused by the 4f–5d transition of Eu^{2+} ions in the crystals and this behaviour is based upon the thermal activation of holes from traps followed by the emission of Eu^{2+}. Such electron transitions have been reported to be affected by the electrical surroundings of Eu^{2+} ions. Thus, the color of the phosphor is dependent on the crystal structure of the main phases [4–8].

Frits are glass particles prepared by heating suitable batches to a high temperature in a gas or oil-fired furnace or in an electric melting unit. Batch constituents are chosen amongst the readily available inorganic raw materials. Frits are employed as a glaze component, a special bonding material in abrasives, a flux in subsidiary ceramic processes like decorating, a coating for electronic components and a cement in ceramic, metal and glass/metal seals [9].

In the present study, long-lasting phosphorescent bluish-green and yellowish-green pigments were developed and produced. Additionally, a low melting transparent frit composition was synthesized and produced for glazed wall tile vetrosa applications. In order to achieve vetrosa decorated wall tiles with long lasting phosphorescence ability, developed pigments were added into the new frit at certain ratios.

The determination of the optimum pigment addition % into the frit, the effect of decoration firing temperature and

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Table 1
Batch recipes for the production of phosphors.

Raw materials	For bluish-green phosphors (BGP) (Moles)	For yellowish-green phosphors (YGP) (Moles)
H_3AlO_3	9–14	0.23–0.48
H_3BO_3	0.5–1.2	0.01–0.03
Eu_2O_3	0.001–0.02	0.001–0.003
Dy_2O_3	0.01–0.08	0.002–0.006
$SrCO_3$	2–4	0.25–0.46
Nd_2O_3	0.001–0.002	–
Y_2O_3	–	0.001–0.003

time and the thickness of vetrosa layer were searched to receive decorations with long lasting, high intensity phosphorescence.

2. Materials and methods

2.1. Production of bluish-green (BG) and yellowish-green (YG) phosphorescent pigments

Polycrystalline phosphor powder samples of the $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}, Nd^{3+} and $SrAl_2O_4$:Eu^{2+}, Dy^{3+}, Y^{3+} systems have been synthesized through the solid-state reaction technique. The initial batches of phosphorescent pigments were prepared using high purity materials; H_3AlO_3 (Merck, Hydragillite), $SrCO_3$ (Riedel-de Haen, >99.5%), $BaCO_3$ (Sigma–Aldrich, >99%), Eu_2O_3 (Stanford Materials, 99.99%), Dy_2O_3 (Stanford Materials, 99.9%), Y_2O_3 (Stanford Materials, 99.999%) and Nd_2O_3 (Stanford Materials, 99.95%). The raw materials were weighed according to the following recipes (Table 1).

The weighed batches were milled in zirconium oxide bowls using zirconium oxide balls and isopropyl alcohol at 200 rpm for 1–4 h (Planetary mill, Fritsch/Pulverisette 5). The mixed slurries were dried in an oven at 75 °C for 24 h. The dried powders were ground and thoroughly mixed. Afterwards, sintering was conducted in alumina crucibles in a tunnel furnace (Protherm PTF 16/50/450) under reducing atmosphere supplied by 95–98.5% N_2 + 5–1.5% H_2 gas mixture at 1350–1600 °C for 1–5 h. Reductive atmosphere condition is necessary to ensure complete reduction of activator ion Eu^{3+} to Eu^{2+}.

Phase identifications were made by XRD at 40 kV and 30 mA with Rigaku Rint 2000 using Cu-Kα radiation. The morphology of sintered powders was designated by Zeiss EVO 55 SEM fitted with an EDX. The photoluminescence (PL) emission spectra were taken on Perkin Elmer LS55 luminescence spectrometer. Each sample was excited with 240–260 nm radiation from a pulsed xenon lamp. The emission spectra were scanned in the range of wavelengths from 360 to 650 nm. To measure the excitation spectra, the analyzer monochromator was set to the maximum wavelength of the emission spectra and then an excitation monochromator was scanned in the range of 200–400 nm.

Table 2
Composition of the base low temperature transparent VF coded frit.

Components	Content (mol%)
$R_2O(Na_2O, K_2O)$	21.54
RO(CaO, MgO, BaO)	9.53
$R_2O_3(B_2O_3, Al_2O_3$, Fe2O3[a])	15.84
$RO_2(SiO_2)$	53.09

[a] Come from some raw materials and their amounts are negligible.

Since commercially available low melting transparent frits were found to be unsuitable for the production of long lasting phosphorescence ability bearing new products, such as vetrosa decoration and wall tile glazes, a new transparent frit composition (VF) was synthesized and produced after 15 trials (Table 2). The behaviour of frit with or without pigment addition was studied by a hot stage microscope (Misura 3.32 ODHT HSM 1600-80) with a heating rate of 10 °C/min up to 1300 °C. The frit viscosities were calculated employing HSM data in association with Tg values obtained from DTA (Netzsch STA 409 PC). In order to determine thermal expansion coefficient values samples were heated in a dilatometer (Netzsch DIL 402 PC) at a rate of 10 °C/min up to 600 °C.

After the production of phosphorescent pigments and the transparent frit (VF), they were mixed at certain ratios. To provide homogenous mixture, dry blending process performed for 10 min. Then, the phosphorescent pigment-added vetrosa frit was applied onto glazed ceramic wall tiles for decoration purposes by screen printing. Besides laboratory studies, industrial firing was also conducted in a fast single-firing decoration furnace with a top temperature of 920 °C for a total firing cycle of 40 min. At this stage the optimum process parameters for producing decorated, glazed wall tiles with phosphorescence ability were investigated. Finally, the microstructure of glazed wall tiles decorated by phosphorescent vetrosa frit was examined by SEM (Zeiss EVO 50 at 20 kV), attached to EDX.

3. Results and discussion

The XRD patterns of bluish-green (BG) and yellowish-green (YG) phosphor samples synthesized under laboratory conditions are shown in Fig. 1.

According to the XRD results, the major crystal phase is seen to be $Sr_4Al_{14}O_{25}$ for BG phosphor and $SrAl_2O_4$ for YG one.

The morphologies of the phosphorescent powders sintered and ground below 63 μm are given in Fig. 2, indicating that the average size distribution of particles are ~10 nm. EDX patterns taken from phosphor powders were presented in Fig. 3.

The excitation and emission spectra of powders were recorded by means of a fluorescence spectrophotometer (Perkin Elmer LS55). Emission spectra of $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}, Nd^{3+} and $SrAl_2O_4$:Eu^{2+}, Dy^{3+}, Y^{3+} system phosphors fired at 1250–1600 °C for 1–5 h are indicated in Fig. 4.

Emission analysis results presented that $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}, Nd^{3+} system has emission intensity at ~490 nm

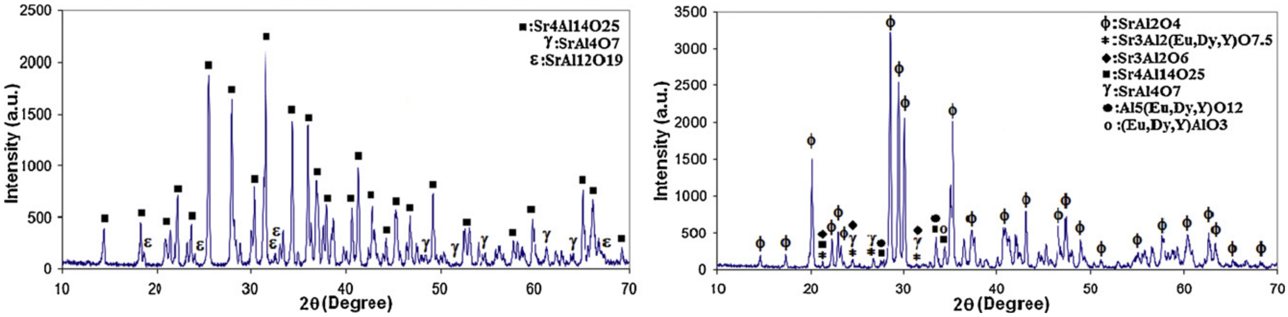

Fig. 1. XRD patterns of (a) BG, (b) YG phosphor samples produced under laboratory working conditions.

(excitation wavelength: 242 nm) and $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, Y^{3+} system at ~520 nm (excitation wavelength: 256 nm). Fig. 5 depicts the decay curves of the afterglow phosphorescence.

These specimens were irradiated by day light for 20 min. After the light source was cut off, they experienced a rapid decay and subsequently long lasting phosphorescence.

In $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} system small amount of Nd_2O_3 increased the emission intensity of the phosphorescent pigment. In $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+}, Nd^{3+} system Eu^{2+} is an emitter, while Dy^{3+} and Nd^{3+} act as the trapping centers. After being excited by the irritation lights, electron and hole pairs are produced in Eu^{2+} ions, and the Nd^{3+} traps captured some of the free holes moving in the valence band. When the excitation source is cut off, some holes capture by the Nd^{3+} traps are thermally released slowly and relax to the excited state of Eu^{2+}, finally, returning to the ground state of Eu^{2+} accompanied with emitting light [10,11]. This should be the reason why the phosphors have good phosphorescence properties.

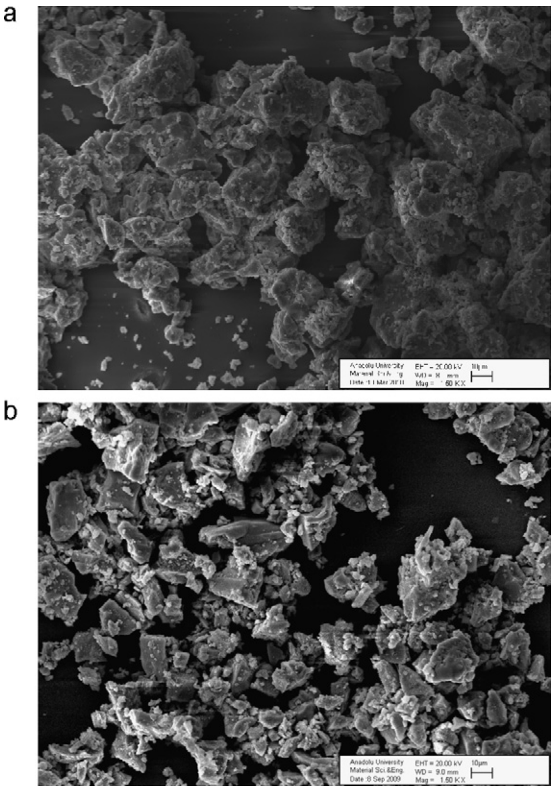

Fig. 2. SEM micrographs of (a) BG ($Sr_4Al_{14}O_{25}$) and (b) YG ($SrAl_2O_4$) phosphor particles.

In $SrAl_2O_4:Eu^{2+}$, Dy^{3+} system yttrium oxide was added to initial pigment recipe to improve phosphorescence properties. In the latter case, yttrium is considered to contribute to promoting the formation of carrier traps or stabilizing carrier traps which contribute directly to the enhancement of phosphorescence brightness and play a role in stabilizing the carrier traps by modifying the aluminate crystal. For these reasons, phosphorescence brightness and intensity increased by its incorporation [12]. In both strontium aluminate systems H_3BO_3 was also added to the starting batch recipes (in the $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+}, Nd^{3+} system as 5 mol% and in the $SrAl_2O_4:Eu^{2+}$, Dy^{3+}, Y^{3+} system as 0.02 mol%) to improve phosphorescence properties and phase stability [6,13].

The frit samples without pigment (VF) and with two types of pigments (VF + BG and VF + YG) were analyzed by means of a hot stage microscope (Tables 3 and 4) (Figs. 6 and 7).

The hot stage microscope analysis indicated that increasing phosphorescent pigment level in the frit caused all the relevant temperature values to increase. It is believed that such a consequence may be occurring due to high alumina content of the pigments limiting their usage in frit at higher amounts. Table 5 indicates the results of hot stage microscope for VF frit containing 10% BG and YG pigments and Fig. 8 their shrinkage behaviours.

Table 3
The hot stage microscope analysis results of VF frit containing 5, 10, 15 wt % BG pigment.

Temperatures (°C)	VF	VF+ 5% BG	VF + 10% BG	VF + 15% BG
Sintering	726	730	738	744
Softening	796	810	820	830
Sphere	–	–	876	–
Half-sphere	888	890	900	912
Fusion	930	936	944	950

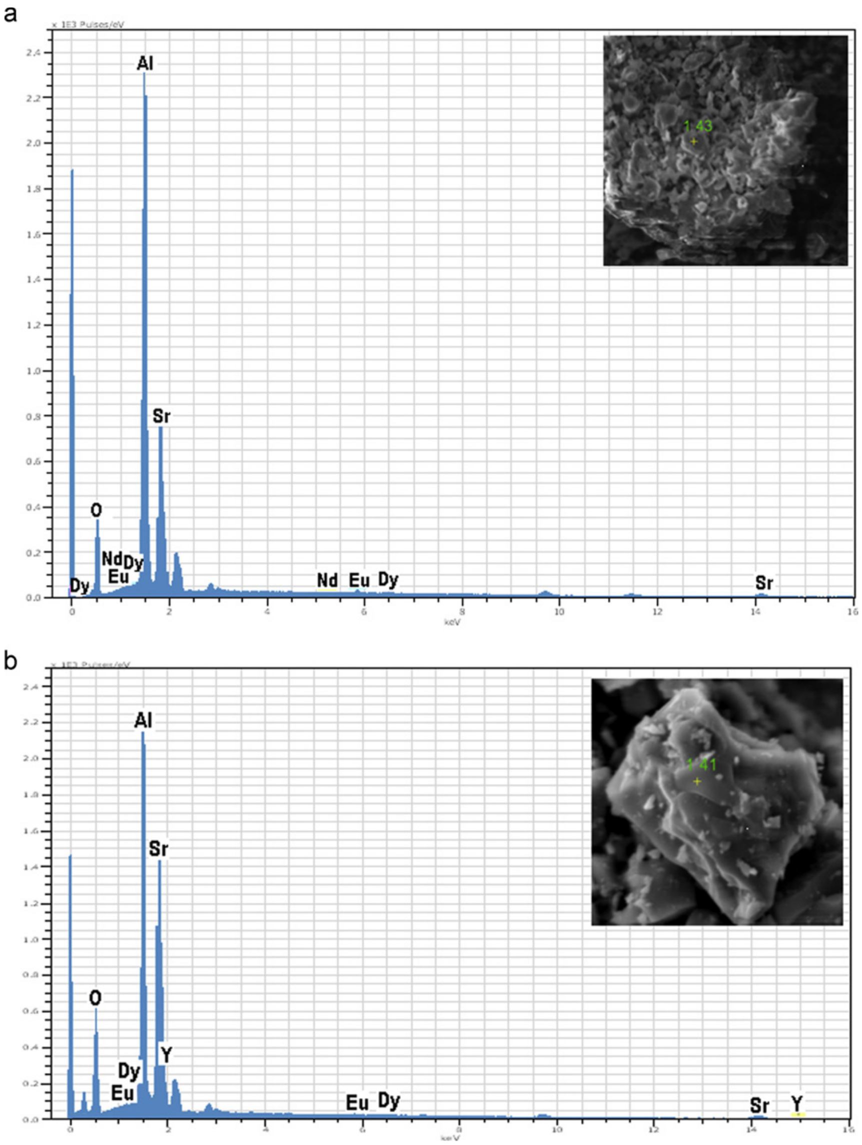

Fig. 3. EDX pattern taken from (a) BG ($Sr_4Al_{14}O_{25}$) and (b) YG ($SrAl_2O_4$) phosphor powders.

Hot stage microscope results strengthened the approach about the effect of alumina content in pigments on raising the relevant temperature values (Table 5). VF frit with BG pigment contains higher level of alumina and naturally all of its relevant values get higher when compared to those having YG one.

Figs. 9 and 10 present the viscosity curves of VF frit with BG and YG pigments.

It can be more clearly seen from the viscosity curves that VF frit has a lower viscosity value than those with pigment incorporation at higher temperatures. When the level of

Table 4
The hot stage microscope analysis results of VF frit including 5, 10, 15 wt % YG pigment.

Temperatures (°C)	VF	VF + 5% YG	VF + 10% YG	VF + 15% YG
Sintering	726	728	732	740
Softening	796	806	812	824
Sphere	–	–	–	886
Half-sphere	888	890	898	908
Fusion	930	932	940	946

Table 5
The hot stage microscope analysis results of VF frit containing 10% YG and BG pigments.

Temperatures (°C)	VF	VF + 10% BG	VF+ 10% YG
Sintering	726	738	732
Softening	796	820	812
Sphere	–	876	–
Half-sphere	888	900	898
Fusion	930	944	940

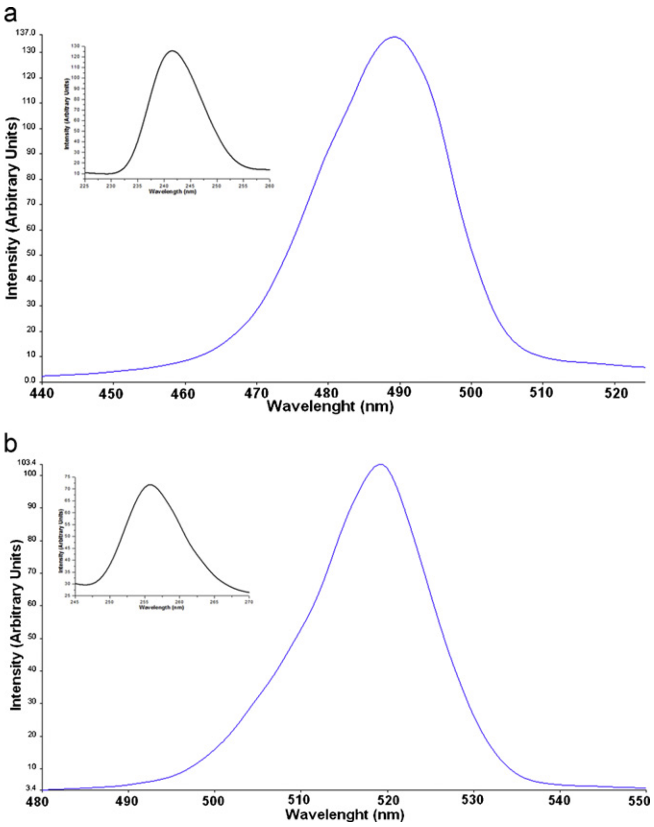

Fig. 4. Emission spectra of (a) BG and (b) YG phosphors exited by the λ = 242 nm and λ = 256 nm UV lights.

pigment was increased, then, frit viscosities also raised. It is thought that this is caused by the major crystalline phases [$Sr_4Al_{14}O_{25}$ ($T_{melting}$: ~1900 °C) and $SrAl_2O_4$ ($T_{melting}$: ~1200 °C)] present in these two different systems raising the melting temperature of VF frit.

Relative viscosity curves of VF frit including 10% bluish-green and yellowish-green pigments are given in Fig. 11. When 10% BG and YG pigment added frits are compared with VF frit without pigment in terms of viscosity it is noticed that pigment addition has an increasing effect on it.

As seen from Fig. 11, bluish-green phosphorescent pigment addition increases the viscosity of VF frit more than yellowish-green one. It is assumed that the reason of such a condition is occurring with bluish-green pigment having the major crystalline phases of $Sr_4Al_{14}O_{25}$, in which strongly bonded aluminum level is higher.

Table 6
Thermal expansion coefficient values of VF frit with 5, 10, and 15% BG pigment (400 °C).

Sample codes	Thermal exp. coeff. ($\times 10^{-7}$ 1/°C)
VF	64.86
VF + 5% BG	64.19
VF + 10% BG	64.68
VF + 15% BG	64.81

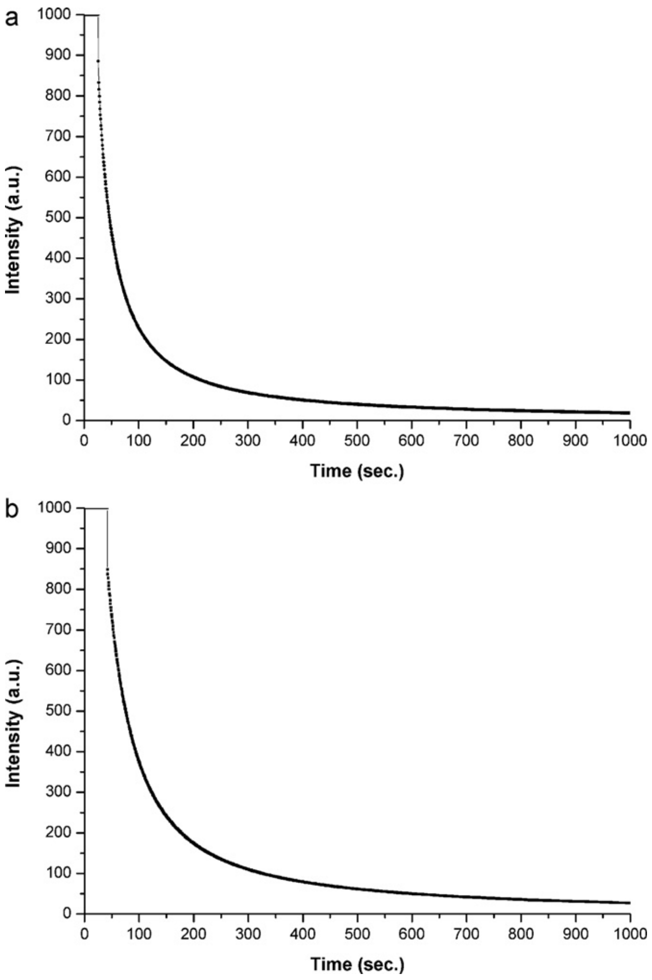

Fig. 5. Decay curves of (a) BG and (b) YG phosphors exited by the λ = 242 nm and λ = 256 nm UV lights.

Table 6 gives thermal expansion coefficient values of VF frit and VF frit with 5–15% BG pigment and Table 7 the values of VF frit with 5–15% YG pigment. In both cases a major change in α values cannot be seen. This is an advantage for the frit not to experience α mismatch between decoration and the glazed

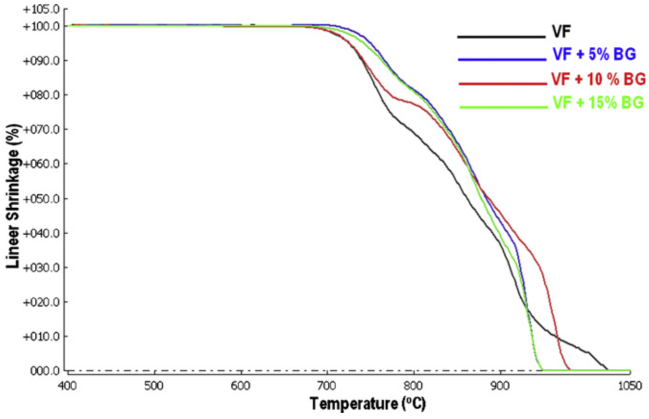

Fig. 6. Shrinkage curves of VF frit with 5, 10, 15 wt% BG pigment.

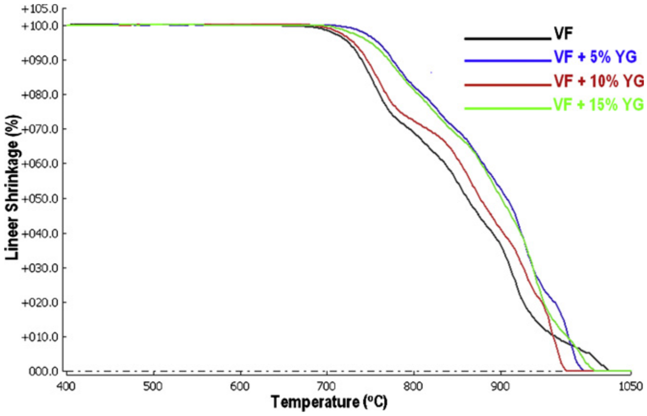

Fig. 7. Shrinkage curves of VF frit with 5, 10, 15 wt% YG pigment.

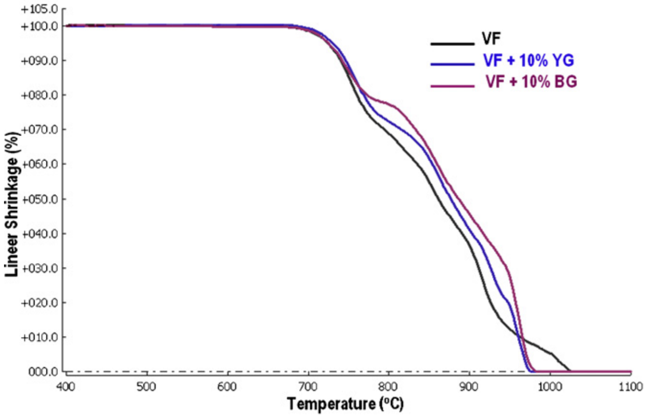

Fig. 8. The shrinkage curves of VF frit with 10% BG and YG pigments.

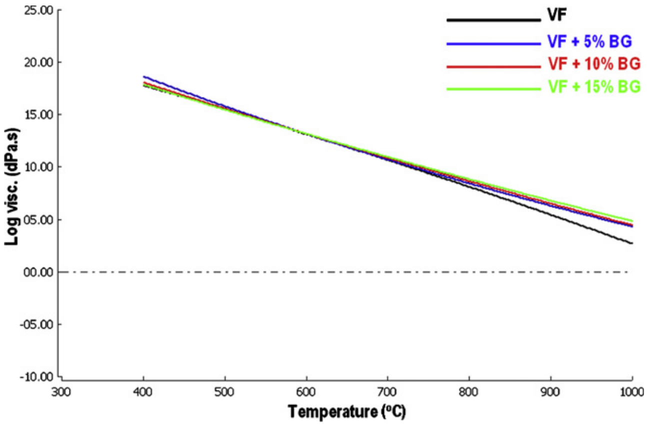

Fig. 9. The viscosity curves of VF frit with 5, 10, 15% BG pigment.

Table 7
Thermal expansion coefficient values of VF frit with 5, 10, 15% YG pigment (400 °C).

Sample Codes	Thermal Exp. Coeff. ($\times 10^{-7}$ 1/°C)
VF	64.86
VF + 5% YG	65.37
VF + 10% YG	65.69
VF + 15% YG	66.05

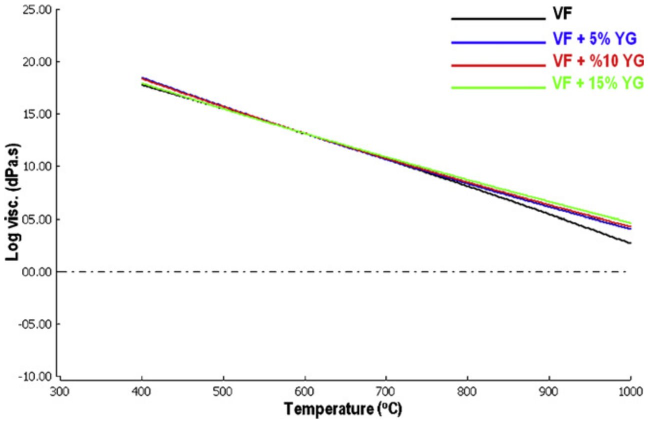

Fig. 10. The viscosity curves of VF frit with 5, 10, 15% YG pigment.

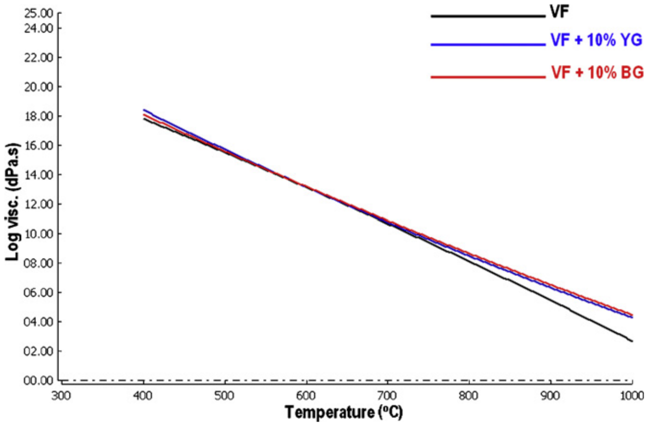

Fig. 11. The viscosity curves of VF frit with 10% BG and YG pigments.

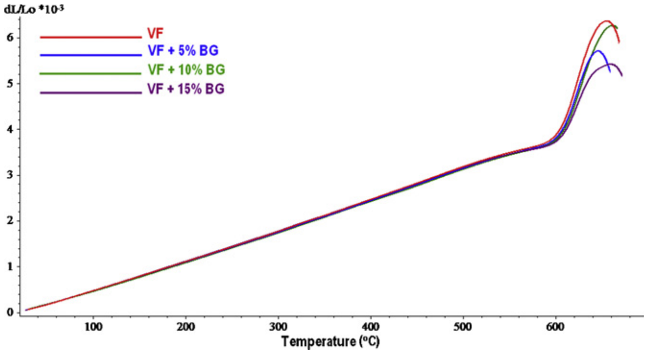

Fig. 12. Dilatometer curves of VF frit with 5, 10, 15% BG pigment.

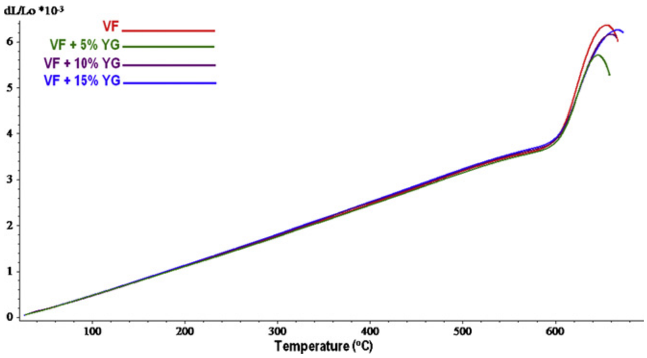

Fig. 13. Dilatometer curves of VF frit with 5, 10, 15% YG pigment.

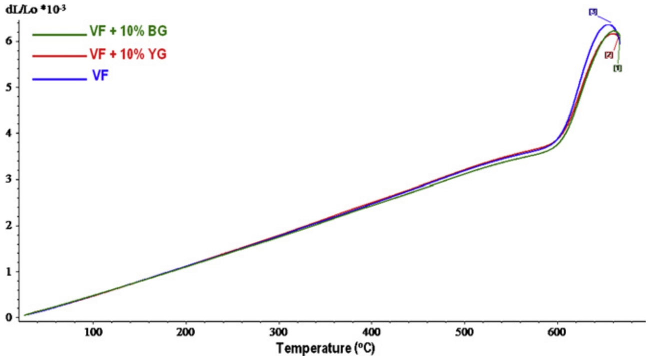

Fig. 14. Dilatometer curves of VF frit without pigment and with 10% BG and YG pigments.

wall tile surface for subsequent application. Figs. 12 and 13 present dilatometer analysis results of the frit samples.

The results confirm that pigment addition into VF frit does not have a considerable effect on α value (Fig. 14).

3.1. Determination of optimum pigment addition into transparent vetrosa frit

To determine the final effects of pigment addition on the phosphorescence ability of the wall tile decoration, the pigments were added into VF frit as 5, 10 and 15 wt.% and the mixtures were applied on the glazed wall tile surfaces.

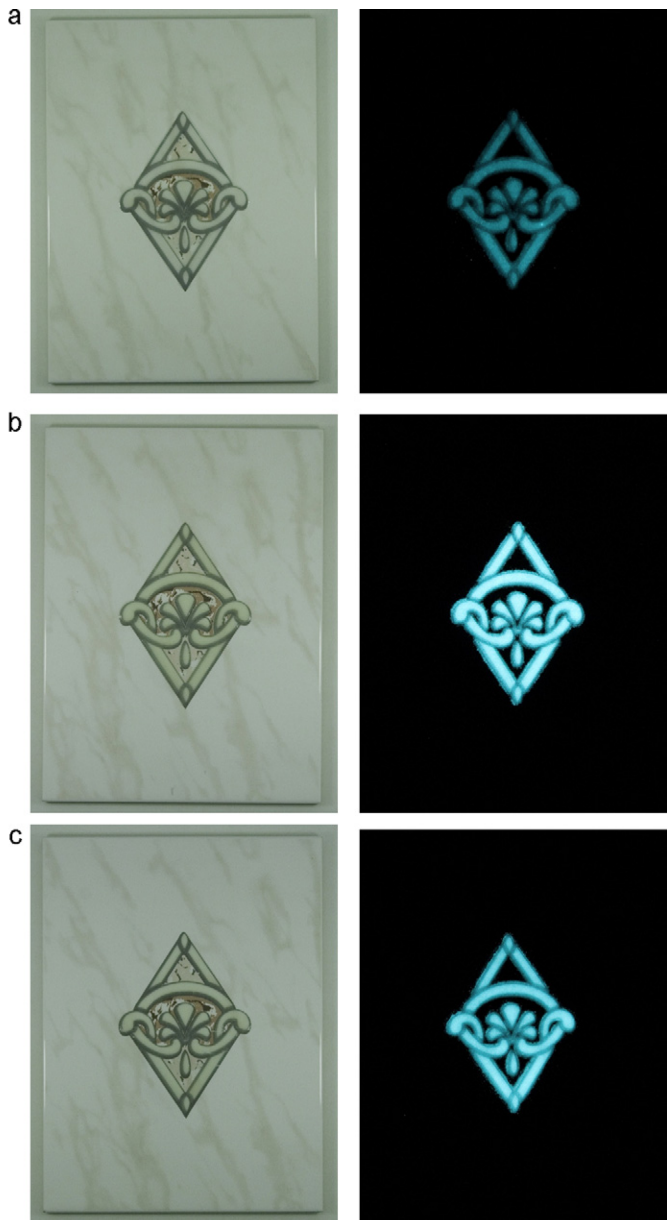

Fig. 15. The glazed wall tiles decorated with BG phosphorescent pigment added frit as (a) 5%, (b) 10%, (c) 15%. Their industrial single fast-firing was conducted in VitrA Karo Inc.

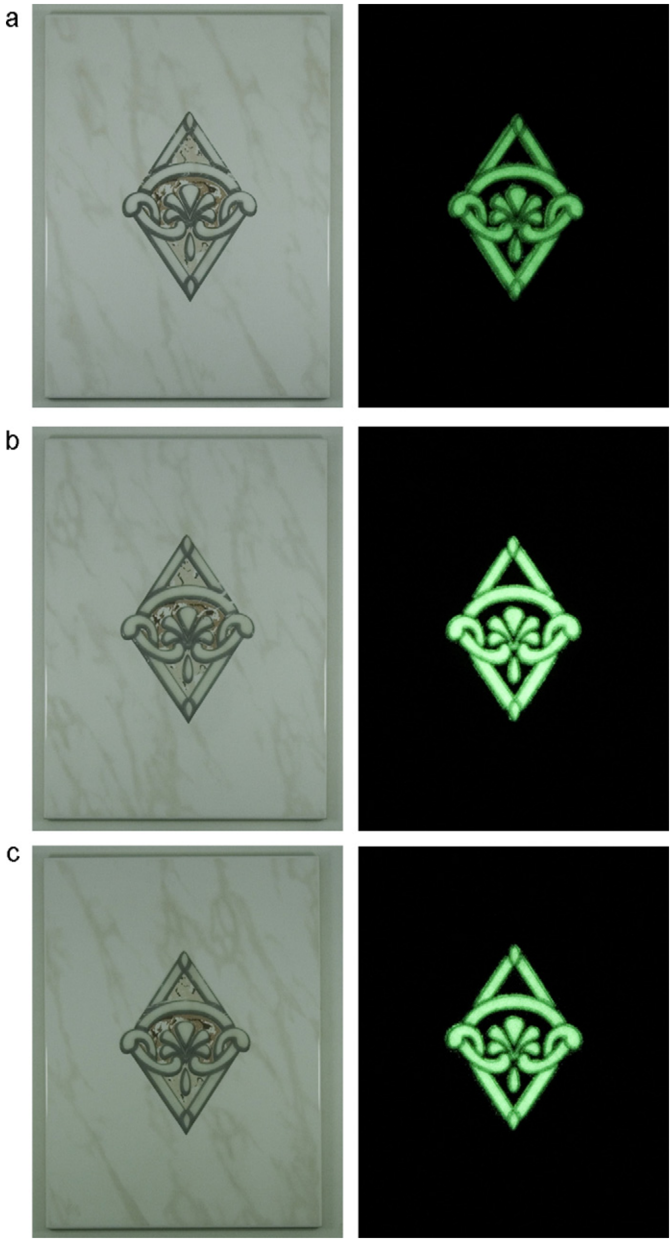

Fig. 16. The glazed wall tiles decorated with YG phosphorescent pigment added frit as (a) 5%, (b) 10%, (c) 15%. Their industrial single fast-firing was conducted in VitrA Karo Inc.

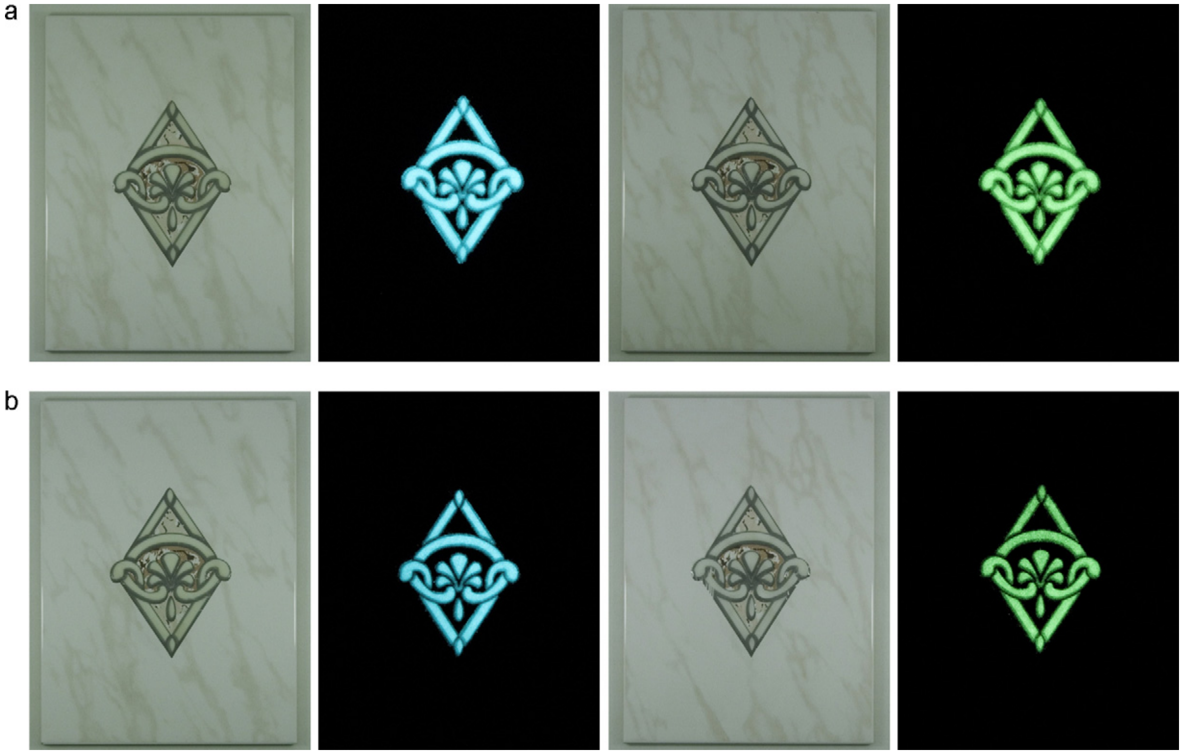

Fig. 17. The final appearances of decorated, glazed wall tiles in the day light and the dark. Decors contain 10% BG and YG pigments and single fast-fired at 920 °C (a) and 980 °C (b) in VitrA Karo Inc.

Figs. 15 and 16 show the final decorated products both in the day light and the dark respectively.

The minimum level of afterglow was observed with the product having 5% BG pigment, although, after firing, desired decoration was obtained with satisfactory maturation and smooth surface. The product with 10% incorporation exhibited comparingly higher afterglow and phosphorescence intensity without any surface defect. In the case of 15% pigment addition frit maturation problem occurred.

As to YG pigment applications, the optimum afterglow was obtained with the usage of 10% pigment in the vetrosa frit. When the addition rate was raised up to 15%, satisfactory decoration could not be achieved.

With 5% pigment addition satisfactory phosphorescence ability of decors cannot be achieved. 15% addition does not attract the attention for cost reasons. Therefore, it was decided that further studies should be carried out with 10% addition.

3.2. The effects of firing temperature and time on the phosphorescence properties of the decoration

The studied decors are matured at temperatures below 1000 °C not to lose phosphorescence ability. Therefore, to determine optimum firing temperatures of decorated glazed wall tile samples they were single fast-fired at 920 and 980 °C in VitrA Karo Inc. in a decoration-firing furnace for a total time of 35–40 min. The appearances of final products are given in Fig. 17.

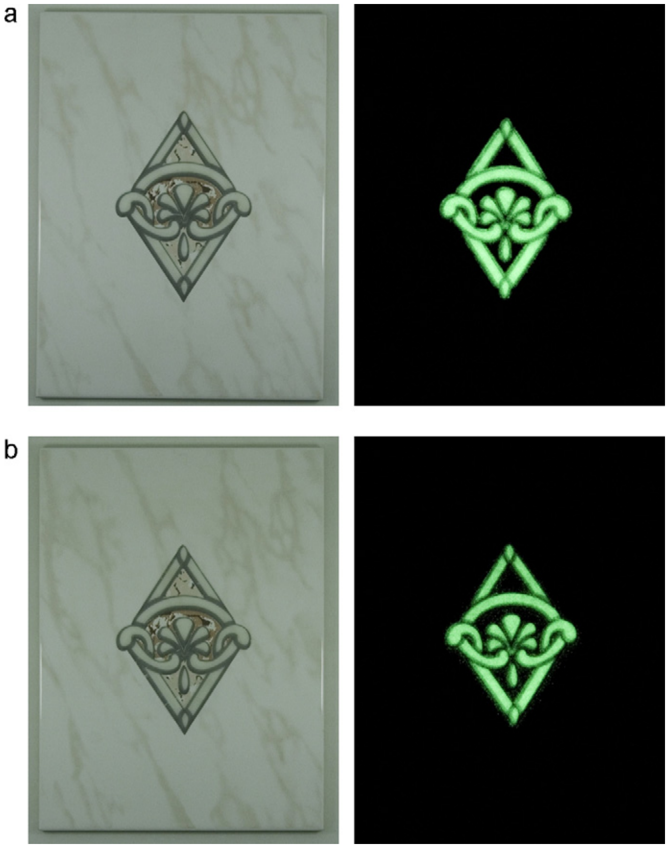

Fig. 18. The final appearances of decorated, glazed wall tiles in the day light and the dark. They were single fast-fired at 920 °C 40 min (a) and 35 min (b) at VitrA Karo Inc.

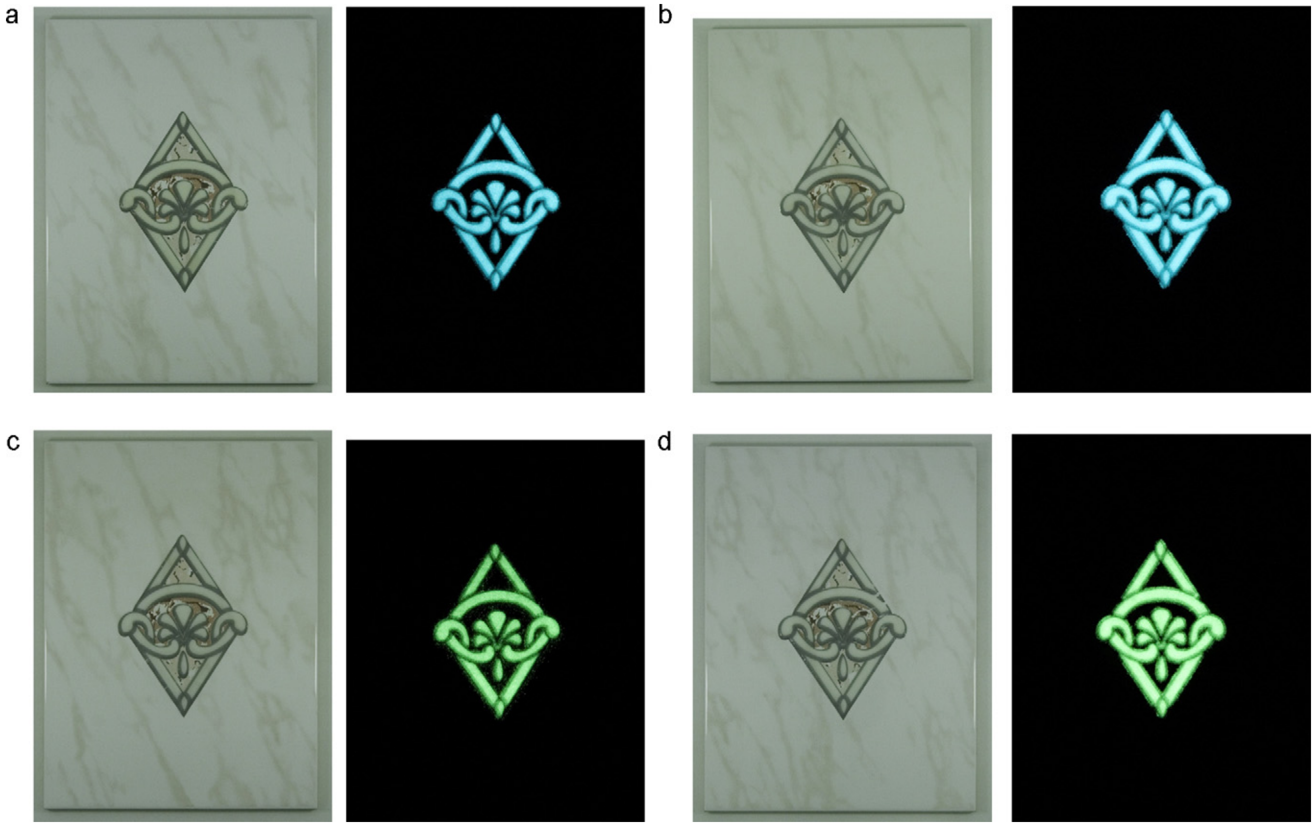

Fig. 19. The final appearance of the decorated glazed wall tiles after single fast-fired at 920 °C for 40 min in VitrA Karo Inc.

As seen from Fig. 17 phosphorescence intensity of YG pigment containing decor comparingly little bit weakens when temperature raises up to 980 °C unlike the one with BG pigment. This indicates the sensitivity of YG pigment added decors to temperature increase.

Under the production condition of VitrA Karo Inc. only YG pigment added decors were studied in order to see the firing time effect on the phosphorescence properties of final products. Fig. 18 depicts the relevant decors fired at 920 °C for 35 and 40 min respectively.

As seen firing time of 40 min supplies better maturation and smoother surface.

3.3. The effect of vetrosa frit thickness on the phosphorescence properties of the decoration

To understand the effects of vetrosa frit level applied onto the glazed wall-tile body on the phosphorescence glow, the amount of industrial standard frit, 3.5 g, and also 1.5 g were studied in the decors (Fig. 19). Naturally, with 3.5 g frit application better afterglow property is achieved. However, with 1.5 g frit satisfactory phosphorescence is also received and the use of this much frit is suggested in order to produce final products with less cost.

SEM and EDX analyses related to $Sr_4Al_{14}O_{25}$ and $SrAl_2O_4$ crystals are presented in Figs. 20 and 21.

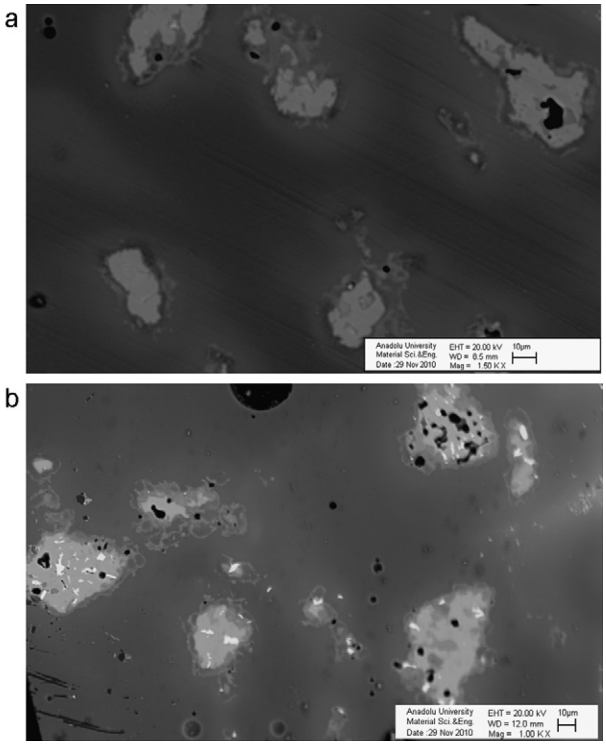

Fig. 20. SEM micrographs taken from the cross section of the decoration part of the piece shown in (a) Fig. 19(a) and (b) of the piece shown in Fig. 19(c).

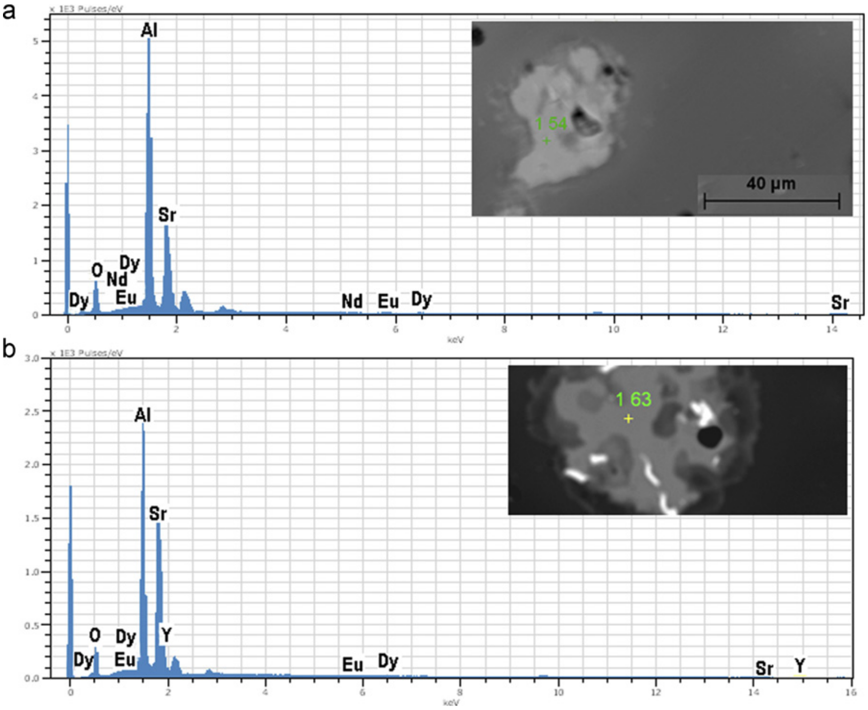

Fig. 21. The EDX analyses of final products given in Fig. 20(a) and (b) respectively.

4. Conclusions

$Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+}, Nd^{3+} and $SrAl_2O_4$:Eu^{2+}, Dy^{3+},Y^{3+} phosphors were synthesized, prepared and produced by the solid-state reaction using H_3BO_3 as a fluxing agent at 1350–1600 °C for 3 h under reductive atmosphere of 95–98.5% N_2 + 5–1.5% H_2. To obtain powders having good phosphorescence properties in both strontium aluminate systems different kinds of rare earths were used. In both systems Nd^{3+} and Y^{3+} have a positive effect on the luminescence.

Results indicated that produced phosphorescence pigments can be added into a suitable low temperature transparent frit for III. firing decoration purposes in order to get more functional and attractive phosphorescence ability having glazed wall tiles.

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