Formation of Zn2sio4:Co2+ Solid Solutions in The Coo-Zno-Sio2 System: Phase Formation and Colorimetric Characteristics

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Abstract

The study examines the synthesis and color characteristics of Co-containing ceramic pigments in the CoO-ZnO-SiO2 system. Pigments were prepared from Zn(NO3)2·6H2O, Co(NO3)2·6H2O, and quartz sand (SiO2) by solid-state firing in air at 1050-1250 °C. X-ray diffraction confirmed willemite-type Zn_2SiO_4 as the main phase; at 1050 °C secondary phases (Co2SiO4, α-SiO2, and traces of ZnO) were detected, while their contribution decreased markedly with increasing temperature, indicating near-complete willemite formation at 1250 °C. Diffuse reflectance colorimetry (CIELAB, D65/10°) showed progressive darkening and saturation of the blue–violet color with temperature (L 58.57→33.43; b* -38.35→-48.65; C* 39.15→49.25) with an almost constant hue angle. The most stable and intense coloration was achieved at 1250 °C (ΔE* vs 1250 °C: 27.17 at 1050 °C and 9.78 at 1150 °C).*

Keywords: Ceramic pigment, willemite, Zn2SiO4, CoO-ZnO-SiO2, solid solution, solid-state synthesis, phase formation, X-ray diffraction (XRD), CIELAB.

Abbreviations: AUC, area under the curve; EGTA, ethylene glycol tetraacetic acid; NCX, Na^{+}/Ca^{2+} exchanger; PMCA, plasma membrane Ca^{2+}-ATPase; ROS, reactive oxygen species.

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1. Introduction

Cobalt-containing ceramic pigments continue to play a key role in ceramic coloration technologies because they can produce intense blue and blue-violet hues in glazes, enamels, and glass-ceramic coatings. Their effectiveness is primarily associated with the fact that Co2+ ions are among the most powerful chromophores in inorganic crystalline matrices and can generate strong coloration even at relatively low additions. Unlike many organic colorants and some less stable inorganic systems, cobalt pigments exhibit high thermal stability: they retain shade and color intensity during high-temperature firing and show resistance to thermochemical effects during sintering and interactions with molten glaze. Consequently, they remain in demand in modern ceramic manufacturing, where color reproducibility, stable quality, and process reliability across various firing regimes are essential [1-4].

The willemite matrix Zn2SiO4 is of considerable interest as a basis for ceramic pigments because it combines chemical durability, thermal stability, and good compatibility with glaze melts [5]. Willemite belongs to stable orthosilicates and, upon firing, forms a robust crystalline lattice capable of reliably incorporating chromophore ions (e.g., Co2+) as solid solutions, which provides reproducible coloration and reduces the risk of color fading. In addition, Zn2SiO4 has a high melting point of about ~1500 °C, making such pigments suitable for high-temperature processing and decreasing the likelihood of pigment degradation or dissolution during firing [6]. Another important practical advantage is the stability of the willemite phase in glazes: in a number of systems, willemite can form and/or remain stable in transparent frits, ensuring consistent coloration within glazed ceramic coatings [7-8].

Co2+ ions are effective chromophores in ceramic pigments because their coloration is governed by intra-ionic d-d transitions within the partially filled d shell. The position and intensity of the absorption bands–and therefore the resulting hue (blue, blue-violet, etc.)-depend strongly on the crystal-chemical environment of Co2+ (coordination geometry, polyhedron distortion, and crystal-field strength) as well as on the ion concentration, which can affect interactions between color centers and may change the distribution of Co2+ among crystallographic sites [9-11].

2. The Experimental Part

The component composition of the synthesized ceramic pigments was designed within the CoO-ZnO-SiO2 system. Water-soluble nitrates Zn(NO3)2·6H2O and Co(NO3)2·6H2O were used as sources of zinc and cobalt cations, while silica was introduced as SiO2 (quartz sand from the Dzheroy deposit). Batch calculations were performed according to the specified molar ratios, with the metal contents recalculated to the corresponding oxides ZnO and CoO, at a fixed SiO2 fraction ensuring the formation of the willemite silicate matrix.

During heat treatment, cobalt and zinc nitrates decomposed stepwise with the release of gaseous products (NO_x, H2O), forming reactive oxide species CoO/Co3O4 and ZnO, which subsequently reacted with silica. As a result of solid-state interaction, depending on the temperature and component ratio, the willemite phase Zn2SiO4 and its cobalt-containing solid solutions Zn2-xCoxSiO_4 were predominantly formed, governing the pigment coloration in the blue to blue-violet region. The synthesis was carried out in air in a muffle furnace at 1050-1250 °C with a 2 h holding time. After firing, the pellets were ground to a powder for subsequent characterization.

To determine the mineralogical composition of the synthesized pigment samples, X-ray diffraction (XRD) analysis was performed using a Shimadzu LABX XRD-6100 diffractometer with CuKα radiation (Ni β-filter, λ = 1.5418 Å, 30 mA, 30 kV). Data were collected in the ω/2θ mode at a scanning rate of 4°/min with a step size of 0.02° over the 2θ = 4-80° range.

The color characteristics of the samples were determined by diffuse reflectance spectrophotometry using a spectrophotometer–colorimeter, and the CIELAB (L*, a*, b*) coordinates were calculated under standard conditions D65/10°. To improve reproducibility, measurements were performed at least three times for each sample and the results were averaged. The samples were prepared as a compacted powder layer in a measuring cell.

Figure 1. shows the X-ray diffraction patterns of the samples fired in the temperature range of 1050-1250 °C with a soaking time of 180 min.

According to the XRD results, at 1050 °C the formation of the willemite phase (Zn_2SiO_4) is observed, which is confirmed by the presence of the most intense and characteristic reflections with interplanar spacings d ≈ 0.435, 0.349, 0.284, 0.264, and 0.232 nm. In addition, reflections corresponding to olivine Co_2SiO_4 (d ≈ 0.278, 0.252, 0.246, 0.175, and 0.149 nm), α-quartz SiO_2 (d ≈ 0.334, 0.245, 0.228, and 0.213 nm), as well as trace amounts of ZnO (d ≈ 0.245, 0.190, and 0.148 nm) are detected, indicating that the solid-state reaction is not yet complete.

As the temperature increases to 1150 °C, the positions of the main willemite reflections remain nearly unchanged, indicating preservation of the Zn_2SiO_4 crystal structure, while the intensities of the reflections associated with secondary phases decrease.

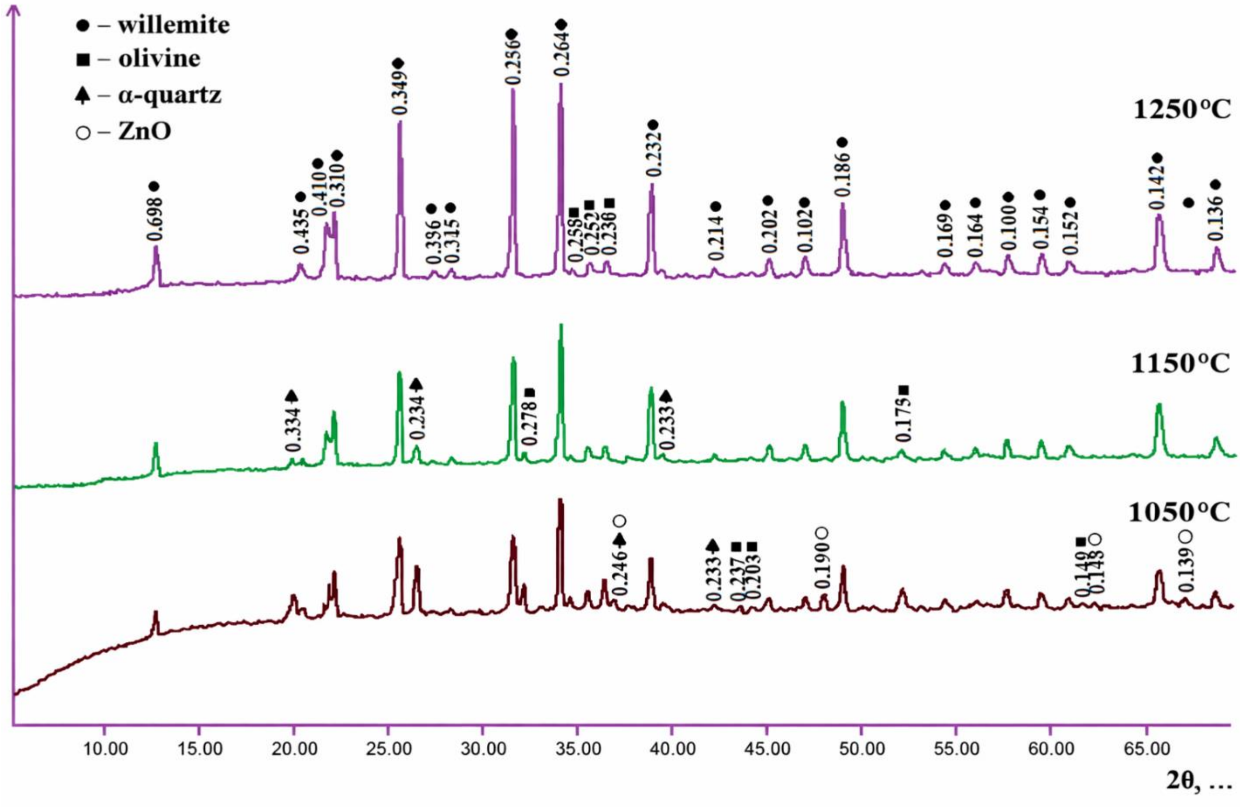

Figure 1. XRD patterns of the synthesized pigments

(1050-1250 °C, 180 min).

At 1250 °C, a pronounced increase in the intensity of willemite peaks is observed together with a reduction in the amount of secondary phases; only trace amounts of olivine are retained. This effect is attributed to the intensification of willemite formation due to the interaction of free quartz with zinc oxide, resulting in the nearly complete formation of the crystalline pigment phase with a willemite-type structure.

After the X-ray diffraction analysis, the color parameters of the synthesized pigments were determined in the CIELAB system. It was established that increasing the firing temperature from 1050 to 1250 °C leads to a systematic change in the L*, a*, and b* coordinates, reflecting variations in the pigments' lightness, saturation, and hue. Overall, as the temperature increases, the coloration becomes more stable, which is associated with an increased fraction of the crystalline willemite phase and a reduced amount of accompanying phases.

Table. CIELAB coordinates and derived parameters for samples synthesized at 1050-1250 °C (holding time 180 min).

Sample	T, °C	L*	a*	b*	C*	h°,°	ΔE* (к Р-1250)	Hue
$Co_{0.5}Zn_{1.5}SiO_4$	1050	58,57	7,89	-38,35	39,15	281,63	27,17	
$Co_{0.5}Zn_{1.5}SiO_4$	1150	42,65	7,75	-45,40	46,06	279,69	9,78	
$Co_{0.5}Zn_{1.5}SiO_4$	1250	33,43	7,65	-48,65	49,25	278,94	0,00	

According to the table data, increasing the pigment synthesis temperature from 1050 to 1250 °C results in a pronounced change in color characteristics in the CIELAB system. With increasing temperature, the lightness L* decreases significantly from 58.57 to 33.43, which corresponds visually to a transition from a lighter to a darker and "deeper" blue tone. At the same time, the b* coordinate becomes more negative (-38.35 → -48.65), indicating an enhanced blue component, whereas the a* values remain nearly constant (7.89 → 7.65), i.e., the red–green component changes only slightly.

The calculated derived parameters confirm an increase in color intensity: the chroma C* rises from 39.15 to 49.25, which agrees with the visually observed increase in saturation in the powder photographs. The hue angle h° changes only slightly (281.63-278.94°), indicating that the overall hue remains in the blue–violet region and that the main effect of temperature is associated with changes in lightness and saturation rather than a shift in hue. The color difference relative to the 1250 °C sample amounts to ΔE* = 27.17 (for 1050 °C) and 9.78 (for 1150 °C), demonstrating a noticeable color difference at lower temperatures and confirming that the most stable and saturated tone is achieved at 1250 °C.

3. Conclusion

Ceramic pigments with a willemite-type Zn2SiO4 structure were synthesized in the CoO-ZnO-SiO2 system (1050-1250 °C, 180 min). XRD results show an increasing fraction of willemite and a decreasing contribution of Co2SiO4, α-SiO2, and ZnO impurities with increasing temperature. The CIELAB data indicate a darker and more saturated color (L* 58.57→33.43; b* -38.35→-48.65; C* 39.15→49.25) with nearly unchanged hue (h° ≈ 281.6-278.9°); the most stable and intense blue-violet tone is achieved at 1250 °C (ΔE* vs 1250 °C: 27.17 at 1050 °C and 9.78 at 1150 °C).

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