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Influence of firing temperature on the color developed by a $(Zr,V)SiO_4$ pigmented opaque ceramic glaze

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Abstract

The analysis of the physical interactions between pigments, opacifiers and glazes is fundamental to understand the optical behavior of ceramic glazes. Furthermore is important to verify if the glaze devitrifies because the crystallized phases can contribute to the optical properties of the system. The size and the quantity of the formed crystals can change significantly the glaze color. The mean goal of this study was to evaluate the influence of firing temperature on the color stability of an opaque ceramic glaze colored by a blue vanadium–zircon pigment taking into account all the optical components. Quantitative X-ray diffraction analysis was conducted in order to evaluate the pigment dissolution at the three studied temperature and the quantity of the *in situ* formed zircon crystals from the used frit. The reported study demonstrated the importance to consider all the components in a multicomponent optical system as a ceramic glaze.

Keywords: Colour; Spectroscopy; X-ray methods; Traditional ceramics; Glazes; $(Zr,V)SiO_4$

1. Introduction

In the ceramic industry one of the mean goal in the application of a glaze is to improve the aesthetic of the finished product. In this context the grain size distribution of both pigments and crystals devitrified by glaze, and the chemical and physical interaction between pigments and glazes during firing is fundamental in order to control the coloring process. The same pigment, in fact, can develop slightly different colors depending on both firing temperature and chemical composition of glaze to color.[1]

Crystallization control and prevention of pigments dissolution in glazes and ceramic matrix during firing is important for optimizing the properties, appearance and reproducibility of products. Multi-oxide frits are the predominant materials in fast-firing glazes,[2–4] and zircon ($ZrSiO_4$) doped pigments are the most commonly used colorants. Compared to other batch components, frit normally has the lowest melting temperature but are the most corrosive to ceramic pigments. Frits for whiteware coatings generally include SiO_2 as the main glass former, alkalis (Na_2O and K_2O), B_2O_3, ZnO or SrO as the main fluxes, CaO, MgO, and Al_2O_3 to increase the coating hardness and durability.[5,6] In addition, opaque whiteware coatings, which are the most widely manufactured, normally incorporate ZrO_2.[7] Opacity and whiteness are obtained through crystallization of zircon. The resulting micro heterogeneities (<10 μm size) have a significantly higher index of refraction (2.05–2.40) than the glassy matrix (1.50–1.70) and thus effectively scatter light.[8] Infact the Mie scattering calculations[9] identify that maximum light scattering and whiteness with zircon occur with a particle size range of 0.60–0.75 μm and a mass fraction of 0.16.

Zircon-doped pigments are the most stable ceramic colorants up to ~1200 °C. Zircon tetragonal structure has the ability to accommodate vanadium and praseodymium substitutionally and inglobate hematite, and its high chemical and thermal stability make it ideal for use in ceramic coatings.[10,11] The zircon triaxial system is commonly used to color industrial glazes. It is based on

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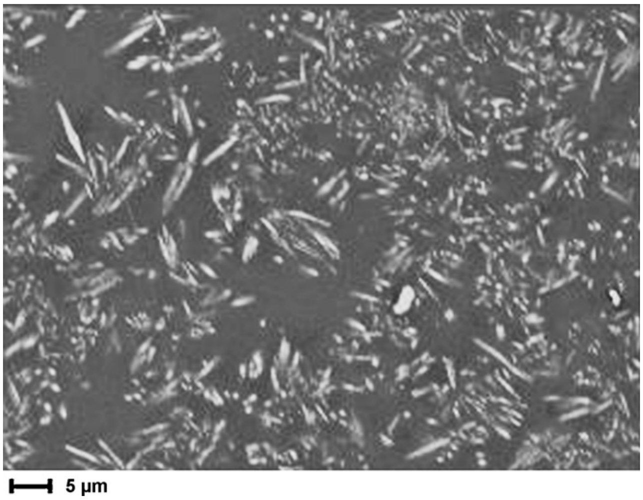

Fig. 1. SEM micrograph of the zircon crystals formed in the glaze at 1175 °C.

Table 1
Chemical composition of the opaque frit

Oxide	wt%
SiO_2	56.00
ZrO_2	7.40
ZnO	9.60
Al_2O_3	5.07
R_2O ($K_2O + Na_2O$)	3.40
RO (CaO + MgO)	12.80
B_2O_3	5.65
Fe_2O_3	0.08

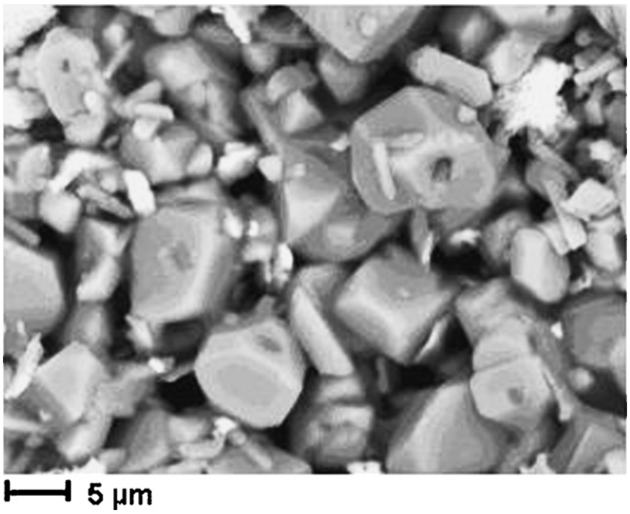

Fig. 2. SEM micrograph of the blue zircon–vanadium pigment used in this study.

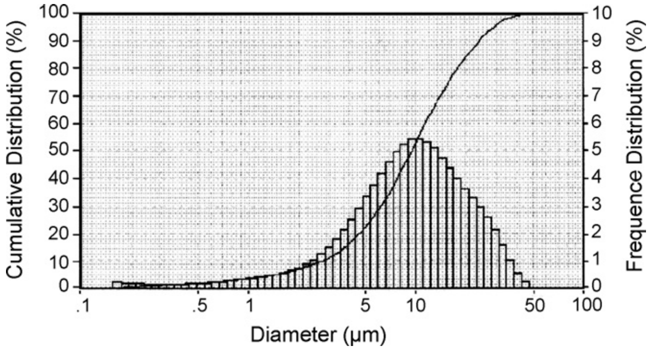

Fig. 3. Grain size distribution of the blue zircon–vanadium pigment used.

blending zircon–vanadium (Zr–V) blue, zircon–iron coral, and zircon–praseodymium yellow to obtain a wide range of colors. Zircon pigments are normally added to glaze batches in range of 0.1–5.0% by weight, and their solubility during firing varies with the frit composition.[7]

When studying the optical behavior of pigments and opacifiers in a glaze, it is important to understand the physical interactions between the pigments, the opacifiers, and the glaze. The following possibilities exist when zircon pigments are used in a glaze: the zircon crystals can be stable and be unaffected by the glaze during firing, the zircon particles can partially dissolve in the glaze during firing with the dissolved portion either remaining in solution or reprecipitating, or the zircon particles can totally dissolve.[1]

The optical properties of an object depend on the energy distribution at every wavelength (reflectance) that is a function of the absorbed and scattered light. This means that for each frequency in the visible all the components of the glaze (pigments, opacifiers ad crystals formed from frit) have both an absorption and scattering coefficient, each one contributing to the optical properties of the glaze. For this reason it is important to consider all components of a multicomponent optical system. Normally the major emphasis is placed on the pigments, even if to define a color, the other optical elements of the system

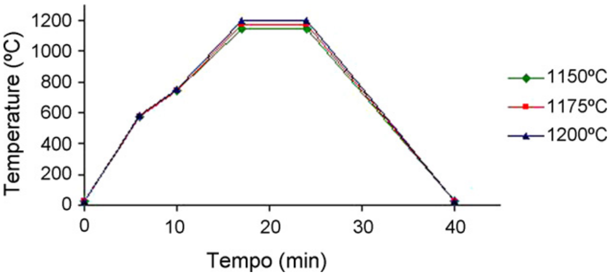

Fig. 4. Firing cycles applied to the glazes.

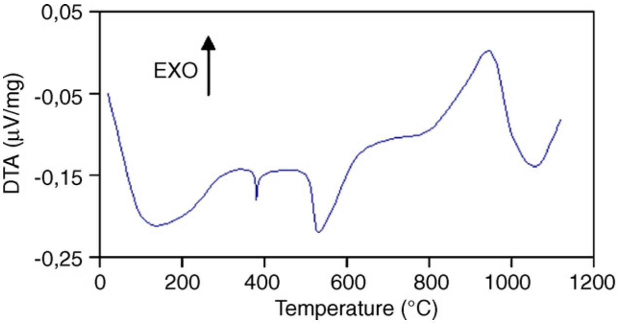

Fig. 5. DTA curve of the glaze with 5 wt% of blue zircon–vanadium pigment.

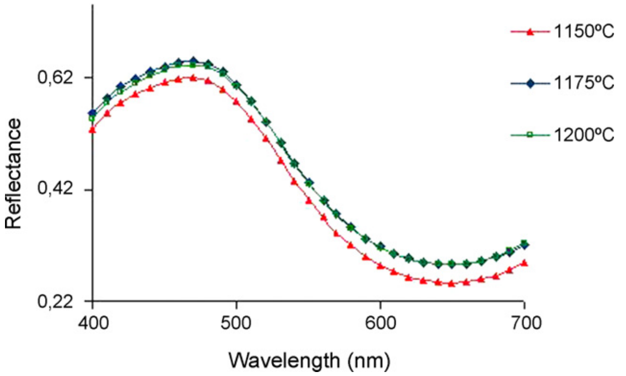

Fig. 6. Observed (crosses), calculated (continuous line) and difference curve from the Rietveld refinement of the glaze fired at 1200 °C. Markers representing the phase reflections correspond to V-doped zircon, corundum and Zircon respectively (from bottom to top).

(opacifiers and the crystalline phases formed by the frit during firing with refractive index greater of vitreous phase) are equally important.[9]

Aim of this work was to evaluate the influence of firing temperature (1150, 1175 and 1200 °C) on the color developed by a blue vanadium–zircon pigment in an opaque ceramic glaze taking into account all the optical elements of the system.[12]

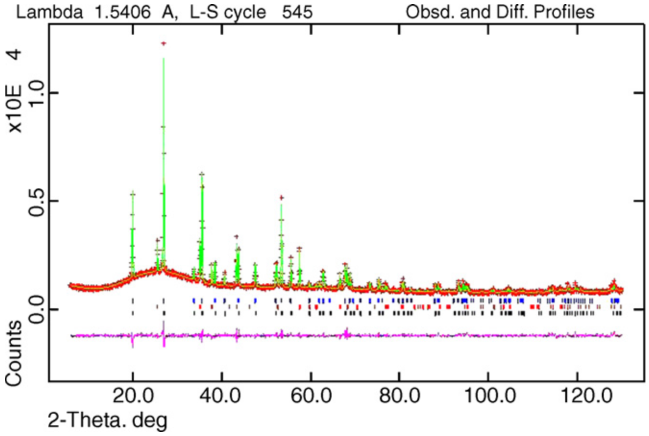

Fig. 7. Reflectance curves of the glazes fired at the studied temperatures.

2. Experimental procedure

The colored glazes were prepared by mixing 92 wt% frit, 8 wt% kaolin and adding 5 wt% of commercial blue zircon–vanadium pigment (Ferro). Powders were wet milled (50 wt% water) in ball mill for 20 min. The frit and the zircon–vanadium pigment used were completely characterized. The frit used was a white frit that during firing devitrifies zircon crystals as showed in Fig. 1. Its chemical composition is reported in Table 1. The morphology of the pigment particles is

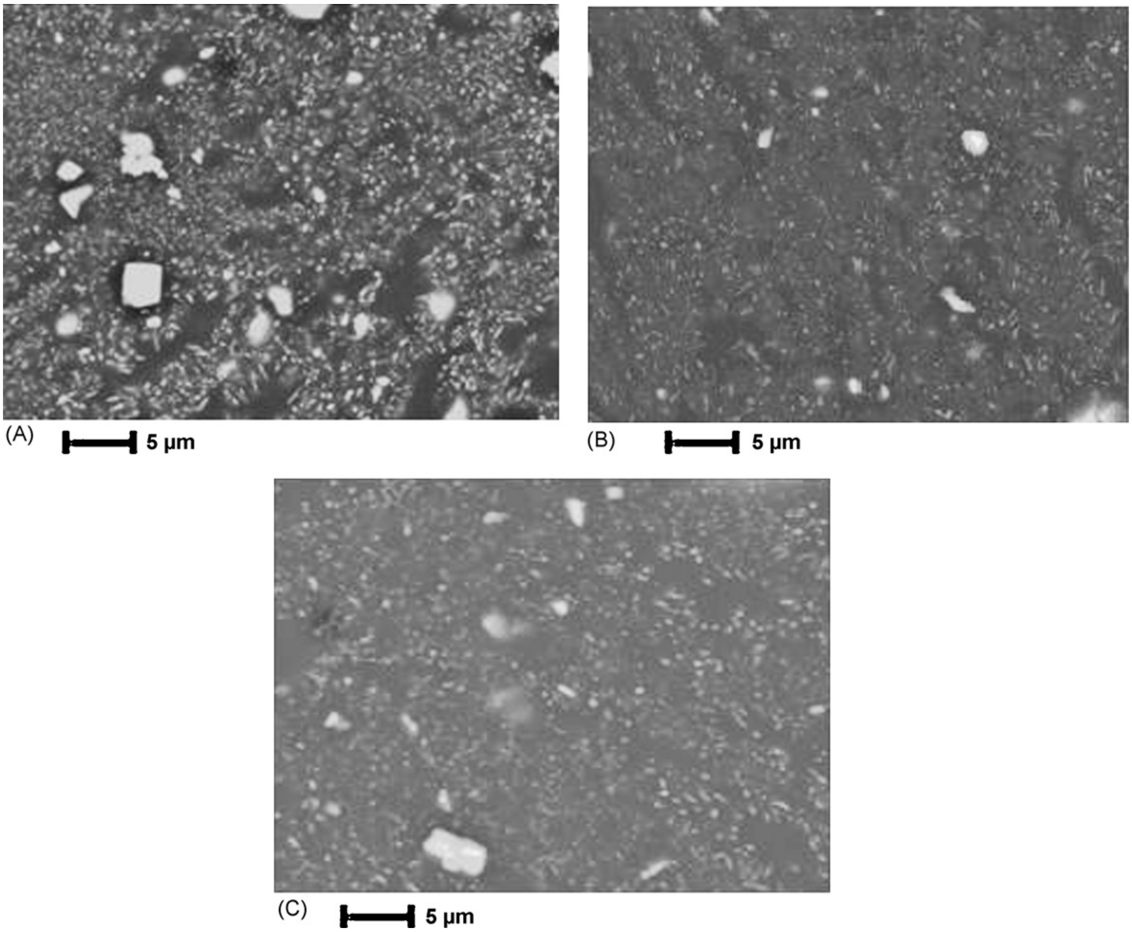

Fig. 8. SEM micrographs of the glazes fired at 1150 °C (A), 1175 °C (B) and 1200 °C (C).

Table 2
L^*, a^*, b^* parameters of the colored glazes fired at different temperatures

Firing temperature (°C)	L^*	a^*	b^*
1150	73.4	−9.3	−16.9
1175	77.3	−8.8	−17.6
1200	76.8	−8.9	−17.3

presented in Fig. 2. The blue zircon–vanadium pigment presents a monomodal grain size distribution with mean particle size of 9.43 μm as showed in Fig. 3. Cylindrical samples (25 mm diameter and 6 mm thickness) of glaze were prepared by pressing the powder (6 wt% of water) with a laboratory press. The samples were fired in a semi industrial kiln at 1150, 1175 and 1200 °C with a total cycle firing of 35 min. The thermal cycles used are reported in Fig. 4.

The L^*, a^*, b^* parameters and the reflectance curves of the fired samples were measured by a Datacolor-Spectraflash 600 spectrophotometer with optical geometry d/8, illuminant D65 and observer 10°.

To evaluate the thermal and chemical stability of the pigment in the glaze the thermal analysis of the glaze containing 5 wt% of blue zircon–vanadium pigment was realized. To determine the thermal and chemical stability of the blue zircon–vanadium pigment in the used glaze and to quantify the devitrified zircon, a quantitative X-ray diffraction analysis of the powdered glazes fired at the studied temperatures was performed by the combined Rietveld-R.I.R. (reference intensity ratio) method.[13] A 10 wt% of corundum (NIST SRM 674a annealed at 1500 °C for 1 day to increase the crystallinity to 100 wt%) was added to all samples as internal standard. The mixtures, ground in an agate mortar, were side-loaded in an aluminium flat holder in order to minimize the preferred orientation problems. Data were recorded in the 5–140° 2θ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld-R.I.R. refinements, using GSAS software, were rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized. The background was successfully fitted with a Chebyshev function. The peak profiles were modelled using a pseudo-Voigt function with one Gaussian and one Lorentzian coefficient. Lattice constants, phase fractions and coefficients corresponding to sample displacement and asymmetry were also refined.

The sample morphology was evaluated by a Philips scanning electron microscope, (SEM, Philips model XL 40) and the grain size distribution and the shape of the *in situ* formed crystals were determined by an image analysis software (Image Pro-plus 4.5.1 with Materials Pro module) from the SEM images.

3. Results and discussion

Fig. 1 shows the morphology of the zircon crystals formed at 1175 °C in the glaze. Spherical and needle shape crystals of about 5 μm in length are presents. The DTA curve of the glaze with 5 wt% blue zircon–vanadium pigment (Fig. 5) do not show

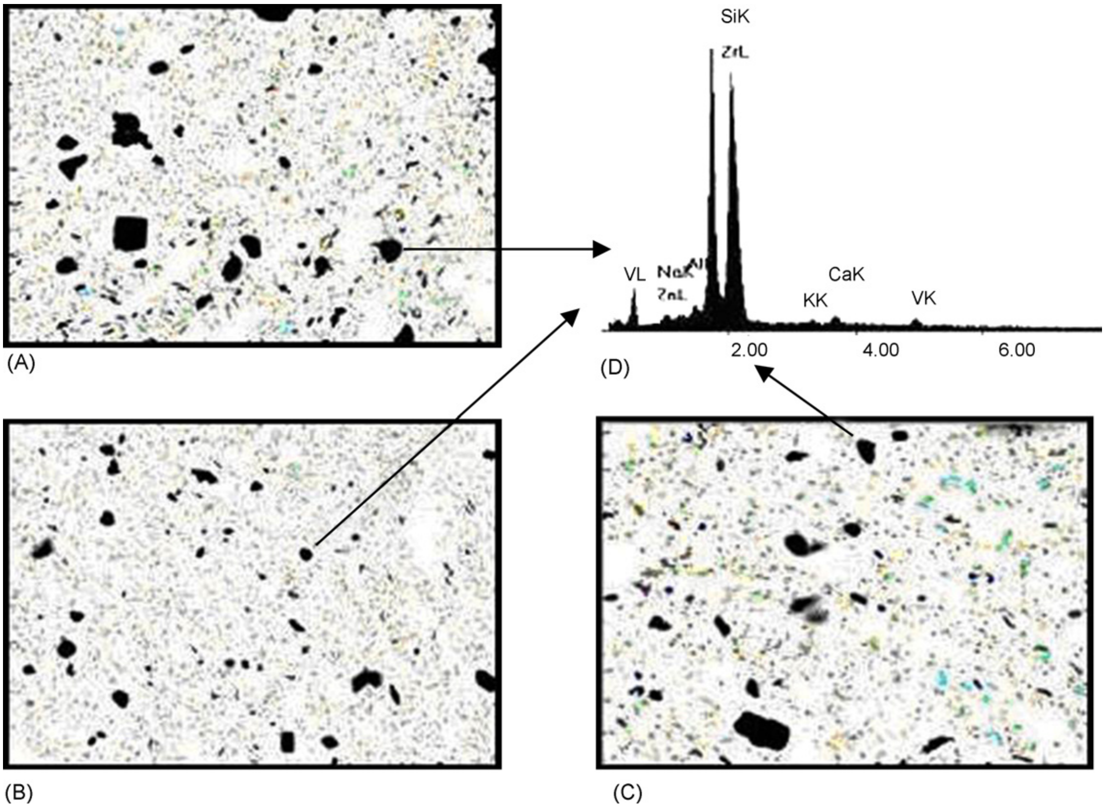

Fig. 9. Classification (obtained with image analysis software) of the *in situ* formed zircon crystals of the glazes fired at 1150 °C (A), 1175 °C (B) and 1200 °C (C) and EDS spectra (D) of pigment particles.

Table 3
Results of Rietveld–R.I.R. quantitative analysis (wt%) for the glazes fired at different temperatures. The structures have tetragonal $I4_1/amd$ symmetry

Phase	Temperature (°C)		
	1150	1175	1200
V-doped zircon			
a (Å)	6.6050(1)	6.6040(1)	6.6041(1)
c (Å)	5.9802(1)	5.9792(1)	5.9793(1)
wt%	4.18(3)	4.26(2)	4.03(2)
Zircon			
a (Å)	6.6141(3)	6.6131(1)	6.6141(3)
c (Å)	5.9967(5)	5.9959(5)	5.9971(5)
wt%	7.45(2)	6.63(2)	6.82(2)
Amorphous phase	88.27(5)	89.01(4)	89.06(5)
Total	99.9	99.9	99.9
χ^2	2.07	1.87	1.90
Rwp	0.042	0.040	0.041
Rp	0.032	0.031	0.031

Table 4
Grain size distribution of the *in situ* formed zircon crystals as a function of the glazes firing temperature obtained by SEM images analysis

Mean diameter (μm)	Mean area (μm)^2	Particles (%)	Particles range (%) 0.60–0.75 μm
1150 °C			
0.165	0.022	62.70	1.69
0.304	0.063	19.34	
0.392	0.103	9.06	
0.458	0.143	4.15	
0.486	0.181	1.69	
0.581	0.224	1.34	
0.634	0.267	0.58	
0.656	0.293	0.53	
0.690	0.336	0.35	
0.711	0.373	0.23	
1175 °C			
0.202	0.038	70.00	8.77
0.447	0.140	18.73	
0.605	0.246	6.29	
0.753	0.344	2.48	
0.832	0.438	1.19	
0.949	0.557	0.43	
0.971	0.662	0.38	
1.002	0.763	0.14	
0.909	0.808	0.14	
1.015	0.963	0.19	
1200 °C			
0.073	0.005	20.30	5.64
0.244	0.048	57.27	
0.458	0.147	10.15	
0.529	0.206	6.26	
0.599	0.267	2.26	
0.655	0.327	2.01	
0.649	0.378	0.62	
0.708	0.439	0.38	
0.760	0.485	0.38	
0.887	0.553	0.38	

the formation of new crystalline phases from the reactivity of the glaze with pigment. The curve presents only the kaolin deoxydrilation, the zircon devetrification from the used frit and the glaze fusion. Fig. 6 shows the reflectance curves of the colored glazes fired at the three studied temperatures. The reflectance of the glaze fired at 1150 °C is weaker than others indicating a minor light diffusion and thus a blue colored glaze darker or less luminous, as shown also by the L^*, a^*, b^* parameters reported in Table 2. No significant differences were observed in the reflectance curves of 1175 and 1200 °C fired samples.

Quantitative X-ray diffraction analysis was performed to quantify both the dissolution behavior of the pigment particles and the *in situ* formed zircon crystals. Table 3 shows the results obtained by the Rietveld-R.I.R. combined method (Fig. 7). The results show that the amount of the vanadium-doped zircon phase is practically the same at the three studied temperatures underlining the thermal and chemical stability of the V-doped zircon pigment in the selected glaze. Moreover, the amount of crystallized zircon is higher in the glaze fired at 1150 °C with respect to the other investigated temperatures. The lattice parameter values clearly show that vanadium causes a contraction of the primitive cell of $ZrSiO_4$ according to the difference in the ionic radii of V^{4+} and Zr^{4+} (0.72 and 0.87 Å respectively). On the contrary the $ZrSiO_4$ cell parameters are unaltered with respect to the values reported in literature for pure zircon.[14]

However, the results of the quantitative diffraction analysis do not explain the reflectance behavior of the glazes. In particular the glaze fired at 1150 °C characterized by the higher amount of *in situ* formed zircon phase should have greater reflectance curve due to the scattering features of these crystals. This apparent discrepancy can be explained by examining the size and shape of the zircon particles from the SEM micrographs (Fig. 8), with an image analysis software that classifies the crystals as shown in Fig. 9. In particular the black particles are V-doped zircon crystals removed from the classification. The zircon crystals size distribution obtained by the software analysis is reported in Table 4. While in Table 5 the aspect ratio distribution (ratio between greater and smaller axis of the equivalent ellipse of object) is reported.

Although the glaze firing at 1150 °C have greater quantity of zircon Tables 4 and 5 evidence that the glazes fired at 1175 and 1200 °C have a major quantity of crystals with a particle size ranging from 0.60 to 0.75 μm (range that provoke the maximum scattering). Moreover these particles tend to a spherical shape due to the greater reactivity with the vitreous phase contributing to the greater values of reflectance.

Table 5
Aspect ratio distribution of the *in situ* formed zircon crystals as a function of the glazes firing temperature obtained by SEM images analysis

Mean aspect	% of particles		
	1150 °C	1175 °C	1200 °C
1	–	–	20.30
1.1 and 1.4	–	0.34	–
1.7 and 1.9	–	70.02	74.67
>2	100	29.64	5.03

4. Conclusions

The obtained results demonstrated that the blue zircon–vanadium pigment is thermally and chemically stable in the opaque glaze at the studied firing temperatures. In particular the quantitative X-ray diffraction analysis performed by Rietveld-R.I.R. combined method evidences that the glazes are characterized by the same amount (approximately 4 wt%) of undissolved pigment and thus that the changes evidenced in the color are not related to the instability of the pigment used. These changes are provoked by the differences in the grain size and morphology of zircon crystals formed during the firing from the used frit contributing significantly in the scattering of the light. This result demonstrates the extreme importance to consider the properties of all the components in a multicomponent optical system as a ceramic glaze principally when devitrification phenomena are present during the firing of the glazes.

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