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Synthesis and color characteristics of willemite-structured ceramic pigments using microsilica

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Kadyrova Zulayho Raimovna, Usmanov Khikmatulla Lutpullayevich, Eminov Azizjon Ashrapovich, Tairov Saidamir Saidmalikovich, Tairov Saidamir Saidmalikovich, & Kodirova Umida Aslonovna. (2025). Synthesis and color characteristics of willemite-structured ceramic pigments using microsilica. The American Journal of Applied Sciences, 7(8), 154–158. https://doi.org/10.37547/tajas/Volume07Issue08-11

Kadyrova Zulayho Raimovna

Doctor of Chemical Sciences, Prof. Institute of General and Inorganic Chemistry of Academy of Sciences of the Republic of Uzbekistan, Uzbekistan

Usmanov Khikmatulla Lutpullayevich

Doctor of Sciences, Prof. Institute of General and Inorganic Chemistry of Academy of Sciences of the Republic of Uzbekistan, Uzbekistan

Eminov Azizjon Ashrapovich

Doctor of Sciences, chief researcher, Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Uzbekistan

Tairov Saidamir Saidmalikovich

PhD, senior researcher, Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Uzbekistan

Kodirova Umida Aslonovna

PhD, senior researcher, Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Uzbekistan

Abstract: The development of ceramic pigments with a willemite structure through the utilization of industrial by-products, such as microsilica, represents a promising and sustainable research direction. In this study, pigments in the ZnO–CoO–SiO2 system were synthesized using microsilica as a silica source. The influence of raw material composition and firing conditions on phase formation, crystal structure, and color characteristics of the pigments was investigated. X-ray diffraction (XRD) analysis confirmed the formation of willemite-based solid solutions. The colorimetric properties were evaluated in the CIE Lab* system, demonstrating that the obtained pigments exhibit stable blue and violet hues with high thermal and

chemical resistance. The results highlight the potential of microsilica recycling for the production of cost-effective, environmentally friendly ceramic pigments suitable for glaze and ceramic applications.

Keywords: Ceramic pigment; blue color; willemite; microsilica; isomorphic substitution; solid-state synthesis; physico-technical properties.

Introduction: The development of the ceramic industry requires the use of thermally resistant and chemically stable pigments capable of retaining their color and structure during high-temperature firing. As noted in [1], in modern ceramic production, the main components are synthetic pigments, which include colored metal oxides as well as complex compounds with spinel, mullite, garnet, willemite, corundum, sillimanite, and other structures. According to [2], such ceramic pigments are widely used in the production of colored glazes, in the formation of color shades of mastics, as well as in underglaze and overglaze heat-resistant ceramic paints.

It should be noted that one of the effective approaches to modifying the color characteristics of willemite compounds is the introduction of transition metal ions through the mechanism of isomorphic substitution. The substitution of Zn^{2+} ions with Co^{2+} makes it possible to obtain pigments with an intense blue coloration, suitable for use in ceramic glazes and coatings [3–5].

It is well established [6–9] that ceramic pigments are traditionally produced by the solid-state synthesis method from chemically pure reagents at high temperatures (1300–1400 °C). In order to expand the color palette and reduce the synthesis temperature parameters, alternative raw material sources, including abundant natural materials and industrial waste, have been actively investigated in recent years. However, the use of natural mineral raw materials and industrial by-products not only reduces the cost of pigment production but also contributes to the improvement of the environmental situation [10].

In this regard, an urgent task is the low-temperature synthesis of ceramic pigments based on zinc silicate (Zn2SiO4) with isomorphic substitution of Zn2+ ↔ Co2+, employing microsilica, a technogenic by-product generated during ferrosilicon production at JSC “Uzmetkombinat.” The present work is focused on studying the structure formation of crystalline phases in the synthesized ceramic pigments and their color characteristics, as well as assessing the potential for using this industrial by-product in their synthesis.

THE EXPERIMENTAL PART

In the course of the study, the chemical and mineralogical compositions, as well as the physico-technical characteristics of microsilica from JSC “Uzmetkombinat,” were investigated.

Microsilica is a technogenic ultrafine powder product formed during the high-temperature gas-phase condensation of silicon oxide (SiO2) vapors in dry gas-cleaning units during ferrosilicon production [15].

According to the results of chemical analysis, the content of silicon dioxide (SiO2) in microsilica is not less than 92 wt.%, which confirms its high purity. The particle size distribution is characterized by a high degree of fineness, with the majority of particles having a size below 1 μm, confirming its ultrafine nature. The chemical composition and physico-technical characteristics of microsilica are given in Table 1.

Table 1.
Chemical composition and physico-technical characteristics of microsilica from JSC “Uzmetkombinat”

Oxide content, wt.%								Moisture, %	Bulk density, g/cm^3	Fractional composition, μm
SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	MnO	SO_3	LOI	<2.0	0.3-0.4	<1.0
>92.0	<0.9	<1.0	<0.5	<0.5	<0.5	<0.6	5.0			
*Includes hygroscopic, constitutional, and crystallized water, organic and volatile substances, and CO_2.										

To identify the crystalline phases present in microsilica samples, X-ray diffraction (XRD) analysis was employed

Fig. 1.

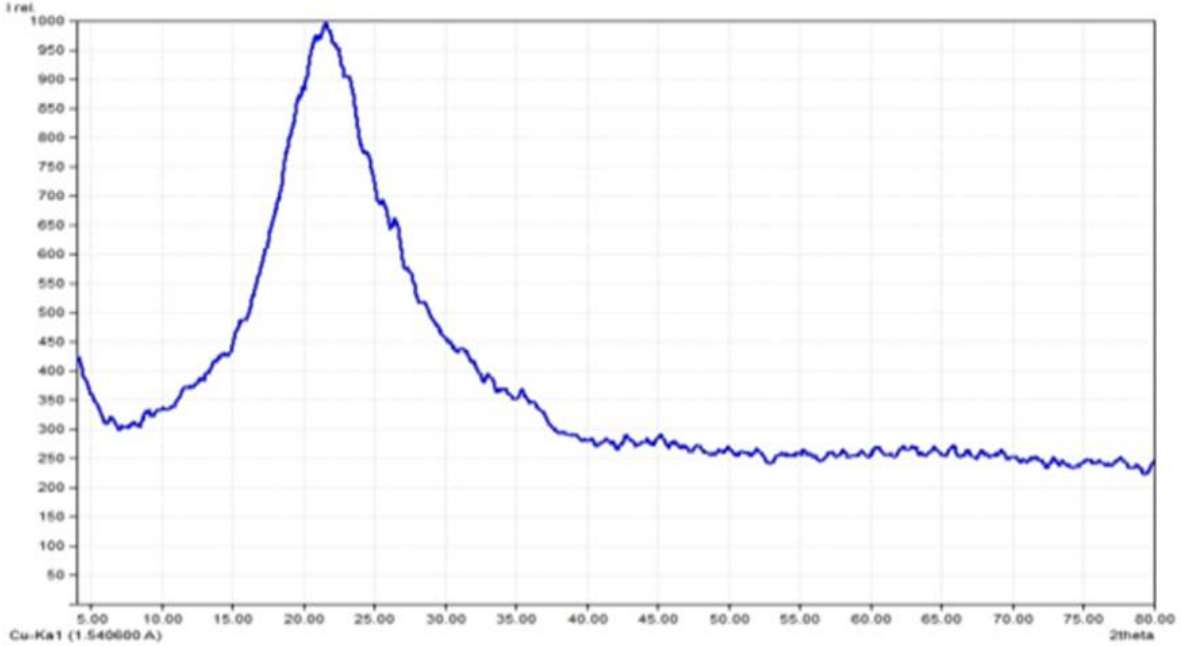

Fig. 1. X-ray diffraction pattern of microsilica from JSC "Uzmetkombinat".

The results of X-ray diffraction analysis showed that microsilica consists mainly of an amorphous phase. According to the literature, the ultrafine amorphous form of silica is more chemically reactive than the crystalline form.

For the synthesis of ceramic pigments with a willemite structure, a series of compositional formulations was developed with the general formula Zn2-xCoxSiO4, varying the cobalt content within the range x = 0.2–1.8. The chemical reagents used (ZnO, CoO) and microsilica were pre-dried at 110 °C to constant weight in order to remove moisture and stabilize the mass of the components. After drying, the components were weighed with high accuracy on an analytical balance according to the calculated batch compositions.

Homogenization of the batch was carried out by dry mixing in an agate mortar. The prepared batch compositions were fired at 1150 °C in a muffle furnace, with a dwell time of 180 minutes at the maximum temperature. The crystalline phase composition of the fired samples was determined by X-ray diffraction Fig. 2.

The component compositions and color characteristics of the obtained ceramic pigment samples synthesized at 1150 °C with a holding time of 180 minutes are presented in Table 2.

Table 2.
Component compositions and color characteristics of the obtained pigment samples synthesized at 1150 °C with a dwell time of 180 min.

Sample	Pigment composition (wt.%)			CIE Lab* coordinates			Visual color
	ZnO	CoO	Microsilica	*L**	*a**	*b**	
Zn_2SiO_4	73.0	-	27.0	-	-	-	white
$Zn_{1.8}Co_{0.2}SiO_4$	65.70	7.30	27.0	38.57	7.89	-38.35	
$Zn_{1.6}Co_{0.4}SiO_4$	58.40	14.60	27.0	39.08	7.65	-44.42	
$Zn_{1.4}Co_{0.6}SiO_4$	51.10	21.90	27.0	38.65	7.75	-45.40	
$Zn_{1.2}Co_{0.8}SiO_4$	43.80	29.20	27.0	38.04	7.95	-46.27	
$Zn_{1.0}Co_{1.0}SiO_4$	36.50	36.50	27.0	37.56	7.89	-47.26	

$Zn_{0.8}Co_{1.2}SiO_4$	29.20	43.80	27.0	36.43	7.65	-48.65	
$Zn_{0.6}Co_{1.4}SiO_4$	21.90	51.10	27.0	35.54	6.43	-49.62	
$Zn_{0.4}Co_{1.6}SiO_4$	14.60	58.40	27.0	34.78	6.89	-50.24	
$Zn_{0,2}Co_{1,8}SiO_4$	7,30	65,70	27,0	33,56	5,98	-51,25	
$Co_{2,0}SiO_4$	-	73,0	27,0	32,44	5,24	-52,32	

As a result, it was established that the obtained ceramic pigment with a willemite structure of composition Zn2SiO4 exhibits a white color with slight grayish shades and crystallizes in the hexagonal system. Samples with partial isomorphic substitution of Zn2+ ions by Co2+, in the compositional range from Zn1.8Co0.2SiO4 to Zn1.0Co1.0SiO4, are characterized by a color palette varying from blue to dark blue, with the corresponding b* color coordinate values ranging from –45.40 to –47.26. Pigments with a higher cobalt content, from Zn0.8Co1.2SiO4 to Co2.0SiO4, acquire intense violet-blue and violet shades, demonstrating a similar chromatic tendency in the coordinates of the CIE Lab* color space.

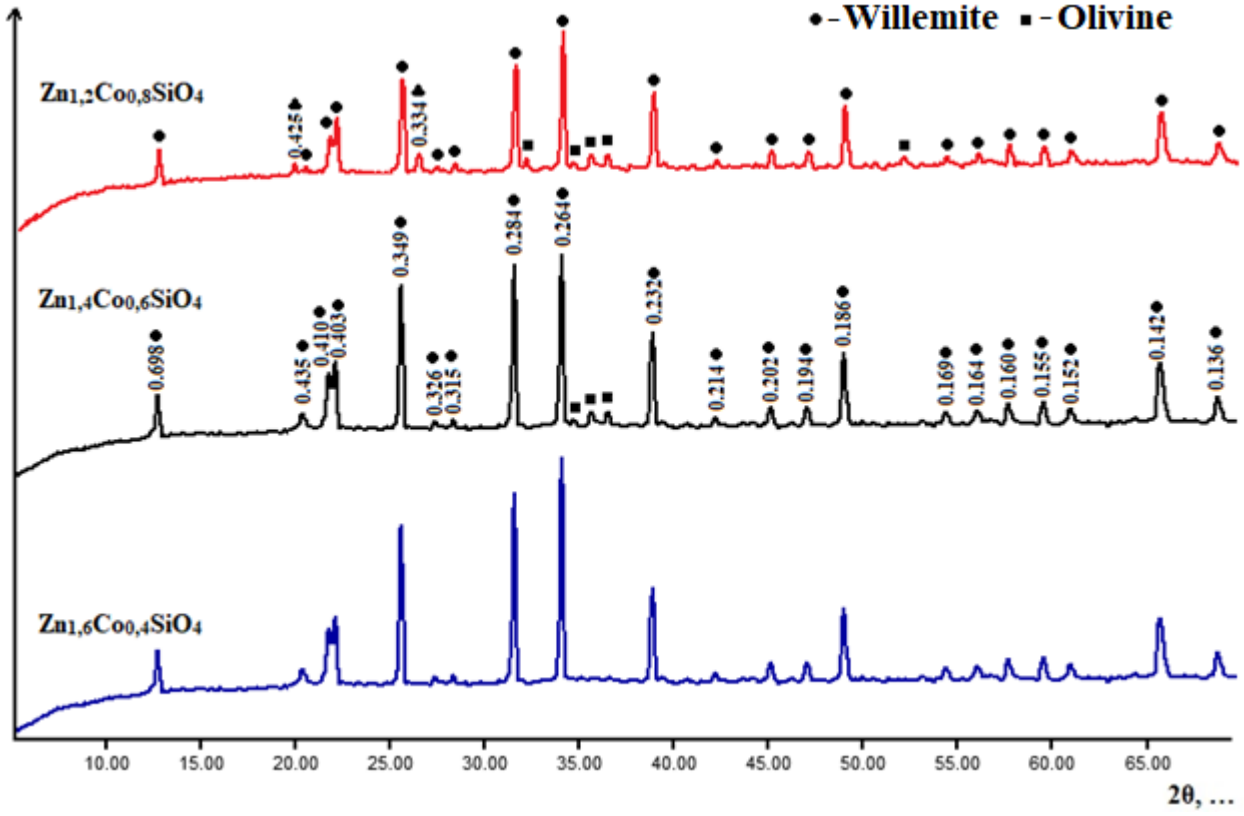

Fig. 2. X-ray diffraction patterns of the synthesized pigment samples.

The results of X-ray diffraction analysis showed that when cobalt is introduced in amounts up to 0.4 mol into the mixture of zinc and cobalt silicates (Zn2-xCoxSiO4), a limited series of solid solutions with a willemite structure is formed. These are characterized by diffraction maxima with interplanar spacings d = 0.698, 0.410, 0.403, 0.349, 0.326, 0.315, 0.284, 0.264, 0.232, 0.214, 0.202, 0.186, 0.169, 0.164, 0.160, 0.155, 0.152, 0.142, and 0.136 nm. With an increase in cobalt content above 0.4 mol, the pigment structure becomes more complex due to the formation of several crystalline phases, including willemite, olivine (d = 0.278, 0.258, 0.252, 0.246, 0.175 nm), as well as a minor amount of α-quartz (d = 0.334, 0.245, 0.228 nm)

CONCLUSION

Thus, the obtained research results demonstrated that the use of microsilica contributes to lowering the synthesis temperature of ceramic pigments to 1150 °C. Samples with compositions Zn1.6Co0.4SiO4, Zn1.4Co0.6SiO4, and Zn1.2Co0.8SiO4 provide an intense and saturated blue coloration. X-ray diffraction analysis confirmed the formation of the willemite

crystalline structure, while higher cobalt oxide contents led to the formation of additional phases such as olivine and α-quartz. These pigments exhibit color characteristics comparable to imported spinel pigments and can be considered a promising and economically viable alternative for application in the ceramic and glass industries.

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