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The Stability of Gahnite Doped with Chromium pigments in Glazes from the French Manufacture of Sèvres

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Abstract

The French manufacture of Sèvres, famous for its production of fine porcelain artefacts, has been synthesizing pink pigments mainly composed of the spinel phase $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ with x varying from 0.25 to 0.41 since the middle of the 19th century. This kind of pigment is mixed with an uncolored frit to obtain decorations for porcelain artefacts. However, the pink color of

the pigment is altered in a particular uncolored frit and a brownish color appears. The mechanism of this color change was investigated. Observations under a scanning electron microscope revealed the formation of a phase rich in Cr resulting from reactions between the uncolored frit and the pigment during firing. X-Ray Diffraction combined with Rietveld refinements and X-Ray Absorption Near Edge Structure at the Cr K-edge measurements showed that the new formed phase belongs to the same spinel phase $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ than the pigment, but with a higher Cr content x . We showed that its formation and thus the stability of the pigment is driven by the Al content in the uncolored frit.

I. Introduction

Pink decorations on porcelain artefacts can be obtained using different kinds of pigments, such as cassiterite,^{1,2} malayaite,³⁻⁵ or spinel doped with chromium.⁶ Recently, several studies have focused on the spinel solid solution gahnite-zincochromite $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ due to its change in coloration with the chromium content.⁶⁻⁹ The introduction of a few ppm of chromium in the colorless gahnite ZnAl_2O_4 gives a pink coloration to the material. Due to its optical properties, this oxide can be used as a pigment for porcelain. The French manufacture of Sèvres, famous for its production of fine porcelain artefacts,¹⁰ has been synthesizing pigments composed of gahnite doped with chromium since the 19th century. They have been extensively used to obtain salmon pink decoration on porcelain artefacts between the end of the 19th century and the beginning of the 20th century (Fig. 1). The detailed synthesis of Sèvres's pigments has been reported by D'Albis.¹⁰ Mixtures of these pigments with an uncolored frit are applied on the porcelain and fired at high temperature to form a glaze, i.e. a decorative glassy layer on the porcelain with a typical thickness between 100 and 500 μm . Two main compositions of uncolored frit are used at the manufacture of Sèvres depending on the chemical composition of the porcelain they are applied on: one is used only on a porcelain

fired at 1380°C, while the other one is used on a porcelain fired at lower temperature, 1280°C. $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ type pigments are only used in the former to obtain pink decorations. In the second one, we observed an alteration of the pink color of the pigment: a brownish hue appears after the thermal treatment of the glaze.



Fig. 1. *Vase from Achères* (1900), from the collection of the Cité de la céramique, ©RMN-Grand Palais. The pink colour is typical of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ type pigment.

The coloring properties of a glaze are not only dependent on the crystal structure of the initial pigment, but also on possible reactions which can occur between the pigment and the uncolored frit during firing.¹¹⁻¹³ The interaction of pigments with glazes was investigated in the literature on various systems such as Fe-Cr corundum base pigments.^{14,15} However a complete study of the mechanism of dissolution of a spinel pigment in a particular frit or glaze has never been undertaken to our knowledge.

We aim in this work at investigating by a multi-analytical approach the stability of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ type pigment during firing processes. We were able to understand the mechanism of color changes observed, and to discuss the role of chromium and aluminium in the reactivity of spinel in silicate melts.

II. Experimental procedure

(1) Sample preparation

The palette of pigments used at Sèvres for porcelain decoration is composed of 138 references, indexed from 10001 to 10138.¹⁰ Their synthesis were developed at the laboratory of the manufacture between the middle of the 19th century and the 20th century. Four of them are composed of a phase belonging to $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ with x varying from 0.25 to 0.41. The pigment numbered 10045 was selected for this study because it is the most commonly used at the manufacture. It is synthesized from ZnO, $\text{Al}(\text{OH})_3$ and Cr_2O_3 with the use of NaNO_3 as a flux (Zn : Al : Cr : Na = 1.54 : 1.61 : 0.39 : 0.42), and calcined at 1400°C without a plateau. Besides pigment 10045, three compositions along the solid solutions $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ with $x = 0.4, 1.0$ and 1.4 were synthesized. Reagent-grade chemicals ZnO, $\gamma\text{-Al}_2\text{O}_3$ and Cr_2O_3 were weighted in the right stoichiometric proportions, mixed, ground in an agate mortar with ethanol and calcined in a platinum crucible at 1400°C during 20 hours.

Glazes are obtained by mixing 0.5 g of the coloring agent (pigment 10045 from Sèvres or synthesized references) with 4.5 g of an uncolored crystallized frit named CI. The mixture is milled in a planetary agate mortar during 10 minutes at 300 rpm. This procedure was applied to each glaze in order to have a similar particle size distribution for each sample. The frit is composed of feldspar, kaolin, quartz and chalk in proportions specific to the porcelain of Sèvres. To assess the effect of the frit, the classical uncolored frit CI from Sèvres was

modified by the addition of 0.20 or 0.45 g of α -Al₂O₃ to 4.5 g of CI. Table 1 gives the chemical composition of the different frits CI, CIA11 and CIA12. The mixture of the pigment and the frit is painted on a round porcelain mount, which is then fired with the following heat treatment in use at the manufacture: 1000°C is reached in ten hours (linear heat-up ramp of 100°C per hour), then 1280°C is reached in 5h30 (linear heat-up ramp of approximately 50.9°C per hour). Once 1280°C is reached, the kiln is either maintained at a plateau or immediately turned off and slowly cooled down to room temperature. The atmosphere of the kiln is not controlled for the preparation of this kind of decoration. The sample obtained with this procedure is called R-1280. To follow the evolution during firing, the kiln was also turned off at 1180, 1200, 1220, 1240 and 1260°C and the resulting samples are called R-1180, R-1200, R-1220, R-1240 and R-1260. Table 2 summarizes the name and characteristic of the different glazes obtained by varying the different parameters (temperature of firing, composition of the pigment or composition of the uncolored frit).

Table 1: Chemical composition in molar percentage of the uncolored frit CI from Sèvres and the two frits CIA11 and CIA12 modified by the addition of 0.2 and 0.45 g of α -Al₂O₃ in 4.5 g of CI, respectively.

	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	MgO	TiO ₂	Fe ₂ O ₃
CI	74.36	8.53	12.04	2.46	2.36	0.07	0.09	0.09
CIA11	72.34	11.02	11.71	2.39	2.30	0.07	0.09	0.08
CIA12	69.97	13.93	11.33	2.31	2.22	0.06	0.09	0.08

Table 2: Summary of the different glazes prepared by mixing pigment and uncolored frit and obtained after the heating treatment (final temperature and plateau).

Sample Name	Pigment	Uncolored frit	Final temperature (°C)	Plateau (hours)
R-1280	10045	CI	1280	0
R-1260	10045	CI	1260	0
R1240	10045	CI	1240	0
R-1220	10045	CI	1220	0
R-1200	10045	CI	1200	0
R-1180	10045	CI	1180	0
R-1350-10h	10045	CI	1350	10
R-1280-5h	10045	CI	1280	5
R-1200-5h	10045	CI	1200	5
R-1160-5h	10045	CI	1160	5
R-AlCr04	ZnAl _{1.6} Cr _{0.4} O ₄	CI	1280	0
R-AlCr10	ZnAl _{1.0} Cr _{1.0} O ₄	CI	1280	0
R-AlCr14	ZnAl _{0.6} Cr _{1.4} O ₄	CI	1280	0
R-CIA11	10045	CiA11	1280	0
R-CIA12	10045	CIA12	1280	0
R-CIA11-1350-10h	10045	CIA11	1350	10
R-CIA12-1350-10h	10045	CIA12	1350	10

(2) Analytical Methods

X-ray diffraction (XRD) data were collected using a PANalytical X'Pert PRO diffractometer with Cu K α radiations ($\lambda_{\text{Cu,K}\alpha 1} = 1.54056 \text{ \AA}$, $\lambda_{\text{Cu,K}\alpha 2} = 1.54439 \text{ \AA}$) operating under 40kV and

40mA. XRD patterns for the pigment 10045 were measured on powdered samples, between 5 and 130°, with a step of 0.008° 2 θ and a counting time of 25 s/step. XRD patterns were measured directly on the glazes without specific preparation, between 10 and 130°, with a step of 0.016° 2 θ and a counting time of 550 s/step. The lattice parameters of the different phases were determined using the Rietveld method,¹⁶ as implemented in the FullProf Suite program.¹⁷

Diffuse reflectance spectra were measured using a Perkin Elmer Lambda 1050 spectrometer with an integrating sphere. The pigment 10045 was finely ground and the powder was deposited on a sample holder. The spectra were recorded between 4000 and 36000 cm⁻¹ directly on the glaze surface, without specific preparation. The white reference was a perfectly flat tablet of BaSO₄. Reflectance data were converted into absorption spectra using the Kubelka-Munk remission function $F(\rho_{\infty})$.¹⁸

Cross sections were cut from the porcelain shard with the glaze on the top. These fragments were embedded in a resin block, polished using diamond pastes down to 3 μm and carbon coated. Scanning Electron Microscopy (SEM) analyses were conducted with a Zeiss Ultra55, with an acceleration voltage of 15 keV, a working distance of 7.5 mm and a backscattered electron detector, associated to an Energy Dispersive Spectroscopy (EDS) microprobe. Based on this analysis, areas of interest were selected for the X-ray absorption Near Edge Structure (XANES) measurements at the Cr K-edge.

X-ray fluorescence (XRF) maps and macro and micro XANES data at the Cr K-edge (5989 eV) were collected on the ID21 beamline at ESRF (Grenoble, France). The powdered pigment 10045 was fixed on a thin film XRF tape and covered with ultralene film. The cross sections of the glazes were fixed directly on the sample holder. The incident beam was monochromatized using a Si(220) monochromator calibrated with a Cr metallic foil. The beam size on the powdered pigments was 200x200 μm^2 . To characterize the glaze, the beam

was focused down to $0.2 \times 0.7 \mu\text{m}^2$. μ -XRF maps were acquired on areas of interest previously selected under the SEM. XRF spectra were batch fitted using the software PyMCA,¹⁹ used to generate elemental maps and identify points of interest for μ -XANES measurements. XANES spectra were recorded in XRF mode between 5960 eV and 6210 eV with a step of 0.2 eV and an accumulation time of 1 s/step. Five and ten scans were recorded for the powdered pigment 10045 and the regions of interest of the glazes, respectively. The scans were summed and the resulting spectrum was normalized using the software PyMCA.

III. Results

(1) Crystalline nature of the pigment 10045

In order to determine the crystalline phases present in the pigment 10045, a XRD investigation was carried out. Fig. 2 presents the XRD pattern of the pigment 10045 used for the glaze and its Rietveld refinement. The lattice parameter a of the phase $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ is linked with the chromium occupancy x by the equation:

$$a(\text{\AA}) = 0.1215x + 8.086(\text{\AA}) \quad (1)$$

derived from our previous XRD investigation on this solid solution.⁹ Both lattice parameter and chromium occupancy are fitted during the refinement and they are in good agreement. Since a and x are nicely correlated, we prefer to use the equation (1) to obtain x from a . Two phases are found in the pigment 10045: a small amount of ZnO and a majority of $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$. ZnO remains in 10045 probably because reagents are not used in stoichiometric proportion for the synthesis of this pigment. Indeed, the crystalline purity of the pigment is not necessarily looked for at Sèvres, but rather its coloring properties in a glaze. The small chromium content of the $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ gives a pink coloration to this pigment.

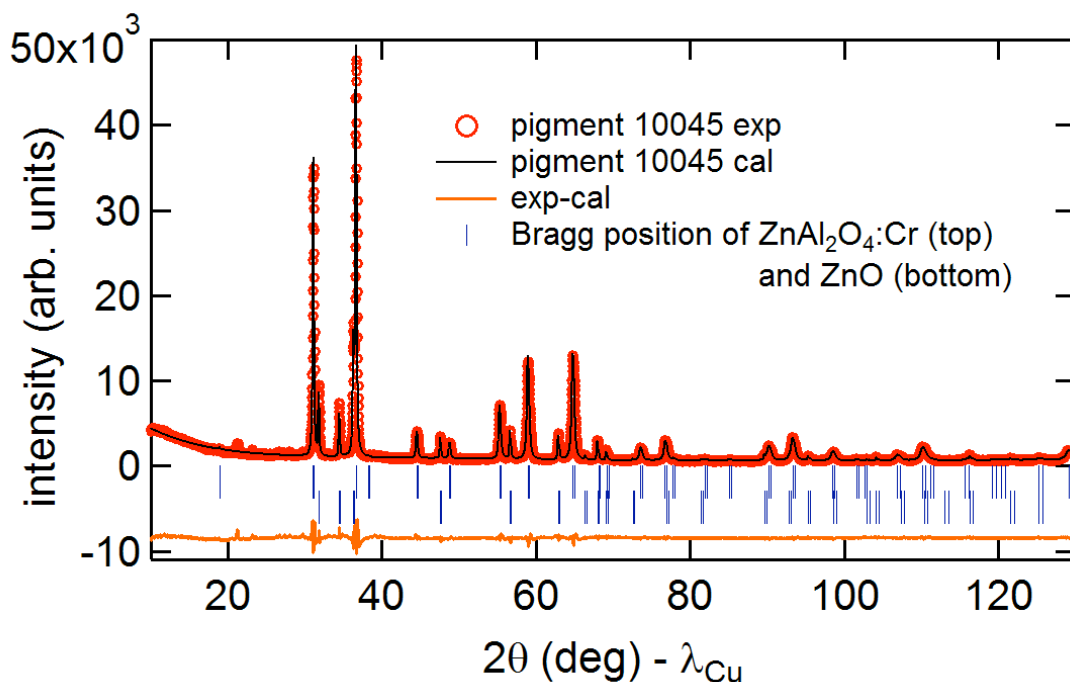


Fig. 2. Rietveld refinement of the pigment 10045 showing two phases: $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ and ZnO . The red dots are the observed intensities, the black line is the calculated intensity. Blue vertical tick marks indicate Bragg positions in space group $Fd\bar{3}m$ (top) for $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ and $P6_3mc$ (bottom) for ZnO . The orange line plots the difference between observed and calculated intensities.

(2) Evolution of the pigment in the glaze

When the pink pigment 10045 is used in a particular frit CI, the glaze becomes brown after the thermal treatment (see pictures of the samples in Fig. 3). The pigment and the glaze were characterized by optical absorption spectroscopy. Fig. 3 shows the remission function $F(Q_\infty)$ of the initial pigment 10045 and from the glaze R-1280. The high absorption of pigment 10045 in the near UV region can be explained by the presence of ZnO , a semi-conductor compound, with a gap energy located at 26600 cm^{-1} in the visible region. The spectra show

two main intense absorption bands, typical of trivalent chromium, Cr^{3+} , in a slightly distorted octahedral symmetry.^{9,20,21} The bands position varies between the initial pigment and the glaze, from about 18350 to 17890 cm^{-1} (ν_1) and from about 26250 to 24330 cm^{-1} (ν_2). The shift in energy of the absorption bands is due to the diminution of the crystal field parameter. It indicates that the pigment 10045 reacts during the thermal treatment, which results in the simultaneous color modification.

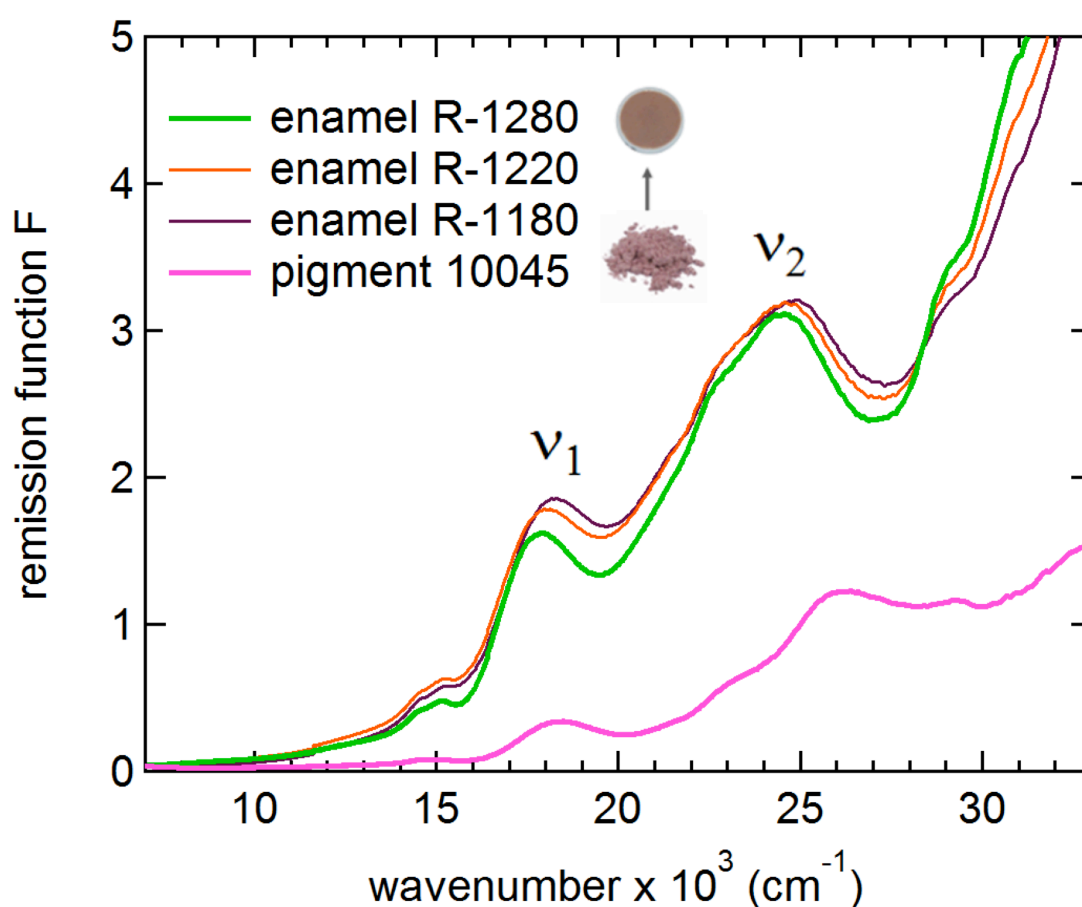


Fig. 3. Remission function $F(Q_\infty)$ calculated from the diffuse reflectance spectra of pigment 10045 (pink line) and glazes prepared with this pigment R-1280, R-CIA11 and R-CIA12.

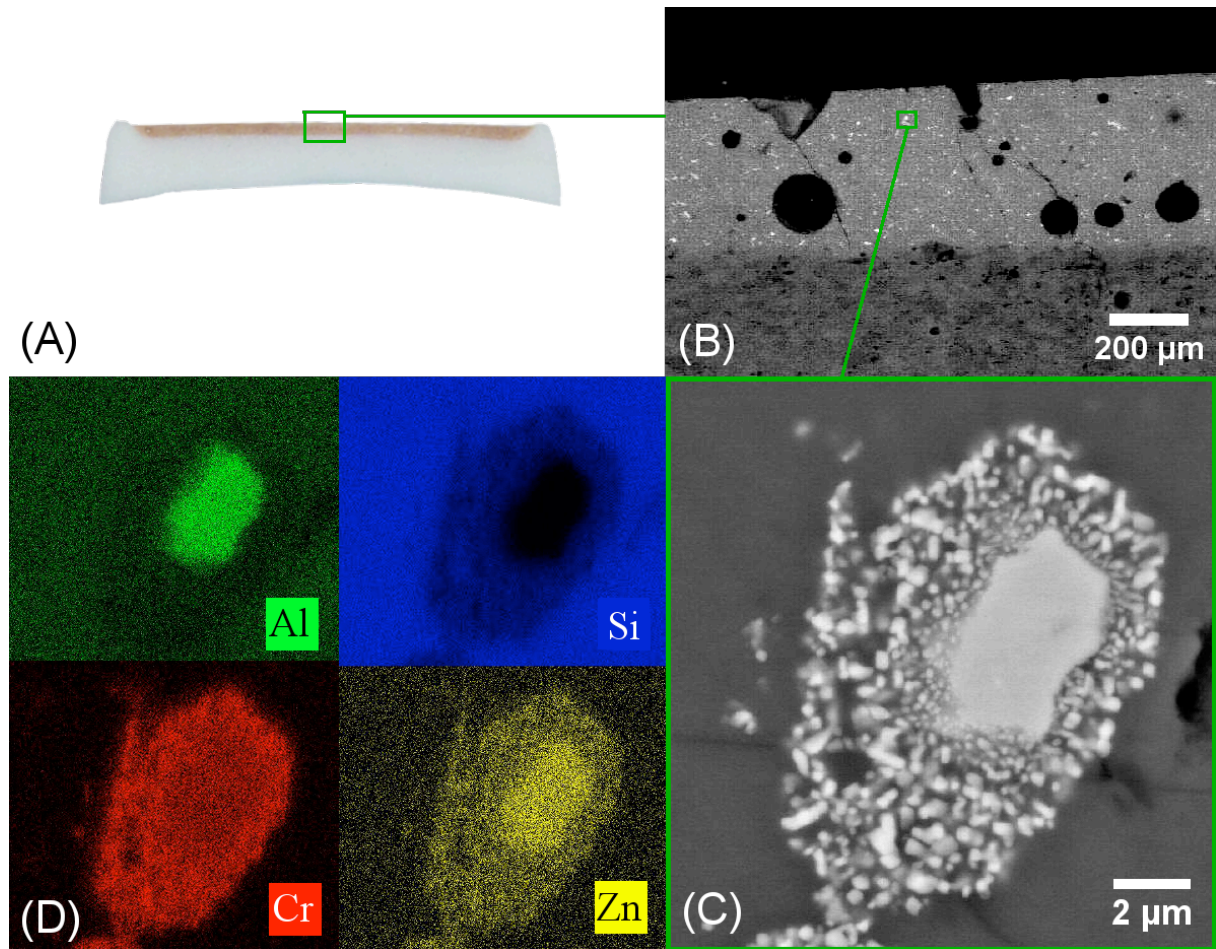


Fig. 4. (A) Picture of a cross-section of sample R-1280; the colored layer corresponds to the glaze and the white part is the porcelain mount; (B) SEM image of the cross-section; (C) Focus on a grain of pigment embedded in the glassy matrix (Signal: ASB, EHT = 15 kV);(D) EDX map of the main elements present in the glaze: Al (green), Si (blue), Cr (red) and Zn (yellow).

Fig. 4(A) and (B) show representative visible and SEM images of a cross section of the glaze obtained after the heat treatment. The glaze is heterogeneous, composed of bubbles and crystallized grains, embedded in a glassy matrix. Fig. 4(C) focuses on a specific crystalline grain embedded in the glassy matrix resulting from the melting of the uncolored frit. We observe an interesting difference in morphology between the center of the grain and the

periphery. The center looks homogeneous while the periphery is fragmented, which corresponds to a difference of chemical composition: indeed, the phase in periphery is richer in Cr whereas the center of the grain is richer in Al (EDX map in Fig. 4(D)). Some other grains in the glaze are characterized by the same difference of morphology and composition between the center and the periphery. Smaller grains are also present in the glaze, completely fragmented and rich in Cr. SEM observations at different heating treatments allow us to conclude that such crystals are the initial pigment grains, gradually altered by reaction with the frit melt. Furthermore, a glaze composed of pigment 10045 was quenched and the same difference of morphology and composition between the centre and the periphery of grains were observed: it means that the two phases are not resulting from recrystallization during cooling down.

Fig. 5 presents the evolution of the XRD pattern of the glaze after different thermal treatments. We can first observe the formation of a glassy signal with the appearance of a diffuse background near $2\theta \approx 26^\circ$, likely resulting from the melting of the uncolored frit. However, the melting process is not completely achieved since Bragg peaks due to quartz SiO_2 are detected up to the highest temperature. The initial phase $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ gradually disappears in favor of a phase with the same characteristic peaks, but shifted towards lower 2θ . This corresponds to an increase of the lattice parameter a , which is observed when the chromium content x is higher in $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$.⁹ Using equation (1), the composition of the new formed phase is $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$. The peaks of $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ and $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$ (zoom in Fig. 5) do not shift in position during heating, which indicates a bimodal distribution between the two phases rather than a continuous change in composition.

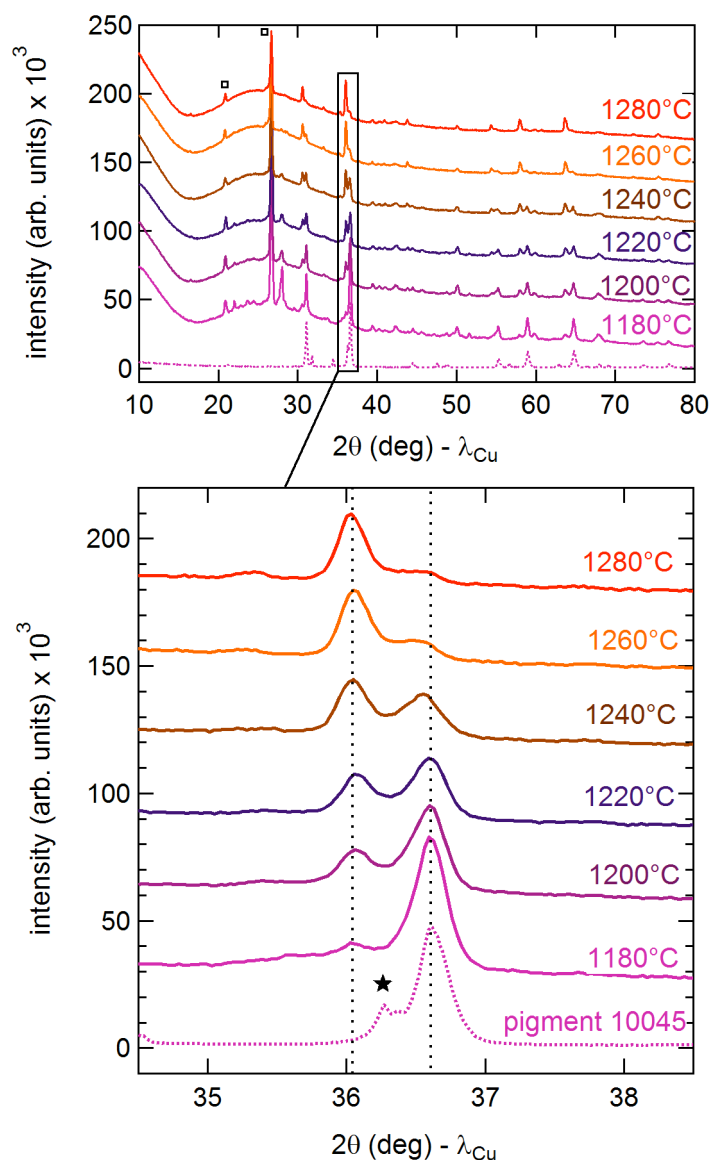


Fig. 5. In solid lines, XRD patterns of the samples fired at different temperatures: R-1180, R-1200, R-1220, R-1240, R-1260 and R-1280. In dotted line the initial pigment 10045. Peaks indexed with squares and stars correspond to quartz SiO_2 and ZnO.

To determine how Cr surrounding is changed with the formation of the Cr-rich phase $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$ during firing, μ -XANES analyses at the Cr K-edge were performed (Fig. 6) to locally probe the chromium environment in the periphery and in the center of the grain. The inset (C) in Fig. 6 is the XRF map acquired on the grain of pigment previously observed

under SEM. The XANES spectra (Fig. 6(A)) exhibit three features *a*, *b* and *c*, which are typical of Cr³⁺ in octahedral symmetry in spinels.⁹ While the positions of *a* and *b* are the same for the two areas, *c* is shifted by 0.92 eV towards lower energies between the center of the grain and the periphery. The pre-edge region (inset (B) in Fig. 6) shows two features α and β common to the two areas and a third feature γ only present on the spectra in the periphery of the grain. The shift towards lower energies of the peak *c* and the appearance of the feature γ are observed when the Cr content increases along the solid solution ZnAl_{2-x}Cr_xO₄.⁹

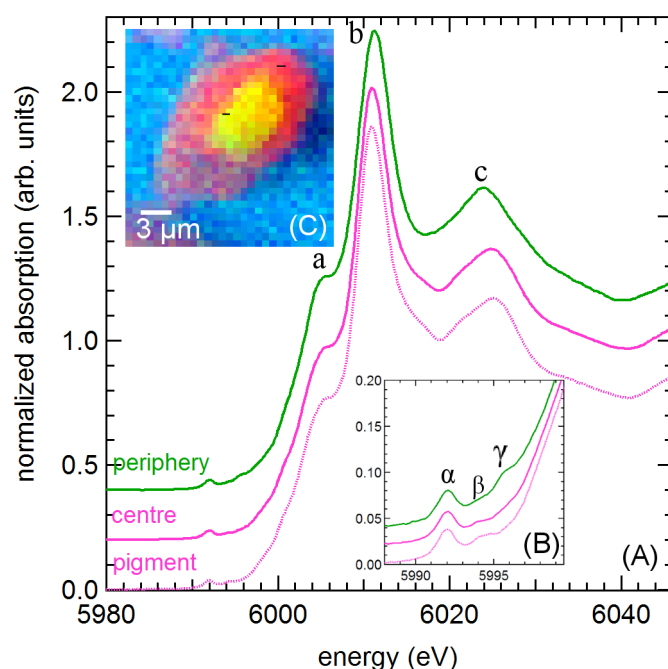


Fig. 6. (A) XANES spectra at the Cr K-edge acquired on the pigment 10045 (dotted line), and on two different areas of the glaze: the centre of the grain of pigment (pink) and the periphery (green). (B) Focus on the pre-edge region. (C) XRF map of the main elements constituting the pigment: Al (green), Si (blue) and Cr (red). The black dashes represent the areas where the XANES data were acquired and their sizes correspond to the spatial beam size ($0.2 \times 0.7 \mu\text{m}^2$).

(3) Influence of the thermal treatment on the stability of Cr-spinel in the glaze

When wood-fired kilns were used at the manufacture of Sèvres, it was particularly difficult to maintain a constant temperature. The heat ramp was then controlled to be slow enough to fire the porcelain and, once the desired firing temperature was reached, the kiln was turned off. This process is still in use at the manufacture. As the initial pigment is not completely dissolved or transformed in the melt, we decided to change the usual firing process and to test the influence of an isotherm at 1280°C with a plateau of 5 hours. XRD and SEM images combined with EDX measurements highlight that the initial grains of pigment totally disappear after the plateau and are replaced by the phase enriched in chromium. Furthermore, isotherms at 1160°C and 1200°C during 5 hours do not change the composition of the new formed phase. However the process of reaction of the pigment is less advanced when the temperature is lower.

(4) Influence of the initial pigment composition

The composition of the pigment was modified to investigate the influence of the initial chromium content. Three compositions along the solid solution $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ were chosen: $x = 0.4$, composition closed to the 10045 one, $x = 1.4$, which is closed to the phase formed when the pigment 10045 is fired in the glaze, and $x = 1.0$, which is an intermediate composition. Using $\text{ZnAl}_{1.6}\text{Cr}_{0.4}\text{O}_4$ as a starting reference excludes any potential influence of ZnO. Fig. 7 represents the evolution of the lattice parameter a with the chromium content x in the solid solution $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ (Fig. 7A) and an example of Rietveld refinement for the sample ZnAlCrO_4 ($x = 1$) and its corresponding glaze R-AlCr10 (Fig. 7B). For the composition $x = 0.4$, the pigment reacts with the frit to form the phase $\text{ZnAl}_{0.52}\text{Cr}_{1.48}\text{O}_4$, which is a composition close to the one obtained from pigment 10045. For the compositions $x = 1$

and $x = 1.4$, a higher chromium enrichment in the final phases is observed: $\text{ZnAl}_{0.32}\text{Cr}_{1.68}\text{O}_4$ and $\text{ZnAl}_{0.16}\text{Cr}_{1.84}\text{O}_4$, respectively.

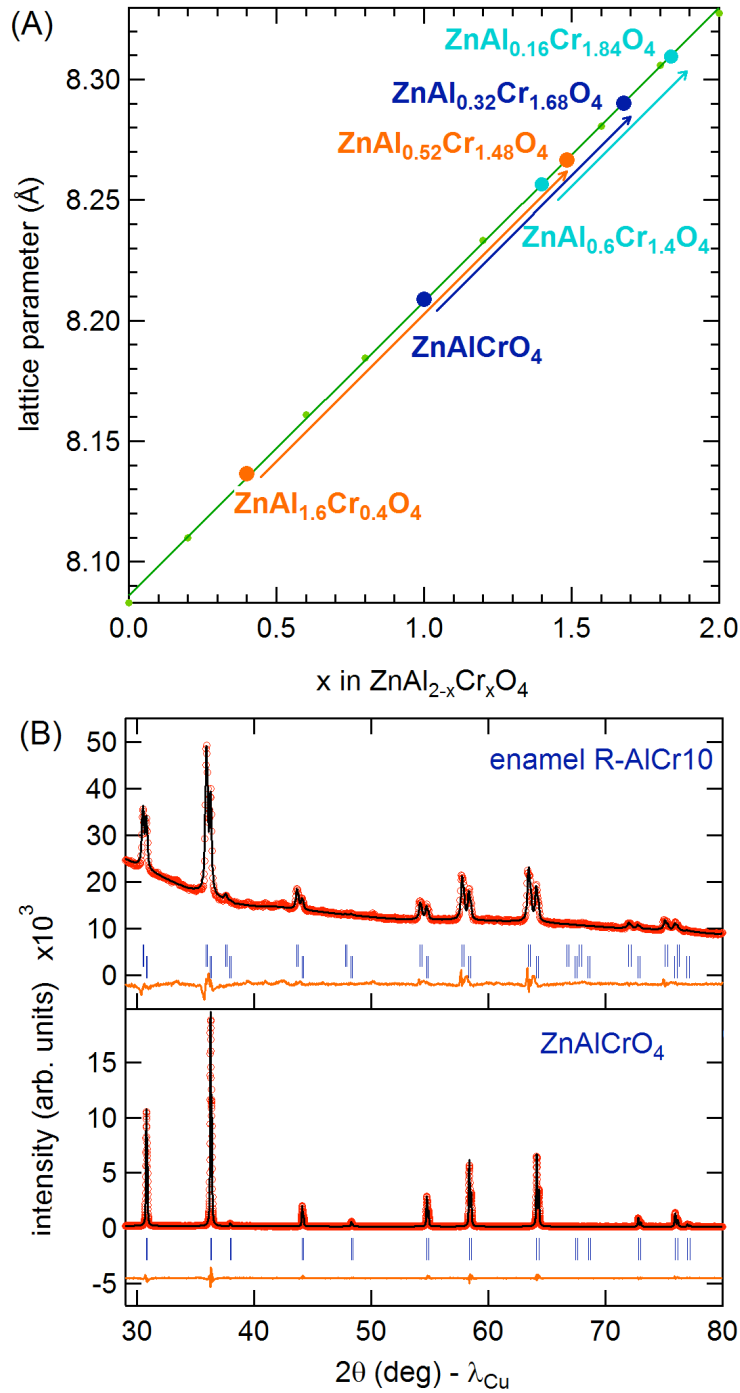


Fig. 7. (A) In green, variation of the cubic lattice parameters a (Å) of $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ as a function of Cr concentration x from Verger *et al.*;⁹ the initial compositions of the references

ZnAl_{1.6}Cr_{0.4}O₄, ZnAlCrO₄ and ZnAl_{0.6}Cr_{1.4}O₄ and their evolution in their respective glazes R-AlCr04, R-AlCr10 and R-AlCr14 after the thermal treatment are placed in the diagram. (B) Example of a Rietveld refinement for the reference ZnAlCrO₄ and the corresponding glaze R-AlCr10 (the same color code is used than in Fig. 2).

There is thus a systematic trend to transform the pigment to a phase richer in Cr than the initial phase. The chromium content of the final phase strongly depends on the initial pigment composition.

(5) Influence of the uncolored frit composition

The influence of Al and Zn content in the melt on the spinel alteration was investigated, by controlling the composition of the uncolored frit. Since the main difference between uncolored frits from the manufacture of Sèvres regards the Al content, we will not discuss here the influence of Zn.

In a calcium aluminosilicate melt/glass, an important parameter is the charge compensation of the AlO₄ tetrahedra by alkali and alkaline-earth cations. The following ratio determines the peraluminosity of the frit:

$$R = n_{Al_2O_3} / (n_{Na_2O} + n_{MgO} + n_{K_2O} + n_{CaO}) \quad (2)$$

where $n_{Al_2O_3}$ and $(n_{Na_2O} + n_{MgO} + n_{K_2O} + n_{CaO})$ are the molar contents in alumina and alkali and alkaline-earth oxide in the sample, respectively. When $R < 1$, the glass is peralkaline, and when $R > 1$, the glass is peraluminous. The peraluminosity of the frit CI is equal to 0.50 and was increased by adding α -Al₂O₃ giving the frits CIA11 and CIA12 (Table 2) with R of 0.67 and 0.88, respectively. Glazes are firstly obtained with the standard treatment (1000°C in 10 h and 1280°C in 5.5 h). The pink color of the Al-rich glazes (CIA11 and CIA12) appears

preserved after the thermal treatment. Fig. 3 shows the remission function $F(\rho_\infty)$ of the initial pigment 10045 and the glazes obtained from the different frits. The positions of the two main absorption bands of R-CIA11 and R-CIA12 glazes are shifted towards lower wavenumbers compared to the pigment, but they are less shifted than R-1280.

This result is confirmed by SEM observations. Fig. 8 shows grains of pigment in R-CIA11 and R-CIA12. Reaction layers between the grains of pigment and the frit are smaller than the one observed for the R-1280 glaze (Fig. 4). This has been observed over many grains of pigments and is representative of the sample.

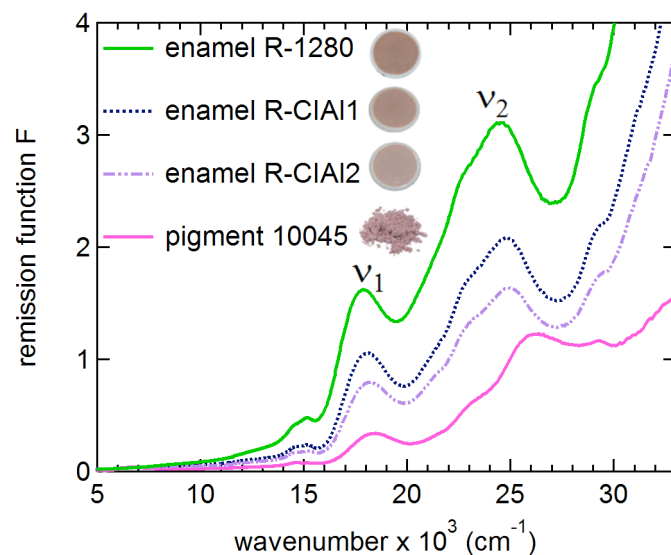


Fig. 8. SEM images of a grain of pigment from the glazes R-CIA11 (left) and R-CIA12 (right).

After the standard heating treatment, R-CIA11 and R-CIA12 are only partially melted because the addition of Al_2O_3 reduces fusibility of the mixture. The presence of phases remaining from CIA11 and CIA12 makes Rietveld refinements more complex. Therefore, the temperature of firing was increased to 1350°C and a plateau of 10 h was applied to fully vitrify the frits. Fig. 9 presents the XRD diagrams for the three glazes fired with this new thermal treatment.

We observe that when the Al content increases in the frit, the new phase formed has a higher Al content, indicating that Al migrates less in the glass.

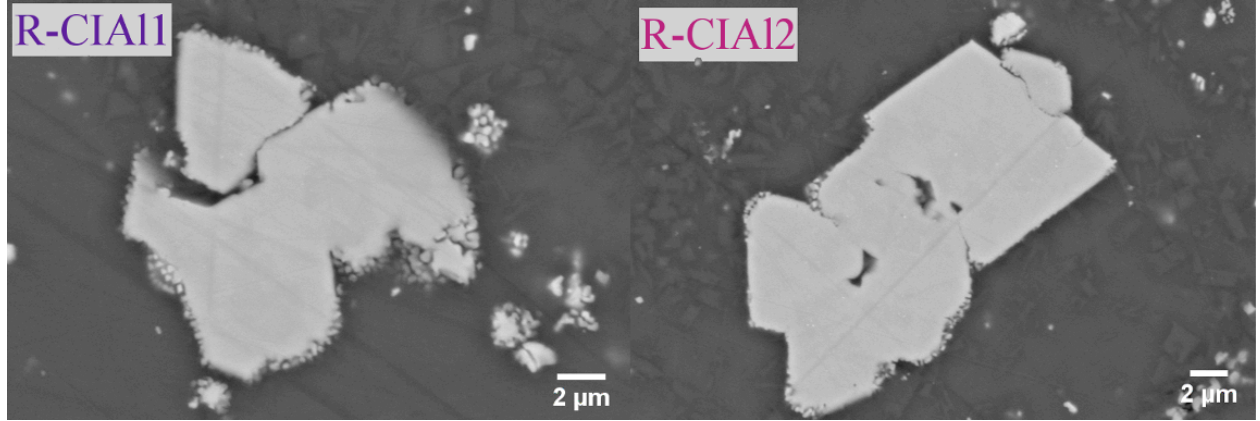


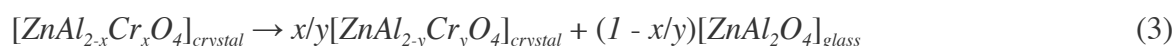
Fig. 9. (A) In green, variation of the cubic lattice parameters a (Å) of $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ as a function of Cr concentration x from Verger *et al.*,⁹ the initial composition of the pigment 10045 and its evolution in the uncolored frits CI (green), CIA11 (purple) and CIA12 (pink) after the thermal treatment are placed in the diagram. (B) XRD patterns of the samples R-1350-10h, R-CIA11-1380-10h and R-CIA12-1350-10h between 30° and 70° 2θ .

IV. Discussion

(1) Relationship between pigment stability and the color of glazes

A reaction occurs between the grains of pigment and the silicate melt during firing of the glaze. It results in the formation of a Cr-enriched gahnite, belonging to the solid solution $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ as the initial pigment. The modification of composition from $x = 0.41$ (pink) to $x = 1.46$ (brownish) explains the change of color between the pigment and the glaze after firing due to a change of the crystal field around Cr^{3+} ions. As explained previously,⁹ at high Cr content, the presence of other Cr^{3+} neighbors in the second shell of a Cr^{3+} ion generates an electronic potential that affects the e_g and t_{2g} orbitals separation or the orbital mixing between

the Cr *d* states and the neighboring O *p* states. These changes in the Cr environment are at the origin of the color modification. Therefore, the color change results from a modification of the Cr content in the spinel structure, without modification of Cr valency or the crystalline structure. Since there is no source of Cr in the system, the Cr-enrichment of the spinel phase results from the decrease of Al and Zn contents, with both elements migrating towards the melt. This process can be summarized by the following equation:



where $x = 0.41$ et $y = 1.46$ with experimental conditions used in part III.(2) (temperature of firing and chemical composition of CI). Al migration towards the silicate melt is driven by the low peraluminosity of the frit and therefore by the amount of free alkali or alkaline-earth cations in the melt.

The color alteration found here has a different mechanism compared to previous studies investigating the stability of corundum-like pigment in ZnO-rich frit.^{14,15} Indeed, corundum type pigment $(Fe,Cr)_2O_3$ forms a reaction layer composed of spinel $(Zn,Fe)(Cr,Fe)_2O_4$ and, in this case, the color change is due to a Fe valency modification from Fe^{3+} to Fe^{2+} and results from the spinel crystallization and Fe diffusion in the glaze.

Other pigments used at Sèvres, which are composed of spinels, were studied with the same approach: pigment 10024 composed of $MgAl_{2-x}Cr_xO_4$ and pigment 10014 composed of $Co_{1-y}Mg_yAl_{2-x}Cr_xO_4$. Both systems react in the same way in the frit CI: gradual dissolution of the initial pigment leading to a Cr-enriched phase and therefore a color change. At the manufacture of Sèvres, almost 60% of pigments containing chromium oxides are spinel-type. However, they are not used for the porcelain decoration described in this article using the uncolored frit CI. Our study shows that stabilizing the Cr-doped spinel structure appears challenging due to the low peraluminosity of glass/melt, resulting in a poor control of the final

glaze coloration. A way to stabilize Cr-doped gahnite is to increase the peraluminosity of the frit. However, this requires an increase of the firing temperature to obtain a glassy aspect for the glaze. Another possibility is to crystallize Cr-doped gahnite during firing of the glaze. This can be achieved by adding ZnO in the frit CI, and by using an initial pigment composed of $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ instead of $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$, in a similar way as observed by Martos *et al.*¹³

(2) The role of Cr, Al and Zn in the dissolution of spinel in glass melt

Our study shows that the initial pigment is strongly altered by the aluminosilicate melt formed from the uncoloured frit. This partial dissolution at 1280°C results in Cr-rich spinel that are even less stable at high temperature such as 1380°C, as Cr is likely to diffuse in the melt. We did not look at the Cr diffusing in the glass because its quantity is very small and is unlikely to modify the color of the glaze. A complete study, beyond the scope of this article, of the solubility of spinel belonging to the system $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ in glass melt controlling the temperature and the oxygen fugacity would be interesting to understand better the physicochemical properties of Cr in melts.²²⁻²⁴

Al and Zn play a key role in this dissolution process. By controlling the Al proportion in the uncolored frit, the Cr content x or $\text{Cr}/(\text{Cr}+\text{Al})$ is modified in the resulting spinel phase. It is then possible to stabilize the spinel phase in the uncolored frit. Roeder *et al.* showed that the Al_2O_3 content in the melt correlates well with the quantity $\text{Cr}/(\text{Cr}+\text{Al})$ found in the spinel phase.²⁵ Even if the mechanism is not the same (crystallization of spinel or reentrant magmas in the article by Roeder *et al.*,²⁵ and dissolution of spinel in our case), both are driven by the quantity of Al_2O_3 in the melt. This explains why pigments composed of gahnite (ZnAl_2O_4) doped with Cr are usually used at the Manufacture on glaze fired at 1380°C, solely: the

uncolored frit used at this temperature is richer in Al than the one fired at 1280°C and thus the initial pink color of the pigment is preserved.

V. Conclusions

At the manufacture of Sèvres, a pink pigment mainly composed of the spinel phase $\text{ZnAl}_{1.59}\text{Cr}_{0.41}\text{O}_4$ has been synthesized for more than a century. Used in a particular composition of uncolored frit to obtain a glaze, an undesired brown color appears. We showed that the initial pigment reacts during firing: it gradually dissolves in favor of a phase richer in chromium $\text{ZnAl}_{0.54}\text{Cr}_{1.46}\text{O}_4$, responsible for the color change. We also showed that the composition of the final phase depends on (i) the composition of the initial spinel phase and (ii) the composition of the uncolored frit, in particular the Al_2O_3 content. Alteration of the pigment occurs despite modification of the temperature of firing of the glaze and the initial Cr content. The stability of the spinel phase is driven by the amount of Al in the uncolored frit. This study brings useful information on the particular role of Al, Cr and Zn in spinel stability in melts. The reactivity (dissolution or crystallization) of minerals in silicate melts gathers interest for geologists (formation of minerals in magmas),²⁶⁻³⁰ chemists (corrosion of materials by molten glasses)²² and in the optoelectronic field (controlled crystallization of nano particles in glass).³¹⁻³³

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