

Article

Sol–Gel Synthesis and Characterization of Mullite–Spinel Ceramics Doped with Divalent (Co^{2+} , Ni^{2+}) Transition Metal Ions

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Abstract

Co- and Ni-doped mullite–spinel ceramics were synthesized via a sol–gel method followed by high-temperature sintering in order to investigate the influence of dopant type on the phase evolution, microstructure, and optical properties. X-ray diffraction analysis confirmed the formation of a multiphase system consisting of mullite and spinel phases, with a residual amorphous fraction, the amount of which decreases with increasing temperature. FTIR and Raman spectroscopy indicate progressive structural ordering of both spinel and aluminosilicate networks during thermal treatment, with differences in crystallization behavior between Co- and Ni-containing system. UV–Vis spectroscopy revealed characteristic absorption bands arising from d–d electronic transitions of Co^{2+} and Ni^{2+} ions in the ceramic matrix, reflecting differences in their local coordination environments and optical behavior. Colorimetric analysis showed that Co-doped samples exhibit intense blue coloration, whereas Ni-doped ceramics display greenish-blue hues. The temperature-dependent evolution of the L^* , a^* , and b^* parameters correlate with structural changes. The results suggest that the type of additive influences the phase evolution and optical response in mullite–spinel ceramics, in agreement with structural and spectroscopic analyses.

Keywords: pigments; color; ceramics; mullite; spinel; cobalt; nickel



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1. Introduction

Ceramic pigments are essential components of the ceramic and glass industries, where stable and reproducible coloration under high-temperature firing conditions is required. Unlike organic colorants, ceramic pigments derive their color from transition-metal ions incorporated into thermally and chemically stable inorganic matrices. The coloration mechanism is governed by crystal-field splitting of the partially filled d orbitals of transition-metal ions. The interaction between the metal cation and surrounding oxygen ions produces a separation of the d energy levels, enabling electronic d–d transitions in the visible spectral region. Selective absorption of visible light by these transitions gives rise to the characteristic colors of ceramic pigments. This structural incorporation provides excellent resistance to heat, light, and chemical attack, while coloration arises from stable electronic transitions

within the crystal lattice, ensuring long-term color durability even under severe firing conditions. Consequently, the development of novel ceramic pigment systems with precisely controlled colorimetric properties remains an active area of research, driven by both aesthetic requirements and industrial performance demands [1–6]. Among inorganic pigment systems, spinel-based oxides (AB_2O_4) are some of the most widely used due to their high structural flexibility and strong capacity to accommodate chromophoric ions within tetrahedral and/or octahedral coordination sites [5–12]. In addition to their importance as blue ceramic pigments, cobalt aluminate spinels have been investigated for catalytic, sensing, and energy-related applications because of their excellent thermal and chemical stability [13–16].

The spinel crystal structure with the general formula AB_2O_4 crystallizes in the cubic space group $Fd-3m$ and is based on a cubic close-packed arrangement of oxygen anions. Within this lattice, 96 interstitial sites are available per unit cell, including 64 tetrahedral and 32 octahedral sites. However, only 8 tetrahedral and 16 octahedral sites are occupied by cations. Two ideal cation distributions are typically distinguished. In the normal spinel, divalent cations occupy tetrahedral sites A, while trivalent cations B reside in octahedral sites. Cobalt aluminate ($CoAl_2O_4$) is typically considered a nearly ideal normal spinel. In this structure, Co^{2+} ions preferentially occupy tetrahedral sites, while Al^{3+} ions remain in octahedral positions. Such a preference of Co^{2+} is related to electronic configuration ($3d^7$), which leads to stabilization in tetrahedral environments. Numerous studies have demonstrated that tetrahedrally coordinated Co^{2+} is primarily responsible for the characteristic intense blue color of cobalt aluminate pigments through d–d electronic transitions of Co^{2+} ions [7–9]. Variations in cation inversion and oxidation state can significantly modify color saturation and hue.

In contrast, nickel aluminate ($NiAl_2O_4$) often shows a higher tendency toward cation disorder and partial inversion. In practice, many spinel oxides exhibit partial inversion, where cations occupy both tetrahedral and octahedral sites. The Ni^{2+} with electronic configuration ($3d^8$) has a significant crystal field stabilization energy in octahedral coordination, which favors its occupation in octahedral sites. Although Ni^{2+} shows a strong preference for octahedral coordination due to crystal field stabilization energy, its actual distribution in spinel structures depends on synthesis conditions and may result in partial occupation of tetrahedral sites. Consequently, a fraction of Ni^{2+} cations may migrate from tetrahedral to octahedral positions, while a corresponding amount of Al^{3+} moves to tetrahedral sites to maintain charge balance. These differences in cation distribution can significantly influence magnetic, catalytic, and electronic properties of materials [10,11,16,17].

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is an important ceramic phase widely valued for its low thermal expansion, excellent thermal shock resistance, high creep resistance, and chemical inertness. Although mullite itself is not an effective chromophore, its incorporation into pigment systems provides significant advantages, including enhanced thermal stability, suppression of excessive grain growth, and improved compatibility with ceramic glazes and bodies. As a result, mullite-containing compositions are widely used in high-temperature refractories and advanced ceramic applications [18,19]. From a crystal chemical perspective, mullite is capable of incorporating considerable amounts of trivalent transition-metal cations, however, the incorporation of divalent ions such as Co^{2+} and Ni^{2+} is extremely limited by structural and charge constraints. The mullite crystal structure is orthorhombic which is built from chains of AlO_6 octahedra parallel to c-axis and interconnected AlO_4 and SiO_4 tetrahedra. Divalent cations as Co^{2+} and Ni^{2+} mainly substitute for Al^{3+} in octahedral sites. As these ions have a lower charge, a charge imbalance must be compensated for by defects such as oxygen vacancies. This requirement limits their solubility in the mullite lattice. Popović et al. [20] demonstrated that even after sintering at 1600 °C, the solubility limit

of Co^{2+} in mullite is approximately 0.6 at%, with excess cobalt segregating to form CoAl_2O_4 spinel. This behavior indicates that increasing the cobalt content beyond the solid solution limit inevitably leads to the formation of a secondary spinel phase. Consequently, compositions containing higher cobalt concentrations are expected to form mullite–spinel biphasic systems, in which the spinel phase provides color, while the mullite matrix ensures thermal and structural stability. Such composite systems are therefore particularly attractive for high-temperature pigment applications requiring stable and consistent color development.

In addition to crystal structure, the synthesis route of ceramic pigments plays a decisive role in controlling the homogeneity, phase assemblage, particle size distribution, and color performance of spinel–mullite ceramics. Conventional solid-state synthesis typically requires high calcination temperatures, which may lead to inhomogeneous incorporation of divalent chromophoric ions (Co^{2+} or Ni^{2+}); dopant volatilization, particularly of cobalt; exaggerated grain growth; and spatially non-uniform color development. These limitations often result in spatial fluctuations in composition, thereby reducing the reproducibility of the CIE L^* , a^* , and b^* color coordinates [21]. In contrast, the sol–gel method offers significant advantages by enabling molecular-level mixing of precursors through the formation of a polymeric inorganic network, ensuring a highly uniform distribution of metal cations prior to calcination. This homogeneous chemical environment shortens diffusion paths and lowers the thermodynamic and kinetic barriers for the formation of spinel and mullite phases, allowing crystallization at reduced temperatures. Consequently, finer and more uniformly distributed crystallites are obtained. From an optical perspective, the improved homogeneity minimizes local variations in ligand field strength around chromophoric ions, leading to more consistent electronic transition and enhanced color uniformity and reproducibility. However, sol–gel-derived pigments may exhibit slightly higher L^* values and reduced chroma, corresponding to paler hues, which can be attributed to the finer particle size and more homogeneous dispersion of chromophoric ions within the ceramic matrix [22]. In the Al_2O_3 – SiO_2 system, divalent transition-metal ions, such as Co and Ni, form $\text{TM}^{2+}\text{Al}_2\text{O}_4$ spinel phases that coexist with mullite in Al_2O_3 – SiO_2 -rich compositions. Compared with single-phase doped spinel or mullite ceramics, the biphasic system combines the strong chromophoric response of the spinel with the excellent thermal stability and microstructural control provided by mullite. We expect this synergistic effect to result in increased color intensity, improved thermal and chemical stability, suppressed grain growth, and superior color reproducibility, making these systems extremely attractive for high-temperature ceramic pigment applications. The formation of these phases can be efficiently achieved by sol–gel synthesis followed by controlled thermal treatment. Due to the molecular homogeneity and high reactivity of the sol–gel precursors obtained, spinel and mullite phases can crystallize at relatively low temperatures ($\approx 1200^\circ\text{C}$), although equilibrium phase diagrams show higher formation temperatures [23,24]. This behavior reflects kinetically driven phase formation, where reduced diffusion distances and increased reactivity significantly lower the activation barriers for crystallization. Furthermore, the presence of mullite contributes to microstructural stabilization, limits grain growth, and helps to preserve the oxidation state of the divalent additives, leading to more uniform and thermally stable coloration.

However, the interplay between dopant-controlled cation distribution, phase evolution, and optical response in mullite–spinel systems remain insufficiently understood.

In this study, Co^{2+} - and Ni^{2+} -doped mullite–spinel ceramic pigments were synthesized by a sol–gel method followed by thermal treatment in the temperature range of 1000 – 1200°C . The phase composition and microstructural evolution were analyzed by X-ray diffraction, scanning electron microscopy, and infrared and Raman spectroscopy, while the optical and color properties were evaluated using spectrophotometry and pre-

sented in the CIE L*a*b* color space. The relationships between dopant incorporation, phase evolution, and the resulting colorimetric parameters are discussed, demonstrating the potential of doped mullite–spinel systems as thermally stable blue and green ceramic pigments for high-temperature applications.

2. Materials and Methods

2.1. Method of Synthesis

The calculations were carried out for a 15.72 g mullite-based material. The required oxide amounts were calculated as 10.77 g Al₂O₃, 4.2 g SiO₂, and 0.75 g CoO or NiO. Based on these quantities, the CoO/NiO content corresponds to approximately 5 mol% of the total oxide composition. These oxides were introduced through their respective precursors: (Al(NO₃)₃·9H₂O 39.6 g), cobalt nitrate hexahydrate or nickel nitrate hexahydrate (Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O, 1.4 g), and tetraethylorthosilicate (Si(OC₂H₅)₄ (TEOS), 15.7 mL). All reagents were of analytical grade and purchased from Merck KGaA, Darmstadt, Germany.

The precursors were dissolved and mixed to form a homogeneous solution. TEOS was first hydrolyzed under controlled conditions, and the resulting sol was stirred at 60 °C. After approximately 48 h, gelation occurred, forming a viscous gel mass. The gel was then dried sequentially at 120 °C and 180 °C to remove residual water and decompose nitrates. Once fully dried, the material was ground in an agate mortar to ensure homogeneity and subjected to heat treatment at 1000, 1100, and 1200 °C, each with an isothermal holding time of 2 h at the maximum temperature, to promote crystallization and incorporation of Co²⁺ or Ni²⁺ ions. The resulting powders were subsequently characterized for phase composition, microstructure, and dopant incorporation.

As a result of high-temperature firing, six samples with the same initial Co or Ni concentrations were obtained. The samples were sintered at 1000, 1100, and 1200 °C and are designated as Co-1000 °C, Co-1100 °C, Co-1200 °C, Ni-1000 °C, Ni-1100 °C, and Ni-1200 °C, respectively.

2.2. Methods for Characterization

Phase composition was analyzed using a Bruker D8 Advance X-ray diffractometer (Bruker Corporation, Billerica, MA, USA) equipped with Cu K α radiation and LynxEye detector in the range of 5–90°2 θ with step 0.02°2 θ , counting time 17 s/step. Phase identification was carried out using Diffracplus EVA 4 software in conjunction with the ICDD-PDF2 (2024) database. Unit-cell parameters and average crystallite sizes were refined with full pattern fitting procedure of TOPAS 4.2, applying the fundamental parameters approach for peak-profile description and incorporating corrections for instrumental broadening according to actual diffractometer geometry [25]. Quantitative phase analysis was performed using Rietveld refinement. The degree of crystallinity (X_c) was calculated from the X-ray diffraction (XRD) patterns by comparing the integrated intensity of the crystalline reflections (*I_c*) with that of the amorphous contribution (*I_a*), according to the following equation:

$$X_c(\%) = \left(\frac{I_c}{I_c + I_a} \right) \times 100$$

The quality of the Rietveld refinement was evaluated using the weighted profile residual factor (R_wp), defined as $R_{wp} = \sqrt{[\sum w (Y_o - Y_c)^2 / \sum w (Y_o)^2]}$. The R_wp values range from 5.04 to 7.43%, corresponding to 5.38, 5.65, and 7.43% for the Co-containing samples and to 5.15, 5.05, and 5.04% for the Ni-containing samples. These values indicate a good fit between calculated and experimental diffraction patterns.

SEM images and EDS analyses were acquired using an IT800SHL scanning electron microscope (JEOL, Tokyo, Japan) equipped with a JED-2300 energy-dispersive X-ray spectroscopy (EDS) system. The analyses were performed at an accelerating voltage of 10 kV. Elemental maps of Al, Si, O, and Co or Ni were collected from representative areas of each sample.

FT-IR spectra were recorded on a Bruker Tensor 37 spectrometer with a resolution of 4 cm^{-1} by averaging 128 scans. Measurements were performed at room temperature in the spectral range $400\text{--}4000\text{ cm}^{-1}$ using standard KBr pellets.

UV-Vis reflectance spectra were recorded using a Cary 4000 (Agilent) spectrophotometer equipped with an internal DRA 900 diffuse reflectance accessory. UV-Vis transmittance spectra were recorded using a solid sample accessory. Measurements were performed in the $200\text{--}800\text{ nm}$ spectral range with a spectral resolution of 1 nm . The spectrum was processed to remove baseline fluctuations and diffuse reflectance spectra were converted to absorbance using the Kubelka–Munk function, $F(R) = \frac{(1-R)^2}{2R}$, in order to enable comparison of optical absorption features.

The color of the pigments was measured using a Lovibond Tintometer RT 100 and expressed in the CIE $L^*a^*b^*$ color space.

Raman spectra were recorded using a WiTec mobile alphaCART confocal Raman system with a 532 nm laser and a $\times 50$ objective, producing a laser spot of $\sim 1\text{ }\mu\text{m}$ with an acquisition time of 5 s and averaged over 250 accumulations to improve the signal-to-noise ratio.

3. Results and Discussion

3.1. Phase Composition

The phase composition of the ceramics sintered at 1000 , 1100 , and $1200\text{ }^\circ\text{C}$ was determined from powder X-ray diffraction (XRD) patterns (Figure 1). Phase composition, quantitative phase content, unit-cell parameters, and crystallite sizes are summarized in Table 1.

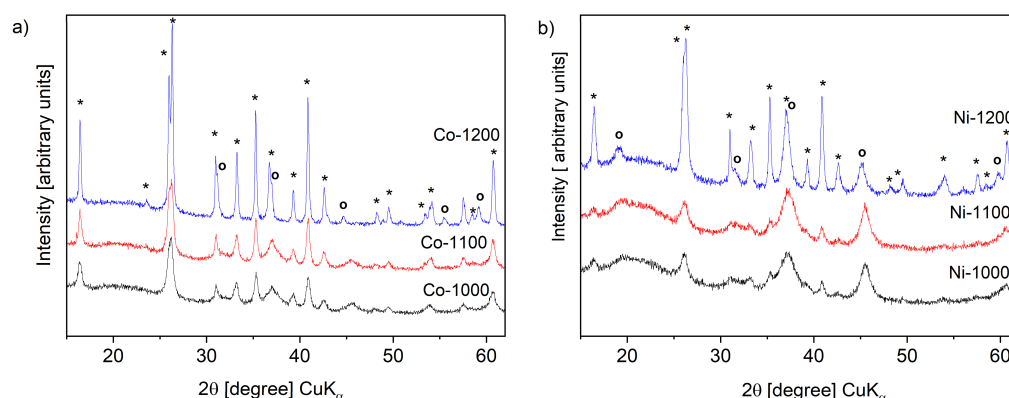


Figure 1. Powder XRD patterns of (a) Co- and (b) Ni-doped mullite–spinel ceramics, *—mullite phase, o—spinel phase.

The changes in phase composition with increasing temperature illustrate the progressive evolution of the mullite–spinel system from a predominantly amorphous state toward a more crystalline structure (Table 1). At lower calcination temperatures, the materials contain a substantial amorphous fraction together with weakly developed crystalline phases. As the firing temperature increases, the amorphous aluminosilicate matrix gradually crystallizes, favoring mullite formation through interactions between silica- and alumina-rich domains. At the same time, the spinel phase becomes more structurally

ordered, which is evidenced by the appearance of sharper and more intense diffraction reflections accompanied by a decrease in the diffuse amorphous halo.

Table 1. Phase composition, quantitative phase content, unit-cell parameters, and crystallite sizes of Co- and Ni-doped mullite–spinel ceramics.

Sample	Mullite Phase Mass% Average Size Unit-Cell Parameters a, b, c	Spinel Phase Mass% Average Size Unit-Cell Parameter a	Amorphous Part Mass%
Co(1000 °C)	46% 26 nm 7.549(2) Å, 7.695(2) Å, 2.875(1) Å	19% 5 nm 7.961(3) Å	35%
Co(1100 °C)	53% 30 nm 7.543(1) Å, 7.694(1) Å, 2.880(1) Å	17% 6 nm 7.984(3) Å	30%
Co(1200 °C)	70% 58 nm 7.5352(6) Å, 7.6933(7) Å, 2.8836(2) Å	8% 38 nm 8.1085(8) Å	24%
Ni(1000 °C)	17% 16 nm 7.513(7) Å, 7.658(9) Å, 2.863(3) Å	39% 5 nm 7.934(9) Å	44%
Ni(1100 °C)	16% 17 nm 7.516(7) Å, 7.657(9) Å, 2.868(3) Å	40% 6 nm 7.938(7) Å	44%
Ni(1200 °C)	53% 36 nm 7.547(1) Å, 7.695(1) Å, 2.8836(4) Å	19% 38 nm 8.031(1) Å	28%

The diffraction patterns of Co-doped ceramics, sintered at 1000 °C, reveal the presence of both mullite and spinel phases together with a significant amorphous contribution. Comparison of the quantities and mean crystallite size of mullite, 26 nm, and spinel, 5 nm, points to the fact that, at this temperature, the crystallization of mullite is more intensive. With increasing firing temperature, progressive crystallization of the amorphous phase occurs, accompanied by grain growth, as seen in ceramics at 1100 °C, where the relative content of the mullite phase increases and the crystallite size increases slightly for both phases. The rate of crystallization is further accelerated at 1200 °C, where the relative content of the amorphous phase decreases to about 24%. Mullite becomes the dominant phase, forming large crystallites, but the rate of crystallization of the spinel phase is even higher at this temperature, with a remarkable increase in the average crystallite size from 6 nm at 1100 °C to 38 nm at 1200 °C.

The evolution of the unit-cell parameters of the two crystalline phases in this system provides additional information on the structural changes occurring during thermal treatment. The observed gradual contraction of the a-parameter together with the increase of the c-parameter suggests structural rearrangement and improved ordering of the mullite framework during calcination. For the spinel phase, the refined unit-cell parameter increases with firing temperature, thus reaching the common value for CoAl₂O₄ spinel (ICDD-PDF2-00-038-0814). These observations can be interpreted in two ways: at lower temperatures, the spinel phase exhibits broad diffraction peaks, indicating limited crys-

tallinity and small size. In nanocrystalline materials, the refined unit-cell parameters may differ from bulk values due to size-related effects and the presence of structural defects, as reported in the literature [12,26–29]. In addition, cation deficiency may also affect the unit-cell parameter of a defect spinel, such as γ -Al₂O₃ and γ -Fe₂O₃. Increased temperature promotes long-range cation transport and facilitates cobalt redistribution between mullite and spinel phases, leading to enhanced formation of CoAl₂O₄ at 1200 °C. This trend is consistent with progressive structural ordering, as evidenced by lattice parameters approaching those of bulk CoAl₂O₄.

The XRD also allowed us to follow the phase evolution of the Ni-containing ceramic system. At lower temperatures (1000–1100 °C), a substantial amorphous fraction is observed, higher than that observed for the Co-containing system. Furthermore, a weakly crystalline spinel phase dominates the mullite content. On the other hand, the unit-cell parameter of the spinel at 1000 and 1100 °C is close to that of γ -Al₂O₃, which may indicate the formation of an intermediate spinel phase with a low level of Ni²⁺ incorporation. This fact, together with the observed low values of the unit-cell parameters of the mullite phase, suggest that, at these temperatures, nickel is predominantly present in the amorphous constituent. Therefore, we can assume that Ni²⁺ ions play a less active role in the crystallization of the mullite phase at low temperatures when compared with Co²⁺ ions. When the temperature is increased to 1200 °C, a pronounced phase transformation occurs and mullite becomes the dominant phase. This transition is accompanied by a reduction in the amorphous content to about 28%. The significant increase in crystallite size with temperature from ~16 nm for mullite to 36 nm and from ~5 nm to 38 nm for spinel reflects active crystal growth. Furthermore, the observed increase in lattice parameters for both mullite and spinel phases suggests a reduction of lattice defects and internal stresses. The lattice parameters of mullite show minor changes between 1000 and 1100 °C, while at 1200 °C a clear increase in all lattice parameters is observed, which may suggest increased incorporation of Ni into the mullite structure and/or structural reorganization towards a more equilibrium state. At the same time, the observed increase in the spinel lattice parameter may be associated with increased Ni incorporation into the spinel phase. At 1200 °C, the unit-cell parameter of the spinel phase reaches 8.031 Å, which is close to the value of 8.05 Å reported for stoichiometric NiAl₂O₄ (ICDD-PDF2-01-078-1601), suggesting progressive evolution toward a more Ni-rich spinel structure.

3.2. SEM-EDS

The Co elemental maps (Figure 2) indicate a non-uniform spatial distribution of cobalt within the ceramic microstructure. In contrast, the area-averaged EDS results show an approximately constant Co content across samples sintered at different temperatures (Table 2), suggesting that the overall cobalt concentration remains stable, while its local distribution varies within the analyzed regions.

Table 2. EDS mean composition of Co- and Ni-doped mullite–spinel ceramics, presented as mass%.

Element	Co 1000	Co 1100	Co 1200	Element	Ni 1000	Ni 1100	Ni 1200
O	46.49 ± 0.12	46.89 ± 0.13	46.06 ± 0.14	O	37.19 ± 0.10	39.71 ± 0.10	41.06 ± 0.38
Al	23.36 ± 0.09	21.60 ± 0.10	26.39 ± 0.11	Al	27.19 ± 0.09	28.62 ± 0.09	21.49 ± 0.29
Si	28.33 ± 0.11	30.02 ± 0.13	25.67 ± 0.13	Si	28.53 ± 0.11	23.51 ± 0.09	30.35 ± 0.38
Co	1.82 ± 0.16	1.49 ± 0.17	1.89 ± 0.19	Ni	7.09 ± 0.39	8.16 ± 0.39	7.10 ± 1.35
Total	100.00	100.00	100.00	Total	100.00	100.00	100.00

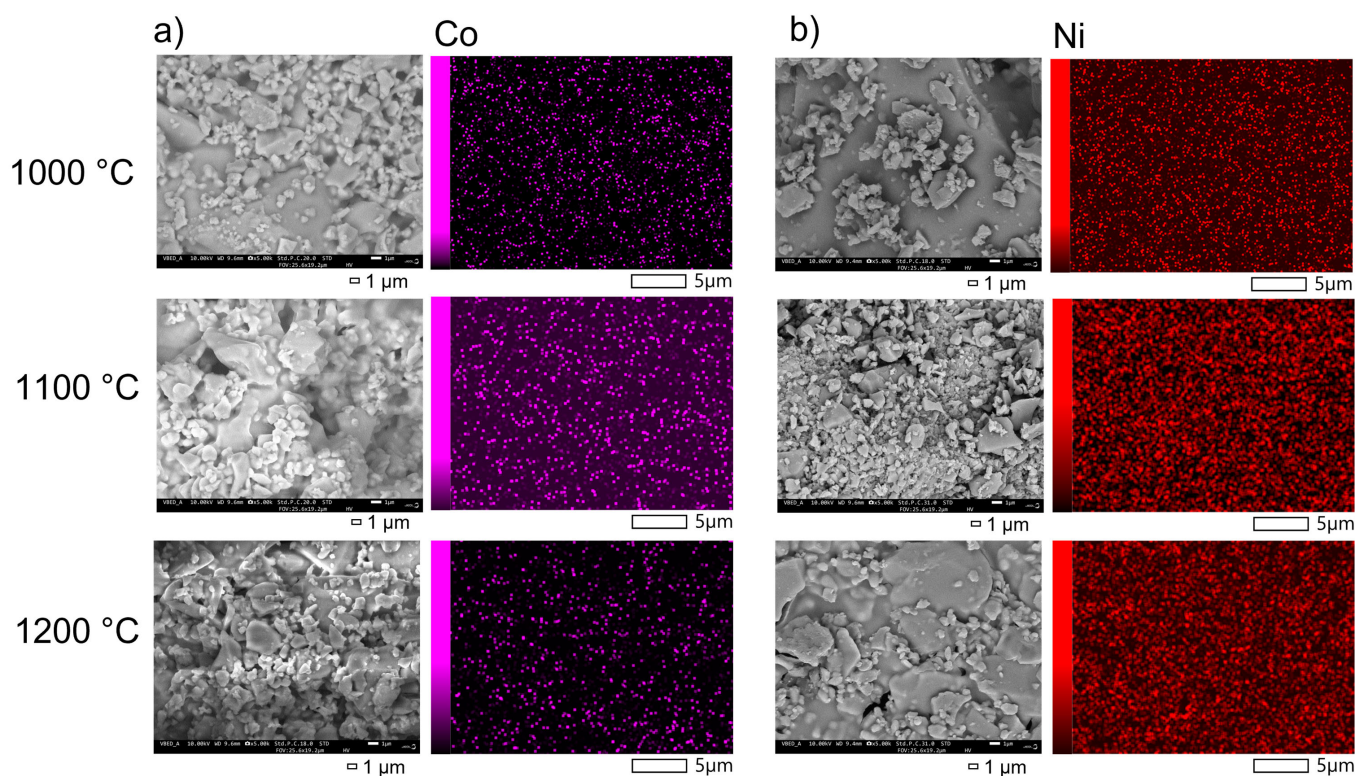


Figure 2. Backscattered electron (BSE) images and corresponding elemental maps of Co- and Ni-doped samples, showing the spatial distribution of (a) Co and (b) Ni within the microstructure.

For Ni-containing samples, the elemental maps suggest a comparatively more uniform spatial distribution of Ni within the microstructure. The corresponding area-averaged EDS data indicate relatively consistent Ni levels across the investigated samples.

The observed differences in spatial distribution suggest different incorporation behavior of Co and Ni during thermal treatment.

3.3. FT-IR Spectra

FTIR spectra reveal temperature-dependent structural changes in Co- and Ni-doped aluminosilicate ceramics (Figure 3). The spectral region between approximately 470–650 cm^{-1} is associated primarily with metal–oxygen vibrations arising from both spinel-type structures and aluminosilicate networks, involving contributions from tetrahedrally coordinated M–O and octahedrally coordinated AlO_6 units [30,31]. However, strong overlap between spinel, mullite, and aluminosilicate vibrations prevent unambiguous assignment of individual bands (Table 3). In the Co-doped samples, progressive sharpening of bands near 470 and 562 cm^{-1} with increasing temperature indicates modification in the local structural environment associated with the ordering of spinel-related and aluminosilicate units. In the nickel-doped ceramics, the appearance of a band at $\sim 563 \text{ cm}^{-1}$, and only at 1200 °C, indicates a similar overlapping contribution. In both systems, these observations are consistent with the phase and structural changes already detected by XRD. The spectral region between approximately 650 and 1000 cm^{-1} contains overlapping contributions from mullite and amorphous aluminosilicate phases, including Al–O vibrations, Si–O–Al linkages, and Si–O stretching modes [32–34]. A noticeable shift of the peak $\sim 888 \text{ cm}^{-1}$ at 1000 °C to $\sim 906 \text{ cm}^{-1}$ at 1200 °C is observed in the Co-doped samples. This behavior indicates progressive reorganization of the aluminosilicate network, associated with increased polymerization and structural ordering of Si–O–Al linkages. The shift toward higher wavenumbers is consistent with densification of the aluminosilicate framework and enhanced development of mullite-related structural units during high-temperature

treatment. The 900–1200 cm^{-1} range is dominated by Si–O stretching vibrations and is highly sensitive to the degree of aluminosilicate network polymerization. The broad bands observed at lower temperatures, especially in the Ni-containing samples, indicate a substantial amorphous fraction, in agreement with the XRD results. With increasing temperature, band sharpening and increased intensity reflect a reduction of amorphous contributions and progressive development of more ordered aluminosilicate environments.

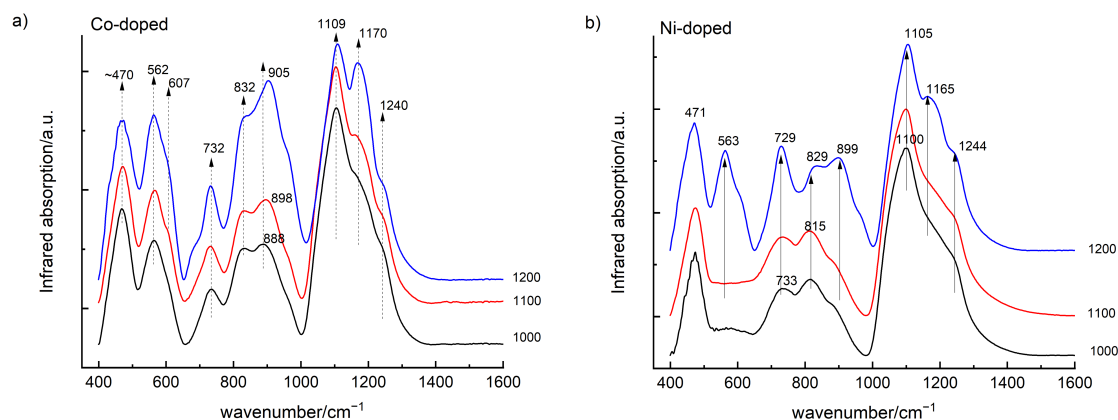


Figure 3. IR spectra of (a) Co-doped and (b) Ni-doped mullite–spinel ceramics.

Table 3. Infrared and Raman peak position, possible assignment, and phases.

Raman	IR	Peak Assignment	Possible Phase Contribution /Overlap	Ref.
170–190		$F_{2g}(1)$ translation involving tetrahedral M–O units	Spinel	[31,35,36]
282–296		AlO_6 deformation	Mullite	[32–34]
320		Lattice mode	Mullite	[32–34]
385–406		O–Si–O bending E_g mode	Mullite/spinel	[31,33,35]
480	470	$F_{2g}(2)$ M–O tetrahedral str. O–Si–O bending	Spinel/mullite/residual amorphous	[31,33,35,37]
593–601	562	$F_{2g}(3)$ M–O vibration Al–O stretching (AlO_6)	Spinel/mullite	[31,33,35,36]
700–788	732–832	Si–O–Al/Si–O–Si stretching	Mullite/residual amorphous	[32,33,37]
899–950	888–906	Si–O stretching in $Si(Al)O_4$	Amorphous/mullite	[32,33,37]
1090–1113	1105	Si–O–Si stretching	Residual Al–Si network	[33,37]
	1170	Asym. Si–O–Si /Si–O–Al stretching	Residual Al–Si network	[33,37]

3.4. Raman Spectra

Raman spectroscopy reveals different crystallization behaviors of Co- and Ni-doped aluminosilicate ceramics (Figure 4). In the Co-containing samples, peaks at 170–189 cm^{-1} , assigned to the $F_{2g}(1)$ translational mode involving tetrahedral M–O units (Table 2), are observed at all firing temperatures, indicating the formation of $CoAl_2O_4$ spinel [35,38]. With increasing temperature, this band shifts from approximately 170 to 189 cm^{-1} and becomes better defined, suggesting changes in local environment associated with spinel phase evolution. In the Ni-containing ceramics, no corresponding low-frequency band is clearly resolved. As XRD confirms the presence of a spinel, the absence of this Raman peak may be attributed to low crystallinity, nanoscale crystallite size, or overlap with aluminosilicate vibrations. Bands in the range of 282–406 cm^{-1} are associated with mullite-related vibra-

tions, including AlO_6 deformation, lattice mode, and O–Si–O bending [36,37,39]. These bands are present in the Co-containing ceramics and become more clearly resolved in the Ni-containing series only after firing at 1200 °C, consistent with the temperature-dependent evolution of crystalline phases, observed by XRD. A band at $\sim 480\text{ cm}^{-1}$, attributed mainly to spinel $F_{2g}(2)$ vibrations, appears only in the Co-1200 sample, which is consistent with the increased crystallinity and growth of the spinel phase. The band at $593\text{--}601\text{ cm}^{-1}$ contains overlapping contributions from spinel-related metal–oxygen $F_{2g}(3)$ vibrations and Al–O stretching in mullite. In Ni-containing ceramics, a slight shift from 599 to 601 cm^{-1} and increase in intensity with temperature suggest progressive structural ordering of the spinel phase. The appearance of the FTIR band at $\sim 563\text{ cm}^{-1}$ in only the Ni-1200 sample supports this interpretation.

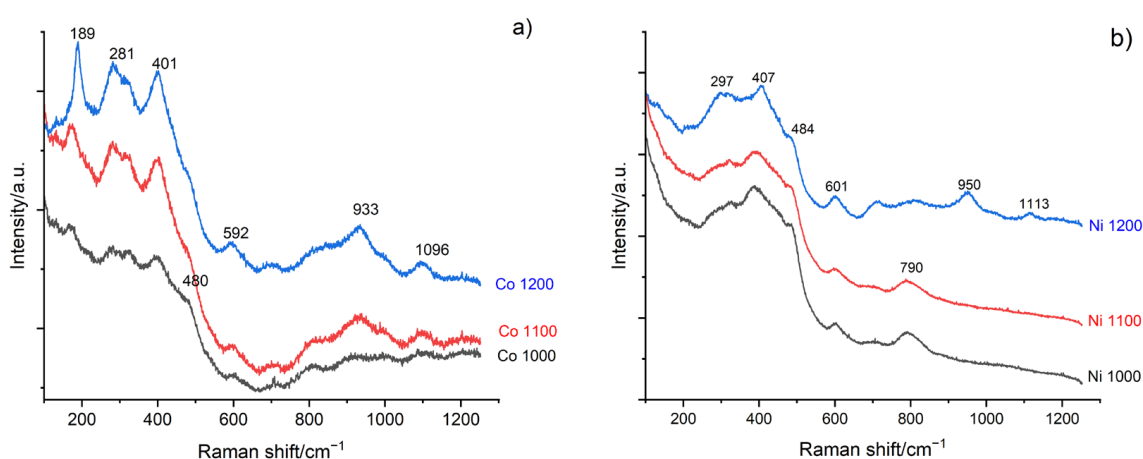


Figure 4. Raman spectra of (a) Co-doped and (b) Ni-doped mullite–spinel ceramics.

The A_{1g} mode characteristic of well-crystallized spinels is not resolved, most likely due to nanoscale crystallite size, structural disorder, and overlap with intense Si–O–Si and Si–O–Al stretching vibrations of mullite and the residual amorphous aluminosilicate phase.

The higher wavenumber bands at $700\text{--}788$, $910\text{--}950$, and $1090\text{--}1113\text{ cm}^{-1}$ originate mainly from Si–O–Si and $\text{Si}(\text{Al})\text{O}_4$ vibrations associated with mullite and the residual amorphous aluminosilicate phases [37]. The band at 788 cm^{-1} is observed only in Ni-containing samples and may indicate differences in the degree of polymerization of the aluminosilicate network. The shift of the $\text{Si}(\text{Al})\text{O}_4$ stretching vibration from 910 cm^{-1} in Co-1000 to 931 cm^{-1} in Co-1200 and the appearance of the corresponding band at 950 cm^{-1} in Ni-1200, are in good agreement with FTIR trends and reflect progressive structural reorganization of the aluminosilicate framework during firing.

Overall, the Raman results indicate earlier crystallization of spinel and mullite phases in the Co-doped ceramics, whereas the Ni-containing system retains a higher degree of structural disorder up to 1100 °C and undergoes more pronounced crystallization only at 1200 °C. These observations are consistent with FTIR and XRD results.

3.5. UV–Vis

The UV–Vis spectra of the Co- and Ni-doped mullite–spinel ceramics provide insight into the electronic structure and cation distribution within the phases. Although measurements were performed in the $200\text{--}800\text{ nm}$ range, only the $400\text{--}800\text{ nm}$ region is shown in Figure 5 because the UV region is dominated by intense charge-transfer absorption and diffuse scattering contributions that obscure the weaker d–d transitions responsible for coloration.

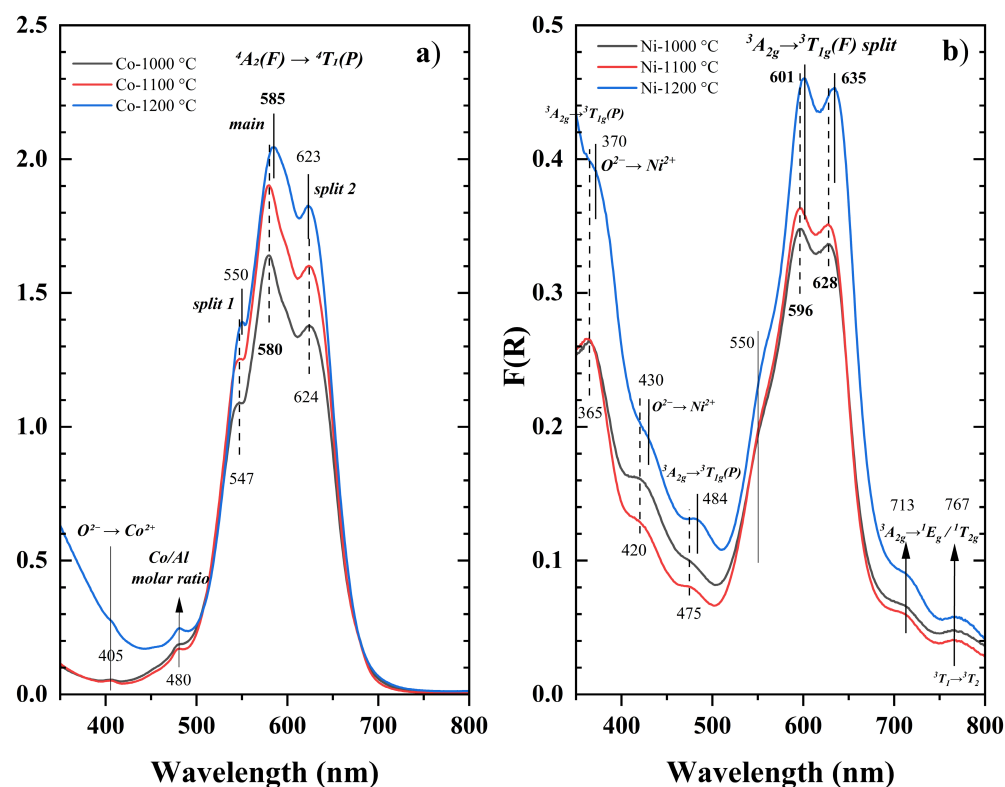


Figure 5. UV-Vis spectra of (a) Co-doped and (b) Ni-doped mullite-spinel ceramics.

The Co-doped ceramics exhibit characteristic broad absorption bands at ~540–560, ~580–620, and ~650 nm (Figure 5), which are attributed to crystal-field d–d transitions of Co^{2+} ions in tetrahedral coordination. These bands correspond to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ crystal-field transition of Co^{2+} in tetrahedral sites (CoO_4), characteristic of Co-containing spinels [36,40]. Additional contribution from Co incorporated into the mullite structure or present in an amorphous aluminosilicate matrix may lead to band broadening. The absorption in the 540–650 nm region is consistent with the transmission of blue light, explaining the observed blue coloration of the samples.

The Ni-doped samples exhibit several characteristic absorption features associated with Ni^{2+} ions. A broad and intense band in the 380–450 nm region is attributed to $\text{O}^{2-} \rightarrow \text{Ni}^{2+}$ charge-transfer transitions. The absorption band observed at 600–630 nm ($15,800\text{--}16,700\text{ cm}^{-1}$) agrees well with the characteristic Ni^{2+} crystal-field transitions reported for Ni-containing spinels. Sakurai et al. [41] observed absorption features near 17000 cm^{-1} in Ni^{2+} -doped MgAl_2O_4 spinels and assigned them to crystal-field transitions of octahedrally coordinated Ni^{2+} ions. The similarity of the spectral position supports the assignment of the present band to the spin-allowed ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition [36,40,42]. The observed band broadening and partial splitting suggests a deviation from ideal cubic symmetry, which may arise from local lattice distortions, cationic disorder, or vibronic interaction. With increasing temperature, the bands become more intense and better defined, reflecting progressive crystallization and stabilization of Ni^{2+} ions, predominantly in octahedral sites, although minor contributions from tetrahedrally coordinated Ni^{2+} cannot be excluded. The preference for octahedral coordination is consistent with the strong crystal-field stabilization energy of Ni^{2+} in octahedral sites [16].

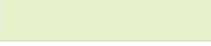
3.6. Color

The color of the samples was characterized using the CIE $L^*a^*b^*$ color space, where L^* represents lightness (0 = black, 100 = white), a^* denotes the red–green axis (positive

values indicate red and negative values indicate green), and b^* denotes the yellow–blue axis (positive values indicate yellow and negative values indicate blue).

The initial Co- and Ni-containing gels exhibit significantly different color coordinates compared with the sintered ceramics, reflecting the transformation of the transition-metal ions from hydrated and structurally disordered precursor environments into more ordered crystalline coordination sites during thermal treatment. The Co-containing gel shows a light, weakly reddish coloration, whereas, after sintering, the ceramics develop intense blue color with strongly negative b^* values (Table 4). In contrast, the Ni-containing gel exhibits a light yellow-green color that gradually evolves into darker green-blue tones after sintering. This change is associated with Ni^{2+} ions predominantly in octahedral coordination, present in spinel, mullite, and possibly residual amorphous aluminosilicate phases.

Table 4. Results obtained from the measurement of the color coordinates, presented in the CIE Lab* color space.

Sample	Color	L^*	a^*	b^*
Initial gel		80.7	11.1	−4.0
Co(1000 °C)		62.8	1.2	−39.5
Co(1100 °C)		62.1	0.9	−43.1
Co(1200 °C)		60.9	−8.3	−33.5
Ref. [7]		25–77	−4	−27 to −29
Initial gel		94.3	−9.3	18.1
Ni(1000 °C)		80.5	−11.2	−6.0
Ni(1100 °C)		79.8	−11.5	−8.9
Ni(1200 °C)		78.7	−13.1	−5.9
Ref. [43]		75–96	−1 to −12	−1 to −8

The colorimetric properties of the Co-doped samples are strongly influenced by firing temperature. The parameter b^* becomes more negative with increasing temperature, with a maximum observed at 1100 °C ($b^* = -43.1$). This indicates a strong increase in the blue coloration, which is typical of Co^{2+} in tetrahedral coordination in cobalt aluminate spinel [40,44,45]. The a^* values shift from slightly positive in the gel to negative at higher temperatures, indicating the disappearance of red hues and minor greenish contributions at 1200 °C. Overall, the data indicate that optimal blue coloration of a mullite–spinel ceramic system is achieved around 1100 °C. The slight reduction in blue intensity at 1200 °C may reflect changes in the relative proportions of mullite, spinel and residual amorphous phase.

The Ni-doped ceramics show a decrease in lightness and increasingly negative a^* values, indicating development of a stronger green component due to Ni^{2+} electronic transitions. Simultaneously, b^* changes from positive values in the precursor gel to negative values (−6 to −9) after sintering indicating a transition from yellowish to green-blue coloration. This color evolution is primarily associated with the formation and crystallization of $NiAl_2O_4$ spinels [17,43] and crystal-field transitions of Ni^{2+} ions in octahedral coordination. However, contributions from Ni incorporated in mullite-related environments and the amorphous aluminosilicate phase may also influence the final optical response by modifying the overall absorption behavior and color saturation.

The results obtained from XRD, SEM-EDS, IR, Raman, UV–Vis spectroscopy, and colorimetric analysis provide complementary evidence for the compositional and temperature-

dependent evolution of the Co- and Ni-doped mullite–spinel ceramics. XRD, FTIR, and Raman analyses reveal progressive crystallization of mullite and spinel phases with increasing temperature, accompanied by a reduction of the amorphous fraction. The diffraction patterns indicate that the Co-doped system develops defined crystalline phases at lower temperatures than the Ni-containing system, which shows broader diffraction features and undergoes substantial crystallization only at 1200 °C. The evolution of the refined cell parameters is consistent with these structural changes. The spectroscopic results are consistent with the structural trends defined by XRD. FTIR and Raman spectra reveal gradual changes in band position and intensity with increasing temperature, reflecting modifications of the crystalline phases and the aluminosilicate network.

SEM-EDS mapping shows different spatial distributions of the transition metal dopants. The elemental maps of Co exhibit a locally heterogeneous distribution, while Ni appears more homogeneously distributed in the analyzed regions. At the same time, area-averaged compositions remain approximately constant with temperature for both systems, indicating that the total dopant concentration is preserved during thermal treatment. These observations are consistent with the multiphase nature of the ceramics revealed by XRD.

The optical properties correlate well with the observed structural evolution. Co-containing ceramics develop an intense blue coloration, whereas Ni-containing ceramics exhibit greenish-blue hues. These differences are accompanied by systematic changes in the UV–Vis absorption spectra and the CIE L^* , a^* , and b^* color coordinates. The optical response therefore reflects the combined influence of phase evolution, changes in the local coordination environment of transition-metal ions, and progressive reduction of the amorphous fraction during firing. Taken together, the results indicate that the Co- and Ni-containing systems follow different crystallization behavior during heat treatment. The Co-doped ceramics show earlier phase development and higher structural ordering at lower temperatures, while the Ni-containing system crystallizes more significantly only at 1200 °C.

4. Conclusions

Co- and Ni-doped mullite–spinel ceramics were synthesized and their structural, microstructural, and optical behaviors were studied as functions of firing temperature. In both systems, progressive crystallization of mullite and spinel phases occurs with increasing temperature, together with a decrease in the amorphous fraction. The Co-doped ceramics reveal earlier crystallization and higher structural ordering, whereas the Ni-doped system shows delayed crystallization and a higher degree of structural disorder at lower temperatures.

Spectroscopic and colorimetric analyses suggest that Co^{2+} is predominantly associated with tetrahedral sites in CoAl_2O_4 spinel, giving rise to the characteristic intense blue coloration. In contrast, Ni^{2+} appears to be distributed among spinel, mullite, and residual amorphous material, leading to green-blue color and more complex optical response. Overall, the results demonstrate that the type of transition-metal dopant plays a key role in controlling the crystallization behavior and optical response of mullite–spinel ceramics, emphasizing the relationship between synthesis conditions, phase evolution, and functional properties.

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References

- Enríquez, E.; Reinosa, J.; Fuertes, V.; Fernández, J. Advances and challenges of ceramic pigments for inkjet printing. *Ceram. Int.* **2022**, *48*, 31080–31101. [\[CrossRef\]](#)
- Ibreva, T.; Dimitrov, T.; Titorenkova, R.; Markovska, I.; Tacheva, E.; Petrov, O. Synthesis and characterization of willemite ceramic pigments in the system $x\text{CoO} \cdot (2-x)\text{ZnO} \cdot \text{SiO}_2$. *Bulg. Chem. Commun.* **2018**, *50*, 31–37.
- Titorenkova, R.; Kostov-Kytin, V.; Dimitrov, T. Synthesis, phase composition and characterization of Co-diopside ceramic pigments. *Ceram. Int.* **2022**, *48*, 36781–36788. [\[CrossRef\]](#)
- Gazulla, M.; Gomez, M.; Barba, A.; Orduña, M. Chemical and phase characterisation of ceramic pigments. *X-Ray Spectrom. Int. J.* **2007**, *36*, 82–91. [\[CrossRef\]](#)
- Vereshchagin, V.I.; Radishevskaya, N.I. Spinel-Based Pigments. In *Concise Encyclopedia of Self-Propagating High-Temperature Synthesis*; Borovinskaya, I., Gromov, A., Levashov, E., Maksimov, Y., Mukasyan, A., Rogachev, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2017; pp. 358–360.
- Melo, D.M.; Cunha, J.D.; Fernandes, J.D.; Bernardi, M.I.; Melo, M.A.; Martinelli, A.E. Evaluation of CoAl_2O_4 as ceramic pigments. *Mater. Res. Bull.* **2003**, *38*, 1559–1564. [\[CrossRef\]](#)
- Zhang, W.; Li, Z.; Wu, G.; Wu, W.; Zeng, H.; Jiang, H.; Zhang, W.; Wu, R.; Xue, Q. Effects of Coloration of Spinel CoAl_2O_4 Cobalt Blue Pigments: Composition, Structure, and Cation Distribution. *Inorganics* **2023**, *11*, 368. [\[CrossRef\]](#)
- Monari, G.; Manfredini, T. Coloring Effects of Synthetic Inorganic Cobalt Pigments in Fast-Fired Porcelainized Tiles. In *A Collection of Papers Presented at the 97th Annual Meeting and the 1995 Fall Meetings of the Materials & Equipment/Whitewares: Ceramic Engineering and Science Proceedings*; Wachtman, J.B., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1996.
- Llusar, M.; Forés, A.; Badenes, J.; Calbo, J.; Tena, M.; Monrós, G. Colour analysis of some cobalt-based blue pigments. *J. Eur. Ceram. Soc.* **2001**, *21*, 1121–1130. [\[CrossRef\]](#)
- Gaudon, M.; Robertson, L.; Lataste, E.; Duttine, M.; Ménétrier, M.; Demourgues, A. Cobalt and nickel aluminate spinels: Blue and cyan pigments. *Ceram. Int.* **2014**, *40*, 5201–5207. [\[CrossRef\]](#)
- Truong, K.T.; Pham, T.H.; Pham, K.T.; Phu, H.P. Microwave combustion synthesis of Co-Ni aluminate spinel for electrophoretic deposition. *Chim. Techno Acta* **2026**, *13*, 9286.
- Sales, M.; Valentín, C.; Alarcón, J. Cobalt aluminate spinel–mullite composites synthesized by sol–gel method. *J. Eur. Ceram. Soc.* **1997**, *17*, 41–47. [\[CrossRef\]](#)
- Sadek, H.E.; Khattab, R.M.; Gaber, A.A.; Zawrah, M.F. Nano $\text{Mg}_{1-x}\text{Ni}_x\text{Al}_2\text{O}_4$ spinel pigments for advanced applications. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *125*, 353–358. [\[CrossRef\]](#)
- Lv, Y.; Yan, H.; Liu, T.; Xu, J.; Xu, X.; Fang, X.; Wang, X. Manufacturing AAI_2O_4 (A = Cu, Co, Ni, Zn) spinel catalysts for toluene combustion: Elucidating the A-site replacement effect on the reactivity. *ChemCatChem* **2024**, *16*, e202301264. [\[CrossRef\]](#)
- Gul, E.M.; Dumanli, S.; Tugce, F.; Emek Moroydor, D. Cobalt aluminates prepared by ultrasonic-assisted synthesis using different surfactants for Congo red photocatalytic degradation. *Int. J. Mater. Res.* **2025**, *116*, 114–122. [\[CrossRef\]](#)
- Dumanli, S.; Tugce, F.; Moroydor Derun, E. Hydrothermal synthesis of CoAl_2O_4 spinel: Effect of reaction conditions on the characteristic and morphological features. *Int. J. Mater. Res.* **2022**, *113*, 1062–1070. [\[CrossRef\]](#)

17. Roelofsen, J.N.; Peterson, R.C.; Raudsepp, M. Structural Variation in Nickel Aluminate Spinel (NiAl_2O_4). *Am. Mineral.* **1992**, *77*, 522–528.
18. Roy, R.; Das, D.; Rout, P. A review of advanced mullite ceramics. *Eng. Sci.* **2022**, *18*, 20–30. [[CrossRef](#)]
19. Dondi, M.; Raimondo, M.; Zanelli, C. Clays and bodies for ceramic tiles: Reappraisal and technological classification. *Appl. Clay Sci.* **2014**, *96*, 91–109. [[CrossRef](#)]
20. Popović, J.; Tkalčec, E.; Gržeta, B.; Kurajica, S.; Schmauch, J. Cobalt incorporation in mullite. *Am. Mineral.* **2007**, *92*, 408–411. [[CrossRef](#)]
21. Acharjee, N.; Ganguly, S.; Sarangi, B.; Srivastava, A. A review of various ceramic pigment preparation and characterization methodologies for applications. *J. Aust. Ceram. Soc.* **2023**, *59*, 303–323. [[CrossRef](#)]
22. Molinari, C.; Conte, S.; Zanelli, C.; Ardit, M.; Cruciani, G.; Dondi, M. Ceramic pigments and dyes beyond the inkjet revolution: From technological requirements to constraints in colorant design. *Ceram. Int.* **2020**, *46*, 21839–21872. [[CrossRef](#)]
23. Mazza, D.; Delmastro, A.; Ronchetti, S. Co, Ni, Cu aluminates supported on mullite precursors via a solid-state reaction. *J. Eur. Ceram. Soc.* **2000**, *20*, 699–706. [[CrossRef](#)]
24. Taguchi, M.; Nakane, T.; Hashi, K.; Ohki, S.; Shimizu, T.; Sakka, Y.; Matsushita, A.; Abe, H.; Funazukuri, T.; Naka, T. Reaction temperature variations on the crystallographic state of spinel cobalt aluminate. *Dalton Trans.* **2013**, *42*, 7167–7176. [[CrossRef](#)] [[PubMed](#)]
25. Topas, Bruker AXS. V4. 2. *General Profile and Structure Analysis Software for Powder Diffraction Data-User Manual*; Topas, Bruker AXS: Karlsruhe, Germany, 2009.
26. Batyrow, M.; Ozturk, H. Surface Effect of Small Nanocrystals on the Accuracy of Structural Parameters Obtained by Pair Distribution Function Analysis. *Cryst. Growth Des.* **2025**, *25*, 2376–2391. [[CrossRef](#)]
27. Kimmel, G.; Sahartov, A.; Sadia, Y.; Porat, Z.; Zabicky, J.; Dvir, E. Non-monotonic lattice parameters variation with crystal size in nanocrystalline CeO_2 . *J. Mater. Res. Technol.* **2021**, *12*, 87–99. [[CrossRef](#)]
28. Vladioiu, R.; Mandes, A.; Dinca, V.; Matei, E.; Polosan, S. Synthesis of Cobalt–Nickel Aluminate Spinel Using the Laser-Induced Thermionic Vacuum Arc Method and Thermal Annealing Processes. *Nanomaterials* **2022**, *12*, 3895. [[CrossRef](#)] [[PubMed](#)]
29. Schneider, H.; Schreuer, J.; Hildmann, B. Structure and properties of mullite—A review. *J. Eur. Ceram. Soc.* **2008**, *28*, 329–344. [[CrossRef](#)]
30. Zayat, M.; Levy, D. Blue CoAl_2O_4 particles prepared by the sol-gel and citrate-gel methods. *Chem. Mater.* **2000**, *12*, 2763–2769. [[CrossRef](#)]
31. White, W.B.; DeAngelis, B.A. Interpretation of the vibrational spectra of spinels. *Spectrochim. Acta Part A Mol. Spectrosc.* **1967**, *23*, 985–995. [[CrossRef](#)]
32. Jin, X.H.; Gao, L.; Guo, J.K. The structural change of diphasic mullite gel studied by XRD and IR spectrum analysis. *J. Eur. Ceram. Soc.* **2002**, *22*, 1307–1311. [[CrossRef](#)]
33. Voll, D.; Angerer, P.; Beran, A.; Schneider, H. A new assignment of IR vibrational modes in mullite. *Vib. Spectrosc.* **2002**, *30*, 237–243. [[CrossRef](#)]
34. Perná, I.; Zárybnická, L.; Mácová, P.; Šupová, M.; Ševčík, R. Physico-mechanical properties of geopolymers after thermal exposure: Influence of filler, temperature and dwell time. *Constr. Build. Mater.* **2024**, *451*, 138893. [[CrossRef](#)]
35. D'Ippolito, V.; Andreozzi, G.B.; Bersani, D.; Lottici, P.P. Raman fingerprint of chromate, aluminate and ferrite spinels. *J. Raman Spectrosc.* **2015**, *46*, 1255–1264. [[CrossRef](#)]
36. Gingasu, D.; Oprea, O.; Marinescu, G.; Calderon Moreno, J.M.; Culita, D.C.; Preda, S.; Surdu, V.-A. Structural, Morphological, and Optical Properties of Single and Mixed Ni-Co Aluminates Nanoparticles. *Inorganics* **2023**, *11*, 371. [[CrossRef](#)]
37. McMillan, P.F.; Piriou, B. Raman Spectroscopic Studies of Silicate and Related Glass Structure: A Review. *Bull. Minéralogie* **2018**, *106*, 57–75.
38. Bouchard, M.; Gambardella, A. Raman microscopy study of synthetic cobalt blue spinels used in the field of art. *J. Raman Spectrosc.* **2010**, *41*, 1477–1485. [[CrossRef](#)]
39. Laguna-Bercero, M.A.; Sanjuan, M.L.; Merino, R.I. Raman spectroscopic study of cation disorder in poly- and single crystals of the nickel aluminate spinel. *J. Phys. Condens. Matter* **2007**, *19*, 186217. [[CrossRef](#)] [[PubMed](#)]
40. Lever, A.B.P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, The Netherlands, 1968.
41. Sakurai, T.; Ishigame, M.; Arashi, H. Absorption spectrum of Ni^{2+} ions in spinel. *J. Chem. Phys.* **1969**, *50*, 3241–3245. [[CrossRef](#)]
42. Lorenzi, G.; Baldi, G.; Di Benedetto, F.; Faso, V.; Lattanzi, P.; Romanelli, M. Spectroscopic study of a Ni-bearing gahnite pigment. *J. Eur. Ceram. Soc.* **2006**, *26*, 317–321. [[CrossRef](#)]
43. Ahmed, I.S.; Dessouki, H.A.; Ali, A.A. Synthesis and characterization of $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ nano ceramic pigments via a combustion route. *Polyhedron* **2011**, *4*, 584–591. [[CrossRef](#)]

44. Taran, M.N.; Koch-Muller, M.; Feenstra, A. Optical Spectroscopic Study of Tetrahedrally Coordinated Co^{2+} in Natural Spinel and Staurolite at Different Temperatures and Pressures. *Am. Mineral.* **2009**, *94*, 1647–1652. [[CrossRef](#)]
45. Andreozzi, G.B.; D'Ippolito, V.; Skogby, H.; Hålenius, U.; Bosi, F. Color Mechanisms in Spinel: A Multi-Analytical Investigation of Natural Crystals with a Wide Range of Coloration. *Phys. Chem. Miner.* **2018**, *46*, 343–360. [[CrossRef](#)]

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