

# Effect of sol–gel method on colour properties of the classical cobalt olivine ( $\text{Co}_2\text{SiO}_4$ ) ceramic pigment

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MS received 2 February 2016; accepted 4 July 2016

**Abstract.** A sol–gel method based on  $(\text{H}_2\text{Si}_2\text{O}_5)_{\text{aq}}$  as silicon precursor in the presence of NaCl and KCl mineralizers was used for the synthesis of the classical cobalt olivine ( $\text{Co}_2\text{SiO}_4$ ) ceramic pigment. The effect of this synthesis route on the colour properties was studied. Highly pure olivine phase was obtained after firing at  $1200^\circ\text{C}$  for 3 h. The resulting powders exhibited very intense violet colour, while their addition at only 1 wt% to an industrial transparent glaze was enough to produce a very intense blue–violet colouration. Based on the aspect of glazed ceramics, addition of pigments even at 0.5 wt% to the glaze resulted in a very interesting colour and opacity. By this appropriate minimization of the used pigment amount without compromising the colouring properties required during application, the obtained Co olivine could be more efficient, less toxic and less expensive.

**Keywords.** Sol–gel processes; cobalt olivine;  $\text{Co}_2\text{SiO}_4$ ; ceramic pigment; optical properties.

## 1. Introduction

Although cobalt is used since antiquity as a traditional chromophore source to obtain blue colours in ceramics [1,2], olivine ( $\text{Co}_2\text{SiO}_4$ ) and spinel ( $\text{CoAl}_2\text{O}_4$ ) are the two main cobalt-containing crystalline structures commonly used for blue pigmentation [3]. However, due to the requirement of higher concentrations of cobalt with only modestly stronger colour, the olivine structure is less preferred [2]. This has been shown more appropriately in a previous work of Llusar *et al* [4], in which colouring efficiency of different Co-bearing structures was compared. The results have shown that the accommodation with low amount of  $\text{Co}^{2+}$  in tetrahedral coordination provided by spinel structure is the main reason for its highly saturated blue colour and great colour stability. In contrast, the relatively poor blue colour obtained by dispersing  $\text{Co}_2\text{SiO}_4$  into ceramic glazes is mainly attributed to the evolution of  $\text{Co}^{2+}$  initially in octahedral coordination of olivine structure to tetrahedral coordination of glassy phase.

On the other hand, regarding the growing concern on Co costs and environmental impact, most of the current research activities concerning Co-based blue pigments have been focused upon the minimization of the employed amount of Co in their formulation (thus reducing both the economic costs and the toxicity). Accordingly, several studies have been previously reported on inorganic structures doped with very low Co, resulting in pigments with an optimal blue colouring performance, among which gahnite ( $\text{ZnAl}_2\text{O}_4$ ) and willemite ( $\text{Zn}_2\text{SiO}_4$ ) are two candidates [4,5]. In this respect,

we have recently reported about cobalt-doped forsterite ( $\text{Co-Mg}_2\text{SiO}_4$ ) solid solution blue pigments [6]. The materials showed high performance, which was mainly attributed to their formation as single-phase products. This, in turn, was achieved using a sol–gel method based on  $(\text{H}_2\text{Si}_2\text{O}_5)_{\text{aq}}$  as silicon precursor in the presence of NaCl and KCl mineralizers.

Taking into account that the preparative method also has a significant contribution in determining the value of a given ceramic pigment [7], the aims of this study, therefore, were as follows: (1) to explore the effect of the mentioned sol–gel synthesis route on the colour properties of this classical pigment (generally prepared by the conventional ceramic procedure [8]) and (2) to achieve an alternative way to minimize the costs and also the environmental concerns related to the high Co content of  $\text{Co}_2\text{SiO}_4$ . To the authors' best knowledge, no other similar study was reported.

In this paper we describe the synthesis and characterization of cobalt olivine ( $\text{Co}_2\text{SiO}_4$ ) as ceramic pigment. Results of this investigation will be compared to those obtained for both  $\text{Mg}_{2-x}\text{Co}_x\text{SiO}_4$  olivine phases [6] and  $\text{Co}_2\text{SiO}_4$  prepared by the conventional ceramic procedure [4].

## 2. Materials and methods

### 2.1 Preparation of silicon precursor

The silicon precursor  $(\text{H}_2\text{Si}_2\text{O}_5)_{\text{aq}}$  was obtained from an aqueous solution of  $\text{KHSi}_2\text{O}_5$  that was prepared by reacting silicon powder with potassium hydroxide in an aqueous medium on heating at  $80^\circ\text{C}$  for 10 min. The potassium cations were then exchanged on a cation-exchange resin (Amberlite type) to yield an aqueous solution of  $\text{H}_2\text{Si}_2\text{O}_5$  with a pH of about 4.

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**Table 1.** Sample codes, synthesis parameters and colour parameters (CIE- $L^*/a^*/b^*$ ) of Co olivine pigments.

Sample	Mineralizer	Method	Temperature	Colour $L^*/a^*/b^*$	
				Powder	Enamelled
CO1	NaCl	Hydrothermal	1200°C/3 h	47.05/16.13/-20.70	32.30/10.30/-22.91
CO2	NaCl	Reflux	1200°C/3 h	46.64/15.90/-20.51	32.94/9.30/-20.61
CO3	KCl	Hydrothermal	1200°C/3 h	43.01/15.61/-20.40	31.11/9.20/-20.22
CO4	KCl	Reflux	1200°C/3 h	41.90/13.60/-18.80	31.10/9.84/-21.94

## 2.2 Synthesis of cobalt olivine powders

( $\text{H}_2\text{Si}_2\text{O}_5$ )<sub>aq</sub> and cobalt acetate tetrahydrate ( $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ , Panreac, 99% purity) were used as silicon and cobalt precursors, respectively, while NaCl and KCl salts were used as the mineralizers. The aqueous mixture was prepared with the stoichiometric molar ratio of cobalt olivine (Co:Si = 2:1), by pouring the metal salt into the aqueous solutions of  $\text{H}_2\text{Si}_2\text{O}_5$ . The mineralizers were then added to these solutions and then stirred for 30 min at room temperature to give the starting solutions, whose pH was measured to be about 6. An NaCl- or KCl-to-cobalt acetate weight ratio of 10% was used.

The starting solutions of each sample were both placed in a Teflon cup with a total volume of 60 ml and then placed into a stainless-steel autoclave that was heated to 200°C in an oven for 3 days (hydrothermal method) and refluxed at 120°C under stirring for 3 days (reflux method) to form a gel. The gels of all samples were dried at 120°C for 12 h to give xerogels, which were ground and then dried to ensure complete dehydration. The resulting powders were subsequently fired in an electric furnace at a temperature of 1200°C for 3 h at a heating rate of 10°C min<sup>-1</sup>. Sample codes and synthesis parameters of the resulting Co olivine samples are depicted in table 1.

## 2.3 Preparation of enamelled pigments

The colouring efficiency of the pigments was tested by applying them in an industrial double-firing transparent lead-free glaze for earthenware application (composition (wt%):  $\text{SiO}_2 < 60\%$ ,  $\text{Al}_2\text{O}_3 < 15\%$ ,  $\text{CaO} < 10\%$ ,  $\text{BaO} < 10\%$ ,  $\text{Na}_2\text{O} < 5\%$ ,  $\text{ZnO} < 5\%$ ,  $\text{ZrO}_2 < 1\%$ ) by preparing mixtures whose weight% base was (1 wt% of pigment + 99 wt% of glaze). After homogenization, 1.3 cm diameter pellets were pressed and fired at 1060°C using 30 min soaking time and 5°C min<sup>-1</sup> heating rate in the electric furnace in air.

In order to qualitatively test the colouring efficiency obtained by varying the amount of the synthesized pigments in the glaze and get an idea about their covering performance, aqueous slips composed of mixtures for which each pigment was added at 0.5 and 1.5 wt% to glaze were prepared. The slips were uniformly deposited on traditional ceramics biscuits having a red-brick colour and then dried at room temperature for 4 h, giving glaze layers of thickness around

0.5 mm. The glazed ceramics were then fired following the same thermal cycle as that used for pellets.

## 2.4 Characterization

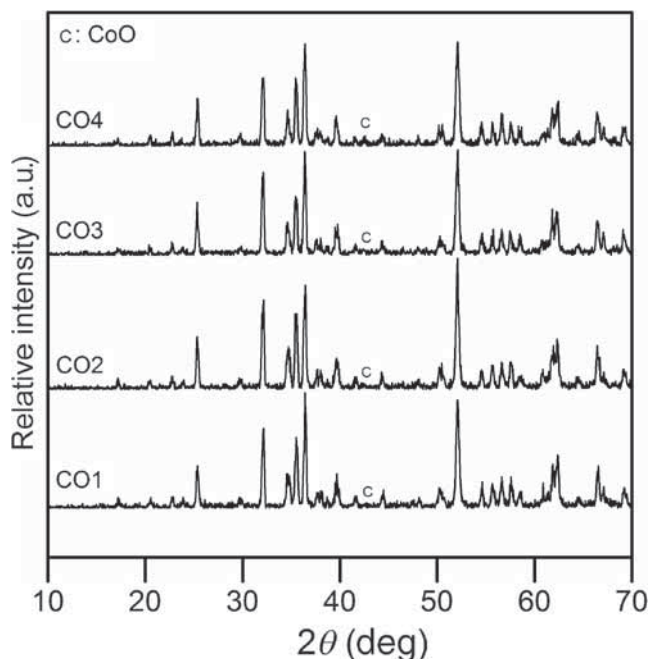
The crystalline phases present in the solids were identified by X-ray diffraction (XRD, Philips Xpert using  $\lambda_{\text{Cu-K}\alpha} = 1.5418 \text{ \AA}$  radiation at 40 kV and 30 mA). Determination of the vibrational modes was performed using a Fourier transform infrared spectroscope (FTIR, Bomem, 100 MB). The powder morphology was observed by scanning electron microscopy (SEM, Quanta 200). The optical properties of pigments and enamelled samples were analysed by diffuse reflectance spectroscopy (UV-visible-near-infrared (NIR)) performed with a Shimadzu (UV-3101) spectrophotometer with  $\text{BaSO}_4$  integrating sphere in a range between 200 and 1600 nm, and their colour was evaluated using the same Shimadzu spectrophotometer in the 380–780 nm range and according to the Commission Internationale de l'Eclairage (CIE) through  $L^*/a^*/b^*$  parameters using a D65 illuminant and 10° standard observer. In this system  $L^*$ ,  $a^*$  and  $b^*$  measure the brightness and the red/green and yellow/blue hue intensities, respectively [9].

## 3. Results and discussion

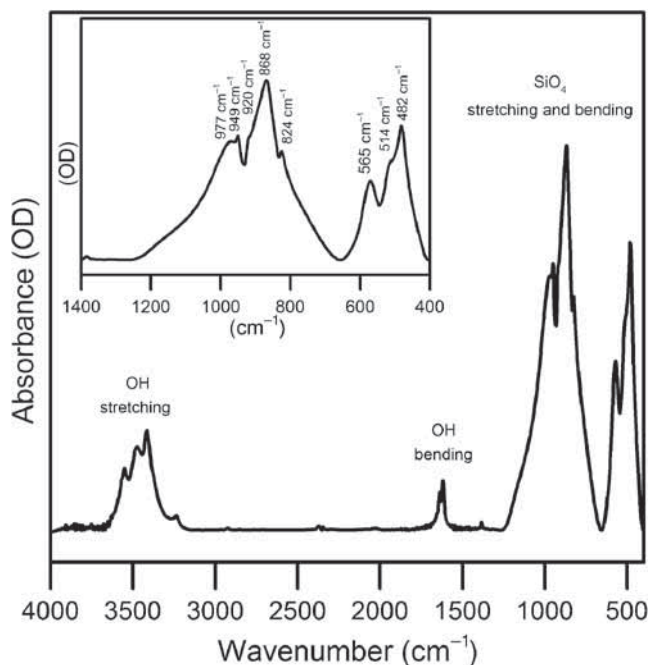
### 3.1 XRD and FTIR characterizations

The XRD patterns of powders fired at 1200°C for 3 h are depicted in figure 1. Strong diffraction peaks related to Co olivine phase ( $\text{Co}_2\text{SiO}_4$ ; PDF number 84-1298) are the most observed, indicating that highly pure Co olivine was obtained by this sol-gel route, at a relatively lower formation temperature. However, a very weak diffraction peak attributed to CoO is also detected in each diffractogram, showing the presence of a small amount of cobalt oxide. A lower intensity of CoO peak is registered for sample CO1, suggesting that the particular use of NaCl (mineralizer) and the hydrothermal method results in the improvement of the purity of the prepared Co olivine.

Infrared spectrum of sample CO1 fired at 1200°C for 3 h is shown in figure 2. This spectrum shows bands at 977 (shoulder), 949, 920 (shoulder), 868 and 824 cm<sup>-1</sup>, attributed to stretching vibrations of  $\text{SiO}_4$  tetrahedra, and at 565, 514 (shoulder) and 482 cm<sup>-1</sup>, assigned to bending vibrations of

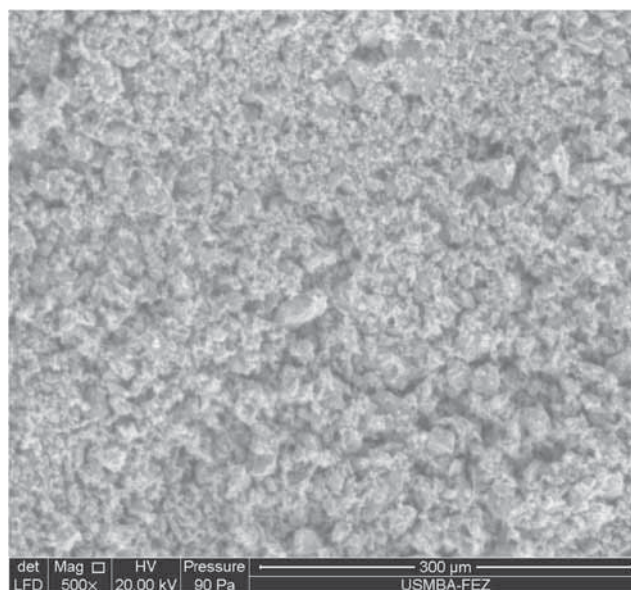


**Figure 1.** XRD patterns of Co olivine CO1–CO4 samples fired at 1200°C for 3 h.



**Figure 2.** FTIR analysis of Co olivine sample CO1 fired at 1200°C for 3 h. Inset is in the range of 1400–400  $\text{cm}^{-1}$ .

Si–O–Si bonds. The observed bands are in good agreement to previously reported work [10], confirming, then, the successful formation of highly pure and more regular Co olivine. On the other hand, the bands spanning the range from 3200 to 3600  $\text{cm}^{-1}$  and that around 1600  $\text{cm}^{-1}$  are assigned to the stretching and bending vibrations related to OH, respectively. The presence of hydroxides is frequently observed in



**Figure 3.** SEM micrograph of Co olivine sample CO1 fired at 1200°C for 3 h.

powders prepared by this sol-gel route based on silicic acid [11,12].

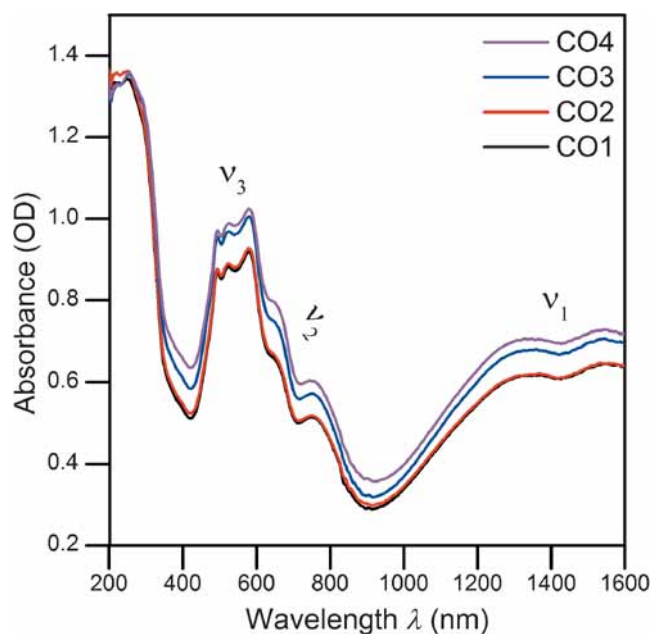
As mentioned in the Introduction section, the same preparation method was used in the synthesis of Co-forsterite ( $\text{Mg}_{2-x}\text{Co}_x\text{SiO}_4$ ;  $x = 0.2, 0.4, 0.6, 0.8$  and 1) solid solutions [6]. The only difference in the case of Co olivine is the employment of mineralizers (NaCl and KCl) at 10 wt% instead of 2.5 wt%. This change was made in order to improve the purity of the obtained Co olivine. Indeed, the use of a ratio of 2.5 wt% resulted in the formation of cobalt oxide (CoO) to higher extent after firing at 1200°C for 3 h. Accordingly, the formation reaction of  $\text{Co}_2\text{SiO}_4$  can be assumed to be slower than that of  $(\text{Mg}_{2-x}\text{Co}_x)\text{SiO}_4$  solid solution phase.

### 3.2 Microstructure

SEM micrograph of sample CO1 fired at 1200°C for 3 h is shown in figure 3. The sample is formed of compact agglomerates constituted by smaller particles, with irregular morphologies and a size of about 1–5  $\mu\text{m}$ . Separate grains with a relatively large size (around 10  $\mu\text{m}$ ) were also observed. Formation of grain boundaries between some of the agglomerated particles may lead to such increase in the size (i.e., sintering process). The other samples show practically the same morphology, and the mean particle size of the obtained powders is in agreement with that for inorganic pigments used in most applications (i.e., between 0.1 and 10  $\mu\text{m}$  [13]).

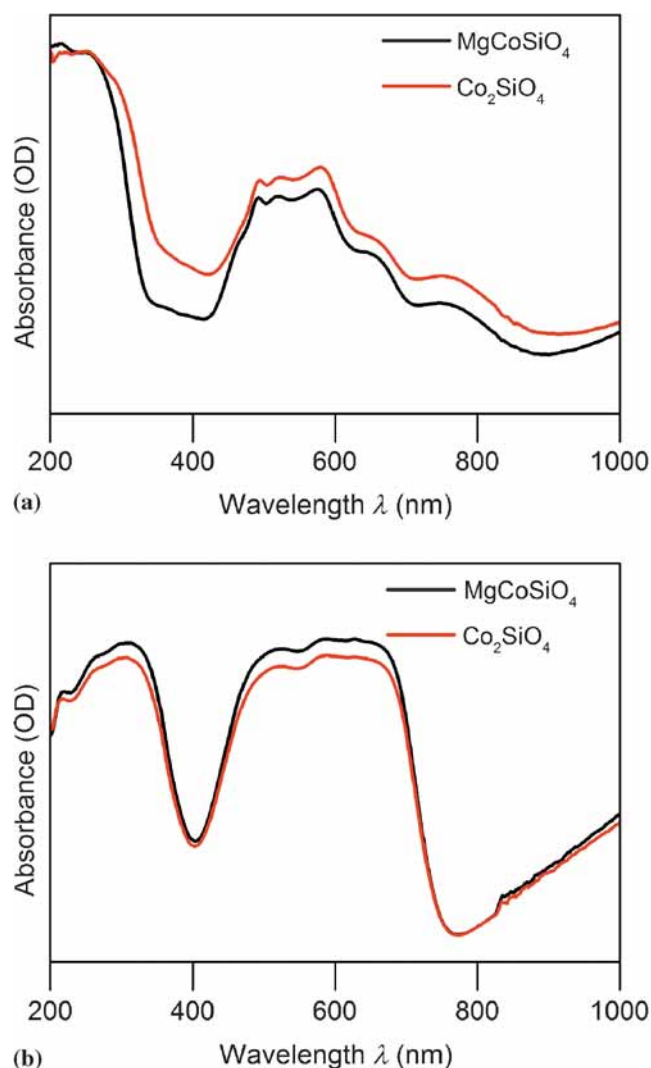
### 3.3 Optical spectroscopy (powders)

Since  $\text{Co}_2\text{SiO}_4$  mineral owes its violet colour to the crystal field transitions within  $\text{Co}^{2+}$  ions present in the octahedral M1 and M2 sites provided by olivine crystal structure [14], UV-visible-NIR spectroscopy was carried out on the fired



**Figure 4.** Optical spectra of Co olivine CO1–CO4 samples fired at 1200°C for 3 h.

pigments at 1200°C for 3 h to gain information about their colour origin (see spectra in figure 4). As can be seen, the spectra of the four samples are very similar and exhibit multiple absorption bands (with peaks centred at around 490, 520 and 580 nm; visible region), two absorption bands located at about 660 and 770 nm (visible region) and two broad absorption bands in the vicinity of 1300 and 1560 nm (infrared region). As three spin-allowed transitions are expected from the energy level diagram for octahedrally coordinated  $\text{Co}^{2+}$  (with configuration  $3d^7$ ), the obtained spectra display characteristic features for cobalt-containing olivines. Indeed, for the visible region, multiple bands are assigned to  $\nu_3$  spin-allowed transitions from the ground state  ${}^4T_1(F)$  to the excited state  ${}^4T_1(P)$  of  $\text{Co}^{2+}$  ions in both M1 and M2 sites of olivine lattice, while the bands located at about 660 and 770 nm are attributed to  $\nu_2$  spin-allowed transitions to the excited state  ${}^4A_2(F)$  of  $\text{Co}^{2+}$  in M1 and M2 sites, respectively. For the infrared region, the bands centred at around 1300 (M1 sites) and 1560 nm (M2 sites) correspond to the  $\nu_1$  spin-allowed transitions to the excited term  ${}^4T_2(F)$ . These assignments are in good agreement with those reported in earlier works [15–17]. Furthermore, spin-forbidden d–d transitions to the other excited terms could be contributing to the absorbance at still higher energies (up to 300 nm) in the near-UV region [17]. However, these bands as well as those in NIR region (900–1600 nm) do not contribute to the absorption in the borders of visible zone and thus, they do not have any optical effect. Accordingly, the violet colour of the synthesized pigments is due mainly to the crystal field bands corresponding to  $\nu_3$  ( ${}^4T_1(F) \rightarrow {}^4T_1(P)$ ) and  $\nu_2$  ( ${}^4T_1(F) \rightarrow {}^4A_2(F)$ ) spin-allowed transitions, which are responsible for the absorption over all the visible spectra except the violet region around



**Figure 5.** Comparative optical spectra (200–1000 nm) of  $\text{Co}_2\text{SiO}_4$  (sample CO2) and  $\text{MgCoSiO}_4$ : (a) powders and (b) enamelled.

400–450 nm. The high absorbance occurring in this zone indicates that the pigments display an intense violet colour.

On the other hand, comparative analysis between spectra of the different samples (measured in the same conditions) shows that the absorbance increase in the series in the sequence  $\text{CO1} < \text{CO2} < \text{CO3} < \text{CO4}$  may be a result of a possible darkening effect caused by residual  $\text{CoO}$ , exhibiting generally a black–grey colour. It may be concluded that the tendency of  $\text{CoO}$  to darken can be significant even by a very low amount. Thus, the observed sequence suggests that the hydrothermal method and  $\text{NaCl}$  salt (mineralizer) are more appropriate for complete formation of Co olivine, which is in accordance with XRD observations.

The presence of the main typical crystal field bands of  $\text{Co}^{2+}$  octahedrally coordinated in UV–visible–NIR spectra of the different samples with their higher intensities present a very good sign that the adopted method results in obtaining more pure and crystallized cobalt olivine.

On the other hand, based on the previously measured crystal field spectra for  $\text{Mg}_{2-x}\text{Co}_x\text{SiO}_4$  [6], it was found that spectrum profiles and peak positions were less affected by compositional variations. The first feature reflected less cation ordering in M1 and M2 sites, while the second was attributed to the comparably sized  $\text{Co}^{2+}$  replacing  $\text{Mg}^{2+}$  ions in the forsterite lattice. In contrast, increasing the amount of cobalt ( $x = 0.2$  to  $x = 1$ ) induced a progressive increase in the band intensities, which was correlated with the intensity of colour.

From comparison of crystal field spectrum of CO2 sample and that of  $\text{MgCoSiO}_4$  (prepared also by the NaCl mineralizer and reflux method) [6] presented in figure 5a, it may be concluded that these trends are maintained up to composition  $x = 2$  ( $\text{Co}_2\text{SiO}_4$ ). Accordingly, the violet of  $\text{Co}_2\text{SiO}_4$  (with high band intensities) is expected to be slightly more intense than that reached for Co–forsterite ( $\text{Mg}_{2-x}\text{Co}_x\text{SiO}_4$ ) solid solutions.

### 3.4 Colour (powders)

Generally, the violet colour can be described as the pairing of the two colours: blue and red. The shade of the mixture can vary from blue–violet to purple depending on whether blue or red is of a higher amount, respectively. Regarding the violet colour characteristics achieved for the synthesized pigments, their colour parameters (CIE- $L^*/a^*/b^*$ ) are summarized in table 1. Negative values for parameter  $b^*$  (around  $-20$ ) corresponding to the blue hue and positive values for parameter  $a^*$  (around 15) corresponding to the red hue are registered for the four samples; they match well with violet colouration. The slightly higher values of the blue component ( $-b^*$ ) compared with those of the red component ( $+a^*$ ) indicate that the pigments display violet shade instead of purple. Values of less than 50 registered for the lightness parameter ( $L^*$ ), which correlates implicitly with the intensity of colour (higher the  $L^*$ , lighter the colour), show, on the other hand, the intense violet of the pigments.

Differences among the quite similar values of colour parameters obtained for the four samples may be significant in order to confirm once again the potential effect of residual CoO mentioned earlier. Comparative analysis among  $L^*/a^*/b^*$  parameters indicates that  $L^*$  value becomes lower in the series in the sequence CO1 ( $L^* = 47.05$ ) > CO2 ( $L^* = 46.64$ ) > CO3 ( $L^* = 43.01$ ) > CO4 ( $L^* = 41.90$ ), as expected from optical spectrum of each sample (figure 4; higher the absorbance, lower the  $L^*$ ). However,

accompanying increase of colour intensity does not necessarily mean reinforcement of colour. In fact, both blue and red components became lower in the same sequence: CO1 ( $b^* = -20.70$ ;  $a^* = 16.13$ ) > CO2 ( $b^* = -20.51$ ;  $a^* = 15.90$ ) > CO3 ( $b^* = -20.40$ ;  $a^* = 15.61$ ) > CO4 ( $b^* = -18.80$ ;  $a^* = 13.60$ ), which should be accompanied by a slight decrease of colour saturation. Thus, since good colour saturation depends generally on improved crystallinity and/or chemical homogeneity of the pigments [18], these observations suggest that the decrease in lightness as well as the increase in absorbance intensity (figure 4) when passing from CO1 to CO4 sample is due to the increased amount of residual CoO in the same direction. Therefore, method–mineralizer combinations may be classified according to their ascending contribution to the formation of Co olivine as follows: (reflux–KCl) < (hydrothermal–KCl) < (reflux–NaCl) < (hydrothermal–NaCl).

On the other hand, the previously reported study [6] indicates that the colour development across  $\text{Mg}_{2-x}\text{Co}_x\text{SiO}_4$  solid solutions with respect to the cobalt content was more significant (i.e., significant change in  $L^*$ ,  $a^*$  and  $b^*$  values) from compositions  $x = 0.2$  (lilac colour) to  $x = 0.4$  (violet colour). Furthermore, the increased amount of Co chromophore (up to  $x = 1$ ) was accompanied by a stability of the blue component ( $-b^*$ ), a slight increase in the red component ( $+a^*$ ) and a slight decrease in the lightness ( $L^*$ ), in turn, resulted in a slight increase of the violet intensity. For deducing the colour evolution up to  $\text{Co}_2\text{SiO}_4$  composition, the  $L^*/a^*/b^*$  parameters of  $\text{MgCoSiO}_4$  [6] pigment are summarized in table 2. As observed, the increase of Co content up to  $x = 2$  ( $\text{Co}_2\text{SiO}_4$ ) did not yield an important change in the chromatic coordinates. In fact, the blue component ( $-b^*$ ) maintained its stability and the lightness ( $L^*$ ) continued its slight decrease, while a decrease in the red component ( $+a^*$ ) was observed. Accordingly, it may be concluded that the violet colour of the obtained Co olivine ( $\text{Co}_2\text{SiO}_4$ ) is slightly darker and bluish (i.e., lower  $L^*$  and  $a^*$ ) than that reached for ( $\text{Mg}_{2-x}\text{Co}_x\text{SiO}_4$ ) compositions.

Now, regarding the effect of the preparation method, the  $L^*/a^*/b^*$  parameters of  $\text{Co}_2\text{SiO}_4$  prepared by the ceramic procedure (fired at  $1300^\circ\text{C}$  for 1 h) [4] are presented in table 2. The very low values registered for  $a^*$  and  $b^*$  chromatic coordinates resulted in an achromatic violet. This observation suggests that Co olivine pigment is more sensitive to the preparation method. Therefore, the use of this sol–gel method results in an appreciable enhancement of  $\text{Co}_2\text{SiO}_4$  colour as powder. This in turn may be related to the higher purity (as deduced from XRD) and/or crystallinity

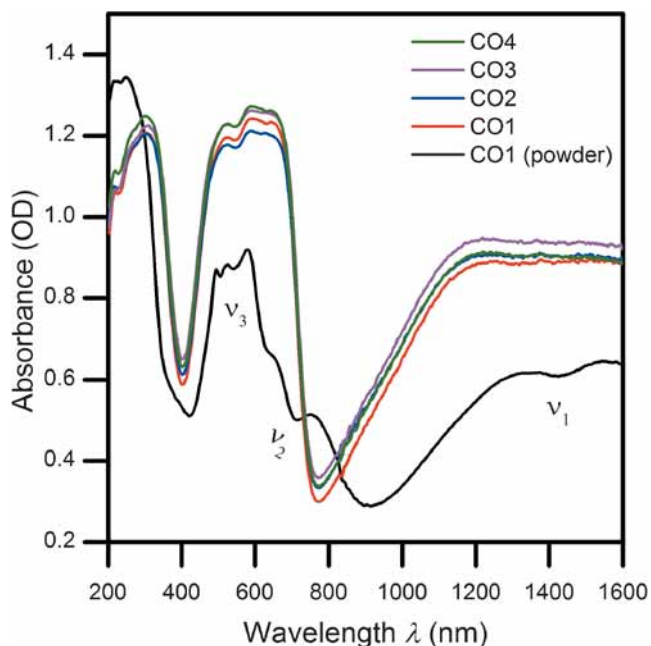
**Table 2.** Colour parameters (CIE- $L^*/a^*/b^*$ ) of olivine-related pigments.

Compound	Method	Colour $L^*/a^*/b^*$		Ref.
		Powder	Transparent glaze	
$\text{Co}_2\text{SiO}_4$	Ceramic procedure	45.70/5.10/–3.20	29.00/11.20/–25.60	[4]
$\text{MgCoSiO}_4$	Sol–gel	50.51/19.42/–22.37	29.19/7.97/–17.61	[6]

(as deduced from FTIR and optical spectroscopies). However, what really matters for a ceramic pigment is its developed colour in a particular application [19]. Accordingly, the CO1–CO4 samples were 1 wt% enamelled within the selected transparent glaze, which appears more suitable to evaluate their technological behaviour (a transparent glaze is required to make a glaze with a dark colour [2]).

### 3.5 Optical spectroscopy (enamelled)

In order to gain information about the colour origin in application and then the stability of the dispersed pigments in the glaze, UV–visible–NIR spectroscopy was carried out on the enamelled CO1–CO4 samples. As it may be seen (figure 6), the spectra present distinct features than those of  $\text{Co}^{2+}$  ions in octahedral coordination and consist of two very broad and intense bands. The first one spans the visible zone with triple peaks between 500 and 600 nm, while the second extends in the NIR region from 1100 to 1600 nm. The profiles and intensities of these bands are characteristic of tetrahedral  $\text{Co}^{2+}$  ions [4,20], which indicates that an evolution of cobalt ions from octahedral to tetrahedral coordination provided by the glassy matrix has occurred. These results are not surprising at all, since the main serious problem with Co-containing pigments is their partial solution, resulting in the diffusion of Co ions in the glaze, the effect or process referred to as *cobalt leaching* [2,21]. During this process, an undesirable hue shift may occur depending on the pigment crystal lattice [22]. For olivine structure (as shown in figure 6), the change in the  $\text{Co}^{2+}$  ions coordination leads to highly absorbing optical band in the red–yellow region (500–700 nm), hence giving rise to a very nice blue–violet colour

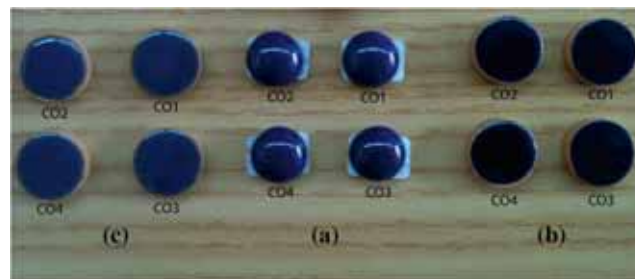


**Figure 6.** Optical spectra of enamelled Co olivine CO1–CO4 samples.

for enamelled samples. The similarity observed in the spectra indicates that the different pigments have practically the same behaviour in application. Thus, the effect of residual  $\text{CoO}$ , when dissolved in glazes, yields also blue shades and can be assumed to be negligible after enamelling. According to Leite *et al* [19], another consequence of cobalt-leaching effect is the consideration of Co olivine as a dye (i.e., being totally dissolved in the glaze). However, the broadening of optical band in the visible zone (figure 6) is still higher than what it should be for Co ions totally in tetrahedral coordination [4,20], reflecting, thus, the contribution of the dispersed  $\text{Co}_2\text{SiO}_4$  pigments in the optical properties of enamelled samples. This is a positive sign, indicating that the obtained Co olivine has a certain degree of stability towards the molten glaze, despite its very small amount used (1 wt%).

### 3.6 Colour (enamelled)

Regarding the performance of the prepared Co olivine as blue–violet ceramic pigment during application, the colour parameters ( $\text{CIE-}L^*/a^*/b^*$ ) of enamelled samples CO1–CO4 are depicted in table 1 and their aspect is presented in figure 7a. After enamelling, very similar values of colour parameters are observed for the enamelled samples, suggesting again that the different pigments have the same behaviour in the glaze. Comparison between the chromatic coordinates of the fired and tested pigments indicates that changes are stronger in both red component ( $+a^*$ ; values from 15 to around 9) and lightness ( $L^*$ ; values from 50 to around 31), which were diminished notably, while the blue component ( $-b^*$ ; values around  $-21$ ) remained practically stable. According to the optical spectra of enamelled samples (figure 6), decrease in  $a^*$  and  $L^*$  parameters may be related to  $\text{Co}^{2+}$  ions dissolved in the glass phase (higher intensities and more absorption in the red region). In contrast, the stability of the blue component may be attributed to the contribution of  $\text{Co}^{2+}$  ions present in olivine structure (absorption in the blue region), reflecting, then, the relative stability of the dispersed pigments. Thus, the developed colour can be described as a violet (i.e., the initial colour of dispersed pigments), for which the amount of red has reduced and the lightness has decreased due to cobalt-leaching effect, yielding a very nice



**Figure 7.** Aspect of enamelled Co olivine CO1–CO4 samples. (a) 1 wt% of pigments, (b) 1.5 wt% of pigments and (c) 0.5 wt% of pigments.

and an intense blue–violet colouration (see figure 7a for visual evaluation).

Optical spectroscopy and colour analysis performed on enamelled CO1–CO4 show clearly that when using  $\text{Co}_2\text{SiO}_4$  pigment to colour ceramic glaze, most of the blue colour is due to the leaching of Co ions to the glaze (occupying less regular tetrahedral environments). The same result was also found for Co–forsterite solid solutions [6] and  $\text{Co}_2\text{SiO}_4$  [4]. Furthermore, the two other blue Co-containing structures, namely spinel and willemite [4], show also the same trend. However,  $\text{Co}^{2+}$  ions, being more stabilized in tetrahedral sites (due to the relatively higher crystal field stabilization energies), make the latter two to react with glazes to a relatively lower extent than olivine [4].

Therefore, in order to compare the degree of reaction with the molten glaze with respect to composition of the olivine structure (i.e.,  $\text{Co}_2\text{SiO}_4$  vs.  $\text{MgCoSiO}_4$ ), optical spectrum of enamelled  $\text{MgCoSiO}_4$  [6] is presented (together with that of enamelled CO2 sample) in figure 5b, while values of their  $L^*/a^*/b^*$  parameters are included in table 2. In this case, the amount of Co introduced to the transparent glaze by  $\text{MgCoSiO}_4$  (Co wt% = 28.07%; added at 2% to glaze) is similar to that introduced by  $\text{Co}_2\text{SiO}_4$  (Co wt% = 56.14%; added at 1% to glaze). Interestingly, UV–visible spectrum as well as  $L^*$ ,  $a^*$  and  $b^*$  values of enamelled  $\text{MgCoSiO}_4$  are very close to those reached for enamelled  $\text{Co}_2\text{SiO}_4$ . This similarity suggests that these two members of olivine structure react with the glaze in the same manner by releasing practically the same Co amount, regardless of their composition. Accordingly, the main factor dominating the colour of the glaze is the high leachability of Co ions incorporated in tetrahedral coordination of the glassy phase.

Returning to the effect of preparation method, the  $L^*$ ,  $a^*$  and  $b^*$  values of  $\text{Co}_2\text{SiO}_4$  prepared by the ceramic method [4] in transparent glaze are quite similar to those of  $\text{Co}_2\text{SiO}_4$  herein obtained, which indicates that the two pigments develop the same colour in application. However, the latter was only 1 wt% enamelled while the first was added at about 16 wt% to the glaze. It may be concluded, then, that the use of this sol–gel method results in a significant reduction of the required quantity of Co olivine to impart an interesting blue colour to the glaze.

Regarding now the colour development resulted by an increase and a decrease of the amount of pigments in glaze, figure 7b and c shows the aspect of glazed ceramics with 1.5 and 0.5 wt% pigments, respectively. As can be seen in figure 7b, a very strong colour was obtained, whose shade tends, however, to be black instead of blue–violet, which indicates that such an increase is really optional and not necessary to promote the colour intensity. In contrast, as a remarkable result, the employment of pigments at only 0.5 wt% did not significantly affect the colour intensity (figure 7c). In fact, a very nice and slight light blue shade was obtained, suggesting that an optimal blue colouration can be maintained. Also noticeable in this case, the ability of glaze layers to completely hide the previous red-brick colour of substrates is extremely higher, suggesting that the synthesized pigments

are more opaque and have a very good covering performance. Accordingly, with regard to this appropriate minimization of the required pigment quantity, a compromise, between performance on one hand and economic and environmental concerns on the other hand, can be achieved.

#### 4. Conclusions

Cobalt olivine ( $\text{Co}_2\text{SiO}_4$ ) pigment, frequently prepared through the conventional ceramic method, was synthesized in this work by an alternative sol–gel route at relatively lower formation temperature (1200°C). According to the results obtained in this investigation, the effect of the adopted method was to provide more purity and crystallinity to this classical pigment, which, in turn, yielded interesting colour properties, either as powder or after enamelling. On the other hand, concerning the high Co content of  $\text{Co}_2\text{SiO}_4$ , the fact that a smaller quantity (0.5–1 wt%) of this pigment is needed to impart an interesting blue colour to the glaze could well offer an alternative way to minimize the costs and also the environmental concerns.

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