# STUDY OF THE PHOTOCHROMIC EFFECT EXHIBITED BY SPHENE-OPACIFIED GLAZES

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## ABSTRACT

White glazes opacified by sphene, based on the system $SiO_2$-CaO-$TiO_2$, are an alternative to the glazes in which the opacifying phase is zircon. However, it has been observed that this type of glaze displays photochromism (reversible change of colour after exposure to a light source), involving the appearance of a yellowish shade after the glaze has been subjected to sunlight for several hours, which then disappears after a few days. This effect has led to limited use of this type of glaze.

In this study, a method of quantifying the photochromic effect by means of a UV light source is established. The microstructural characterisation of glazes with a pronounced tendency to display a photochromic effect has allowed the possible causes of the photochromic effect to be determined. Finally, a series of tests have been conducted that show that the photochromic effect is related to the impurities present in the glaze, as well as to the type and quantity of crystalline phases contained in the glaze.

The available literature on sphene-opacified white glazes is very scarce. Oxide systems are involved that have drawn little attention for use in the manufacture of glazed ceramic tiles, this being the first study conducted on the determination of the causes of photochromism in this type of glaze.

# 1. INTRODUCTION

White glazes opacified by sphene, based on the system $SiO_2$-CaO-$TiO_2$, are an alternative to the glazes in which the opacifying phase is zircon. However, it has been observed that this type of glaze displays photochromism (reversible change of colour after exposure to a light source)[1], involving the appearance of a yellowish shade after the glaze has been subjected to sunlight for several hours, which disappears after a few days when there is no light. This effect has limited the use of these glazes.

The main objective of this study was to determine the causes of the photochromic effect in sphene-opacified white glazes, and to propose lines of work for the obtainment of glazes that do not exhibit this effect.

The available literature on sphene-opacified white glazes is very scarce[2][3][4][5], and no information was found on the existence of the photochromic effect in this type of glaze. However, it is an effect that appears in glazes that contain titanium oxide and, though its causes are not well understood, it has been noted that the intensity of the photochromism depends on the existence of iron oxide impurities and sodium compounds[6]. In one of the studies found[7], it was concluded that the photochromic effect was a property of the crystals that contained titanium, which were suspended in the glassy matrix, but not of the glass itself.

The literature[8] also reports that some anatase pigments of poorer quality exhibited darkening when they were subjected to intense radiation. The changes were reversible and they were related to the presence of $Ti^{+3}$. Other authors[9][10] have suggested that the effect was due to the presence of iron and tantalum impurities: when the samples were irradiated, an electronic transfer took place from the impurity to $Ti^{+4}$, giving rise to $Ti^{+3}$. A patent was also found on the production of a photochromic pigment[11], which consists of anatase with iron impurities.

Some titanium minerals, including sphene ($CaTiSiO_5$), exhibit luminescence[12], which could be the cause of the photochromic effect in the glazes at issue in this study. Luminescence may be due to the existence of luminescent centres such as $Ti^{+3}$ and to different impurities such as $Pb^{+2}$ and $Mn^{+2}$ replacing $Ca^{+2}$, $Cr^{+3}$ or $Mn^{+4}$ replacing $Ti^{+4}$ and $Cr^{+4}$, or $Cr^{+5}$ and $Fe^{+3}$ replacing $Si^{+4}$.

Taking into account the literature found and the results of a number of preliminary tests performed with glazes that exhibited different behaviour on exposure to solar radiation, it was decided to focus the study on the determination of the influence of the content in iron impurities and sphene on the photochromic effect displayed by sphene-opacified glazes.

## 2. PRELIMINARY TESTS

It has been observed in industry that glossy titanium glazes exhibit a change of colour towards yellower shades when they are subjected to exposure to sunlight, whereas matt titanium glazes do not, the effect being more pronounced when kaolin is used in preparing the glazes. This yellowing had never been observed with glazes opacified by zircon devitrification (traditional opaque glazes), and it disappears over time when the tiles are left in the dark. A description of the opaque white glazes used in conducting the preliminary tests is given in Table 1.

| Ref | Finish | Composition | Change of colour with sunlight |
|---|---|---|---|
| B | Glossy | Titanium frit | Yellowing |
| BK | Glossy | Titanium frit, kaolin | Yellowing, more intense |
| M | Matt | Titanium frit | No change |
| MK | Matt | Titanium frit, kaolin | No change |
| STD | Glossy | Zirconium frit | No change |
| STDK | Glossy | Zirconium frit, kaolin | No change |

*Table 1. Description of the glazes used in conducting the preliminary tests.*

With a view to simulating the change of colour, a series of tests were conducted by exposing the glazes to an ultraviolet light source and testing different exposure times. It was verified that the yellowing that occurred in glazes B and BK was similar to that observed when these pieces were subjected to solar radiation, the UV exposure times being relatively short (maximum 3 hours). The results of the colour determination on the glaze coatings before and after their irradiation with a UV light source, as well as the result of the determination of the colour variation ($\Delta E^*$), are detailed in Table 2.

| Ref. | Initial values | | | | UV (3 hours) | | | | $\Delta E^*$ |
|---|---|---|---|---|---|---|---|---|---|
| | $L^*_R$ | $a^*_R$ | $b^*_R$ | $Ib_R$ | L* | a* | b* | Ib | |
| B | 93,9 | -0,27 | 0,95 | 80,7 | 93,1 | 0,15 | 2,66 | 71,0 | 1,9 |
| BK | 92,8 | -0,17 | 1,77 | 74,4 | 91,8 | 0,41 | 4,04 | 61,4 | 2,6 |
| M | 90,6 | -0,46 | 0,60 | 74,7 | 90,2 | -0,32 | 0,77 | 73,1 | 0,4 |
| MK | 91,7 | -0,72 | -0,16 | 80,6 | 91,2 | -0,61 | -0,03 | 79,0 | 0,5 |
| STD | 93,2 | -0,07 | 0,30 | 82,1 | 92,6 | 0,10 | 0,67 | 79,0 | 0,7 |
| STDK | 93,2 | -0,21 | 1,31 | 77,3 | 92,8 | -0,09 | 1,59 | 75,0 | 0,5 |

*Tests performed according to the procedure set out in section 3.1

*Table 2. Glaze starting colour and variation of this colour ($\Delta E^*$) after irradiation with UV light for 3 hours*.*

These results are consistent with what has been observed in industrial practice, and they show that it is the opaque as well as the glossy white glazes prepared from frits containing titanium in their composition that give rise to the yellowing effect when subjected to UV radiation.

With a view to determining whether the photochromic effect exhibited by these glazes was related to the presence of particular crystalline phases, the crystalline phases in the glazes were quantified. The results are detailed in Table 3. The crystalline phases were referenced as follows:

- E: Sphene (Titanite)-$CaTiSiO_5$
- W: Wollastonite-$CaSiO_3$
- D: Diopside-$CaMgSi_2O_6$
- Q: Quartz-$SiO_2$
- Z: Zircon-$ZrSiO_4$
- C: Cristobalite-$SiO_2$
- T: Tridymite-$SiO_2$
- Cl: Clinopyroxene-$NaTiSi_2O_6$
- De: Dellaite-$Ca_6(SiO_4)(Si_2O_7)(OH)_2$

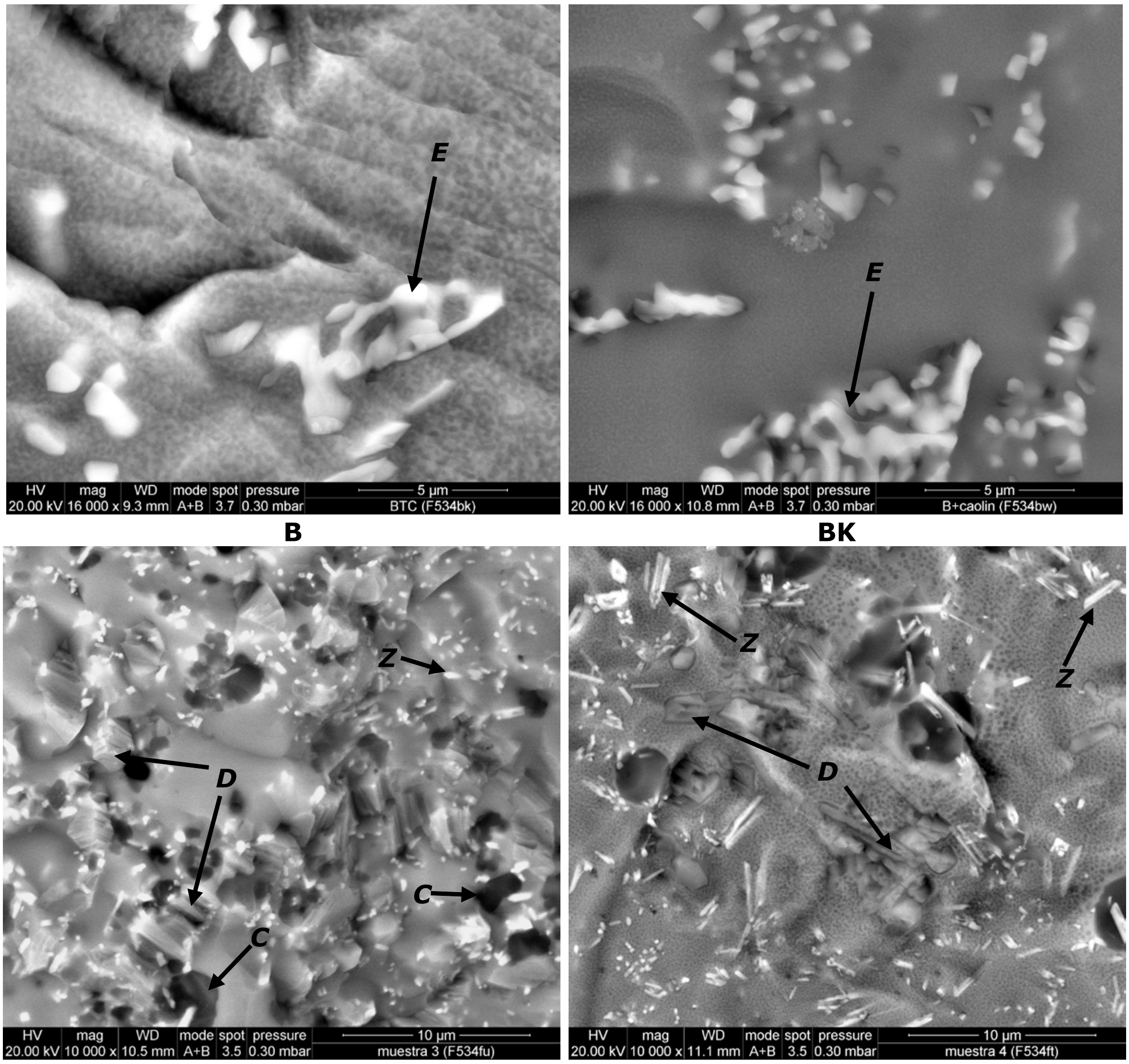
The table shows that the glazes that displayed a change of colour with UV light (B and BK) contained sphene in their composition, the sphene content being the same in the two compositions. Although the matt glazes exhibited a larger quantity of crystalline phases, the presence of titanium phases was very small and no sphene was identified.

| **Ref.** | **Crystalline phases (%)** | | | | | | | | | **Amorphous phase (%)** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **E** | **W** | **D** | **Q** | **Z** | **C** | **T** | **Cl** | **De** | |
| B | 15 | 13 | <0,5 | <0,5 | -- | -- | -- | -- | -- | 75 |
| BK | 15 | <0,5 | <0,5 | <0,5 | -- | -- | -- | -- | -- | 85 |
| M | -- | -- | 26 | <0,5 | 8 | 17 | 2 | 2 | 1 | 44 |
| MK | -- | -- | 23 | 1 | 7 | 4 | 1 | 7 | <0,5 | 57 |

*Tests performed according to the procedure set out in section 3.2

*Table 3. Results of the phase quantification by XRD of the glazes containing titanium.*

Observation of the ceramic glazes by scanning electron microscopy (SEM), figure 1, showed that glazes M and MK exhibited a greater quantity of crystals, which corresponded to the crystalline phases cristobalite, diopside, and zircon in sample M and to diopside and zircon in sample MK. Glazes B and BK exhibited a smaller quantity of crystalline phases, and it was verified by microanalysis that a sphene crystalline phase was involved.



**B** **BK**

**M** **MK**

*Figure 1. Observation of the glossy and the matt glazes prepared with frits containing titanium.*

These results, together with the information found in the literature, suggested that the possible causes of photochromism in these glazes was the presence of sphene and iron impurities, since the introduction of kaolin into the composition hardly changed the sphene content though it did increase the iron content in the glaze. As a result, this study focused on the influence of these two variables.

## 3. EXPERIMENTAL

The study was conducted using a ceramic frit based on the system $SiO_2$-CaO-$TiO_2$, which gave rise to opaque glazes by sphene devitrification, as reference frit. This frit had the following composition (% by weight): 50–60 $SiO_2$, 15–20 CaO, 4–8$TiO_2$, 4–8 $Al_2O_3$, 4–8 $B_2O_3$–4–8 $K_2O$, 1–3 MgO.

The test frits were obtained on a pilot scale by fusion at 1500ºC. The frits were used to prepare glazed test pieces that were fired in a pilot kiln using a 50-minute cycle and peak temperature of 1100ºC. The resulting fired pieces were used to carry out the tests set out below.

## 3.1. Quantification of the photochromic effect

In order to quantify the photochromic effect, a test method was used that resembles the change of colour that glazed tiles undergo when they are subjected to sunlight. The glazed test pieces were exposed to a UV light source from a 400W mercury vapour lamp for three hours. In order to determine in a simple way whether the UV light produced a change of colour in the glaze, half the surface of the test pieces was concealed.

After the exposure time, the pieces were left for 30 minutes in the dark inside the chamber in order to reach an appropriate temperature for making the colour measurement. The difference in colour between the piece before and after UV irradiation was used as a variable to quantify the photochromism.

$$\Delta E^* = \sqrt{(L^* - L^*_R)^2 + (a^* - a^*_R)^2 + (b^* - b^*_R)^2}$$

where:

$L^*_R$, $a^*_R$, and $b^*_R$ are the chromatic coordinates corresponding to the glaze before it underwent the UV-light exposure test.

$L^*$, $a^*$, and $b^*$ are the chromatic coordinates corresponding to the glaze after the irradiation test.

## 3.2. Determination of the $Fe_2O_3$ content

The $Fe_2O_3$ determination was carried out by wavelength-dispersive X-ray fluorescence spectrometry, using reference standards that assured measurement traceability.

## 3.3. Microstructural characterisation

### 3.3.1. Identification and quantification of the phases present in the glazes

The crystalline phases were identified by X-ray diffraction of powdered samples, obtained by firing glaze test pieces in an electric laboratory kiln at 1100ºC and subsequent milling the pieces. The crystalline phases present were quantified by the Rietveld method, using an internal standard to quantify the amorphous phase. Fluorite was used as internal standard.

### 3.3.2. Observation by scanning electron microscopy (SEM)

The pieces fired in the pilot kiln were observed by SEM, coupled to an energy-dispersive X-ray microanalysis (EDXA) instrument. The observations were performed on fresh fractures of the glazes.

## 4. INFLUENCE OF IRON CONTENT

Glaze compositions were prepared, based on the reference frit, modifying the iron content in three ways:

- Use of a frit prepared with purer raw materials.
- Addition of $Fe_2O_3$ to the glaze: two quantities, namely 0,01 and 0,03% $Fe_2O_3$, were tested
- Glaze preparation with and without kaolin.

The iron content in each glaze composition was determined (section 3.2). The glaze compositions were then used to prepare fired glazed pieces in a laboratory kiln. Figure 2 was then obtained by quantifying the change of colour when the fired glaze pieces were exposed to UV light.

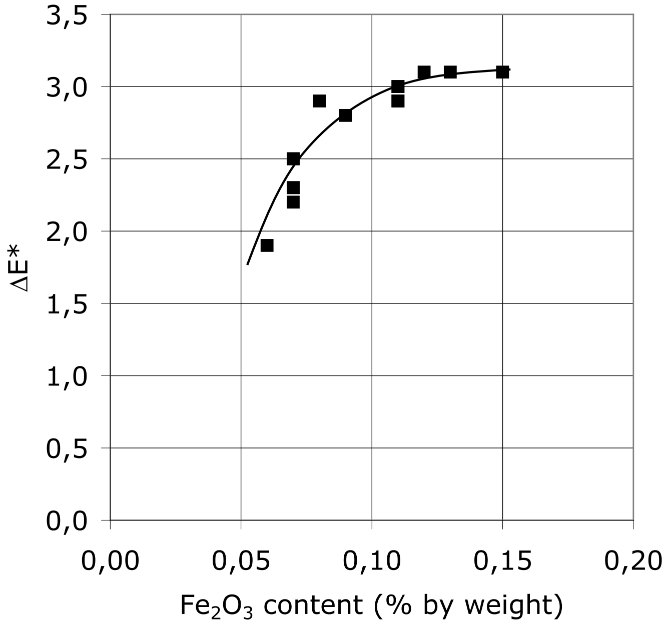


*Figure 2. Variation of the change of colour with $Fe_2O_3$ content in the glaze compositions*

The use of frits prepared from purer raw materials allowed glaze compositions with a 0,06% $Fe_2O_3$ content, by weight, to be obtained. The kaolin addition increased the $Fe_2O_3$ content by 0,04%. Combining the three modification approaches enabled a working range of 0,06% to 0,15% $Fe_2O_3$, by weight, to be obtained.

Figure 2 shows that, at $Fe_2O_3$ contents above 0,1% in the glaze composition, the colour variation stabilised at about 3,0.

These results show that, to reduce the photochromic effect in the studied fired glaze coatings, it was necessary to work with the lowest possible $Fe_2O_3$ contents, which involved using frits prepared with purer raw materials and kaolins containing less $Fe_2O_3$.

## 5. INFLUENCE OF SPHENE CONTENT

Ceramic frits were prepared, using the reference frit that yielded glaze compositions with a 0,08% $Fe_2O_3$ content, by weight, modifying their compositions with a view to reducing the quantity of sphene in the fired glazes. Two series were tested in which the oxides that formed this crystalline phase (CaO, $SiO_2$, and $TiO_2$) were reduced, taking into account sphene stoichiometry:

- 'A' series: reduction of the CaO, $SiO_2$, and $TiO_2$ content at the expense of proportionally increasing the other oxides (A4 and A8).
- 'B' series: reduction of the CaO and $TiO_2$ content at the expense of increasing the $SiO_2$ content, since $SiO_2$ does not limit sphene formation (B4 and B8).

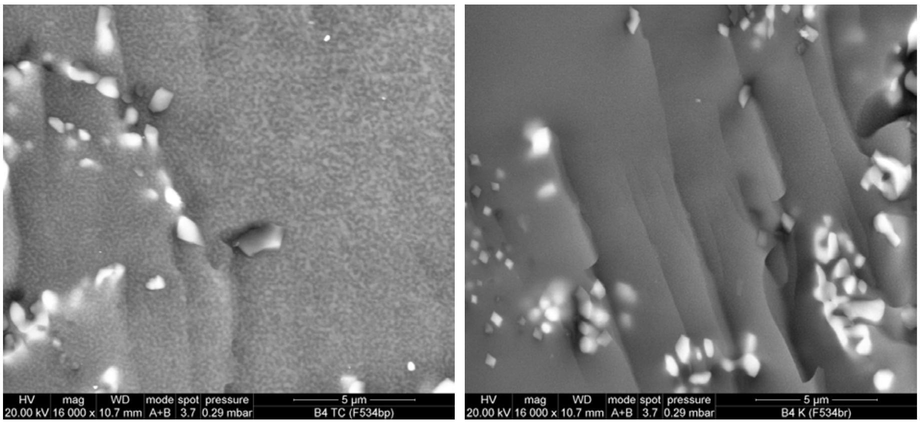
The new frits were used to prepare glaze compositions with and without kaolin (the reference 'K' was added to the samples with kaolin), and eight new compositions were obtained with different crystalline sphene phase contents. The results of the phase quantification conducted on the new glaze coatings, as well as the results corresponding to the starting glazes (B and BK), are detailed in Table 4. The same phases were identified in the eight new glazes as those found in the starting glazes.

| Ref. | Crystalline phases (%) | | | | Amorphous phase (%) |
|---|---|---|---|---|---|
| | E | W | D | Q | |
| B | 15 | 13 | <0,5 | <0,5 | 75 |
| BK | 15 | <0,5 | <0,5 | <0,5 | 85 |
| A4 | 8 | <0,5 | 5 | <0,5 | 87 |
| A4K | 10 | <0,5 | 2 | <0,5 | 88 |
| A8 | 2 | <0,5 | 5 | <0,5 | 93 |
| A8K | 4 | <0,5 | 2 | <0,5 | 94 |
| B4 | 12 | <0,5 | 4 | <0,5 | 74 |
| B4K | 11 | <0,5 | 2 | <0,5 | 87 |
| B8 | 6 | 12 | 4 | <0,5 | 78 |
| B8K | 6 | <0,5 | 2 | <0,5 | 92 |

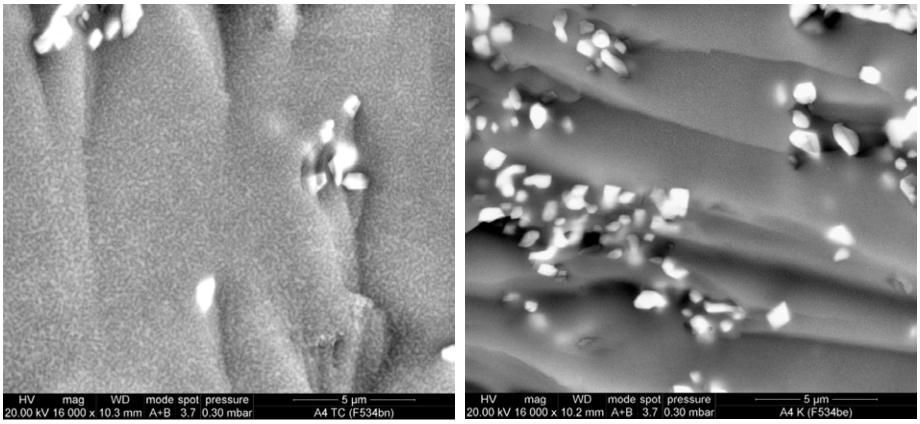
*Table 4. Results of the phase quantification by XRD of the glazes containing titanium.*

It may be observed (Table 4) that the modifications yielded glazes with different sphene contents. When kaolin was added to the compositions, fired glazes were obtained with a greater glassy phase content, i.e. the kaolin inhibited the formation of crystalline phases. The table also shows that a larger reduction in sphene occurred in the 'A' series, in which the quantity of the elements that contained this phase (CaO, $SiO_2$, and $TiO_2$) decreased at the expense of an increase in the other elements.

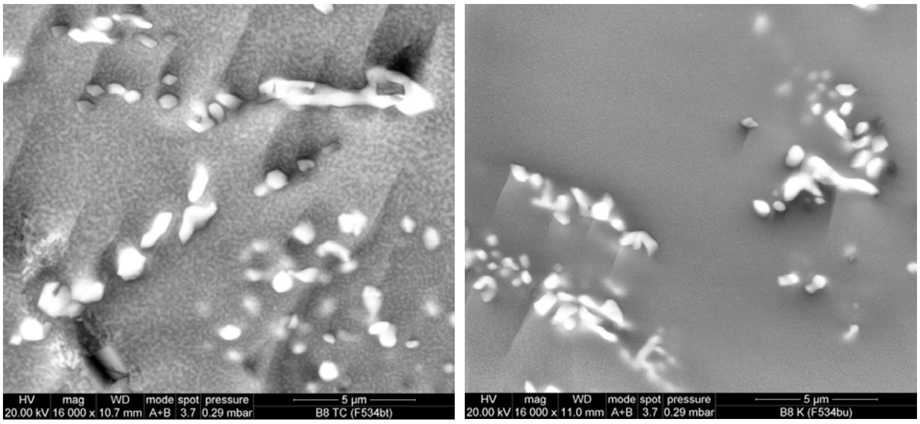
Figure 3 presents views of fresh fractures of the tested ceramic glazes. They show that the major crystalline phase in the glazes was sphene. The glazes prepared without kaolin exhibited a clear phase separation. Kaolin inhibited the formation of this phase separation. No sphene crystalline phase was observed in glaze A8; only a phase separation was observed, which produced the opacity in this glaze.



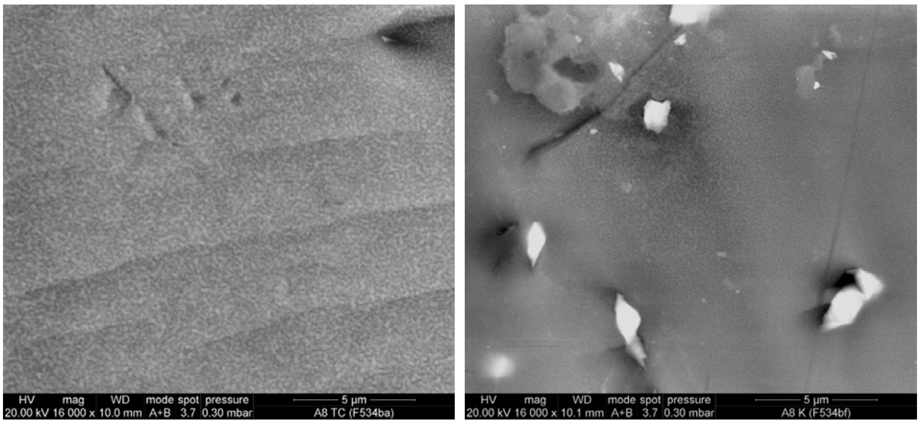
**B4: 12% Esfena** **B4K: 11% Esfena**



**A4: 8% Esfena** **A4K: 10% Esfena**



**B8: 6% Esfena** **B8K: 6% Esfena**



**A8: 2% Esfena** **A8K: 4% Esfena**

*Figure 3. Observation of a fresh fracture in the glazes*

| Ref. | Initial values | | | | UV (3 hours) | | | | $\Delta E^*$ |
|---|---|---|---|---|---|---|---|---|---|
| | $L^*_R$ | $a^*_R$ | $b^*_R$ | $Ib_R$ | $L^*$ | $a^*$ | $b^*$ | Ib | |
| B | 93,9 | -0,27 | 0,95 | 80,7 | 93,1 | 0,15 | 2,66 | 71,0 | 1,9 |
| BK | 92,8 | -0,17 | 1,77 | 74,4 | 91,8 | 0,41 | 4,04 | 61,4 | 2,6 |
| A4 | 92,3 | -0,74 | -0,16 | 82,1 | 91,7 | -0,34 | 1,36 | 73,6 | 1,7 |
| A4K | 91,5 | -0,59 | 0,65 | 76,5 | 90,6 | -0,18 | 2,88 | 63,9 | 2,4 |
| A8 | 90,9 | -1,07 | -1,21 | 84,0 | 90,8 | -1,01 | -0,90 | 82,1 | 0,4 |
| A8K | 85,9 | -0,44 | 0,42 | 65,7 | 85,7 | -0,35 | 1,11 | 61,8 | 0,7 |
| B4 | 94,1 | -0,72 | -0,22 | 86,5 | 93,2 | -0,33 | 1,87 | 74,8 | 2,3 |
| B4K | 93,0 | -0,60 | 0,32 | 81,6 | 92,0 | -0,15 | 2,95 | 66,9 | 2,9 |
| B8 | 92,7 | -0,81 | -0,44 | 84,2 | 92,1 | -0,52 | 0,87 | 76,8 | 1,5 |
| B8K | 90,7 | -0,51 | 0,17 | 77,0 | 89,9 | -0,12 | 2,00 | 66,5 | 2,0 |

*Table 5. Glaze starting colour and variation of this colour ($\Delta E^*$) after UV irradiation for 3 hours.*

Table 5 details the results of the colour determination and of the changes that took place when these samples were subjected to UV light. Figure 4 shows a plot of the colour variation exhibited by the glazes with UV light as a function of their sphene content. It may be observed that, when the sphene content increased, glaze photochromism became more pronounced. In addition, the glazes prepared with kaolin displayed a greater photochromism, at the same sphene content, which may be explained by the larger $Fe_2O_3$ content in these glazes.

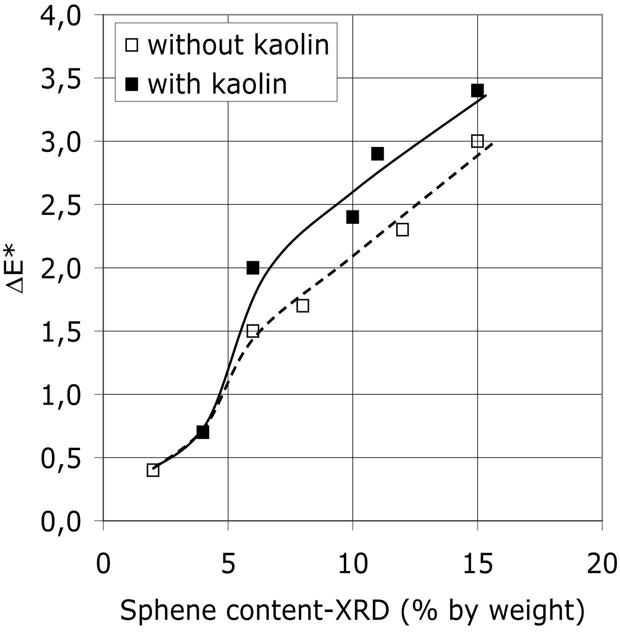


*Figure 4. Variation of the change of colour with glaze sphene content*

Glaze A8 exhibited an acceptable whiteness and practically zero colour variation with UV light, equivalent to that displayed by the zirconium glazes (STD) (Table 6). The opacity of this glaze was not caused by the presence of sphene but by the existence of phase separation and, as a result, even though the opacity was slightly lower (lower values of the chromatic coordinate L*), it displayed a high whiteness caused by its more bluish shade (lower values of b*).

| Ref. | Initial values | | | | UV (3 hours) | | | | ΔE* |
|---|---|---|---|---|---|---|---|---|---|
| | $L^*_R$ | $a^*_R$ | $b^*_R$ | $Ib_R$ | L* | a* | b* | Ib | |
| A8 | 90,9 | -1,07 | -1,21 | 84,0 | 90,8 | -1,01 | -0,90 | 82,1 | 0,4 |
| STD | 93,2 | -0,07 | 0,30 | 82,1 | 92,6 | 0,10 | 0,67 | 79,0 | 0,7 |

*Table 6. Glaze starting colour and variation of this colour (ΔE*) after UV irradiation for 3 hours.*

## 6. CONCLUSIONS

This study has shown that the photochromic effect of fired glazes that contain sphene depends on the content in $Fe_2O_3$ impurities and on the quantity of sphene in the glaze. The magnitude of the photochromic effect increases as these two parameters increase.

Modification of a frit composition with titanium has enabled opaque as well as glossy white glazes to be obtained that exhibited no photochromic effect. In these glazes, the quantity of sphene was practically zero and the opacity was due to the presence of a phase separation in the glaze.

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