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Factors affecting glaze transparency of ceramic tiles manufactured by the single firing technique

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Abstract

Transparency is an extremely important optical property of several glazes used in the ceramic tile sector. The present work aimed to identify the causes of loss of transparency presented by some ceramic glazes composed of frits with chemical compositions typical of optically transparent glasses. After identifying the causes of low transparency presented by several ceramic glazes based on microstructural analyses, X-ray diffraction and scanning electron microscopy, attempts were made to increase the transparency of these glazes by altering their chemical compositions. The results suggest that the addition of alumina – through distinct mineral sources – may be an interesting alternative to prevent the crystallization of calcium silicates, which reduce the transparency of glazes used in the ceramic tile sector.

Keywords: Optical properties; Glass; Al_2O_3; Electron microscopy; Ceramic frits

1. Introduction

1.1. Rationale and objectives

Ceramic glazes[1,2] are applied on the surface of a variety of products to waterproof them, facilitate cleaning and give them their final esthetic appearance. They are applied by different technologies[3] and develop their properties of interest after firing at high temperatures. Given that glazes are responsible for the esthetic properties of glazed ceramic products, their optical properties – such as gloss, color, transparency and opacity – take on a special relevance within the set of properties that glazes should present. In several applications the objective is to achieve transparent glazes[4,5] on the surface of ceramic materials. In the case of ceramic tiles, especially floor tiles, the design of the product is applied in the form of very thin layers of colored glazes, over which a thicker layer of highly transparent glaze must be applied (Fig. 1). This layer of glaze protects the product by preventing the abrasive wear[6] the ceramic tile undergoes when in use from reaching the underlying colored glazes, thus losing their decorative effect. At the same time, the presence of this layer on the surface of the product should not prevent the colors of the designs applied on the lower layers from remaining visible, thus making the high transparency of this protective glaze layer an essential characteristic of the product.

Because the firing cycles used in the manufacture of ceramic tiles are extremely rapid – usually less than 30 min – and the maximum firing temperatures do not exceed 1200 °C, the glazes used on these products consist basically of ceramic frits.[7] However, many of the frits commercially available today present a certain degree of opacity (loss of transparency) when fired in typical conditions of ceramic tile manufacture, especially when the glazes are formulated with high frit contents to produce surfaces with high gloss and minimal roughness. In this situation, the product may undergo shade variations[8] that impair the colors of the end product, since the visibility of the decorations applied

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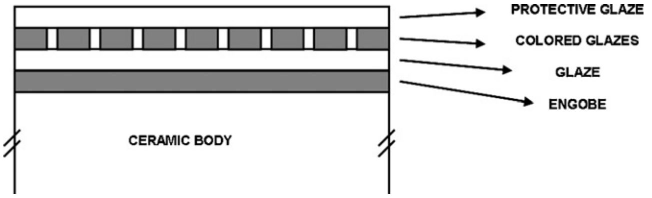

Fig. 1. Diagram of the layers that make up a ceramic tile.

under this layer is impaired by the low transparency of the top layer.

The purpose of this work, therefore, was to contribute to the identification of the causes of loss of transparency of several glossy frits used in ceramic tiles fabricated by the single firing technique and to propose alternatives to maximize the transparency of these frits.

1.2. Interaction of light with glassy materials

To develop highly transparent glazes 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,[9] while opaque materials reflect higher fractions of incident light. Generally speaking, 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. However, heterogeneous glasses may 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.[2]

Considering the nature of ceramic glazes and the process used in the manufacture of ceramic tiles, the possible sources of heterogeneity that can potentially generate loss of transparency in glazes are:

- porosity (air bubbles);
- devitrification (formation of crystalline phases during firing); and
- separation of vitreous phases (generated by the immiscibility of liquids during firing).

All ceramic glazes contain air bubbles,[10,11] which occupy distinct volumetric fractions and present different size distributions according to the nature of the product and the conditions of manufacture. Air bubbles may be formed from gases released by the support during firing, from the combustion of organic substances used in the application of the decorations, from the air that remains occluded among the frit particles in the green compact, or even through the incorporation of air bubbles previously present in the suspensions used for wet glaze application. Since the refractive index of air ($n = 1.0$) is considerably lower than that of glasses ($n = 1.5$), the presence of appreciable volumetric fractions of air bubbles may impair not only the transparency but also other technical properties of glazes.

Glaze devitrification has been studied exhaustively in response to the growing interest in vitroceramic glazes[12–14] in recent years. This phenomenon is directly related to the chemical composition of the starting glaze and to the sintering conditions. Devitrification begins with the appearance of small nuclei, which lead to the growth of crystalline phases in a vitreous matrix. The size and quantity of crystals that are formed, which depend on the nucleation and growth rates, directly affect the properties of the resulting glazes, e.g., their mechanical, optical and chemical properties.[15] Most of the existing studies in the literature involving the devitrification of ceramic glazes deal with the increment of mechanical properties,[16–18] which can be obtained through vitroceramic systems. Some of these systems, such as $Li_2O–Al_2O_3–SiO_2$ and $CaO–MgO–Al_2O_3–SiO_2$, have been explored with greater emphasis for some time.[5,14] However, devitrified crystalline phases usually present higher refractive indices than those of glassy matrices, resulting in glazes with low transparency.

The phenomenon of vitreous phase separation is observed by electron microscopy analysis of many transparent and optically homogeneous glasses. The literature[19] also highlights that the technical properties of the ceramic glazes depend on a lack of structural homogeneities. Aparici et al.[8] states that the loss of transparency of single-fired ceramic frits and the bluish and/or milky aspect of glazes obtained from them occurs as a result of the separation of vitreous phases of certain glaze compositions as a function of the cooling rate applied in rapid firing cycles. When immiscible vitreous phases show significant differences in surface tension, the phase with the highest surface tension adopts the shape of spherical droplets. If the dimensions of the droplets reach the dimensions of the wavelength of visible light, the vitreous material undergoes loss of transparency. Under certain conditions, the heterogeneities may evolve into crystalline nuclei, at which point the separated phase is considered to be in a pre-crystalline state, with a higher degree of order than the glassy matrix.

The great majority of studies about phase separation in glassy materials involve simple glass compositions, such as binary silicate or borosilicate glasses.[20] In these glasses, the nature and molar fraction of the network-modifier elements is a determining factor of the tendency for phase separation.[19] The smaller the size of the network-modifier cation and the higher its electric charge the easier the separation of vitreous phases. The probability of vitreous phase separation decreases considerably as the coordination requirements of the network former and modifier elements become similar.[19] Therefore, alumina can be used to prevent phase separation in these glass material systems, since the Al^{3+} ion can form tetrahedral configurations similar to those found in $SiO_4{}^{4-}$ tetrahedrons.[19] In the case of ceramic tile glazes, several authors[4,21] have studied ranges of chemical compositions of frits and raw materials from which highly transparent glazes can be obtained. Poyraz et al.[4] concluded that pumice – a volcanic material found in the Mediterranean area – could replace feldspar in transparent raw glazes. In fritted glazes, results show design of experiments as a tool for increasing transparency and the role of alumina in this kind of

Table 1
Chemical composition of the frits expressed in wt%.

Oxides	Frit A	Frit B
LOI (%)	–	0.1
SiO_2 (%)	59.8	60.3
Al_2O_3 (%)	6.3	8.1
Fe_2O_3 (%)	0.1	0.2
CaO (%)	15.8	17.3
MgO (%)	0.6	1.0
Na_2O (%)	1.2	2.1
K_2O (%)	4.2	4.0
ZnO (%)	7.3	–
B_2O_3 (%)	4.5	7.0

Table 2
Composition of the glazes expressed in wt% of raw materials.

Raw materials	Glaze A	Glaze B
Frit A (%)	67.6	–
Frit B (%)	–	67.6
Bentonite (%)	0.7	0.7
Sodium tripolyphosphate (%)	0.15	0.15
CMC (%)	0.15	0.15
Water (%)	31.4	31.4

composition,[21] making glaze less prone to immiscible liquid-phase separation.

2. Materials and methods

This work was divided into two steps. First, we sought to identify the possible causes of loss of transparency presented by two commercial glossy frits used in the ceramic tiles sector. In the second step, based on the findings of the first, several experimental tests were carried out aiming to increase the transparency of the frits characterized in the first step.

2.1. Causes of low transparency of ceramic glazes

Samples of two glossy frits were chosen and their chemical compositions were determined by X-ray fluorescence (Table 1), except for the B_2O_3 content, which was analyzed by atomic absorption spectrometry.

The frits were then ground in a rapid milling laboratory ball miller, following the composition of glazes indicated in Table 2. In addition to frit and water, a suspending agent (bentonite), a deflocculant (sodium tripolyphosphate) and a ligand (carboxymethylcellulose – CMC) were used to obtain the suspension. The material was ground until a residue of 2.0% was obtained in an ASTM #325 sieve (44 μm mesh).

The frit suspensions were then applied onto the surface of industrial ceramic tile supports using a regulated glaze applicator for the deposition of raw layers with 0.4 mm thickness. The test specimens were then fired in a laboratory-scale rapid-cycle furnace at a firing temperature of 1060 °C, which, in the laboratory furnace, corresponded to the temperature used industrially to manufacture the product with the support and glaze in question. Heating and cooling rates were about 90 °C/min and the soak time at 1060 °C was 3 min.

The transparency of the glazes was evaluated based on a colorimetric analysis of the glazed surface of the test specimens using a Minolta CM-2600d spectrophotometer. The results are expressed by the trichromatic coordinates: L^* indicates the degree of whiteness; a^* presents the variation between green and red colors; and b^* indicates the variation between blue and yellow colors. Highly transparent glazes show the tile support color and consequently they have low L^* values and more positive a^* and b^* parameters. To complement the results, the gloss of the glazes (β_{60}) was determined by glossmeter analysis, using a Zehntner ZGM1110 equipment.

To better understand the results, the glazes were characterized microstructurally by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The X-ray diffraction was performed from 5° to 70° (2θ scale), at a scan velocity of 3°/min, with the X-ray beam focused directly onto the glazed surface. The SEM analysis was carried out on the cross section of the glaze on the test specimens, which were previously cut and their cross sections sandpapered and polished.

2.2. Effects of the addition of alumina on transparency

This stage of the study consisted of preparing glazes from the same frits used earlier, but with the addition of alumina to the glaze composition. An evaluation was made of the effects of introducing two different contents of Al_2O_3 to the solid fraction of the glaze – 2.4% and 4.0%, using kaolin and calcined alumina of known chemical compositions were evaluated.

Table 3 lists the glaze compositions used in this stage of the study. The glaze processing conditions (grinding, application and firing) were the same as those employed in the previous stage

Table 3
Composition of the glazes with alumina additions expressed in wt% of raw materials.

Raw materials (in wt%)	GIz.A 2.4 K	GIz.A 4.0 K	GIz.A 2.4 AC	GIzA 4.0 AC	GIz.B 2.4 K	GIz.B 4.0 K	GIz.B 2.4 AC	GIz.B 4.0 AC
Frit A	64.2	61.5	66.0	64.9	–	–	–	–
Frit B	–	–	–	–	64.2	61.5	66.0	64.9
Bentonite	–		0.7	0.7	–	–	0.7	0.7
Kaolin	4.1	6.8	–	–	4.1	6.8	–	–
Calcined alumina	–	–	1.6	2.7	–	–	1.6	2.7
Sodium tripolyphosphate	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
CMC	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Water	31.4	31.4	31.4	31.4	31.4	31.4	31.4	31.4

Table 4
Colorimetric coordinates and glossmeter analysis of the Glaze A and Glaze B.

Glazes	Chromatic coordinate			β_{60}
	L^*	a^*	b^*	
Glaze A	67.6	12.0	3.5	89.2
Glaze B	65.8	10.9	12.6	92.6

of this work. Similarly, the transparency and microstructural analysis of the resulting glazes followed the same procedures described earlier herein, in order to ensure the comparability of the results.

3. Results

3.1. *Causes of low transparency of ceramic frits*

Table 1 lists the chemical compositions of the two industrial frits used in this study. Frit A was found to present a chemical composition typical of transparent frits used in the manufacture of porous ceramic tiles by single firing. These frits are characterized by their low content of alkaline oxides and high content of calcium and zinc oxides as network modifiers.[7] Frit B corresponds to a type of frit widely used in Brazil, which consists of an adaptation of traditional glossy frits used in porous products fabricated by single firing, in which the zinc oxide is eliminated from the composition for economic reasons[22] and the content of the other oxides are readjusted correspondingly. The selected frits represent the main types of frits used in the ceramic tile industry today.

Table 4 shows the results of the colorimetric analysis of the transparency of the frits. L^* and b^* parameters show whiteness and yellow or blue color tendency, respectively. In the same table, the results of the glossmeter analysis are expressed. As can be seen, the two frits present low transparency and, most importantly, their surfaces show differences in shade. Note that parameter b^* of Frit A indicates a considerably bluer shade than that of Frit B. The latter, in turn, albeit slightly more transparent and with less bluish shade than frit A, can also be visually classified as a highly milky or opaque frit (as indicated by the parameter L^*), which impairs the visibility of the colors of the substrate on which it is applied. The two frits are glossy, but their gloss values (β_{60}) are not very high.

These samples were characterized microstructurally by SEM and XRD. Figs. 2 and 3 present the SEM images, while Table 5 lists the results of the semi-quantitative chemical analysis carried out by SEM/XRD. Fig. 4 depicts the results of the qualitative XRD analysis of the crystalline phases in the glazes.

These analysis indicated the presence of crystalline phases in the glazes obtained from the two frits under study. Both glazes showed the formation of elongated crystals with lengths varying from 0.5 to 5 μm. The pointwise chemical analysis and X-ray diffractions indicated that calcium silicate crystals were formed in the glazes from the two frits, although the diffraction pattern also revealed that these crystals has distinct crystalline structures. Moreover, it can be stated that the crystals detected in Frit A presented slightly larger sizes, on average, than those found in Frit B, and that the volumetric fraction occupied by these crystals in the glaze was also higher. Determination of the mean crystals sizes indicates 1.47 and 0.81 μm in Glaze A and Glaze B, respectively.

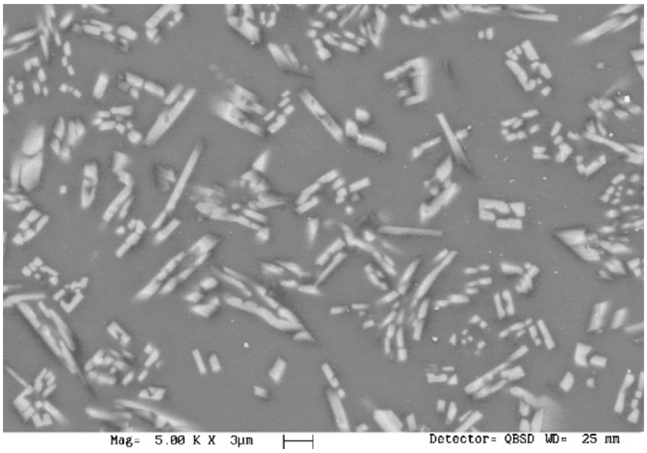

Fig. 2. SEM micrograph of Glaze A.

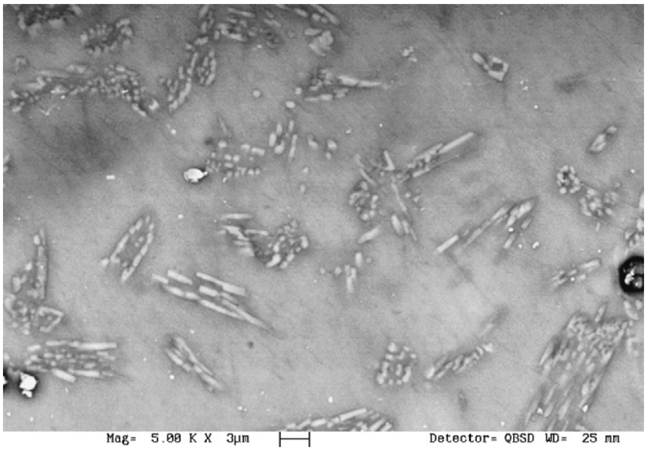

Fig. 3. SEM micrograph of Glaze B.

Since calcium silicate crystals usually present refractive indices of 1.61–1.65,[19] it can be stated that the loss of transparency of the glazes under study is related to the devitrification

Table 5
Semi-quantitative chemical analysis carried out by SEM/XRD.

Elements (%)	Glaze A		Glaze B	
	Matrix	Crystal	Matrix	Crystal
C	0.4	0.4	0.4	0.4
0	2.3	1.7	1.8	1.2
Na	3.2	1.8	0.7	0.4
Mg	0.8	0.9	1.3	0.7
Al	7.2	4.7	10.5	4.5
Si	65.4	61.6	64.1	55.8
K	4.6	3.4	6.8	2.8
Ca	14.5	24.6	14.2	34.0
Fe	–	–	0.2	0.2
Zn	1.6	1.0	–	–

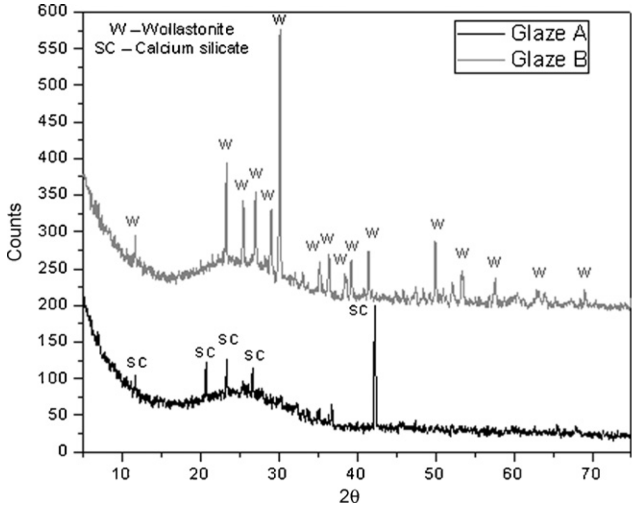

Fig. 4. Diffractograms of the of the glazes obtained from the two frits.

of these crystalline phases. Differences of transparency found between the two frits can be explained by differences in devitrification detected in the SEM analysis. Frit A, rich in ZnO and lower in alkaline elements, probably tends to undergo vitreous phase separation more easily. This phenomenon may occur precursory to devitrification[19] and create more favorable conditions for nucleation and growth of crystals.

3.2. *Effects of the addition of alumina on transparency*

The literature reports that devitrification can be prevented by incorporating small amounts of other components into the vitreous network, such as alumina.[15,19] Therefore, in this stage of the study, an evaluation was made of the influence of the incorporation of alumina – added in the form of kaolin and calcined alumina – on the transparency of these glazes.

Figs. 5 and 6 illustrate the results of the colorimetric analysis of the different glazes obtained with the addition of Al_2O_3 through the introduction of kaolin and calcined alumina in the glazes. The incorporation of small amounts of Al_2O_3 was found to lead to a significant increase in their transparency, as can be seen by the progressive reduction of the chromatic coordinate *L** (loss of milkiness) and the increase in the chromatic coordinate *b** (loss of the bluish aspect and improved visibility of the yellowish color of the ceramic support upon which the glazes were applied).

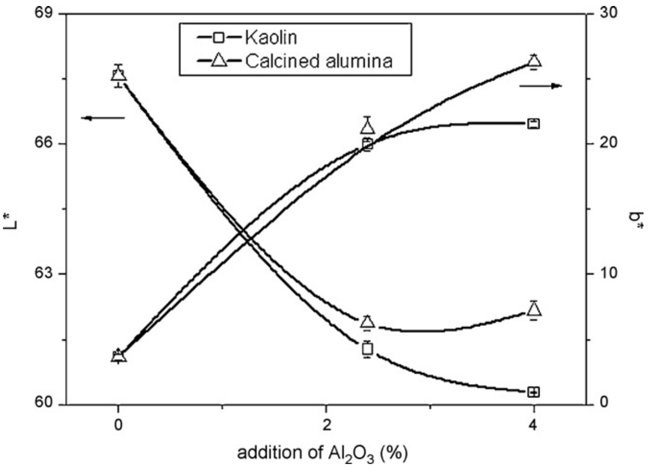

Fig. 5. Influence of the addition of Al_2O_3 on the transparency of Glaze A.

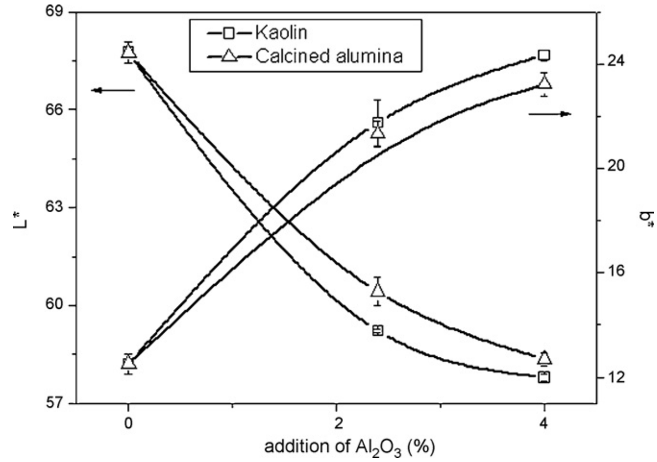

Fig. 6. Influence of the addition of Al_2O_3 on the transparency of Glaze B.

The incorporation of Al_2O_3 into the glazes led to considerable gains in transparency, independently of the mineral source. As can be seen in Figs. 5 and 6, the chromatic coordinates *L** and *b** in the glazes containing kaolin and calcined alumina are very similar at the same added content of Al_2O_3. In addition to increased transparency, the gloss of the glazes shows slight increase (Glz.A 4.0 K presents $\beta_{60} = 98.2$ and Glz.B 4.0 K shows $\beta_{60} = 99.3$).

To confirm the efficacy of the addition of Al_2O_3 as an alternative to increase the transparency of the glazes by preventing their devitrification, the glazed surfaces of samples Glz.A 4.0 K and Glz.B 4.0 K (Glazes A and B with the addition of 4.0% of Al_2O_3 through kaolin) were analyzed microstructurally by SEM and XRD.

Figs. 7 and 8 illustrate the results of the SEM analysis, while Fig. 9 depicts the diffractograms of the surfaces of the glazes. These results explain the high transparency shown by these glazes, indicating that they contain significantly low volumetric

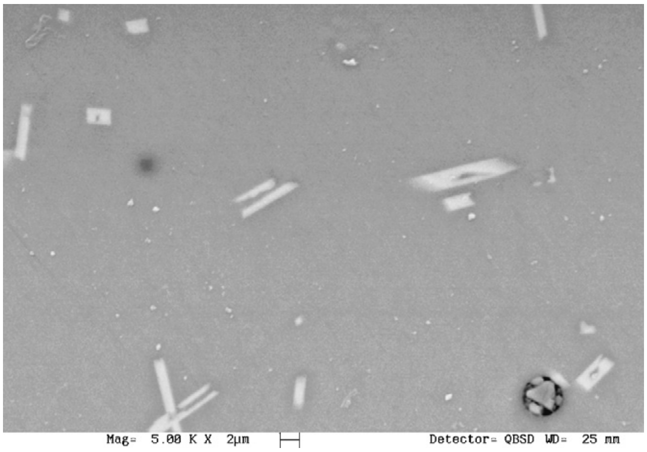

Fig. 7. Micrograph of sample Glz.A 4.0 K.

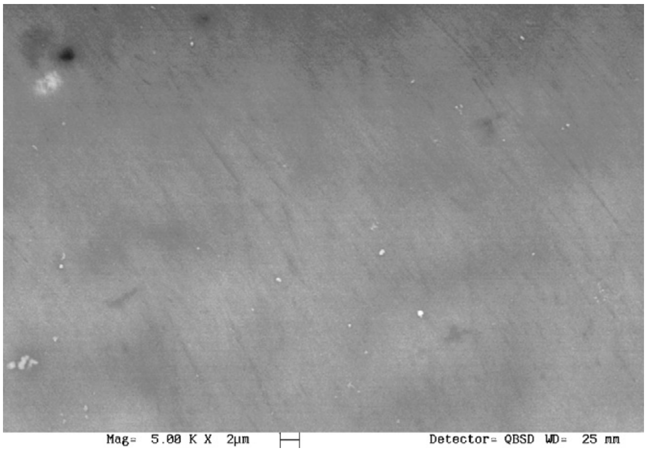

Fig. 8. Micrograph of sample Glz.B 4.0 K.

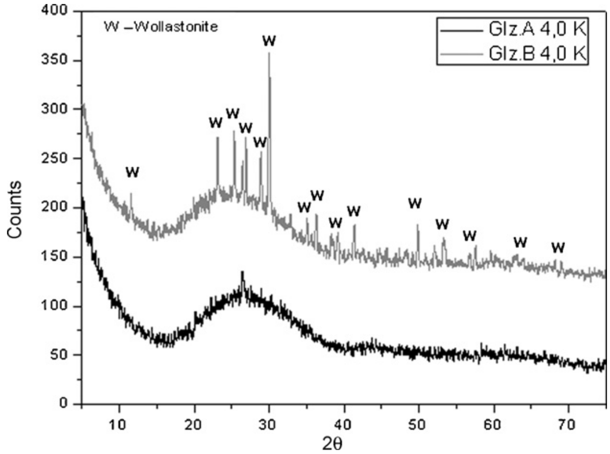

Fig. 9. Diffractograms of the surfaces of samples Glz.A 4.0 K and Glz.B 4.0 K.

fractions of devitrified crystalline phases, unlike Glazes A and B characterized initially.

After the addition of 4.0% of Al_2O_3 in the solid fraction of the glazes through the introduction of kaolin, Glaze B still has a microstructure more heterogeneous than Glaze A. The first, even after the incorporation of Al_2O_3, still showed the formation of crystalline calcium silicate phases, albeit in considerably smaller quantities than observed previously in Glaze A without the addition of Al_2O_3.

4. Conclusions

The results obtained in this work indicated that the loss of transparency presented by some commercial glossy frits used in the ceramic tile sector is associated to the devitrification they undergo during firing. The frits of this study were found to form calcium silicate crystals, which, because they have higher refractive indices than the vitreous matrices, tend to reduce the transparency of the glazes and produce milky and/or bluish colors. Although there are reports in the literature stating that this type of loss of transparency in glazes is associated with the separation of vitreous phases, the results obtained in this study indicated the presence of the aforementioned crystalline phases as the cause of this phenomenon. In this case, the most probably hypothesis is that vitreous phase separation occurs precursory to devitrification. Frit A, rich in ZnO and lower in alkaline elements, has a higher tendency to phase separation and consequently enables the development of larger and more numerous crystals than Frit B.

The incorporation of Al_2O_3 proved to be a viable alternative to maximize the transparency of the glazes obtained from the frits in question. Small additions (in the order of 2.0–4.0%) may suffice to produce substantial increases in transparency. Effects of the alumina addition on the other technical properties were not evaluated in this study. However, considering that the crystals avoided by alumina addition were calcium silicates, losses are not expected to abrasion or chemical resistance.

The incorporation of Al_2O_3 through kaolin of calcined alumina produced very similar results insofar as the transparency of the glazes is concerned. Therefore, the two raw materials can be used successfully for this purpose, and represent very interesting options to increment the transparency of ceramic tile glazes, in which this characteristic is an essential requisite.

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