Synthesis of Ceramic Pigments from the System Al_2O_3 - SiO_2 by Utilization of Rice Husk Ash as Silica Source

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Abstract: - In this work, the synthesis of ceramic pigments from the system Al_2O_3 - SiO_2 by utilization of rice husk ash (RHA) as a silica source is considered. For comparison, pigments from pure raw materials were also synthesized. All compositions were synthesized at 1450°C. The amount of chromophore in the compositions was 5%. Co, Cu, and Ni were used as chromophore elements, introduced respectively as Co_2O_3, CuO, or NiO. The pigments were studied by several methods - XRD, FT-IR, EPR, and spectral colour determination. By X-ray diffraction, a qualitative and quantitative analysis of the synthesized pigments was made. The colour characteristics are determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color. The pigments with cobalt chromophore have the best indicators, in which (b) = - 24.1 when using $SiO_2.nH_2O$ and (b) = -27.4 when using RHA. The possibility of replacing pure silica with one obtained from oxidized rice husks was proven.

Key-Words: - ceramic pigments, solid-phase sintering, waste raw materials, rice husk ash, chromophore ions, color determination.

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1 Introduction

Corundum (α-Al_2O_3) is one of the most widely applied materials in ceramics. Such a huge use is due to its low cost and to its important mechanical, electronic and catalytical properties, [1]. Conventional methods for synthesizing α-Al_2O_3 powder involve solid-state thermally driven transformations from the hydrates of aluminum oxide. The extent of conversion to the corundum structure depends on the temperature and the time of thermal treatment, and total conversion occurs on heating above 1230°C, [2], [3].

One of the challenges in the production of various types of ceramic products is the continuous pursuit of improving quality and diversifying the range offered. The answer to this lies in the development, improvement, and production of ceramic pigments and expanding the colour range of glazes and masses, [4].

Ceramic pigments have been used for many centuries due to their properties of being highly refractory, being able to resist chemical corrosion, and presenting suitable optical characteristics, [5].

Initially, natural-colored minerals and ores containing Co, Fe, Mn, Cr, Cu, etc. were used as pigments, but due to constant and significant fluctuations in their chemical composition, they are currently almost not used. Much later, the development and production of synthetic pigments began, initially obtained empirically, and subsequently - through the synthesis of pigments, [6].

Currently, the synthesis of these pigments is carried out by a conventional ceramic route, consisting of mixing powders of the individual components and subsequent heating at high temperature, [7], [8], [9].

Ceramic pigments are inorganic, coloured, mineral substances that have colouring ability, resistance to high temperatures, atmospheric and chemical influences, light, etc. These characteristics are the reason for their large-scale production and its continuous increase. The purpose of ceramic pigments is the increase of decorative effect through application on ceramic products by using colouring compounds. They must fit certain quality characteristics: to develop a high colouring capacity and colorimetric purity; to have a good coating power; to resist to high firing temperatures and to dissolvent attack of glass melt; to have a good compatibility with used frits for obtaining colours up on the glaze; to favour the linking of oxides in the composition of ceramic colours, [10], [11], [12].

In the ceramic industry, natural and synthetic pigments find applications as colouring agents in glasses, enamels, and unglazed bodies. There has been a great interest in the ceramic industry for developing highly stable pigments that show intense tonalities and that comply with technological and environmental demands. One of the current trends is the search for alternative and less expensive raw materials. Several factors and characteristics should be considered in the selection of pigments for a specific ceramic application. The most important of them are the thermal stability, the intensity, and the uniformity of the obtained colours and the particle sizes of the powders, [6], [13].

In connection with the above, the aim of this work is the synthesis of ceramic pigments from the system Al_2O_3 - SiO_2, by the solid-phase sintering method, from pure raw materials and waste ones, by using rice husk ash as a source of silicon dioxide. Also, the study of the properties of the obtained pigments by applying the methods of X-ray structural analysis, Fourier transform infrared spectroscopy, Electron paramagnetic resonance, and Spectrophotometric colour measurement.

2 Experimental

2.1 Materials

The synthesis of ceramic pigments from the system Al_2O_3 - SiO_2, using waste raw material - rice husk ash, as a source of silica, was carried out by the solid-phase sintering method. For comparison, pigments from chemically pure raw materials were also synthesized.

For the purposes of the experiment, Al_2O_3 and SiO_2 were used as starting raw materials. Silica was introduced into the ceramic masses either as amorphous $SiO_2.nH_2O$ (compositions MP1-5, MP2-5, MP3-5, presented in Table 1) or as ash from rice husks burned in air - RHA (compositions MPR1-5, MPR2-5, MPR3-5 - Table 1).

Table 1. Compositions of ceramic pigments from the system Al_2O_3 - SiO_2, synthesized from pure or waste raw materials - rice husk ash (RHA) at 1450°C

Pure raw materials - Al_2O_3 and amorphous $SiO_2.nH_2O$		
№	Compositions	5 % Chromophore
1	MP1-5	Co
2	MP2-5	Cu
3	MP3-5	Ni
Al_2O_3 and rice husk ash burned in the air - RHA		
1	MPR1-5	Co
2	MPR2-5	Cu
3	MPR3-5	Ni

Since the color of most natural and synthesized, mineral substances are related to the presence of d- or f- elements from the periodic table in their composition, Co, Cu, and Ni ions (Co^{2+}, Cu^{2+}, Ni^{2+}) were selected and introduced as chromophores. These elements are characterized by unfilled d- or f- f-electron orbitals, which determine the electronic transitions under the action of light energy. The amount of chromophore in all compositions is 5%, and Co, Cu, and Ni are introduced as Co_2O_3, CuO or NiO, respectively.

The preparation of ceramic pigments, i.e., all procedures in the course of the technological process are schematically presented in Figure 1.

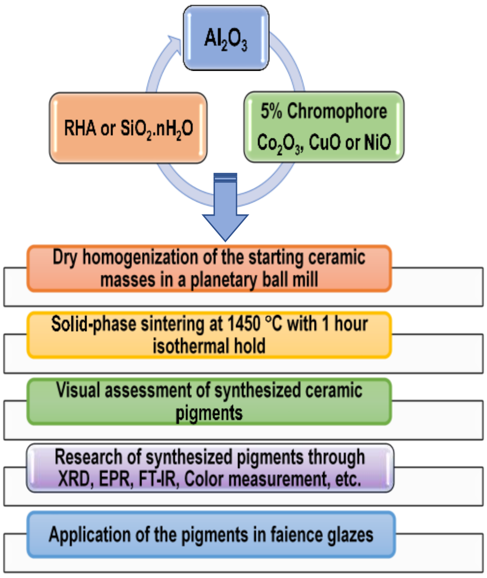


Fig. 1: Schematic representation of the preparation of ceramic pigments by solid-state sintering

The starting components are dry-mixed and homogenized in a planetary ball mill. All compositions are synthesized at 1450°C, and in order to ensure completeness of the reactions, at the maximum temperature in the final stage of the process, a one-hour isothermal hold in a Nabertherm high-temperature furnace was performed in an air environment.

The obtained pigments were studied using the methods of X-ray structural analysis, Fourier transform infrared spectroscopy, and electron paramagnetic resonance. Their colour was determined using a spectrophotometer.

2.2 Methods

X-ray structural analysis. The phase composition was determined using an X-ray diffractometer manufactured by Philips with a PW1830 generator and a PW 1050 goniometer. The device was equipped with an X-ray tube with a copper anode, operating at a voltage of 40 kV and a current of 40 mA. The diffraction patterns were interpreted with the High Score Plus program, using the ICSD (Inorganic Crystal Structure Database) database.

Electronic paramagnetic resonance. EPR spectra were recorded on a Bruker EMX Premium X EPR spectrometer, equipped with a temperature-variable measurement system - ER4141-VT Unit.

Fourier Transform Infrared Spectroscopy - FT-IR. The spectra were made with a Tensor 27 Fourier infrared spectrophotometer FTIR (Bruker, Germany) in the range 400 - 4 000 cm^{-1} at a resolution of cm^{-1}. The measurements were carried out at room temperature, with the test sample (0.3 mg) being tableted with KBr (100 mg) at a pressure of 2 - 4 atm.

Spectrophotometric color measurement. The color determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color.

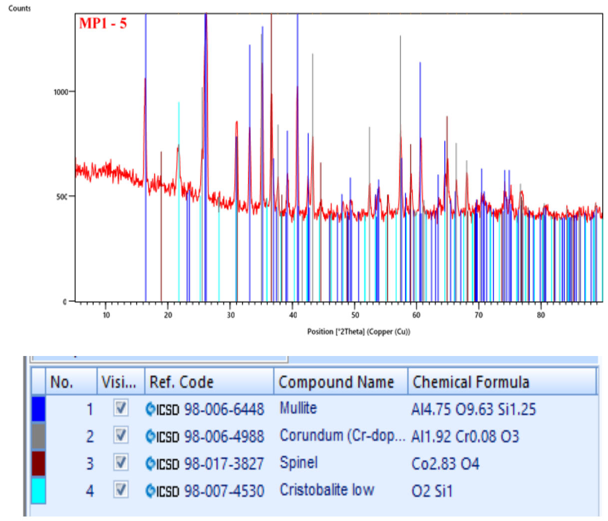
3 Results and Discussion

Two series of finely dispersed ceramic pigments from the system Al_2O_3 - SiO_2 were synthesized by the solid-phase sintering method at a temperature of 1450°C. In the synthesis of the first series of pigments, pure starting materials were used - compositions MP1-5, MP2-5, MP3-5 (Table 1). In the second case, the waste raw material was utilized - ash from rice husks burned in the air (RHA), as a source of silica-ceramic pigments with compositions MPR1-5, MPR2-5, MPR3-5 (Table 1). In the syntheses carried out, in both starting materials (from pure and waste raw materials) as chromophores, in the form of Co_2O_3, CuO or NiO, Co, Cu, and Ni ions were selected and introduced in the amount of 5%.

The obtained ceramic pigments were studied and characterized using X-ray structural analysis, Fourier transform infrared spectroscopy, Electron paramagnetic resonance, and the color characteristics of the pigments were determined spectrally with a Lovibond Tintometer RT 100 Color.

From the X-ray structural analysis performed on the synthesized pigments from pure or waste raw materials, the phase composition of the studied samples was determined. The results are presented in the following figures.

The results presented in Figure 2 indicate that in addition to the main mullite phase, the studied sample also contains reflections of residual cristobalite - the high-temperature modification of SiO_2, spinel, and corundum (Al_2O_3).



	No.	Visi...	Ref. Code	Compound Name	Chemical Formula
🟦	1	☑	ICSD 98-006-6448	Mullite	Al4.75 O9.63 Si1.25
▨	2	☑	ICSD 98-006-4988	Corundum (Cr-dop...	Al1.92 Cr0.08 O3
🟥	3	☑	ICSD 98-017-3827	Spinel	Co2.83 O4
▢	4	☑	ICSD 98-007-4530	Cristobalite low	O2 Si1

Fig. 2: X-ray phase analysis of composition MP1-5 - with cobalt

Figure 3 presents a quantitative diagram from the conducted X-ray diffraction of composition MP1-5.

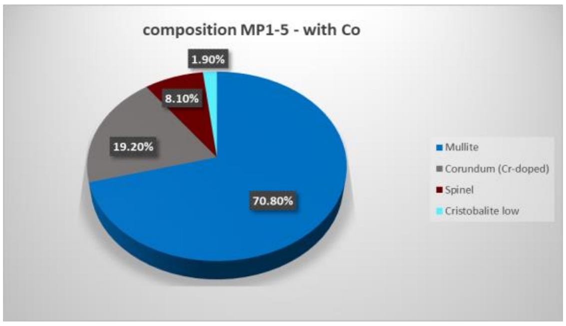
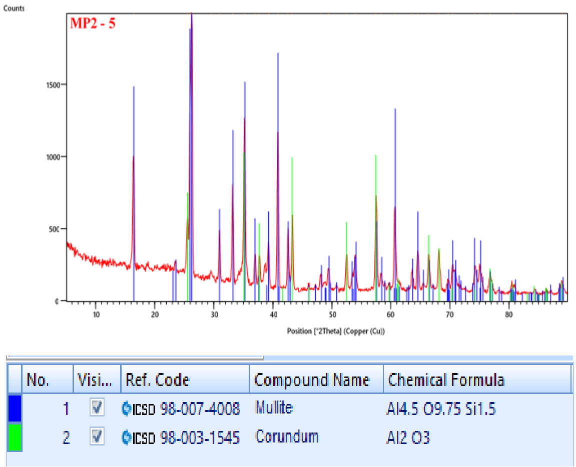


Fig. 3: Quantitative diagram of the X-ray phase analysis of the composition MP1-5

Figure 4 shows the main phase mullite and a small amount of corundum (Al_2O_3). The results obtained for composition MP2-5 - with copper are interpreted quantitatively in a diagram - Figure 5. With this composition, the amount of synthesized mullite is the largest - 78.6 %. The other phase observed in the pigments is corundum, in an amount of 21.4 %.



	No.	Visi...	Ref. Code	Compound Name	Chemical Formula
🟦	1	☑	ICSD 98-007-4008	Mullite	Al4.5 O9.75 Si1.5
🟩	2	☑	ICSD 98-003-1545	Corundum	Al2 O3

Fig. 4: X-ray phase analysis of composition MP2-5 - with copper

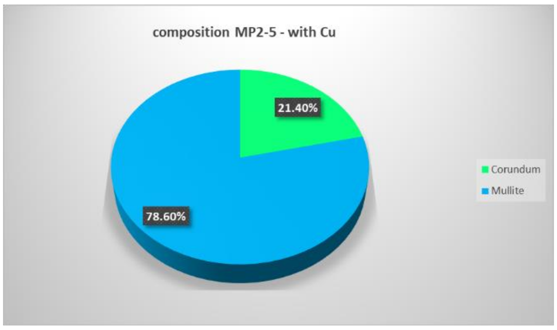
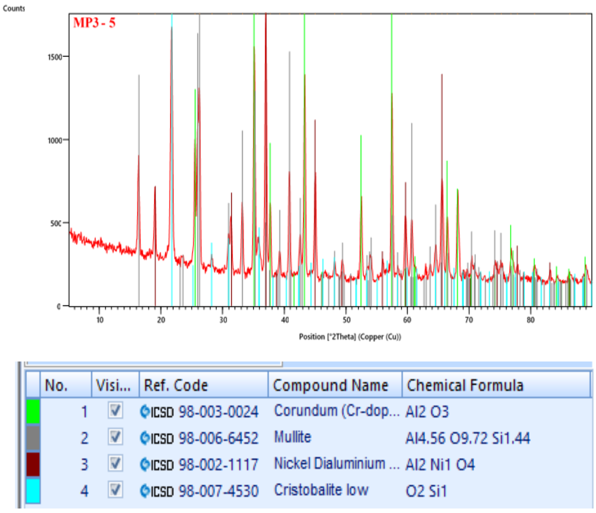


Fig. 5: Quantitative diagram of the X-ray phase analysis of the composition MP2-5



	No.	Visi...	Ref. Code	Compound Name	Chemical Formula
🟩	1	☑	ICSD 98-003-0024	Corundum (Cr-dop...	Al2 O3
⬜	2	☑	ICSD 98-006-6452	Mullite	Al4.56 O9.72 Si1.44
🟥	3	☑	ICSD 98-002-1117	Nickel Dialuminium ...	Al2 Ni1 O4
🟦	4	☑	ICSD 98-007-4530	Cristobalite low	O2 Si1

Fig. 6: X-ray phase analysis of composition MP3-5 (with nickel)

The data in Figure 6 shows that, in addition to mullite, residual cristobalite - the high-temperature modification of SiO_2, dialuminium nickel tetra oxide, and corundum (Al_2O_3) are observed in the composition of MP3-5 - with nickel. In percentage terms, the X-ray diffraction results are expressed in the quantitative diagram in Figure 7.

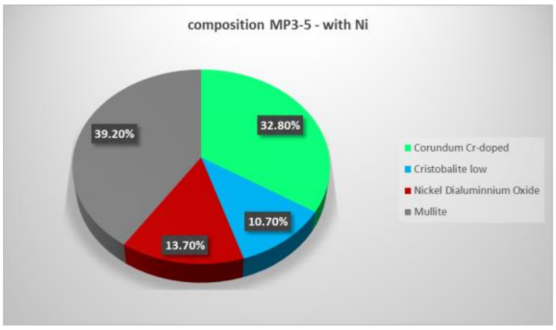
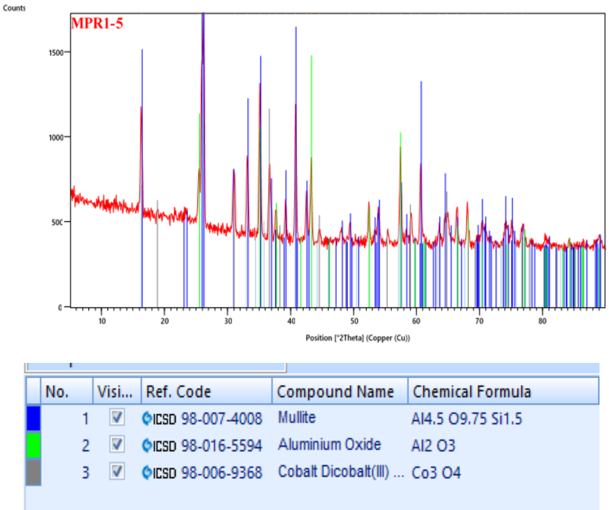


Fig. 7: Quantitative diagram of the X-ray phase analysis of the composition MP3-5



	No.	Visi...	Ref. Code	Compound Name	Chemical Formula
🟦	1	☑	ICSD 98-007-4008	Mullite	Al4.5 O9.75 Si1.5
🟩	2	☑	ICSD 98-016-5594	Aluminium Oxide	Al2 O3
⬜	3	☑	ICSD 98-006-9368	Cobalt Dicobalt(III) ...	Co3 O4

Fig. 8: X-ray phase analysis of composition MPR1-5 - with cobalt

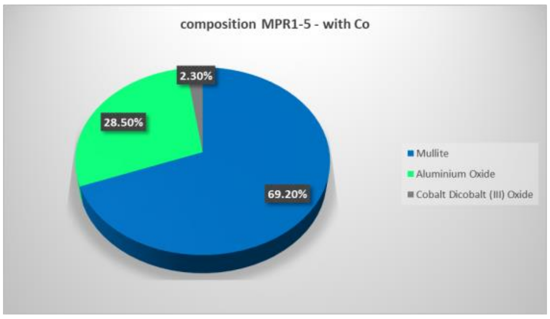
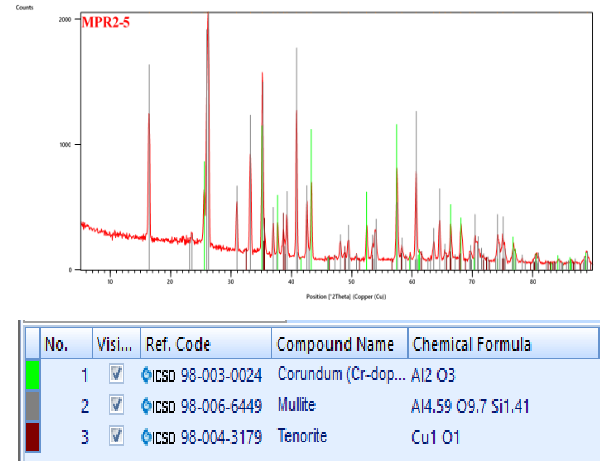


Fig. 9: Quantitative diagram of the X-ray phase analysis of the composition MPR1-5

Figure 8 presents X-ray diffraction studies of the composition MPR1-5, which used rice husk as a source of silica. The data indicate that in addition to mullite, corundum and tricobalt tetroxide phases are present. The quantitative diagram of the X-ray phase analysis of the same composition is presented in Figure 9.



	No.	Visi...	Ref. Code	Compound Name	Chemical Formula
🟩	1	☑	ICSD 98-003-0024	Corundum (Cr-dop...	Al2 O3
⬛	2	☑	ICSD 98-006-6449	Mullite	Al4.59 O9.7 Si1.41
🟥	3	☑	ICSD 98-004-3179	Tenorite	Cu1 O1

Fig. 10: X-ray phase analysis of composition MPR2-5 (with copper)

In addition to the mullite phase, the X-ray diffraction results of composition MPR2-5 (Figure 10) indicate corundum and a minimal amount of tenorite (CuO), which is also confirmed by the quantitative diagram - Figure 11. With this composition of pigments obtained with waste flakes, the amount of synthesized mullite is the largest - 78.7%, respectively, corundum has a content of - 20.4%, and tenorite - 1.0%.

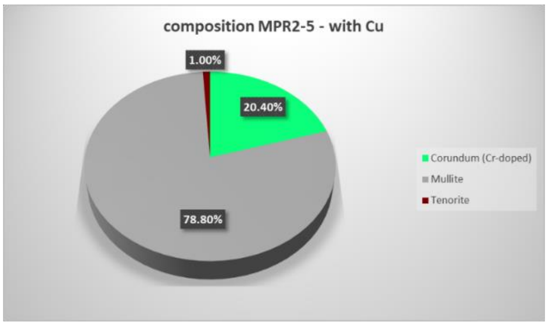
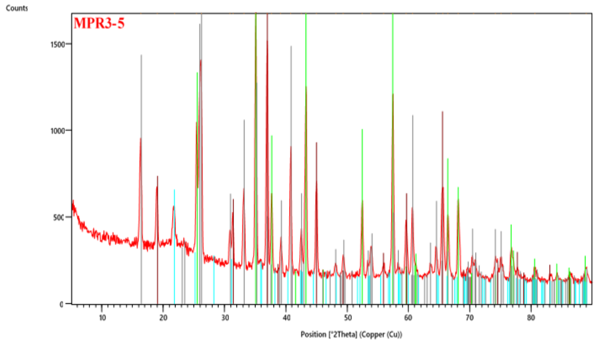
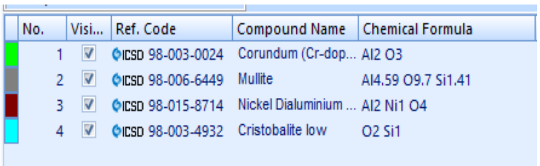


Fig. 11: Quantitative diagram of the X-ray phase analysis of the composition MPR2-5





	No.	Visi...	Ref. Code	Compound Name	Chemical Formula
🟩	1	☑	ICSD 98-003-0024	Corundum (Cr-dop...	Al2 O3
⬛	2	☑	ICSD 98-006-6449	Mullite	Al4.59 O9.7 Si1.41
🟥	3	☑	ICSD 98-015-8714	Nickel Dialuminium ...	Al2 Ni1 O4
🟦	4	☑	ICSD 98-003-4932	Cristobalite low	O2 Si1

Fig. 12: X-ray phase analysis of composition MPR3-5 (with nickel)

In addition to mullite, Figure 12 shows phases of corundum, dialuminium nickel tetra oxide, and reflections of cristobalite. The quantitative diagram reflecting the X-ray phase analysis of composition MPR3-5 is presented in Figure 13.

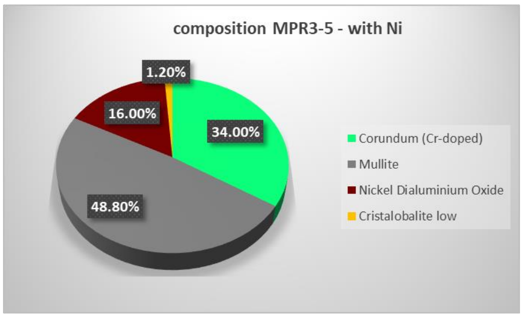


Fig. 13: Quantitative diagram of the X-ray phase analysis of the composition MPR3-5

Using the CIELab system, which gives a numerical expression of the visual sensation of colour, the basic colour characteristics of the pigments were determined - colour, brightness, colour hue - Figure 14.

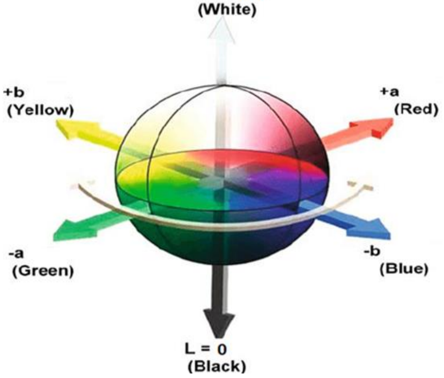


Fig. 14: Colour space of CIELab system, [14]

In the CIELab system, the colour coordinates are as follows [14]:

- L* - brightness, L*=0 - black colour, L*=100 - white colour;
- a* - green colour (-) / red colour (+);
- b* - blue colour (-) / yellow colour (+).

The results of the determined colour parameters of the synthesized pigments from pure or waste raw materials, with chromophore ions of Co, Cu, and Ni in the amount of 5%, are presented in Table 2 and Table 3.

Table 2. Colour coordinates of samples with MP1-5 ÷ MP3-5 compositions

№ sample	T, °C	Colour	L*	a *	b *
MP1-5	1450	🟦	34,8	-1,6	-24,1
MP2-5	1450	⬛	31,1	-3,6	4,3
MP3-5	1450	🟩	67,6	-16,0	-5,4

From the data presented in Table 2, it can be seen that the pigment with the best color characteristics of the synthesized and studied compositions is the pigment with the composition MP1-5 - b = - 24.1 (with cobalt chromophore).

Table 3. Colour coordinates of samples with MPR1-5 ÷ MPR3-5 compositions

№ sample	T, °C	Colour	L*	a *	b *
MPR 1-5	1450	🟦	37,3	2,5	-27,4
MPR 2-5	1450	⬛	32,6	-2,3	3,7
MPR 3-5	1450	🟩	72,7	-13,7	-4,5

From the results presented in Table 3, it can be seen that even in the compositions with rice husks, the pigment with the cobalt chromophore (composition MPR1-5) has the best color characteristics. In comparison with the previous table, it can be seen that under the same conditions, such as isothermal holding temperature and holding time, the coloring of the pigments obtained from rice husks and the chromophore Co, Cu, Ni is stronger than that of the pigments obtained from pure raw materials. This can be explained by the fact that in the ash of rice husks, there are residual elements that play the role of a mineralizer and at the same time contribute to the greater intensity of the resulting coloring.

EPR is a non-destructive method for the study of paramagnetic substances (i.e., those containing unpaired spins) in the form of powder samples - as in pigments. It is applied to the study of paramagnetic ions such as Mn, Cu, Co, Cr, Fe, Ni, Va, Pt, etc.

The results of the EPR analysis of the synthesized pigments from pure raw materials containing Al_2O_3, SiO_2, and chromophores Co, Cu, Ni (compositions MP1-5÷MP3-5) and of the samples containing Al_2O_3, ashed rice husks and chromophores Co, Cu, Ni (compositions MPR1-5÷MPR3-5) are presented in Figure 15 and Figure 16.

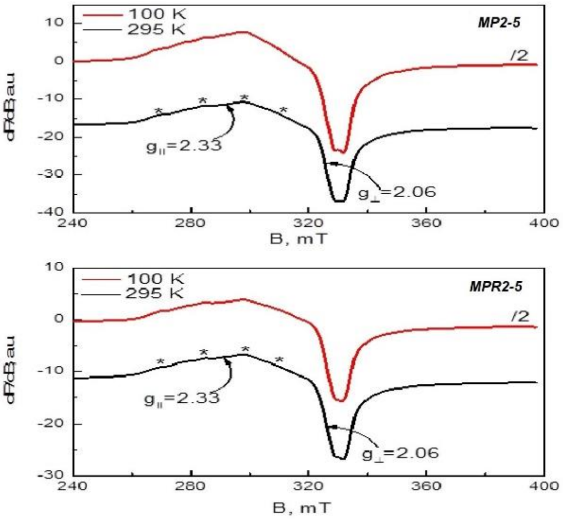


Fig. 15: EPR spectra of compositions MP2-5 (top) and MPR2-5 (bottom), recorded at 100 K and 295 K

In the EPR spectra of samples MP2-5 and MPR2-5, identical signals are found, consisting of a parallel and perpendicular component, characterized by $g_{II}>g_{\perp}$. On the parallel component, poorly resolved lines of an ultrafine structure are observed, and more than one quarter of ultrafine interaction lines can be distinguished. The perpendicular part of the spectra is split, which is again an indication of the presence of more than one type of coordination of the Cu^{2+} ions. The established effective EPR values for one of the quartets of ultrafine interaction lines are the following: $g_{II}=2.32$, $g_{\perp}=2.06$ $A_{II}=15.3mT$. The intensity of the registered signals increases with decreasing temperature, but its temperature dependence does not follow the Curie-Weiss law. Signals with the described EPR characteristics are attributed to isolated Cu^{2+} ions located in tetrahedrally distorted octahedral symmetry. The indicated values of g_{II} and A_{II} are characteristic of the coordination of Cu^{2+} ions with four oxygen atoms.

The EPR spectra of compositions MP1-5, MPR1-5, MP3-5, and MPR3-5 are composed of the same group of signals located in the entire range of the magnetic field - 0-800 mT, with the following g-factors: 14.8, 5.0, 4.25, 2.014, 2.01, 1.93, 1.70, 1.34, 1.18. The same set of signals is visible, in addition to the signal from Cu^{2+} ions, in the spectrum of samples MP2-5 and MPR2-5. In the EPR spectra of

MP1-5, MPR1-5, MP3-5, and MPR3-5, signals from Co and Ni are not registered. Co^{3+} ions, as well as Co^{2+} ions in octahedral symmetry with a high-spin electronic state are invisible in the X-range of registration of the spectra. Ni^{2+} ions have an integer spin number S=1, which makes them difficult to observe at a frequency of electromagnetic radiation of 9.4 GHz.

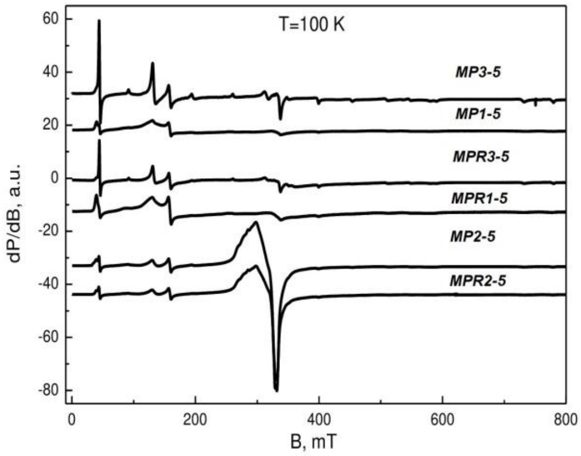
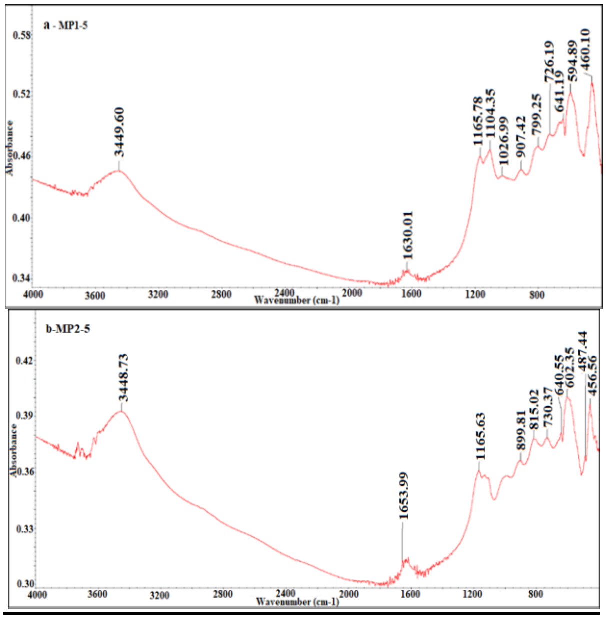


Fig. 16: EPR spectra of MP1-5÷MP3-5 and MPR1-5÷MPR3-5 compositions registered at 100 K

FT-IR analysis was also performed on the two series of compositions synthesized at 1450°C, containing pure or waste raw materials and 5% chromophore introduced as Co_2O_3, CuO, or NiO, respectively. The results of the Fourier transform-infrared spectroscopy are presented in the Figure 17 and Figure 18.



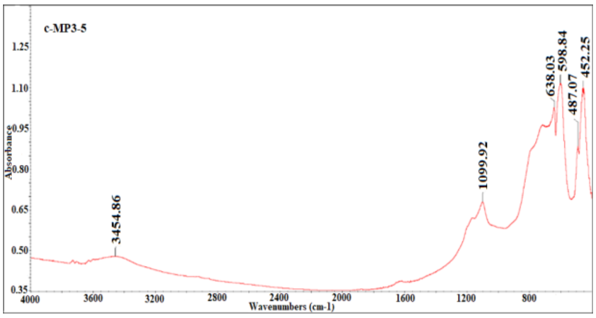


Fig. 17: FT-IR spectra of pigment compositions from pure raw materials and 5% chromophore: a) MP1-5, b) MP2-5, c) MP3-5

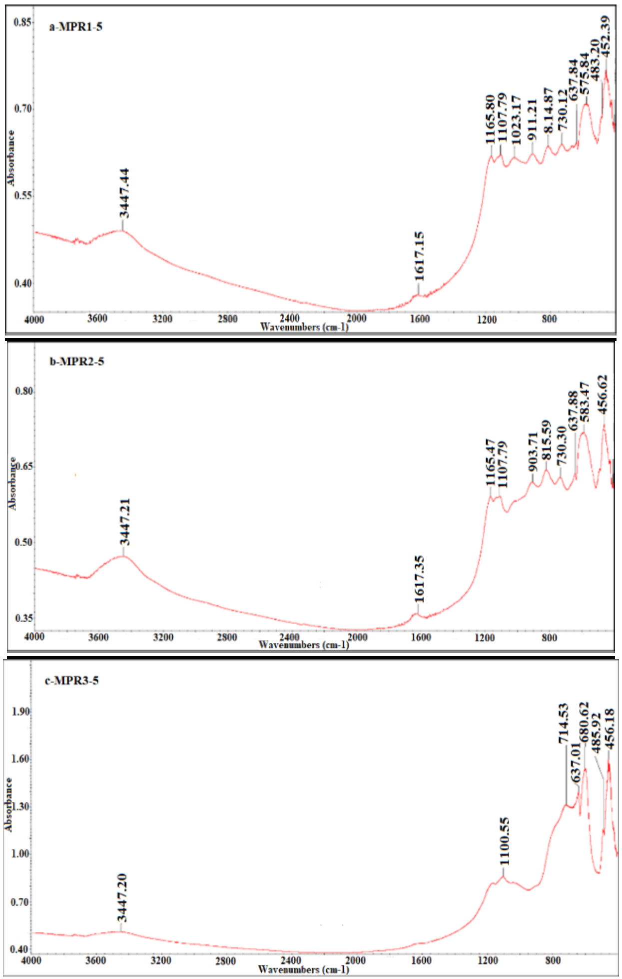


Fig. 18: FT-IR spectra of pigment compositions with waste raw material - RHA and 5% chromophore: a) MPR1-5, b) MPR2-5, c) MPR3-5

The applied FT-IR spectrograms show broad and intense absorption bands with a maximum of ~3447.20 cm^{-1} ÷ ~3454.86 cm^{-1}, which can be associated with the stretching vibrations of the O-H bond in water molecules. The weak band at ~1630.01 cm^{-1} ÷ ~1653.99 cm^{-1} is a result of the deformation vibrations of water molecules (δ-H_2O). The intense bands at about ~1099.92 cm^{-1} ÷ ~1165.80 cm^{-1} are due to the stretching vibrations of the silicon-oxygen tetrahedra - ν_{as} (SiO_4). These bands can be attributed to the stretching vibrations of the Si-O bond of the tetrahedra. The characteristic bands recorded at ~899.81 cm^{-1} ÷ ~911.21 cm^{-1} correspond to the asymmetric stretching vibrations of the silicon-oxygen tetrahedra - ν_{as} (SiO_4). The results of the FT-IR analysis indicate large peaks in the frequency range from ~500 cm^{-1} to ~900 cm^{-1}. They are characteristic of the vibrations of the Al-O bonds in Al_2O_3. The presence of absorption bands in the low-frequency region of the spectrum at ~452.25 cm^{-1} cm^{-1} ÷ 483.20 cm^{-1} can be attributed to the deformation vibrations (δ_{as}) of the Si-O bonds of the SiO_4 tetrahedra.

4 Conclusion

The synthesis and properties of finely dispersed ceramic pigments from the system Al_2O_3 - SiO_2 were studied. The synthesis of both series of pigments was carried out by the solid-phase sintering method. In the first case, pure starting materials were used - Al_2O_3 and $SiO_2.nH_2O$, and the more active - amorphous form of $SiO_2.nH_2O$ was chosen, instead of the crystalline form of SiO_2. For the preparation of the second series of pigments, recycled ash from burnt rice husks - RHA was also used. The syntheses of the pigments were carried out at a temperature of 1450°C with a one-hour isothermal hold. In both starting compositions - from pure and waste raw materials, the amount of chromophore was 5%. Co, Cu, and Ni ions were selected and introduced as chromophores in the form of Co_2O_3, CuO, or NiO. The synthesized pigments from the system Al_2O_3 - SiO_2 were studied by a number of methods, such as X-ray structural analysis, Fourier transform infrared spectroscopy, Electron paramagnetic resonance, and the color characteristics of the pigments were determined spectrally with a Lovibond Tintometer RT 100 Color. The possibility of replacing pure silica with one obtained from oxidized rice husks was proven.

The X-ray structural analysis determined the phase composition of the studied samples. It was established that the main phases in the synthesized pigments from pure raw materials are mullite and corundum, and depending on the introduced chromophore, spinel, dialuminium nickel tetra oxide, and cristobalite reflexes are also observed. X-ray studies on the pigments, in whose compositions rice husks were used as a source of silica, indicate that in addition to the main phases of mullite and corundum, depending on the chromophore used, phases of tricobalt tetroxide, tenorite, and cristobalite are also present.

By FT-IR analysis the main functional groups in the composition of the synthesized ceramic pigments were identified.

The color characteristics of the pigments were determined spectrally with a Lovibond Tintometer RT 100 Color. The best color characteristics of the synthesized and studied pigments are the compositions with cobalt chromophore - composition MP1-5 - b = - 24.1, composition MPR1-5 - b = - 27.4.

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- Irena Markovska, PhD is the head of a research project with the number KP-06-N87/14 at the Ministry of Education and Science of the Republic of Bulgaria, National Research Fund, which is funding this study. The activities were implemented under her leadership.
- Adriana Georgieva, Fila Yovkova, and Mariela Minova carried out the experimental work on the synthesis of the series of ceramic pigments.
- Adriana Georgieva is responsible for the analysis, discussion and interpretation of the obtained results.
- Georgi Avdeev performed some of the analyses of the obtained pigments.
- Desislava Komunova participated in the design of the figures.

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Conflict of Interest

The authors declare no conflict of interest.

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