

Substitution of a fraction of zircon by cristobalite in nano hematite encapsulated pigment and examination of glaze application

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Abstract: Hematite pigment has a long history, but it cannot be used for ceramic application, because it must be thermally and chemically stable at high firing temperature when using a pigment in a glaze or ceramic body. Recently, through encapsulated systems, a new pigment with suitable thermal and chemical stability can be obtained by encapsulating hematite crystals into selected silica or zircon matrices. It means that nano-sized red hematite has been encapsulated into the protected phases. Transmission electron micrographs of hematite encapsulated into silica and zircon matrices by sol–gel method show spherical single crystals with diameter of about 5–10 nm. In order to optimize ceramic glaze formulations for application of the synthesized red inorganic nanocomposite inclusion pigment by sol–gel method, four different types of glazes (i.e., alkalis, borate, earth alkalis, and leaded glazes) have been tested. The results show that the substitution of a fraction of zircon by cristobalite in hematite–zircon pigment produces acceptable stability with red hue.

Keywords: nano hematite; inclusion pigment; zircon; silica; ceramic glaze

1 Introduction

In the production of colored ceramic materials, coloring ions can play their roles by being dissolved in the material (ceramic body or glaze) which we intend to color [1–3]. However, these alternatives do not appear to be recommendable in industrial production, since the solution and/or reduction processes involved are rather difficult to control and good reproducibility must always be guaranteed in industrial production. Instead of these procedures, synthetic pigments are widely used in ceramic industry; in these pigments, the color agent has been already incorporated into an

appropriate host lattice during the calcination stage by some kind of reaction. Of course, the host lattice must have adequate thermal stability and remain insoluble to withstand the aggressive action of the glazes (ceramic frits and/or sintering additives) in which they are formulated. Based on the glaze formulation, some pigments will be useful to apply [4,5].

The inclusion or encapsulation of a reactive, colored or toxic crystal into a highly stable crystalline matrix gives a protection effect to the guest crystal. The guest crystal becomes inactive within the host [6–8]. There is a restricted choice for red/pink and orange colors among synthetic inorganic ceramic pigments to be used in ceramic industry. They are generally easily etched by glasses, and sensitive to the atmosphere and firing temperature; a number of them contain toxic and polluttional elements. Therefore in recent years, there has been a developing interest toward new nontoxic

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inorganic red pigment and applying them into ceramic glazes [4,9–11].

Hematite encapsulated pigment based on silica and/or zircon crystals that protect the occluded red α - Fe_2O_3 chromophore crystals is usually utilized, even if the traditional preparation leads to powders that negatively affect the glaze composition and sintering temperature. In particular, in order to achieve high efficiency of chromophore agent encapsulation, the matrix sintering and/or crystallization must be synchronized with the nucleation and growth of the occluded chromophore agent. Crystallization, sintering and inclusion process are thus considered to take place simultaneously, and consequently, the control of particle size of the raw powders is one of the main steps [5–9,12–16].

Silica may be considered to have a potential to be used in the occluded pigment as a matrix due to its properties, relatively low price, and particularly, the sufficient thermal and chemical stability towards glassy phases. The high thermal stability of the silicon lattices and their properties such as the sinter-ability at relatively low temperature are well known [8–11], but an important question is why the hematite–silica pigment is not applied into glaze by ceramic industry? The hematite–silica system presents better red shade pigment than hematite–zircon system, and the hematite–zircon pigment is more expensive than hematite–silica system [17–19].

Based on these considerations, the aim of the present work is to compare the synthesized inclusion pigments in hematite–silica, hematite–zircon, and hematite–silica–zircon systems of several ceramic glazes for applications.

2 Experimental procedure

2.1 Materials

Samples of 1 mol SiO_2 –0.2 mol Fe_2O_3 , 1 mol ZrSiO_4 –0.2 mol Fe_2O_3 , and (0.5 mol SiO_2 –0.5 mol ZrSiO_4)–0.2 mol Fe_2O_3 compositions were prepared by colloidal sol–gel method. A concentrated aqueous solution was prepared by adding iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Merck) in deionized water and refluxing at 70 °C for 30 min. Then, the required aqueous suspensions of colloidal silica (30 wt% SiO_2 , LUDOX) and zirconium chloride (Merck) based on final composition were added to the aqueous solution by drops of the concentrated solution. The systems were

continuously stirred and maintained at 70 °C until the pH was stabilized at about 4. The resulting gels were dried at 110 °C. 0.2 mol NaF as mineralizer or flux agent was applied to all dried gels by milling. The powders were fired at 1000 °C in an electrical furnace with a soaking time of 3 h. The fired samples were micronized, wet milled and washed in deionized water. Finally three kinds of inclusion pigments were obtained after drying at 110 °C and screening [20].

Constant 5 wt% of the pre-synthesized nano-composite inclusion pigments of the mentioned systems were added to several kinds of transparent ceramic glazes, i.e., earth alkalis (high calcium), borate, alkalis (high sodium), and leaded glazes. All of the colored glazes were formulated by regular amounts of kaolin and additives, then wet milled for 20 min. After air brushing on conventional wall tiles, they were dried at 110 °C for 2 h and fired at 1100 °C in an electrical furnace with a soaking time of 10 min. The heating rate was 20 °C/min.

2.2 Characterization methods

In order to determine the effects of the glaze formulation on the stability of the nanocomposite inclusion pigments and to define the color developed by the samples, a Gretag Macbeth Color-Eye 7000 was used, employing a 10° standard observer. L^* , a^* and b^* color parameters were measured following CIE (Commission International de l'Eclairage) colorimetric method. In this method, L^* is the lightness (black (0) → white (100)) axis, a^* is the green (–) → red (+) axis, b^* is the blue (–) → yellow (+) axis, c^* is the concentration of color, and h^* is the hue factor of color. Particle size analysis of the samples was controlled by a sift mesh (No. 400) and equipment of Mastersizer Malvern with water dispersant.

The microstructures were characterized using a scanning electron microscope (SEM, Leo 1455 VP) equipped with secondary electron (SE) detector and Robinson solid-state backscattered electron (BSE) detector (to display the chemical contrast in the observed objects). The glazes were selected from some ceramic industries; in order to identify their compositions, X-ray fluorescence (XRF) and inductively coupled plasma (ICP) analysis were used.

X-ray diffraction (XRD) patterns have been collected using a conventional powder technique by a Siemens Diffractometer (D500 mod) with Cu $K\alpha$ Ni-filtered radiation to identify the crystalline phases

present in the raw and fired powders.

The powders' microstructure characterization and hematite's morphology have been studied by transmission electron microscopy (TEM, Jeol JEM 2010 with GIF gatan Multiscan Camera 794 and Software Digital Micrograph 3.1).

3 Results and discussion

3.1 Nomenclature of glaze formulations by XRF and ICP analysis

Table 1 shows the formulations and codes of the four types of frits that have been applied in the colored glazes. They are collected among different glazes. The one with the code of A has higher sodium oxide, so it is called alkalis glaze, and similarly, the borate glaze B, earth alkalis (high calcium) E and leaded glaze L.

3.2 Thermal evolution of crystalline phases by XRD analysis

According to the XRD results in Fig. 1, three phases (i.e., hematite, cristobalite and zircon) crystallize after calcination at 1000 °C in (0.5 mol SiO₂–0.5 mol ZrSiO₄)–0.2 mol Fe₂O₃ sample. Before heat treating, just an amorphous phase with iron chloride crystals can be detected (Fig. 1(a)).

Figures 2 and 3 are related to binary systems of

Table 1 Formulations and codes of the applied frits by XRF and ICP (%)

Chemical analysis	Leaded glaze L	Borate glaze B	Alkalis glaze A	Earth alkalis glaze E
SiO ₂	57.7	55.5	51.5	57.4
Al ₂ O ₃	6.82	5.47	4.30	7.53
Fe ₂ O ₃	0.23	0.21	0.28	0.28
Na ₂ O	4.36	5.98	18.4	5.47
K ₂ O	1.53	1.98	4.29	1.16
CaO	5.17	3.21	5.65	11.5
MgO	0.23	0.45	0.15	0.22
B ₂ O ₃	0.14	20.8	4.45	6.24
Pb	22.0	4.05	0.05	1.73
Zn	1.27	2.01	7.20	8.51
Zr	0.40	0.21	0.04	—
Cl	0.06	0.10	3.72	—

hematite–silica and hematite–zircon respectively. XRD results in Fig. 2 detect hematite and cristobalite phases, and hematite and zircon phases are detected in Fig. 3.

3.3 Colorimetric analysis of the colored glazes by CIELab values

CIELab colorimeter results are shown in Tables 2 and 3, providing easy comparison of the stability and color shades of the nanocomposite pigments and a traditional red pigment with code of K4272 made by Reimbold & Strick Company.

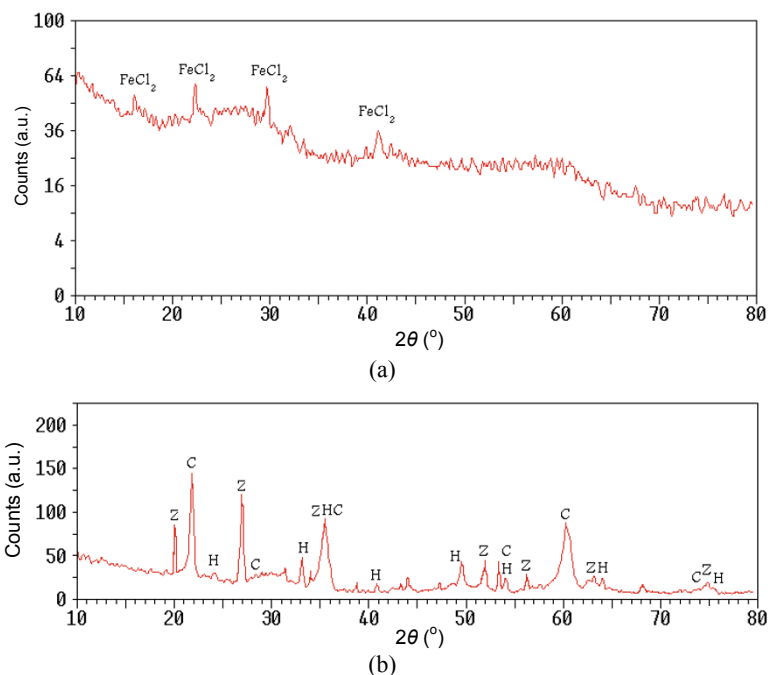


Fig. 1 XRD patterns of (0.5 mol SiO₂–0.5 mol ZrSiO₄)–0.2 mol Fe₂O₃ sample: (a) raw; (b) after calcination at 1000 °C for 3 h. H: hematite, C: cristobalite, Z: zircon.

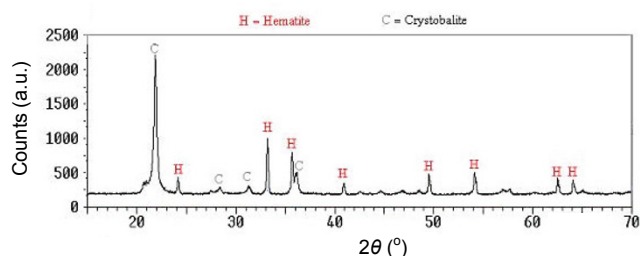


Fig. 2 XRD patterns of the fired sample at 1000 °C for 3 h with composition of 1 mol SiO₂-0.2 mol Fe₂O₃. H: hematite, C: cristobalite.

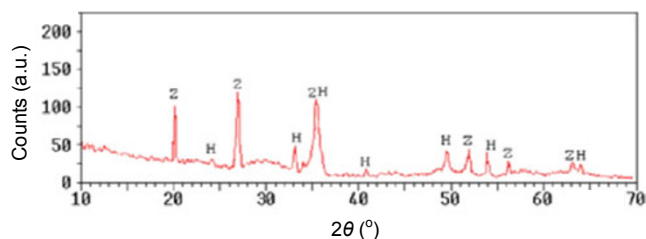


Fig. 3 XRD patterns of the fired sample in 1000 °C for 3 h with composition of 1 mol ZrSiO₄-0.2 mol Fe₂O₃. H: hematite, Z: zircon.

Table 2 Color shades and CIELab values of the colored glazes with 5 wt% of the synthesized nanocomposite inclusion pigments in different systems by light source standard of D65

Code of frit	Color	L^*	a^*	b^*	c^*	h^*
Hematite-silica pigment						
E	Red	39.92	26.59	18.40	32.33	34.69
L	Light red	45.21	27.49	18.80	33.30	34.36
A	Brown	39.26	13.99	11.87	18.35	40.33
B	Brown	41.60	11.51	9.23	14.76	38.72
Hematite-silica-zircon (ternary) pigment						
E	Red	39.46	30.62	23.61	38.67	37.63
L	Red	47.40	30.24	27.34	40.77	42.12
A	Red	45.83	27.45	19.58	33.72	35.50
B	Red (dark)	48.50	27.55	24.41	36.80	41.54
Hematite-zircon pigment						
E	Coral	33.13	17.65	9.92	20.25	29.34
L	Coral	36.79	16.67	10.67	19.80	32.63
A	Coral	33.56	14.82	8.45	17.06	29.69
B	Coral	34.03	17.55	9.54	19.98	28.52

Table 3 Color shades and CIELab values of the colored glazes with 5 wt% of a traditional red pigment in system of Sn-Si-Ca-Cr by light source standard of D65

Code of frit	Color	L^*	a^*	b^*	c^*	h^*
E	Coral	34.47	18.00	12.20	21.74	34.13
L	Coral	35.26	14.73	9.95	17.78	34.03
A	Coral	34.69	15.27	10.38	18.46	34.21
B	Coral	35.40	17.97	11.88	21.55	33.47

The color of the glazed tile after firing depends on the system of nanocomposite pigments and glaze formulation. Table 2 presents color shades and CIELab values of the colored glazes with 5 wt% of the synthesized nanocomposite inclusion pigments in systems of hematite-silica, hematite-silica-zircon (ternary) and hematite-zircon, respectively.

From Table 2 about hematite-silica pigment, it can be seen that the hues of red glazes are different. The

best red shade has been obtained by the frit of code E with high a^* 26.59 and hue factor 34.69; therefore, the glaze based on earth alkalis is more suitable for the application of binary nanocomposite inclusions with colorant agent of hematite and silica matrix. The hematite-silica system of pigment did not have necessary thermal and chemical stability in the glazes except for the earth alkaline frit. Color shades for other glaze formulations are very different from brown to

light red, thus they are not reliable and consistent enough for industrial application. In point of comparison, a traditional hematite–silica red pigment useful for body stain made by INCO Company was not stable in any glaze. In fact, nano hematite encapsulated in cristobalite phases by the mentioned procedure will introduce better inclusion microstructure and therefore better thermal and chemical stability in comparison with an industrial pigment.

The systems of hematite–silica–zircon (ternary) and hematite–zircon (binary) do not dissolve in these selected glazes, and present approximately unique red-orange shade and red-coral glazes respectively. It seems that the color shade of traditional red pigment with code of K4272 is more or less similar to the synthesized hematite–zircon pigment.

The cause of changes in the red hues can be studied by SEM.

3.4 Particle size analysis of the samples

The synthesized pigment was added in glazes after screening. The particle size of the samples is about 10 μm . Figure 4 presents a normal curve of particle distribution with $d(0.5)$: 9.078 μm related to one of the samples (hematite–zircon pigment).

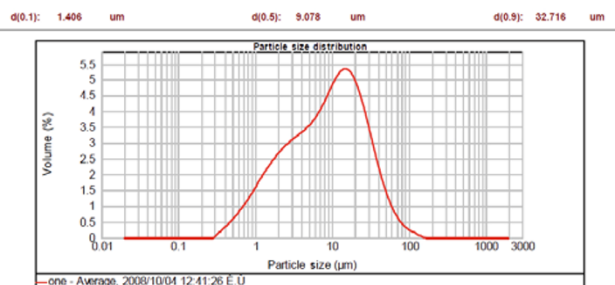


Fig. 4 Particle size analysis of the synthesized hematite–zircon pigment.

3.5 Microstructure analysis of the samples (pigments and glazes) by SEM and TEM techniques

TEM micrographs of hematite crystals encapsulated into silica, zircon and both matrices can be seen in Fig. 5. The spherical nanoparticles have diameter of about 5–10 nm.

Figures 5(a) and 5(b) are high magnifications of nano hematite encapsulated into zircon–silica and zircon crystals, respectively. They show that the morphology and size of nano hematite in different systems is more and less similar as in the

hematite–silica system seen in Fig. 5(c). The morphology of hematite is important for the color of red pigments [21].

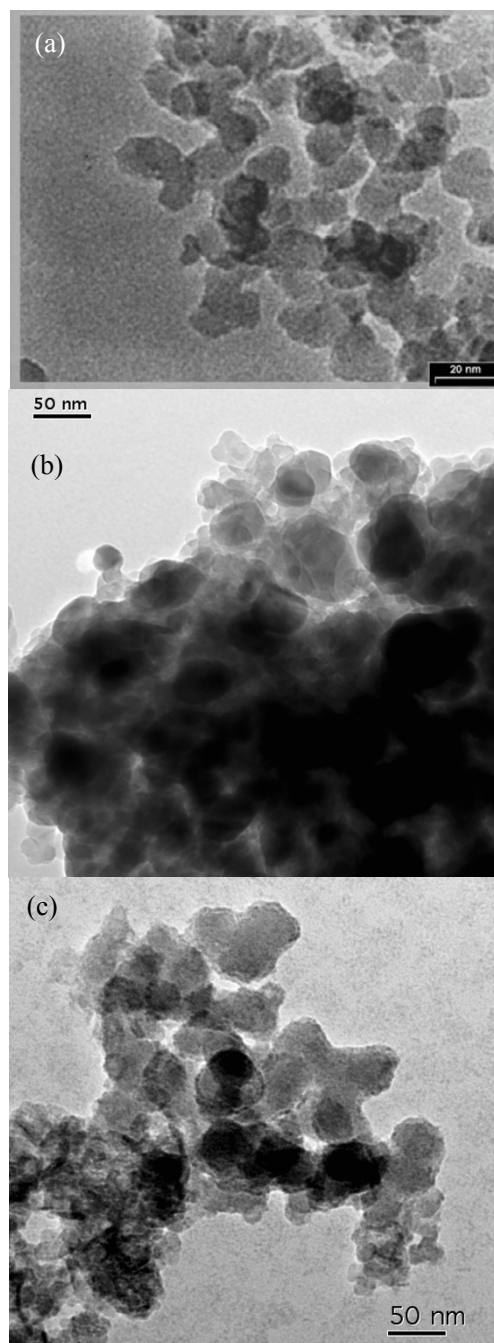


Fig. 5 TEM micrographs of the synthesized (a) hematite–zircon–silica inclusion pigment, (b) hematite–zircon inclusion pigment, and (c) hematite–silica inclusion pigment.

From Fig. 6(a), the microstructure studies of the brown glaze samples related to the colored glaze with 5 wt% of the synthesized inclusion pigments in system

of hematite–silica after firing show only some spherical dissolved particles and/or uniformed glassy phase, which indicate that the borate kind of glaze formulation is not useful for the applied system of the nanocomposite pigments, while hematite–zircon pigment in the same glaze show some dispersed particles in the glassy phase (Fig. 6(c)). Borate, leaded and alkalis glazes have the lower viscosity than earth alkalis in the firing of glazes. The viscosity of a molten

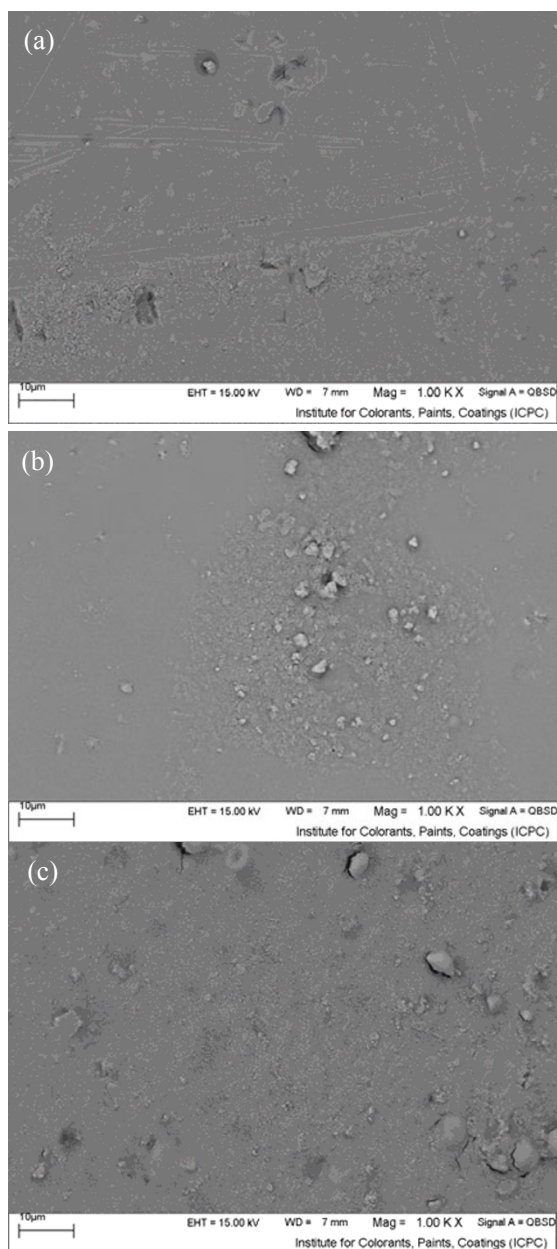


Fig. 6 Microstructures of the brown shade glaze containing 5 wt% of (a) hematite–silica, (b) hematite–silica–zircon, and (c) hematite–zircon nanocomposite pigments with frit of code B by BSE.

glaze affects the mobility of atoms and the speed of diffusion that control the reactions. Gualtieri *et al.* [22] reported the same result about a natural pigment based on hematite–silica.

The SEM analysis of the red shade glaze samples containing 5 wt% of hematite–silica nanocomposite inclusion pigment in frit of code E, and/or 5 wt% of the ternary and binary zircon nanocomposite inclusion pigment in all frits, observe some irregular micron-sized particles dispersed in the glass matrix.

The EDX analysis of the stable particles in the fired glazes prove the presence of Si–Fe and/or Zr–Si–Fe elements. It means that these glaze formulations after melting do not attack to nanocomposite pigments. The microstructures of a red shade glaze and point EDX of a stable pigment particle into glaze can be viewed in Fig. 7 (5 wt% of hematite–silica–zircon nanocomposite pigment with frit of code E) with different magnifications by SE detector.

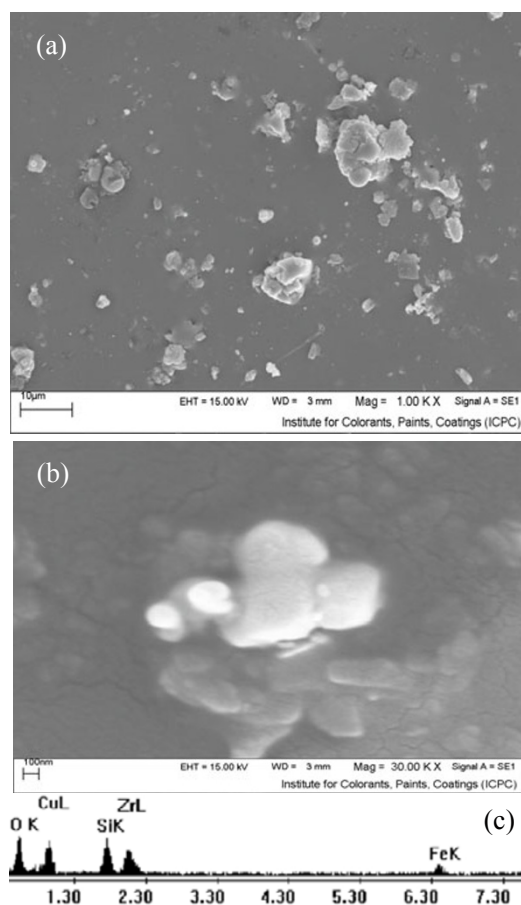


Fig. 7 Microstructures of the red shade glaze (5 wt% of hematite–silica–zircon nanocomposite pigment with frit of code E) by SE detector ((a) and (b)), and point EDX of a stable particle (c).

4 Conclusions

In order to optimize the ceramic glaze formulations for application of the synthesized red inorganic nanocomposite inclusion pigments by colloidal sol–gel method, several ceramic glazes have been tested. The results show that the best formulation of the glaze with hematite–silica inclusion pigment is Si–Ca–Zn system (earth alkalis glaze). This system is almost applied for the monoprosa tile glazes in ceramic industry. hematite–silica–zircon and hematite–zircon systems of the nanocomposite inclusion pigments have more stability in ceramic glazes than the other system.

Colorimeter data of hematite–zircon system show that this pigment presents more or less similar shades in different types of glazes, and its color can be predicted in every application, so it is more respectable. By the way, hematite–silica–zircon inclusion pigment in earth alkaline glaze presents more intense red shade. Due to the thermal and chemical stability of ternary nanocomposite pigment in some glazes, it may be considered to be a suitable red pigment for ceramic applications.

A fraction of zircon is substituted by silica in the mentioned pigment; therefore, it can be obtained cheaper than hematite–zircon pigment. On the other hand, it shifts coral shade of hematite–zircon pigment to better or different red hue and performs new red pigment.

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