COLOR CHARACTERISTICS AND PROPERTIES OF HIGH-TEMPERATURE CERAMIC PIGMENTS, OBTAINED BY UTILIZATION OF BIO-WASTE

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Abstract—The subject of this study are high-temperature pigments from the aluminum-silicon system. For their preparation, both pure starting raw materials and biowaste were used – ash from oxidized rice husks, containing 94.47% SiO_2. Cobalt, copper and nickel oxides were introduced as colorants in the batches. The quantities of the materials were weighed with an accuracy of 0.1 g, then they were mixed and homogenized dry in a Pulverisette-6 planetary mill. The high-temperature firing of the pigments was carried out in a NaberTherm furnace, in an air atmosphere at a final temperature of 1450°C, with a 2-hour isothermal hold. The X-ray phase analysis performed shows that the main phases in all compositions are mullite and corundum. It has been proven that when NiO is introduced into the batches in both series, nickel spinel is also obtained, i.e. nickel shows a strong tendency to form spinel. It has been established that copper ions, in turn, tend to form solid solutions with mullite. Some of them are included in the crystal lattice of mullite, defect it and thus promote the formation of mullite. In terms of color characteristics, the best indicators are those of the compositions with the chromophore cobalt. This chromophore ensures the production of pigments with a saturated blue color. In pigments obtained with the addition of oxidized rice husks as a source of SiO_2, the amount of blue color is $b^* = -28.2$, and in pigments obtained from pure raw materials, the amount of blue color is $b^* = -31.1$.

Keywords: Ceramic pigments, Bio-waste utilization, Rice husk ash, High-temperature synthesis, Color characteristics

I. INTRODUCTION

Ceramic pigments are crystalline inorganic materials responsible for imparting stable and reproducible coloration to glazes, enamels, and ceramic bodies [1-4]. To perform effectively in industrial applications, these pigments must meet a stringent set of criteria. Essential properties include high color intensity, which allows for strong coloration with minimal quantities, and excellent covering power to ensure a dense, uniform application [1,5]. Furthermore, they must exhibit outstanding thermal stability to withstand the high temperatures of ceramic firing processes, as well as chemical inertness to prevent reactions with the ceramic body, glaze or other components [6]. Among the various systems investigated, those based on aluminosilicates are of significant interest due to the exceptional stability of the mullite phase ($3Al_2O_3 \cdot 2SiO_2$). Mullite is a high-performance refractory material, relatively rare in nature and typically synthesized for technical applications. It is widely utilized in traditional ceramics, most commonly produced via solid-state reactions from raw materials such as clays, kaolins, and oxides, though advanced methods like sol-gel and chemical precipitation are also employed.

The SiO_2–Al_2O_3 system provides a robust host matrix, where mullite and corundum act as the primary crystalline phases, ensuring high thermal and structural integrity [7]. This matrix is highly suitable for the incorporation of transition-metal ions, which act as chromophores. The incorporation of transition-metal oxides such as cobalt, nickel, and copper enables the development of intense and varied colors. These elements produce distinct hues- cobalt yields stable blues, nickel imparts green to gray tones, and copper contributes turquoise to green shades- through strong crystal-field effects within the host structure. The stabilization of these chromophores often occurs in secondary crystalline phases, such as spinels, which form alongside the primary mullite matrix. Some of research has focused on developing mullite–corundum-based pigments through solid-state synthesis routes, which

allow for controlled crystallization of both the host and chromophore-containing phases. A key challenge in this process is optimizing the reaction pathway to maximize mullite formation while ensuring the effective integration of chromophores into the coloring phases. In this context, the choice of raw materials, particularly the silica source (e.g., amorphous silica or rice husk ash), plays a critical role in determining the reactivity, final phase composition, and optical properties of the synthesized pigments.
Resently, many scientists are working on the problem of obtaining ceramic pigments from industrial waste [5, 8-12]. Costa et al. [10] report the preparation of ceramic pigments using Al-rich sludge generated in the wastewater treatment unit of an anodising or surface coating industrial plant, and a galvanizing sludge from the Cr/Ni plating process. Bessmertnyi V.S [11] obtained ceramic pigments from Vanadium Production Waste. Paz-Gómez, D.C., [12] et al successfully obtained dark pigments were from the mixtures of T: ES: Co3O4, T: MS and T: IG.
The present study focuses on the synthesis and characterization of ceramic pigments based on SiO_2–Al_2O_3, from pure and waste starting materials (rice husk), doped with chromophores of Co, Ni and Cu oxides. The pigments were prepared by solid-state reaction at high temperature and systematically evaluated with respect to their crystalline phase composition, microstructure and colorimetric properties. Particular attention is paid to the role of mullite as the main host phase and to the formation of secondary phases containing chromophores, which directly determine the color characteristics of the pigments in ceramic applications.

II. MATERIALS AND METHODS

X-ray analysis. The X-ray analysis was performed using an automatic powder X-ray diffractometer, Bruker D8 Advance with CuKα radiation (Ni filter) and registration by a LynxEye solid-state detector. The X-ray spectrum was recorded in the angular range from 5.3 to 80° 2θ with a step of 0.03° 2θ and a counting time of 52.5 sec/step. Qualitative phase analysis was performed using the PDF-2(2009) database of the International Commission on Diffraction Data (ICDD). Quantitative analysis was performed using the Topas 2 software.
Spectrophotometric color measurement. The color determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color.
Microscopic analysis. Microphotographs were taken with a stereo microscope ZEISS SteREO Discovery.V8

A. Materials

Al_2O_3 and SiO_2 were employed as the base materials. Ceramic pigments from the Al_2O_3–SiO_2 system were synthesized via the solid-state sintering method. Rice husk ash (RHA), an agricultural waste product, was used as a silica source. For comparison, additional pigment samples were prepared using chemically pure raw materials. Silica was incorporated into the ceramic compositions either as amorphous $SiO_2 \cdot nH_2O$ (in compositions MP4-5, MP5-5, MP6-5, as listed in Table 2) or as RHA obtained by burning rice husk in air (compositions MPR4-5, MPR5-5, MPR6-5).

Table 2 shows the oxides contained in the oxidized rice husk powder. The amount of SiO2 was determined using the accelerated determination method for SiO_2 in quartz materials; the qualitative composition of the other impurity oxides was determined using emission spectral analysis, and the quantitative composition was determined using chemical analysis methods.

In our experiments, we used rice husk powder burned at 650 °C in an air environment, as the X-ray analysis showed that the powder obtained at this temperature is amorphous, i.e., more reactive. The composition of the oxidized flakes is shown in Table 1.

TABLE I COMPOSITION OF OXIDIZED RICE HUSK POWDER

Component	Quantity, %
SiO_2	94,47
CaO	1,62
Fe_2O_3	1,36
MgO	1,08
Al_2O_3	0,98
MnO_2	0,49
Cu	traces
Pb	traces

The color of most natural and synthetic mineral substances is typically associated with the presence of d- or f-block elements in their composition. For this reason, Co^{2+}, Cu^{2+}, and Ni^{2+} ions were selected and introduced into the system as chromophores. These elements are characterized by unfilled d- or f-electron orbitals, which facilitate electronic transitions when exposed to light energy. In all compositions, the chromophore content was maintained at 5%. The colorant elements were added in the form of Co_2O_3, CuO, or NiO, respectively.

III. EXPERIMENTAL , RESULTS AND DISCUSSION

Table 2 presents the composition of the starting mixtures. For their preparation, both pure starting raw materials and bio-waste – ash from oxidized rice husks containing 94.47% SiO_2 were used. The quantities of the materials were weighed with an accuracy of 0.1g, then mixed and homogenized dry in a Pulverisette-6–6 planetary mill. The high-temperature firing of the pigments was carried out in a NaberTherm high-temperature furnace, Germany, in an air atmosphere in covered porcelain crucibles at a final temperature of 1450 ^{0}C, with a 2-hour isothermal hold.

TABLE IIIII COMPOSITION SYNTHESIZED FROM PURE MATERIALS AND RHA AT 1450 °C, WITH A 2-HOUR ISOTHERMAL HOLD

Sample	**Composition**		**Chromophore, 5%**
MP4-5	Al_2O_3	$SiO_2.nH_2O$	Co
MP5-5	Al_2O_3	$SiO_2.nH_2O$	Cu
MP6-5	Al_2O_3	$SiO_2.nH_2O$	Ni
MPR4-5	Al_2O_3	RHA	Co
MPR5-5	Al_2O_3	RHA	Cu
MPR6-5	Al_2O_3	RHA	Ni

The resulting pigments were characterized using X-ray structural analysis and microscopic analysis. Their color was measured with a spectrophotometer

TABLE IVVVI UNITS FOR MAGNETIC PROPERTIES

Sample	**Corundum (mass%, cryst. size)**	**Cristobalite (mass%, cryst. size)**	**Mullite (mass%, cryst. size)**	**$CoAl_2O_4$ (mass%, cryst. size)**	**$NiAl_2O_4$ (mass%, cryst. size)**	**CuO (mass%, cryst. size)**
MP4-5	19% 120nm	4% 20nm	73% 130nm	4% 113nm	-	-
MP5-5	16% 108nm	-	82% 140nm	-	-	2% 29nm
MP6-5	32% 127nm	8% 40nm	52% 128nm	-	8% 88nm	-
MPR4-5	24% 144nm	-	71% 159nm	5% 156nm	-	-
MPR5-5	56% 154nm	-	42% 136nm	-	-	2% 46nm
MPR6-5	31% 125nm	-	59% 138nm	-	10% 101nm	-

X-ray phase analysis. The figures below show the results of the X-ray analysis of the obtained pigments, and Table 3 gives the phase and granulometric composition of pigments with the composition MP4-5 ÷ MP6-5 and MPR4-5 ÷ MPR6-5

Figures 1 to 6 present comparative diffractograms of the pigments containing the respective chromophores

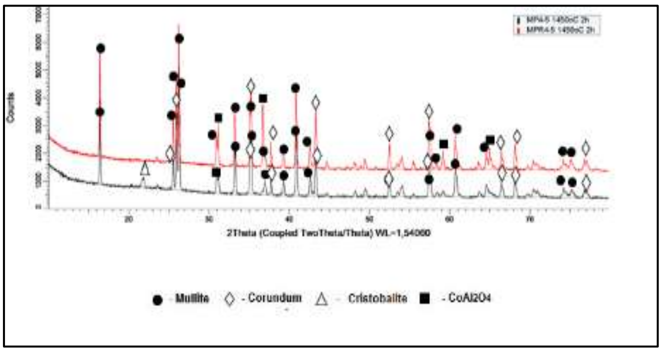


Fig. 1 Diffractogram of pigments containing the chromophore cobalt

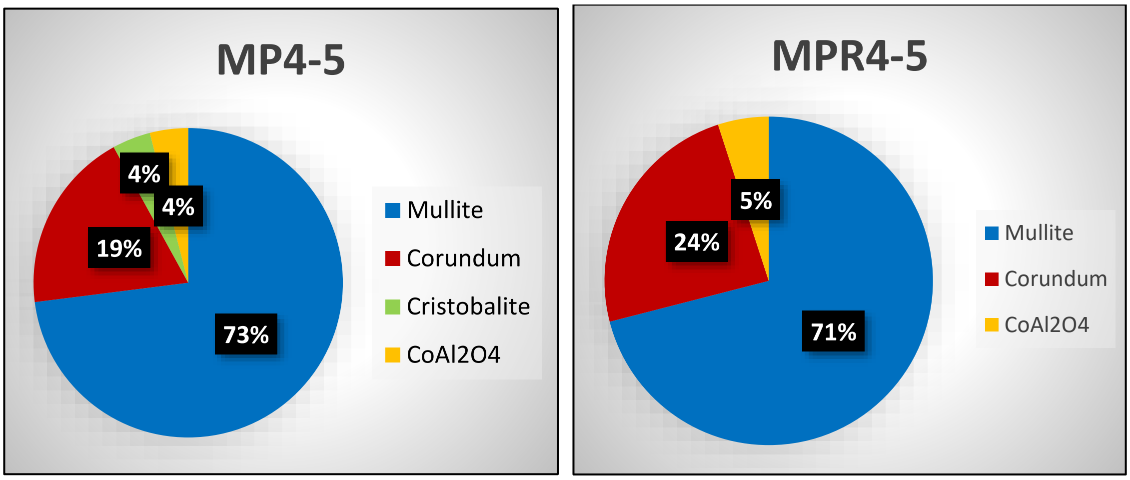


Fig. 2 Quantitative analysis of pigments containing the cobalt chromophore - MP4-5 and MPR4-5

The diffractograms show that the main phases in sample MP4-5 are mullite - 73%, corundum - 19%, cristobalite -4%, $CoAl_2O_4$ (cobalt aluminate spinel) - 4%. The MP4-5 sample demonstrates a complex multiphase structure dominated by mullite, which constitutes 73% of the total composition. Mullite is very stable at high temperatures and is the desired phase in mullite–corundum pigments. Its needle-like microstructure improves mechanical strength and thermal shock resistance in mullite materials. Mullite incorporation usually enhances the stability of color because it acts as a robust crystalline matrix for chromophores.

Corundum (α-Al_2O_3) is also stable, but unlike mullite, it does not incorporate the chromophores well. Corundum, making up 19% of the phases, serves as a reinforcing secondary phase. Its presence contributes to increased hardness and chemical resistance, enhancing the durability of the pigments. In addition, cristobalite, a polymorph form of silica (SiO_2), accounts for 4% of the sample. The presence of cristobalite can influence the thermal expansion behavior of the material due to its unique phase transitions at elevated temperatures. The incorporation of $CoAl_2O_4$ (4) may also affect the microstructure by interacting with the aluminosilicate matrix.

Sample MPR4 contains 71% mullite ($3Al_2O_3{\cdot}2SiO_2$), 24% corundum (α-Al_2O_3), and 5% $CoAl_2O_4$ (cobalt aluminate spinel). The high mullite content confirms a well-sintered aluminosilicate material. Corundum presence shows unreacted or secondary alumina phase, which might influence properties like hardness or translucency. The $CoAl_2O_4$ content is typical for a coloring pigment amount.

Diffractograms of pigments containing the chromophore copper are presented in Figures 3 and 4.

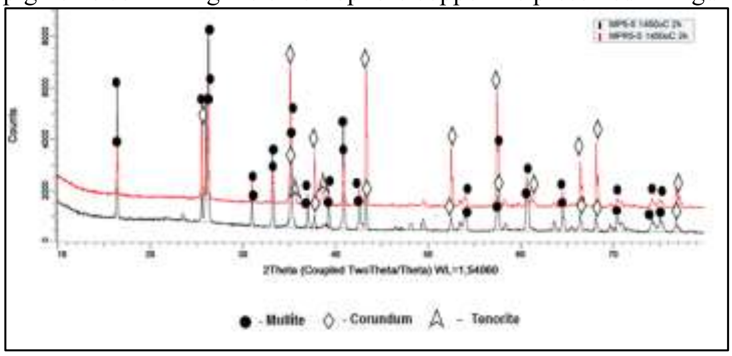


Fig. 3 Diffractogram of pigments containing the chromophore copper

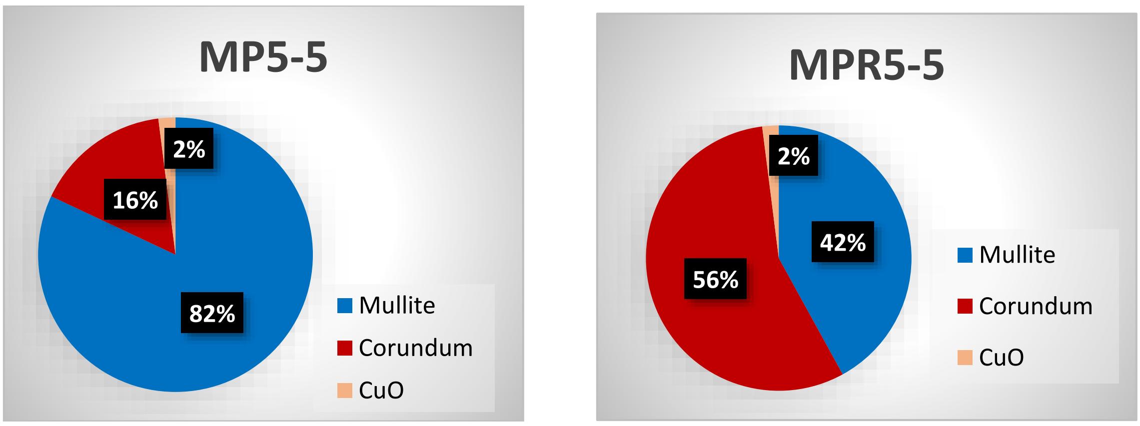


Fig. 4 Quantitative analysis of pigments containing the copper chromophore - MP5-5 and MPR5-5

According to the quantitative phase analysis of sample MP5-5, given in Figure 4, mullite represents the main phase - 82% of the total composition. Corundum, whose content in the pigments is 16%, is identified as a secondary phase, while copper oxide (CuO) is present in a minor amount of approximately 2%. The predominance of mullite guarantees high thermal stability and mechanical strength, which is consistent with the expected phase formation in aluminosilicate systems subjected to high temperature treatment. The presence of mullite usually improves color stability because it acts as a stable crystalline matrix for the Cu chromophore, and it, in turn, forms solid solutions with mullite.
The phase composition analysis reveals noticeable differences between the MP5-5 and MPR5-5 samples. While an MP5-5 sample consists mainly of mullite, the MPR5-5 sample shows a significant change, with corundum becoming the dominant phase (56%), mullite being reduced to 42%, and the amount of unreacted CuO being again 2%. The presence of a residual 2% CuO suggests that a part of the copper ions is incorporated into the mullite, forming a solid solution.

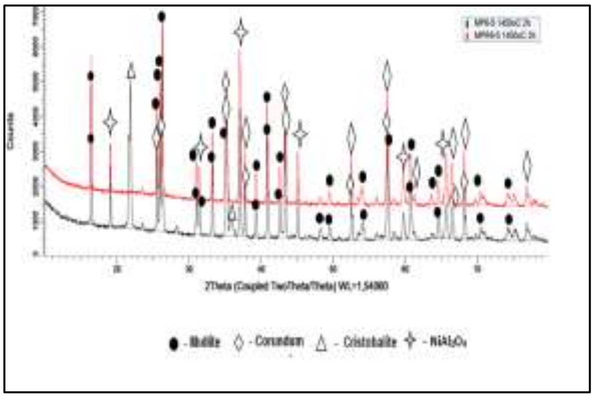


Fig. 5 Diffractogram of pigments containing the chromophore nickel

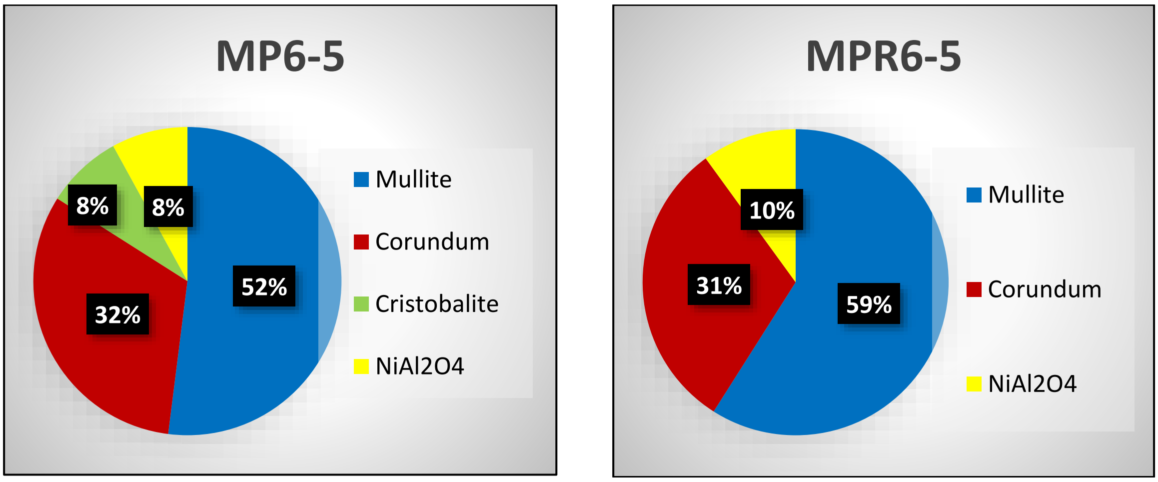


Fig. 6 Quantitative analysis of pigments containing the nickel chromophore – MP6-5 and MPR6-5

The main phases in the composition MP6-5 are mullite - 52%, corundum - 32%, cristobalite - 8% and $NiAl_2O_4$ (nickel aluminate spinel) - 8%. As already noted above, mullite is very stable at high temperatures and is the desired phase in mullite-corundum pigments. Its acicular microstructure improves mechanical strength and thermal shock resistance in ceramics. The relatively high fraction of corundum means that some Al_2O_3 has not completely reacted with SiO_2 → incomplete mullitization. This can reduce the effectiveness of the pigment, but corundum still contributes to the hardness and opacity in ceramic glazes. Cristobalite is probably formed due to excess silica or incomplete reaction. In general, cristobalite is an undesirable phase because it undergoes phase transitions with volume changes that can affect the mechanical properties of the pigment. However, in small amounts, it does not drastically impair the function of the pigment. Nickel aluminate spinel is usually responsible for the appearance of greenish to gray tones. Its presence confirms the reaction of Ni^{2+} ions with Al_2O_3, stabilizing the color. Even in small amounts, spinels strongly influence the optical properties of the pigment.
In an MPR6-5 sample, the phase composition consists of 59% mullite, 31% corundum, and 10% $NiAl_2O_4$ (nickel aluminate spinel). In this composition, the reaction between SiO2 from RHA and corundum has proceeded to a more complete degree, and no residual SiO2 in the form of cristobalite is observed. The similar amount of $NiAl_2O_4$ in compositions MPR6-5 and MP6-5 (respectively 10% and 8%) suggests color properties should be similar between the two samples, which is confirmed by tables 3 and 4, but MPR6-5 likely has better structural and thermal stability.

Color determination. The results of the determined color parameters of the synthesized pigments from pure or waste raw materials, with chromophores - Co, Cu, and Ni ions in an amount of 5%are presented in Tables 4 and 5.

TABLE VIIV COLOR CHARACTERISTICS OF PIGMENTS WITH COMPOSITIONS MP 4–5 ÷ MP 6–5

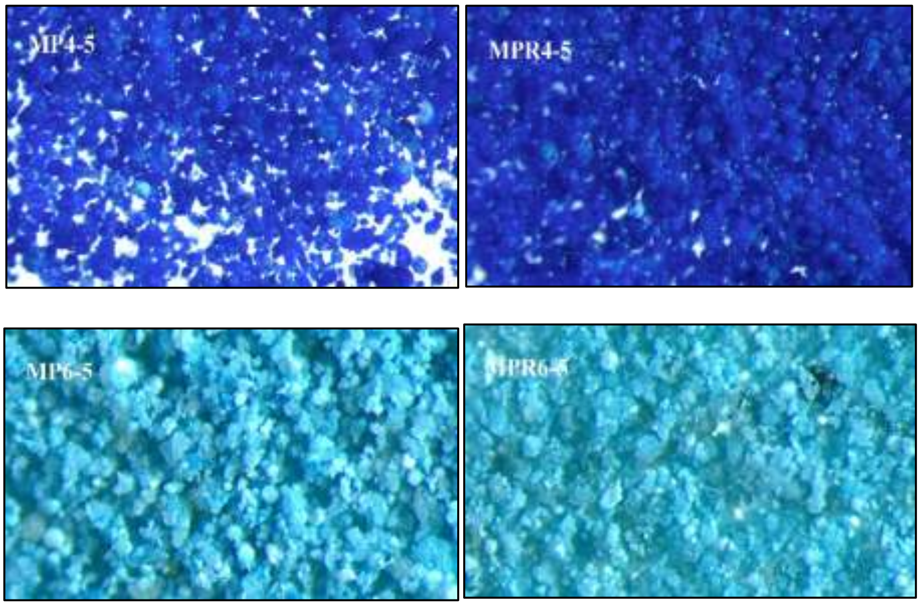
№	**Composition**	**T, °C**	**Colour**	**L***	**a ***	**b ***
1	MP4 – 5	1450		34,5	2,4	**-28,2**
2	MP5 – 5	1450		50,3	-3,7	9,9
3	MP6 - 5	1450		69,8	-17,1	-4,5

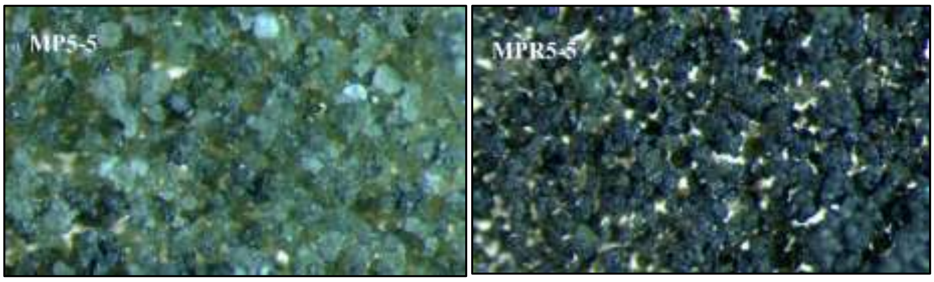
TABLE V COLOR CHARACTERISTICS OF PIGMENTS WITH COMPOSITIONS MPR 4–5 ÷ MPR 6–5

№	**Composition**	**T, °C**	**Colour**	**L***	**a ***	**b ***
1	MPR 4 - 5	1450		39,5	0,7	-31,1
2	MPR 5 - 5	1450		32,6	-2,0	3,4
3	MPR 6 - 5	1450		70,9	-17,4	-2,1

In terms of color characteristics, the best indicators are obtained for compositions with a cobalt chromophore. When a cobalt chromophore is introduced into the starting compositions, pigments with a saturated blue color are obtained. In pigments obtained with the addition of oxidized rice husks as a source of SiO_2, the amount of blue color is b* = -28.2, and in pigments obtained from pure raw materials, the amount of blue color is b* = -31.1.

For comparison, the figures below show images of the pigments taken with a stereo microscope ZEISS SteREO Discovery.V8. The photos in Fig. 7 show that the pigments obtained have beautiful saturated colors and can be used for glazing various ceramic items – ceramic tiles, sanitary ceramics, artistic porcelain, etc.





IV. CONCLUSIONS

Two series of pigments were obtained by the solid-state sintering method at 1450°C with a two-hour isothermal hold. Co, Cu, and Ni ions were introduced as chromophores, with a concentration of 5% in the form of Co_2O_3, CuO, or NiO.
X-ray phase analysis showed that the main phases in the pigments are mullite and corundum, with additional phases of spinel, cristobalite, and CuO depending on the introduced chromophore.
It has been proven that some of the copper ions are incorporated into the crystal lattice of mullite and form a solid solution with it.
It has also been proven that the nickel chromophore has a tendency to form nickel spinel, which ensures stability of the color characteristics of compositions MP6-5 and MPR6-5.
Colorimetric analysis showed that pigments containing cobalt as a chromophore exhibit the best color characteristics. In the MP4-5 composition, the amount of blue color is b* = -28.2, and in the pigments with the MPR4-5 composition, obtained from pure raw materials, the amount of blue color is b* = -31.1.
The results of the colorimetric analysis and stereomicroscopic studies prove that pigments with saturated colors were obtained, which can be used for glazing various ceramic products - ceramic tiles, sanitary ceramics, art porcelain, etc.

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REFERENCES

[1] E. Gerasimov E., A. Gerasimov, A. Atanasov, V. Toshev, D. Petkov et al., Technology of Ceramic Products and Materials, Publisher: Sarasvati, edited by Prof. S. Bachvarov, 2003, 939
[2] Lahlahi-Attalhaoui at.al, “Ultrafast development of blue pigment for in situ laser digital coloration in the ceramic industry”, J. Am. Ceram. Soc., vol. no.108, Issue 9, 2025.
[3] R. Ianoş et al. “Preparation and testing of yellow pigments based on nickel-doped tialite”, Ceram. Intern., vol.51, Issue 21, Part B, pp. 34099-34105, September 2025.
[4] Qi, Menghang et al. Novel orange-red glaze based on in-doped $CaFe_2O_4$ red chromophore: Synthesis, properties and characterizations, Ceram. Intern, vol. 51, no. 20, Part A, pp. 30104-30112, August 2025.
[5] Rodrigo, Marta at al., “Blue inkjet inks from E-waste: Toward a greener ceramic industry”, J. Europ. Ceram. Soc., vol. 45, no. 16, 2025.
[6] Colour, pigments and colouring in ceramics. Editor: S.A.L.A. srl - via Fossa Buracchione 84, 41100 Baggiovara, Modena, Italian Ceram. Soc. 2003
[7] I. V. Pisht, E. N. Maslennikova, Ceramic Pigments, Minsk, Vsshaya Shkola, 1987.
[8] A. Georgieva, M. Minova, I. Markovska, F. Yovkova, G, Avdeev, D. Komunova, “Synthesis of ceramic pigments from the system Al_2O_3 - SiO_2 by utilization of rice husk ash as silica source”, WSEAS trans. Env. Develop., vol. 21, pp. 1001 – 1009, 2025.
[9] N. Duan, S. Peng, C. Lu, Y. Zhang, F. Zhang, “Preparation of Iron Oxide Red from Titanium Industrial Solid Waste and Its Application in Ceramic Black Pigments”, Bull. Chin. Ceram. Soc., 43, no. 12, pp. 4532–4544, 2024.
[10] G. Costa, M. J. Ribeiro, T. Trindade, J.A. Labrincha, “Development of waste-based ceramic pigments”, Bol. Sociedad Espanola de Ceram. Vidrio, vol. 46 no. 5, pp. 363-366, 2006,
[11] Bessmertnyi V.S. et al., “Plasma Synthesis of Black Ceramic Pigment Based on Vanadium Production Waste”, Glass and Ceramics , vol. 98, no. 5, pp. 25-31, 2025,

[12] Paz-Gómez, D.C., et al., "Valorisation of Metallurgical Waste for Inorganic Pigments Production", Waste Biomass Valor., vol. 15, no. 12, pp. 6761–6773, 2024.