



# Synthesis and optical properties of forsterite ceramic pigments using mirror wastes as a flux

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## Abstract

Cobalt-doped forsterite ceramic pigments based on the formula  $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$  ( $x = 0, 0.05, 0.1, 0.2$ ) were synthesized using mirror wastes as a flux. Addition of this flux enhanced forsterite phase formation at lower temperature by as much as 200°C. The resulting pigment particles were in a micron range which is suitable for use in a ceramic glaze. The host structure ( $\text{Mg}_2\text{SiO}_4$ ) could accommodate cobalt cations up to 20 at%. Investigation on the chemical distribution revealed that no chemical species from the flux reacted with pigment grains. Optical properties were examined by UV-vis spectroscopy and colorimetry. Technical performance of the obtained pigments was tested in an industrial low-fire glaze. Alteration in color of the matured glazes was clearly observed, suggesting some instability of the pigments. Using a dense pellet form embedded in a molten glaze, an interfacial layer was observed, indicating interaction between the pigment and corrosive glassy glaze occurred. Stability in all raw materials commonly used in medium-fire glazes was further studied in order to determine which compound might cause such instability. The results would allow a design of glaze's recipe to possess the desired color of the finished products.

## 1. Introduction

Inorganic pigments have been used in several industries including in plastics and ceramics. Compared to their organic counterparts, inorganic pigments are more stable in terms of their chemical, UV radiation, and thermal resistance [1,2]. Coloration can be obtained in glasses and ceramic glazes with the addition of either single-oxide or complex-oxide compounds. The former ones give an intense coloring, although only a limited range of colors are available, whereas the latter ones offer a larger variety of colors. This advantage is achieved by possibilities such as the host structure type and the type and amount of chromophore cations.

Several inorganic compounds have been investigated and reported to be potential pigments for ceramic glazes. Only a limited number of those compounds are commercially available likely due to the complication of cationic doping, cost effectiveness and satisfactory performance. The inorganic compounds include rutile, spinel, malayaite and zircon [3]. Forsterite ( $\text{Mg}_2\text{SiO}_4$ ) is another host phase, which is also refractory, with its structure belonging to the olivine family [1,4-6]. This structure holds high potential for being a new commercial pigment due to its silica network reinforced by octahedral MgO with a lattice size that can fit several transition metals through isomorphic substitution [4]. However, the use of forsterite as a host structure for chromophore cations has rarely been reported in the literature [1,4].

Among ceramists, synthesis of pigment from highly refractory (high melting point) precursors is widely understood to be very difficult

if not impossible [1,2]. The difficulty lies in the fact that the host crystal structure is often very rigid which tends to thermodynamically reject the input of foreign atoms into the original lattice sites. Also, several low-temperature intermediate phases may readily form during the heating process, thereby hindering the formation of desirable single-phase pigments [2].

The problem of the unreactive nature of the solid-state reaction could be alleviated by intentionally introducing a liquid phase (flux) into the system to facilitate diffusion and mass transport. This novel method is also a basic fundamental element of liquid-phase sintering, fluxing, and molten flux synthesis [3,7]. Among these methods, adding a flux in small but sufficient quantities has effectively reduced the firing or calcination temperatures of several oxide-based phases [7,8]. A decrease in the firing temperature as a means of yielding intended phases would be advantageous for energy reduction, which is desirable for the pigment industry.

A majority of fluxing agents are based on halide compounds such as LiF, NaF, NaCl and boric acid [2,8]. However, these are commercially pure materials and relatively expensive. Additionally, they have very low melting temperatures, meaning that their effectiveness during the liquid phase may be inadequate to facilitate the diffusion and mass transportation of the system to create complete reactions. Sublimation of these fluxes could likely occur, especially for pigments which require processing conditions at temperatures higher than 1000°C. A new class of flux is therefore required for this situation. To the best of the author's knowledge, this study is among the first to

utilize cullet (crushed glass) from clear mirrors without using a metallic coating as a fluxing agent in the production of a ceramic pigment. Given the relative similarity of the composition with the glaze, this glass-based flux was expected to alleviate severe chemical degradation of the pigment particles in the molten glaze. The host structure was refractory forsterite ( $\text{Mg}_2\text{SiO}_4$ ) with cobalt as a chromophore. The study examined the effect of flux addition, chromophore incorporation on structural alteration, as well as the optical properties. The coloring performance of an industrial glaze was also tested alongside an examination of the elemental mapping at the pigment-glaze interface.

## 2. Experimental

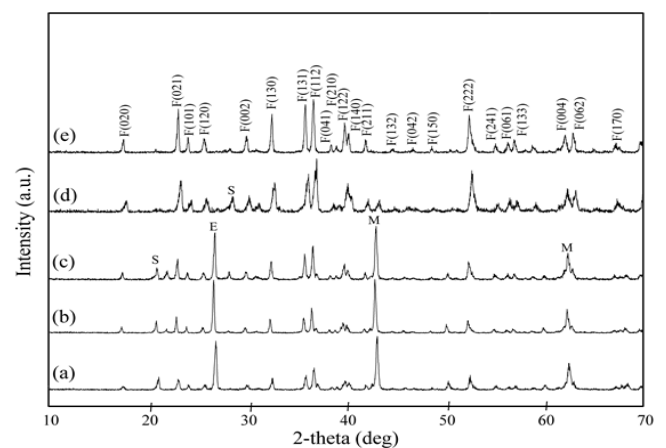
The researchers synthesized the forsterite pigments by employing a conventional solid-state reaction, using a flux to aid the reactivity. The reagent-grade starting precursors that were used included MgO (Himedia),  $\text{SiO}_2$  (Himedia) and  $\text{Co}_3\text{O}_4$  (Amarin). The crushed mirror cullets used as a flux were obtained from Thai Techno Glass Co., Ltd. (BSG Glass). The major compositions (wt%) of the glass, determined by X-ray Fluorescence (XRF), were  $\text{SiO}_2$  (68.6%),  $\text{Na}_2\text{O}$  (12.4%), CaO (9.7%), MgO (4.5%),  $\text{CeO}_2$  (1.5%) and  $\text{Al}_2\text{O}_3$  (1.3%). Other oxides existed as traces (less than 1 wt%). The general formula was  $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$  with  $x = 0, 0.05, 0.1$  and  $0.2$ . Beyond  $x = 0.2$ , the solid solubility was found to be exceeded at the currently examined firing temperatures. The presence of impurity ( $x > 0.2$ ) may provide incorrect information about the color properties, since overlapping of the absorption bands can occur [1]. The addition of the flux varied from 0 wt% to 10 wt% relative to the weight of the starting precursors. The mechanical mixtures were hand-ground in an agate mortar with acetone, and were then pelletized to minimize contamination during calcination in an electric furnace. The ramping rates were  $5^\circ\text{C}\cdot\text{min}^{-1}$  with a soaking time of 12 h. Intermediate grinding was carried out to ensure chemical homogeneity.

The pigment phase formations were examined by X-ray Diffraction (XRD; Shimadzu 6100) with a condition of 30 kV, 20 A and  $10^\circ\cdot\text{min}^{-1}$ . Lattice refinement was carried out using silicon as an external standard. The occurrence of relevant bonds in the forsterite structure was probed by Fourier Transform Infrared Spectroscopy (FTIR; Vertex 70) in the  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  range using KBr (weight ratio of 1:9). The oxidation state of cobalt cation was determined by X-ray Photoelectron Spectroscopy (XPS). Morphology and elemental mapping were examined by a Scanning Electron Microscope (SEM; Hitachi TM3030) equipped with Energy Dispersive Spectroscopy (EDS). The coloration of the obtained pigments and glazes were studied in the CIELab system using a colorimeter (Minolta; CR-10). The optical properties of the pigments were analyzed by UV-vis Spectroscopy (UV-vis; Carry 5000 Agilent) in the visible region (400 nm to 800 nm). The structural stability of the pigments was examined at the interface between the pigment pellet and the molten glaze. The pigment powders were consolidated and sintered to minimize porosity in order to avoid mechanical disintegration of the pellet during the glaze melting process. The selected glaze was an industrial and transparent type with a maturation at  $1000^\circ\text{C}$ . The pigment-glaze samples were fired at  $1000^\circ\text{C}$  for 2 h, cross sections were carefully cut to reveal the interface between the pigment pellet and solidified molten glaze. The surface was polished using SiC papers and later examined by EDS.

## 3. Results and discussion

The influence of flux content on the phase formability of forsterite was examined to select the appropriate amount of flux addition. All mechanical mixtures were calcined at  $1200^\circ\text{C}$  for 12 h for comparison. The XRD patterns of the crushed samples are shown in Figure 1. It is clear that, up to 2 wt% of flux, both starting precursors (MgO and  $\text{SiO}_2$ ) had still not fully reacted as evidenced by the reflections of MgO (JCPDS 04-0829) and  $\text{SiO}_2$  (JCPDS 83-0542) [1]. Intense MgO reflections were accompanied by prominent presence of Enstatite ( $\text{MgSiO}_3$ , JCPDS 07-0216) reflections, suggesting a premature formation of undesirable stoichiometric MgO- $\text{SiO}_2$  ratio [6]. With increasing amount of flux up to 5 wt%, the enstatite phase abruptly vanished whereas the intensity of MgO reflection decreased dramatically. The new phase of  $\text{SiO}_2$  still retained. However, additional flux amount (10 wt%) resulted in all those secondary phases disappearing entirely, yielding single-phase forsterite (JCPDS 04-0768). It is widely known among ceramists that many silicate compounds are difficult to form cleanly using solid-state processing given the refractoriness of the raw materials [1,2,6]. From these results, the mirror waste clearly facilitated the formation of the forsterite phase, potentially through the enhanced diffusion and mass transport in the liquid state during calcination [8]. Hence, a flux amount of 10 wt% was determined to be appropriate and subsequently used throughout this study.

Formation of the forsterite phase with the flux addition was also indirectly confirmed by Fourier Transform Infrared Spectroscopy (FTIR). Figure 2 displays the FTIR spectra of the mechanical mixtures with different amounts of flux that were calcined at  $1200^\circ\text{C}$  for 12 h. Changes in the spectral peaks are clearly observed with increasing amount of flux. The designation of the peaks is summarized in Table 1. At low amounts of flux ( $< 5$  wt%), all peaks could be indexed as various bond vibration modes belonging to undesirable phases such as  $\text{SiO}_2$  and  $\text{MgSiO}_3$ . FTIR peaks from Si-O and Mg-O in the forsterite structure became notable at the flux amount of  $\geq 5$  wt%. These results were in agreement with those reported by Kharaziha and Fathi [9] and Ghariana *et al.* [10]. In addition, their intensity increased with higher flux content. Such sharpening of FTIR peaks could be closely associated with improvement in the crystallinity of the forsterite phase due to the assistance of mirror waste flux.

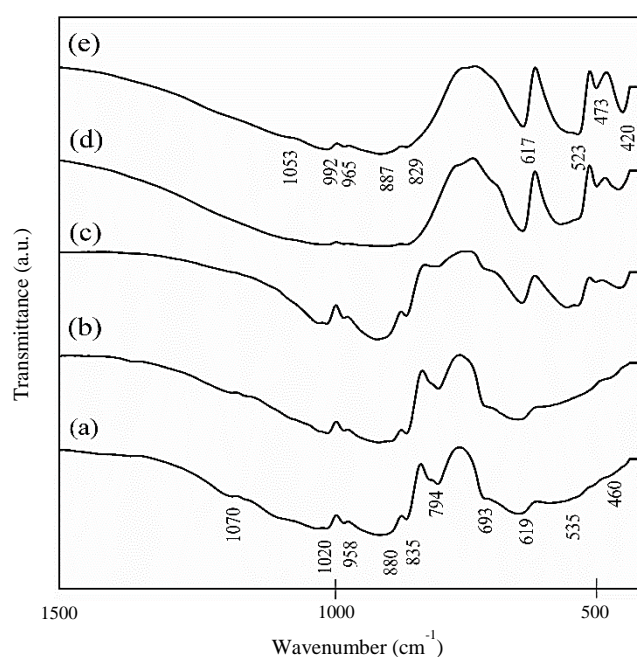


**Figure 1.** XRD patterns of the MgO- $\text{SiO}_2$  mixtures with different amounts of flux calcined at  $1200^\circ\text{C}$  for 12 h. (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, (d) 5 wt% and (e) 10 wt%. The secondary phases are  $\text{SiO}_2$  (S),  $\text{MgSiO}_3$  (E) and MgO (M).

The formation of forsterite phase was comparatively probed by XRD to examine the effectiveness of using mirror waste as a flux. Figure 3 demonstrates the disparity between the forsterite reflections at each of the five calcination temperatures between the two systems (non-fluxed and fluxed). Without the flux, the solid-state reaction was incomplete at all five temperatures, yielding the main phases of the starting precursors ( $\text{SiO}_2$  and  $\text{MgO}$ ) and intermediate phase ( $\text{MgSiO}_3$ ). The forsterite phase began to emerge at  $1100^\circ\text{C}$ , which is contradictory to the fluxed system within which forsterite reflections readily appeared at  $900^\circ\text{C}$ . The addition of the flux successfully suppressed formation of enstatite and also induce a greater reaction between the two starting precursors. It has been reported that enstatite could be detrimental due to its dissociation into silica-rich liquid and forsterite at high temperatures [6]. The new  $\text{SiO}_2$  reflection at  $1100^\circ\text{C}$  was likely associated with the phase formation of the silica itself. Nevertheless, a single-phase forsterite system could be obtained at  $1200^\circ\text{C}$  with the help of the mirror waste as is also shown in Figure 1. This temperature range was lower than the  $1250^\circ\text{C}$  to  $1600^\circ\text{C}$  reported in the literature [2,6,11]. In addition, the resultant phase from the  $900^\circ\text{C}$  heating was comparable to the findings reported in the literature using a sol-gel approach which is significantly more complicated than the fluxed solid-state processing used in this study [10,12].

XRD was used to investigate the ability to dope the cobalt chromophore into the  $\text{Mg}_2\text{SiO}_4$  host. Figure 4 shows the XRD patterns of the  $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$  system calcined at  $1200^\circ\text{C}$  for 12 h with the flux addition. The selected amount of flux was 10 wt% relative to the pigment mixture, since this proportion has been previously proven to be optimal for phase formation. At all compositions (doping concentration), only forsterite reflections were present, suggesting a high probability of a single-phase nature. Beyond the doping concentration of  $x = 0.1$ , secondary phases ( $\text{SiO}_2$ ,  $\text{MgSiO}_3$  and  $\text{MgO}$ ) began emerging which might complicate the subsequent analysis in terms of the coloring performance. Additionally, given the presence of  $\text{SiO}_2$  in the molten flux, there may be a minute amount of amorphous entity in the system that was not detected by XRD. However, such occurrence is unlikely to affect the performance of the pigments as they are intended to be used in silicate glass. A further crucial point arises since there could be a concern whether cobalt cations were

actually situated in the host structure. This may be resolved by a lattice refinement of these doped systems. Due to a difference in the ionic radii between cobalt and magnesium cations, shifts in XRD reflections were expected. According to Shannon radii,  $\text{Co}^{2+}$  (VI, LS) is 9.7% smaller than  $\text{Mg}^{2+}$  in the similar octahedral coordination ( $0.65 \text{ \AA}$  vs.  $0.72 \text{ \AA}$ ), and a shift towards higher 2-theta values was expected. The lattice parameters and unit cell volumes of the  $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$  system are summarized in Table 2. These values are close to those of pure forsterite [5,12]. With increasing amount of cobalt doping, the cell volume gradually decreased from  $290.75 \text{ \AA}^3$  ( $x = 0$ ) to  $289.47 \text{ \AA}^3$  ( $x = 0.2$ ). Changes in lattice parameter were also reported by Hadri *et al.* [1] and Glebycheva *et al.* [11]. Although such reductions were very small, they could be considered as a testament to the successful substitution of cobalt cations into the magnesium lattice sites.



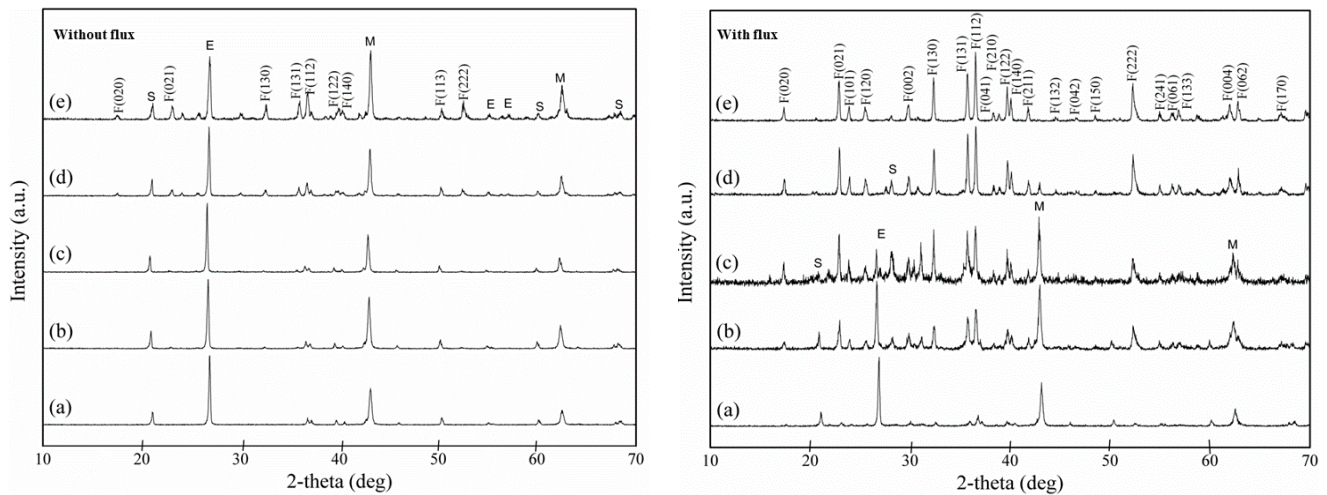
**Figure 2.** FTIR spectra of the  $\text{MgO-SiO}_2$  mixtures with different amounts of flux calcined at  $1200^\circ\text{C}$  for 12 h. (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, (d) 5 wt% and (e) 10 wt%.

**Table 1.** Summary of the type of bonding associated with different compounds.

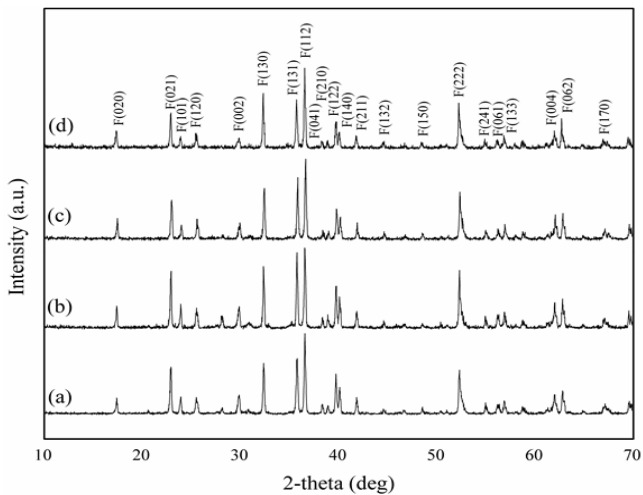
Bonding	Wavenumber ( $\text{cm}^{-1}$ )		
	$\text{SiO}_2$	$\text{MgSiO}_3$	$\text{Mg}_2\text{SiO}_4$
Mg-OH	-	3700	-
Si-O asymmetric stretching	-	1020, 1070	1053
Si-O-Si stretching	-	880, 958	992, 965, 887, 829
Si-O-Si bending	798	460, 693	473, 523, 617
Mg-O stretching	-	535	420

**Table 2.** Summary of lattice parameters and unit cell volumes of the  $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$  system.

Composition	a ( $\text{\AA}$ )	b ( $\text{\AA}$ )	c ( $\text{\AA}$ )	Volume ( $\text{\AA}^3$ )
$x = 0$	$4.7616 \pm 0.0015$	$10.2105 \pm 0.0010$	$5.9802 \pm 0.0014$	290.75
$x = 0.05$	$4.7650 \pm 0.0012$	$10.1857 \pm 0.0008$	$5.9725 \pm 0.0015$	289.87
$x = 0.1$	$4.7680 \pm 0.0013$	$10.1776 \pm 0.0015$	$5.9640 \pm 0.0018$	289.41
$x = 0.2$	$4.7743 \pm 0.0014$	$10.1693 \pm 0.0010$	$5.9521 \pm 0.0007$	288.98



**Figure 3.** XRD patterns of the MgO-SiO<sub>2</sub> mixtures calcined for 12 h at different temperatures comparing between no flux (left) and with flux addition in the 10 wt% amount (right). (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C and (e) 1200°C.

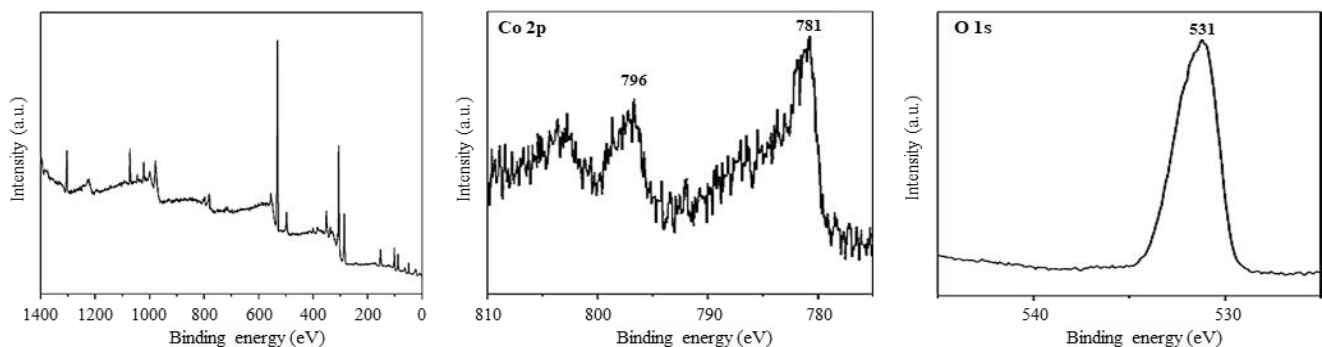


**Figure 4.** XRD patterns of the (Mg<sub>2-2x</sub>Co<sub>2x</sub>)SiO<sub>4</sub> system calcined at 1200°C for 12 h with flux addition in the 10 wt% amount. (a)  $x = 0$ , (b)  $x = 0.05$ , (c)  $x = 0.1$  and (d)  $x = 0.2$ .

Incorporation of cobalt cations into the Mg sites requires them to have a valence state similar to the host to be electrically stable in addition to the size mismatch constraint. The X-ray photoelectron spectroscopy (XPS) spectra of the  $x = 0.2$  composition (Mg<sub>1.6</sub>Co<sub>0.4</sub>SiO<sub>4</sub>) are given in Figure 5. For cobalt with the +2 oxidation state, XPS

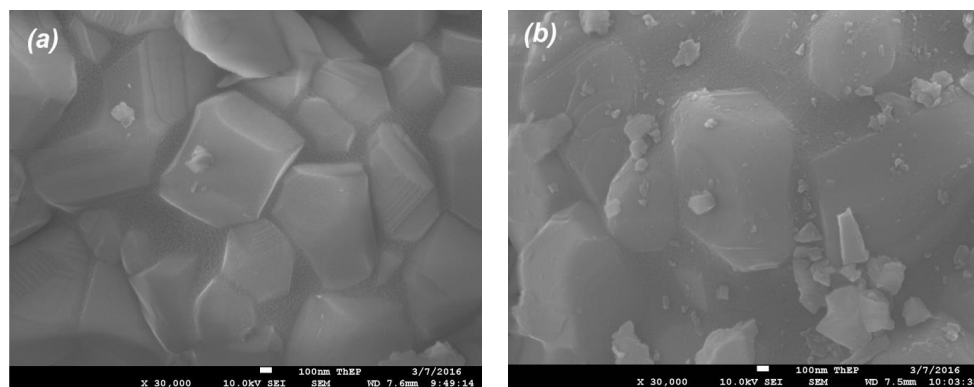
will indicate splitting into two peaks for Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>. The obtained high-resolution spectrum in Figure 5 revealed two peaks at 781 and 796 eV, suggesting that the cobalt cations in the host structure exist as a 2<sup>+</sup> state [13].

The morphology of the synthesized pigments is demonstrated in Figure 6. The majority of the particles lay in the 400 nm to 800 nm range which is similar to the findings of Hadri *et al.* [1] and Ghariani *et al.* [10]. This sub-micron size range appears appropriate for the current application as the pigment particles must be neither too small to be dissolved by aggressive, molten glass, nor too large to ensure a good dispersion within the glass matrix [1]. Agglomeration among the particles due to partial sintering was observed. Elemental mapping by EDS is shown in Figure 7. The magnification of these images was much lower than in Figure 6 due to the EDS detection resolution. Na species were found to mainly distribute on agglomerates of particles, further confirming its role as a flux decorated only on the particle's boundary. The majority of the particles demonstrate that the Mg, Si, Co and O species overlapped each other, suggesting that these synthesized pigments were indeed Co-doped forsterite as previously confirmed by XRD and lattice refinement. The presence of Na and Ca was from the solidified glassy flux either coating around pigment particles or existing as free particles. They are unlikely to affect coloring performance in the glaze since the molten glaze would readily dissolve them during maturation period.

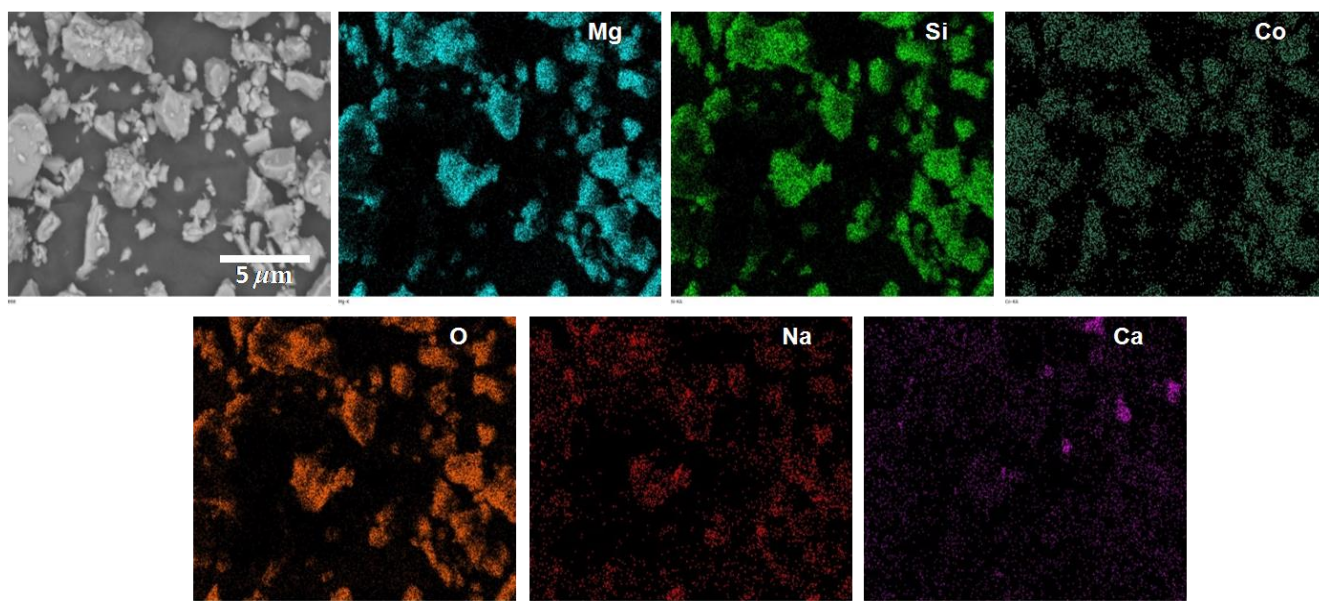


**Figure 5.** X-ray photoelectron spectroscopy (XPS) spectra of the  $x = 0.2$  composition (Mg<sub>1.6</sub>Co<sub>0.4</sub>SiO<sub>4</sub>). High-resolution spectra of both cobalt and oxygen peaks are also included.





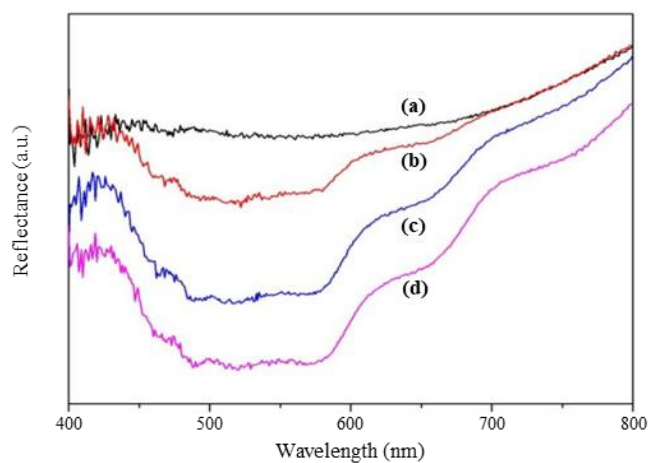
**Figure 6.** SEM images of the pigment samples calcined at 1200°C for 12 h with flux addition in the 10 wt% amount. (a) Undoped ( $x = 0$ ) and (b) Doped ( $x = 0.2$ ).



**Figure 7.** EDS mapping of the  $x = 0.2$  composition ( $\text{Mg}_{1.6}\text{Co}_{0.4}\text{SiO}_4$ ) calcined at 1200°C for 12 h with flux addition in the 10 wt% amount.

The color characteristics of the synthesized pigments in the CIELab system are summarized in Table 3. Increasing the cobalt doping resulted in an enhanced redness (more positive  $a$  value) and blueness (more negative  $b$  value), while this gradually decreased the lightness ( $L$ ). The  $x = 0.2$  composition demonstrated the most intense reddish-purple tone, as was also confirmed by its UV-vis spectrum which had the lowest intensities of reflection bands (a reverse of the absorption bands). The UV-vis spectra of the  $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$  system calcined at 1200 °C for 12 h are shown in Figure 8. The undoped ( $x = 0$ ) sample revealed no reflectance peak as there was no crystal-field energy stabilization from the chromophore. The undoped sample was plain white in color. The lowest degree of reflectance (highest absorbance) occurred in the 470 nm to 600 nm range. There appeared to be three peaks at around 490, 520, 580, 670 and 770 nm, which were also reported by Hadri *et al.* [1]. These optical spectroscopic peaks are characteristics of an octahedral crystal field of  $\text{Co}^{2+}$  in a forsterite or olivine structure. In the green-yellow wavelengths, there was a transition from  ${}^4\text{T}_1(\text{F})$  from  $\text{Co}^{2+}$  ( $3d^7$ ) to  ${}^4\text{T}_1(\text{P})$  in octahedral sites in the olivine structure. The optical peaks at 670 nm and 770 nm occurred from spin-allowed transitions to  ${}^4\text{A}_2(\text{F})$  excited state. Hadri *et al.* [1]. There was no noticeable shift

in the UV-vis peak upon increasing the cobalt content. This could be explained by a small disparity in cation radii between  $\text{Co}^{2+}$  and  $\text{Mg}^{2+}$  Hadri *et al.* [1].



**Figure 8.** UV-vis spectra of the  $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$  system calcined at 1200°C for 12 h with flux addition in the 10 wt% amount. (a)  $x = 0$ , (b)  $x = 0.05$ , (c)  $x = 0.1$  and (d)  $x = 0.2$ .





The synthesized pigment ( $x = 0.2$ ) was tested in a practical industrial low-fire boron-based glaze matured at 1000 °C. The addition of the pigment powders (10 wt%) in the dry glaze resulted in a dramatic change in the  $b$  parameter when compared in Table 3. The blueness enhanced more than three-fold, whereas the lightness decreased from 63.3 (pigment) to 40.0 (colored glaze). The  $a$  parameter remained relatively unchanged. Such alterations yielded a glaze possessing a deep purple tone. This phenomenon was surprising as this purple tone has been known in the industry to be primarily obtained by the malayaite ( $\text{CaSnSiO}_5$ ) phase.

Attempts were made to examine the possible source of this color change. Given the extremely harsh and corrosive environment of the molten glaze, dissolution of the pigment through either a chemical or physical interaction is unavoidable [1]. EDS mapping in the vicinity of the interface between the pigment and glaze entities was investigated to obtain insights into the stability of the currently examined forsterite pigment. Figure 9 displays the distribution of several relevant species within that area. The pigment entity was in a consolidated form that had been previously sintered to achieve a high relative density to prevent itself from disintegrating during the glaze melting. The BSE mode revealed a reaction layer that was approximately 100  $\mu\text{m}$  wide. Within this layer, many species were present at different concentrations compared to the bulk pigment and glaze portions, implying that a significant interaction occurred within this interface region. Na, Ca, Al and B species were found deep in the pigment pellet due to infiltration of the liquid glaze due to the porosity of the pellet. In addition to this inward diffusion, an outward diffusion of cobalt into the molten glaze was clearly








observed at least within the detection limit of EDS. It is commonly understood that adding cobalt oxide to a silicate glass will yield a blue color. Preliminary lattice refinement of these pigments after incorporation into the glaze found the XRD reflections shifting slightly toward lower 2-theta values, implying a small increase in cell volume. This result is in line with the previously observed outward diffusion of cobalt cations from the pigment to the surrounding glaze entity. Therefore, enhanced blueness upon incorporating the forsterite pigment in a practical glaze could be sufficiently explained by this outward diffusion of cobalt species. This is commonly known as cobalt leaching or bleeding [1].

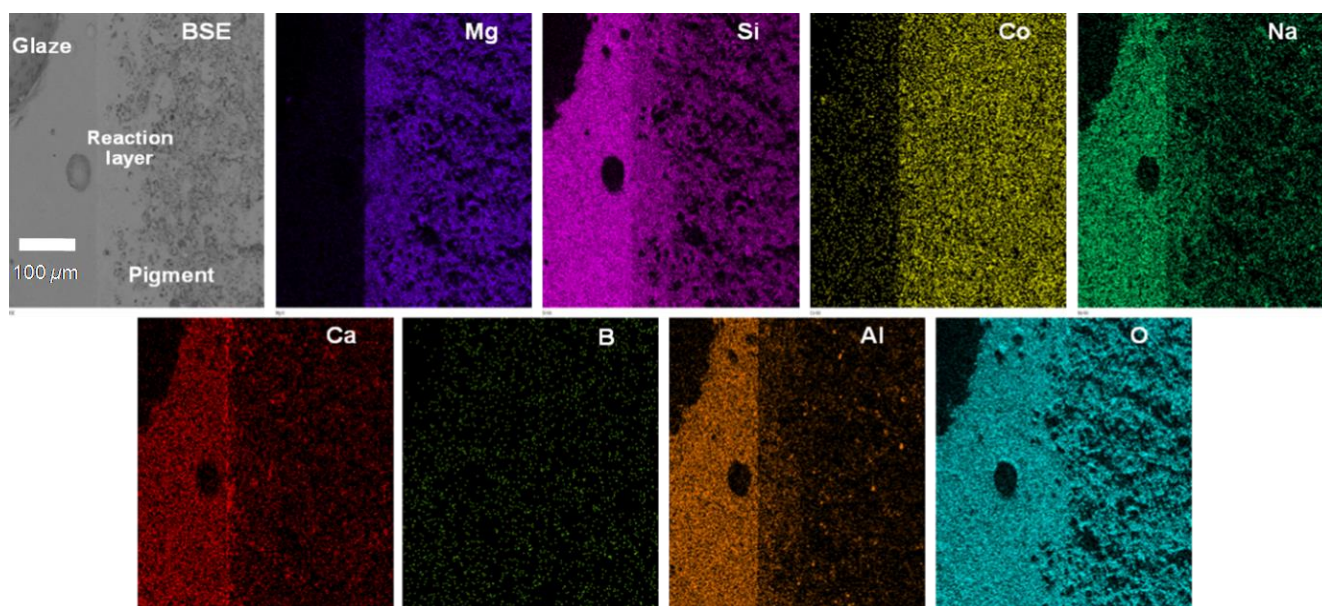
Commercial production of ceramic products is not limited to only low-fire glazes which mature in the 1000°C range. Rather, the more common glazes used in the industry require complete maturation in the 1200°C range given stoneware or porcelain used to form a body. These medium-fire glazes are typically feldspathic, composing of various compounds with different roles. Five compounds were selected in this preliminary study as representatives of raw materials frequently employed industrially. They are Na-feldspar,  $\text{SiO}_2$ ,  $\text{CaCO}_3$ , ZnO and kaolin. The pigment was newly synthesized with addition of both mirror waste (as a flux) and Na-feldspar (as a filler) to mimic the method of “color stain” production. The obtained pigment demonstrated color parameters still close to those of the non-feldspathic one reported previously. The pigment and glaze were mixed in a weight ratio of 1:1 for this stability test. This study was among the first to examine the effect of major raw materials on color changes for the forsterite pigment system.

**Table 3.** Color parameters of the pigments and glaze in the CIELab system. Coloring performance was tested using the  $x = 0.2$  composition in the low-fire industrial glaze fired to reach maturation at 1000°C for 2 h.

Composition	Color parameter			Color
	L	a	b	
$x = 0.05$	$81.7 \pm 0.2$	$5.1 \pm 0.2$	$-1.4 \pm 0.1$	
$x = 0.1$	$69.9 \pm 0.3$	$12.6 \pm 0.3$	$-5.6 \pm 0.5$	
$x = 0.2$	$63.3 \pm 0.1$	$14.1 \pm 0.2$	$-7.6 \pm 0.4$	
In glaze	$40.0 \pm 0.8$	$14.0 \pm 0.5$	$-26.1 \pm 0.7$	

**Table 4.** Color parameters of the pigments and glaze in the CIELab system. Coloring performance was tested using the  $x = 0.2$  pigment newly synthesized to mimic a color stain in the medium-fire industrial glaze fired to reach maturation at 1200°C for 2 h. Selected five raw materials were also tested.

Materials	Color parameter			Color
	L	a	b	
Pigment	$69.8 \pm 0.3$	$11.0 \pm 0.2$	$-4.0 \pm 0.1$	
Pigmented glaze	$10.0 \pm 0.2$	$21.5 \pm 0.2$	$-51.5 \pm 0.3$	
Na-feldspar	$66.4 \pm 0.1$	$16.7 \pm 0.2$	$-15.5 \pm 0.4$	
$\text{SiO}_2$	$80.2 \pm 0.2$	$10.1 \pm 0.5$	$-5.9 \pm 0.3$	
$\text{CaCO}_3$	$70.8 \pm 0.3$	$7.7 \pm 0.2$	$7.2 \pm 0.2$	
ZnO	$51.0 \pm 0.2$	$-19.9 \pm 0.1$	$4.9 \pm 0.3$	
Kaolin	$57.5 \pm 0.3$	$-5.7 \pm 0.1$	$-28.4 \pm 0.2$	



**Figure 9.** EDS mapping at the interface between the pigment ( $x = 0.2$ ) and molten glaze. Both inward and outward diffusion of several species were detected.

Obvious color change was observed in a fired glaze, which became intense blue as reflected by a high negative value of the  $b$  parameter (-51.5). Totally different color tones were obtained for each tested raw material. The redness (positive  $a$  value) was maintained for Na-feldspar ( $\text{NaAlSi}_3\text{O}_8$ ),  $\text{SiO}_2$  and  $\text{CaCO}_3$  while the blueness (negative  $b$  value) only for Na-feldspar and  $\text{SiO}_2$ . Mixing the pigment with  $\text{CaCO}_3$  resulted in a positive  $b$  parameter, making the glaze to appear brownish which is undesirable for the aimed purple color. Both ZnO and Kaolin ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) reacted with the pigment; the mixtures turned greenish and bluish, respectively. Such small alteration in the mixture of Na-feldspar is likely associated with the amorphous nature of the feldspar as it was melted at  $1200^\circ\text{C}$ . This amorphousness with Na modifiers would restrict reactivity of both Al and Si cations in the glass structure. Refractoriness of  $\text{SiO}_2$  could also be the cause for insignificant changes in color parameters; its high melting temperature would limit its own reactivity with the forsterite pigment.  $\text{CaCO}_3$  promptly turned to CaO at approximately  $800^\circ\text{C}$  to  $1000^\circ\text{C}$  and readily combined with leached cobalt to form a brownish Ca-Co-O compound. The green color in the ZnO-pigment mixture was a direct result of successful doping of cobalt in the ZnO lattice as widely known in the ZnO-based varistor field. Outward diffusion of cobalt into the glaze could also be responsible for the bluish color when mixing the pigment with kaolin. Following its structural transformation from metakaolin to spinel, conversion into  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (mullite) occurs. This phase with two oxides might be highly prone to forming  $\text{CoAl}_2\text{O}_4$  and  $\text{Co}_2\text{SiO}_4$  which have been known to be blue pigments. From these results from a medium-fire glaze study, it is comprehensible that, in order to maintain the pigment's purplish tone, both ZnO and kaolin should be avoided or included at their minimal level.

#### 4. Conclusions

Ceramic pigments based on forsterite phase were successfully synthesized by solid-state processing. The addition of a flux (10 wt%) could reduce the forsterite phase starting temperature  $200^\circ\text{C}$ . Cobalt

was employed as a chromophore in the host structure ( $(\text{Mg}_{2-2x}\text{Co}_{2x})\text{SiO}_4$ ). Refinement from X-ray Diffraction yielded a slight reduction in the lattice volume with increasing amounts of cobalt given the smaller ionic radius of cobalt. The solid solubility limit was determined to be  $x = 0.2$ . The incorporation of cobalt into the Mg lattice was further confirmed by Infrared Spectroscopy which demonstrated a red shift in the metal-oxygen peaks. The crystallite sizes were in line with the particle sizes ( $0.5 \mu\text{m}$  to  $1 \mu\text{m}$ ) observed by Electron Microscopy. The oxidation state of cobalt was 2+ according to X-ray Photoelectron Spectroscopy (XPS). Two optical absorption peaks were detected in the 450 nm to 600 nm range ( ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ ) and 600 nm to 750 nm ( ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{A}_1(\text{F})$ ). This transition was a direct result of the substitution of Co in the octahedral coordination of Mg. The addition of cobalt yielded an enhanced redness of the pigment (more positive  $a$  parameters), while the  $b$  parameters decreased towards negativity (blueness). Such changes corresponded with the slight shifts observed in the UV-vis spectra. To be of technological relevance, the synthesized pigments were tested in practical, industrial low-fire glazes. Surprisingly, a color change occurred which yielded a further decrease in the  $b$  parameter. The obtained glaze possessed a purplish tone which has never previously accomplished in the forsterite system. In-depth investigation revealed outward diffusion of cobalt from the pigment, resulting in a reduction in the lattice volume of the forsterite host. Preliminary studies with a medium-fire glaze suggested that ZnO and kaolin should be avoided in the glaze's ingredient to preserve the pigment's original purplish color tone.

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