Bulgarian Chemical Communications, Volume 57, Special Issue E (pp. 17-22) 2025 DOI: 10.34049/bcc.57.E.SIMONS03

Synthesis and properties of Ni-doped finely dispersed ceramic pigments

M. G. Minova*, F. S. Yovkova, I. G. Markovska, A. A. Georgieva

Burgas State University "Prof. Dr. Assen Zlatarov", Department of Chemical Technology, 8000, 1 Prof. Yakimov Blvd., Burgas, Bulgaria

Received: May 05, 2025; Revised: June 06, 2025

This work aims to synthesize finely dispersed ceramic pigments by the solid-phase synthesis method. Two series of pigments were obtained – from pure and waste raw materials. In the first case, pure raw materials - Al_2O_3 and SiO_2 were used. The initial SiO_2 was introduced into the mixtures as amorphous $SiO_2.nH_2O$. An amorphous form of silica - $SiO_2.nH_2O$ was chosen because it is significantly more reactive than ordinary quartz sand and has a degree of particle dispersion in the range of 2÷7 μm. In the second case, Al_2O_3 and oxidized rice husk ash (RHA) were used, which contained 94.47 % of silica. The synthesis was carried out at temperatures of 1350 °C and 1400 °C with 1-hour isothermal period in a Nabertherm oven. The chromophore used was Ni introduced into the mixtures as NiO. The amount of the chromophore was 5 %. Finely dispersed pigments with a blue-green color were obtained. The synthesized pigments were studied by a number of methods - X-ray diffraction, SEM, DSC, etc. Using the CIELab system, which gives a numerical expression of the visual sensation of color, the basic color characteristics of the pigments were determined - color, brightness, color hue. The pigments synthesized from pure raw materials at 1350 °C had the best indicators, respectively, (a) = - 15.2 and (b) = - 4.9.

Keywords: ceramic pigments, Ni-chromophore, rice husk, solid-state sintering, CIELab system

INTRODUCTION

One of the main methods for producing ceramic pigments with different chromophores – such as nickel, copper, chromium, cobalt, vanadium, iron, etc. is solid-phase synthesis [1]. Ceramic pigments are essentially colorants, which, when applied to various materials, give them a certain color. In this regard, they are widely used in the silicate industry, where they are added to glazes for coloring floor and wall tiles (such as monoporosa), inks for decorating ceramic and glass products, etc. When coloring ceramic tiles, the relative production quantities with about 10 million square meters of tiles per year are about 20-30 tons of pigments depending on the models that are produced. That is why the interest in their production, as well as in the development of new types of highly refractory pigments is very high. In the synthesis of inorganic ceramic pigments, nickel compounds are very often used as chromophores. Nickel has the following characteristics: oxidation state 2^+, coordination numbers 4 and 6 (most often), spatial coordination - tetrahedron and octahedron [2]. In silicate systems, the change in the coordination state of nickel varies depending on the ratio of alkali metal oxides and silicon dioxide. The appearance of nickel in quadruple coordination depends on the strengths of the Me-O single bonds in alkali metal oxides [3].

In ceramic pigments, nickel can be found in the form of the following complexes: $[NiO_4]$ - blue color, $[NiO_6]$ - brown color, or Ni_2SiO_4 - green color. Nickel oxide NiO is resistant to the action of high temperatures, but dissolves in ammonia and concentrated mineral acids. Other nickel compounds are easily soluble in water - $Ni(NO_3)_2.6H_2O$, $NiSO_4.7H_2O$, forming green solutions [4].

Wang *et al.* [5] synthesized solid-phase inorganic pigments based on Ni-doped Al_2TiO_5. They used a Ni chromophore, which was added to the batch as NiO. The resulting material has a blue-green color due to the d-d transition of Ni^{2+} in octahedral coordination. It turns out that with the introduction of Ni, the Vickers microhardness values of the composite are higher. Patrocínio *et al.* [6] synthesized a blue pigment based on Ni-doped Zn_2GeO_4. They noted that the pigment is characterized by low toxicity, a bright blue hue, and excellent chemical and thermal resistance.

The present work aims to synthesize finely dispersed ceramic pigments with a nickel chromophore by the solid-phase synthesis method. An innovative and ecological aspect of our work is the fact that we have found a way to utilize agricultural waste, such as rice husks. Millions of tons of rice husks are generated worldwide per year. In some of the compositions, we use rice husk ash

* To whom all correspondence should be sent:
E-mail: *minova_m@abv.bg*

instead of amorphous $SiO_2.nH_2O$. The pigments obtained in this way are in no way inferior to those obtained from pure raw materials. On the contrary, in some cases, they give better colors. From an economic point of view, the price of the produced pigments is lower, since waste material is used.

MATERIALS AND METHODS

Materials

Al_2O_3 with a purity of 99.9 % and SiO_2 were used as starting materials. Silicon dioxide was introduced in some of the compositions as amorphous $SiO_2.nH_2O$, and in others as rice husk ash (RHA). The inorganic part of the raw husk consists of about 20 % SiO_2 and about 5.5 % mixture of: CaO, Fe_2O_3, MgO, Al_2O_3, Na_2O, K_2O, MnO_2 [7]. Ni was used as a chromophore element in an amount of 5 %. Ni was introduced with NiO. Table 1 presents the compositions of the synthesized ceramic pigments.

Fig. 1 shows the scheme for obtaining the pigments.

Table 1. Pigment compositions

Sample №	Composition		Synthesis temperature, °C
M3-5	Al_2O_3	$SiO_2.nH_2O$	1350
MR3-5	Al_2O_3	RHA	1350
P3-5	Al_2O_3	$SiO_2.nH_2O$	1400
PR3-5	Al_2O_3	RHA	1400

The preparation of the pigments involves several stages. First, the components are mixed and homogenized dry. The thus prepared batches are placed in corundum crucibles and fired in a Nabertherm high-temperature furnace. Firing was done at two final temperatures of 1350 °C and 1400 °C with an isothermal hold of 1 hour. This is followed by cooling to room temperature. The synthesized pigments are removed from the furnace and visually inspected. The pigments are ground in an agate mortar.

Methods

- *Color measurement.* The color of the pigments was determined spectrally on a Lovibond tintometer RT 100 Color.
- *SEM.* The samples were analyzed by scanning electron microscopy (SEM) at 10.00 kV accelerating voltage using an IEM11 microscope, Inovenso INC (Turkey).
- *Hot-stage microscopy (HSM).* High-temperature microscope ESS Misura HSM - 1400 ODHT, model 1600/80, Italy (IFH-BAS) was used. The sample was heated to 1400 ºC at a rate of 10 ºC min^{-1}, and the graph reflects the changes that occur during heating.
- *X-ray diffraction.* X-ray diffraction (XRD) was performed on a Bruker D8 Advance automatic powder X-ray diffractometer 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. Qualitative phase analysis was performed using the PDF-2(2009) database of the International Center for Diffraction Data (ICDD). Quantitative analysis was performed with the Topas 2 program.
- *DSC.* The DSC experiments were performed on an apparatus for complex thermal analysis (STA 449 F3 Jupiter), Netzsch, Germany, by heating to 1100 °C at a rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

Mixtures studies

The mixtures were studied by DSC, and the results are presented in Figs. 2 and 3. The DSC curves of the two mixtures are quite different. This is explained by the fact that in the batch with pure raw materials, we have $SiO_2.nH_2O$, while in the other batch, it is replaced by RHA. The first low-temperature endothermic reactions (1) and (2) in Figs. 2 and 3 in both batches can be attributed to the separation of adsorbed water. In Fig. 3 between 400 - 500 °C, we see a large endothermic effect (3), both in height and area. Probably, the unburnt particles in RHA burn. Here the mass loss is the greatest. The endothermic peak (3) in Fig. 2 in the interval 500-550 °C is due to the dehydration of $SiO_2.nH_2O$.

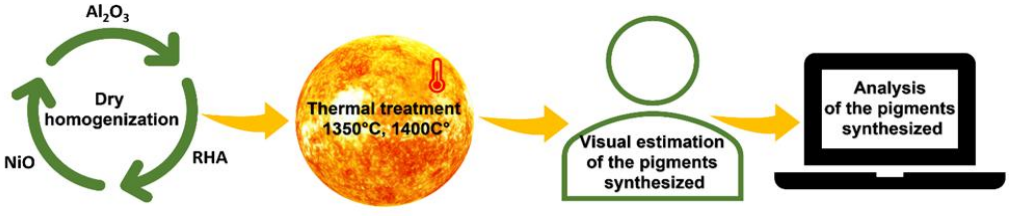

Figure 1. Scheme of pigment preparation

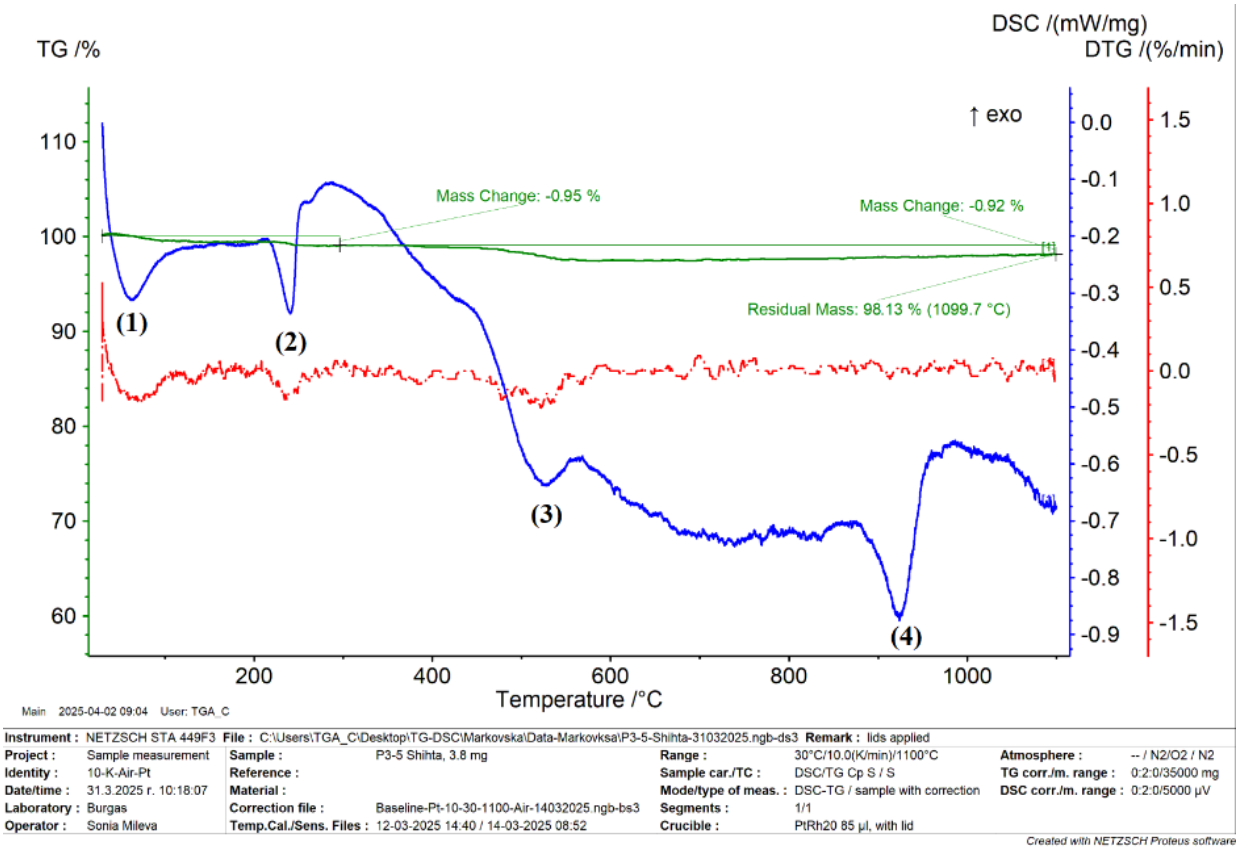

Figure 2. DSC of the mixtures with pure raw materials (Al_2O_3 and $SiO_2.nH_2O$)

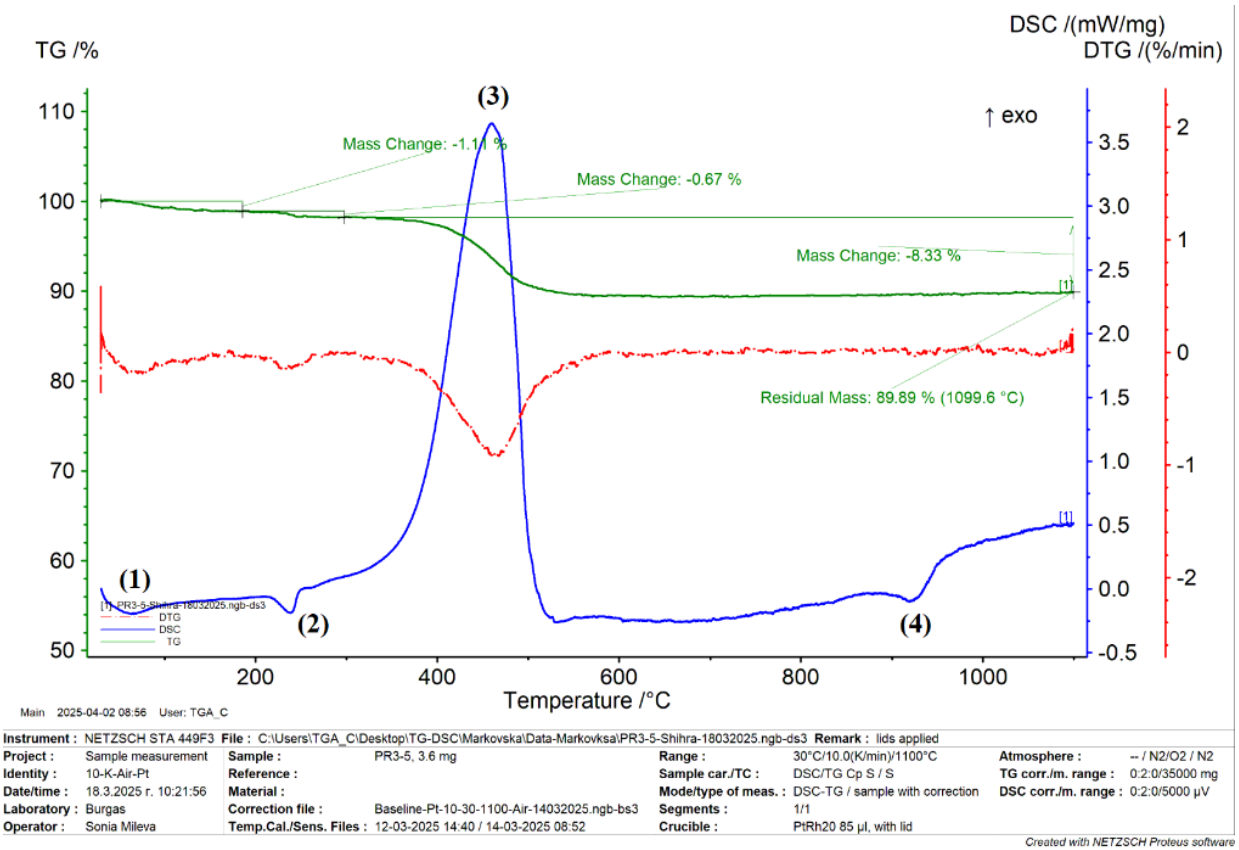

Figure 3. DSC of the mixtures with waste RHA (Al_2O_3 and RHA)

The product of the endothermic processes (4) (Figs. 2 and 3) in the temperature range 900-960 °C is $NiAl_2O_4$ (spinel) which is formed by a chemical reaction between NiO and Al_2O_3. Javanmardi *et al*. also obtained $NiAl_2O_4$ by solid-phase synthesis at about 900-960 °C. However, to reach these low temperatures of synthesis they ground the raw materials for many hours. In our work, due to the addition of RHA to the samples, the process was accelerated, since the impurities contained in RHA act as mineralizers and lower the synthesis temperature of the spinel phase [8].

We could not trace endothermic effects of other high-temperature compounds, since the heating of the samples in this analysis was up to 1100 °C.

Hot-stage microscopy (HSM) results of the mixtures

Figure 4 shows the hot-stage microscopy (HSM) results of mixtures obtained from pure raw materials - Al_2O_3 and $SiO_2.nH_2O$.

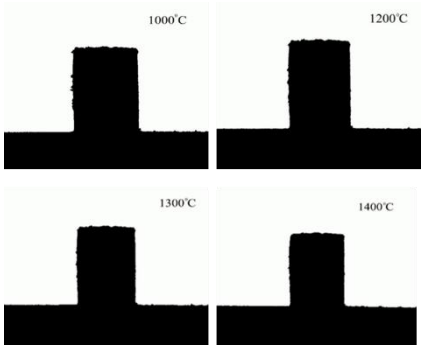

Figure 4. Hot-stage microscopy (HSM) of batches obtained from pure raw materials

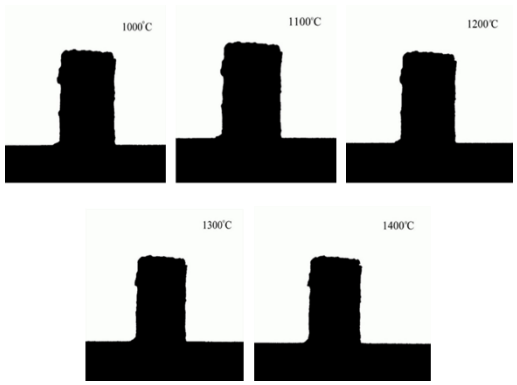

Figure 5. Hot-stage microscopy (HSM) results of mixtures obtained from waste RHA

From Fig. 4 it is seen that up to 1400 °C, the shape of the samples remains constant, without visible changes. Extremely high thermal stability of the samples is observed. Fig. 5 shows the results of hot-stage microscopy (HSM) of mixtures obtained from Al_2O_3 and RHA, as a source of SiO_2.

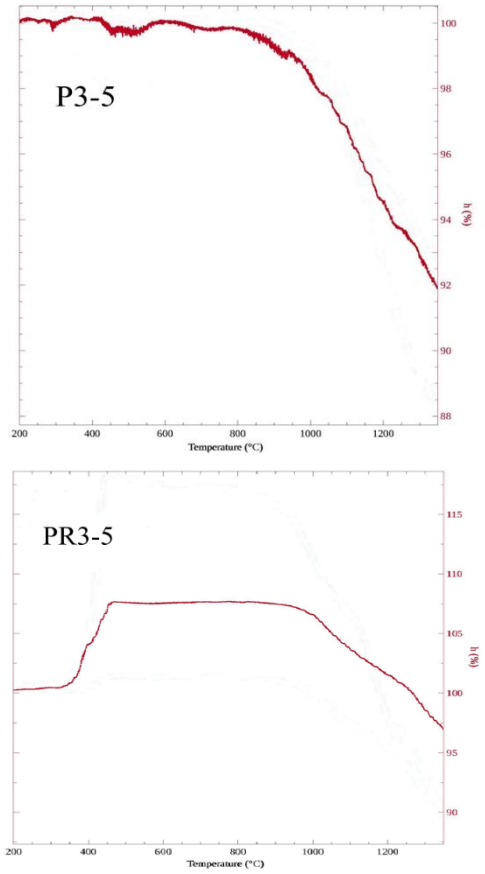

Figure 6. Summary results of hot-stage microscopy for samples without (P3-5) and with rice husk (PR3-5) in their compositions.

The results of Fig. 6 prove the stability of both types of samples. This can be explained in the following way - firstly because the pigments are fired at a lower temperature (1350 °C). Secondly, a tendency to form nickel spinel is observed, in which Al_2O_3 binds to nickel. The remaining Al_2O_3 passes into corundum. SiO_2, due to the inability to bind to Al_2O_3 to mullite, turns into cristobalite.

For comparison, Khattab *et al*. synthesized mullite pigments from waste material containing silica. They reported results similar to ours. At 1300-1350 °C they also obtained corundum and cristobalite as the main phases. With increasing temperature to 1400°C, mullite is mainly formed, while the amount of corundum and cristobalite decreases [9].

Pigments studies

Figure 7 presents the results of the X-ray analysis. It reveals the main phases in the synthesized ceramic pigments, which are: corundum (Al_2O_3), cristobalite (SiO_2), mullite ($3Al_2O_3.2SiO_2$), and nickel spinel ($NiAl_2O_4$). Mullite is detected only in samples P3-5 and PR3-5, fired at 1400 °C. Mullite is not observed in samples M3-5 and MR3-5.

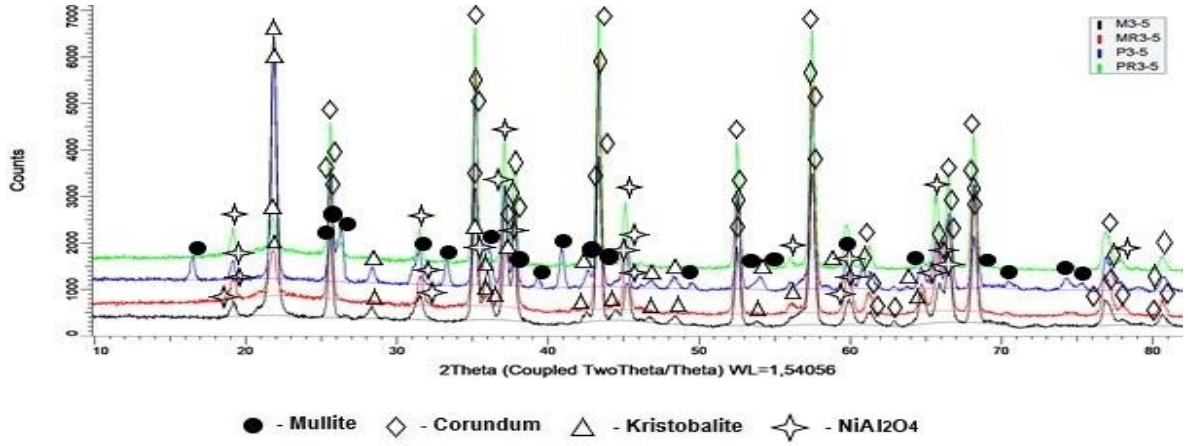

Figure 7. XRD of samples M3-5, MR3-5, P3-5, PR3-5

Figure 8. presents the main phases in the synthesized samples in mass percentages.

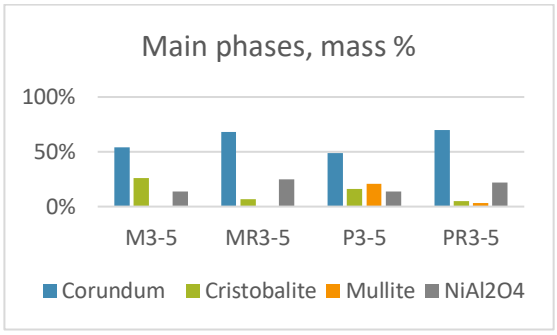

Figure 8. Main phases in the samples

The graph in Fig. 9 shows the crystal sizes of the main phases in the samples.

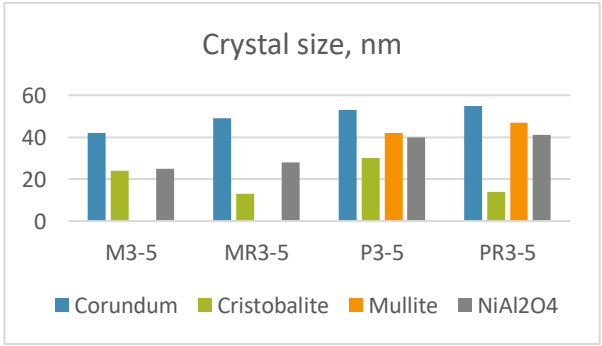

Figure 9. Crystal size of samples.

Table 2. Color coordinates of samples

Composition	T, °C	Color	L*	a *	b *
M3-5	1350		96.3	-15.2	-4.9
MR3-5	1350		79.0	-12.8	-2.9
P3-5	1400		75.2	-15.1	-2.5
PR3-5	1400		76.5	-13.6	-4.2

The size of the crystalline phases varies from 13 nm (MR3-5) to 55 nm (PR3-5), with the average crystal size for each phase being: corundum - 49.75 nm, cristobalite - 20.25nm, mullite - 44.5 nm and $NiAl_2O_4$ - 33.5 nm.

Color measurement

There are different systems for reporting and measuring colors - MKO 1931, CIELuv, CIELab, etc. [10, 11]. For the needs of ceramics in Europe and the USA, the most widely used system is the CIELab system with color coordinates:

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

In our study, the color of the pigments was determined spectrally with a tintometer from the company Lovibond Tintometer RT 100 Color, with the CIELab system.

All synthesized pigments have a beautiful blue-green color due to the d - d transition of Ni^{2+} in octahedral coordination. The pigments synthesized from pure raw materials at 1350 °C had the best indicators, respectively (a) = - 15.2 and (b) = - 4.9 (Table 2).

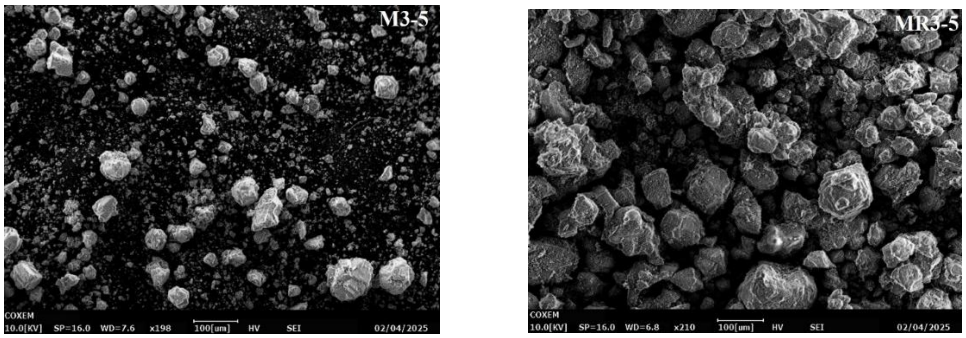

Figure 10. SEM images of samples M3-5 and MR3-5 fired at 1350 ºC

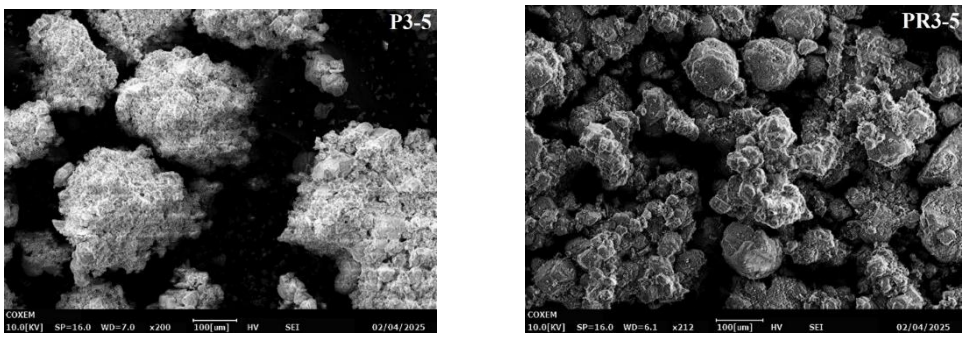

Figure 11. SEM images of samples P3-5 and PR3-5 fired at 1400 ºC

Scanning electron microscopy

The samples were analyzed by scanning electron microscopy (SEM) at 10.00 kV accelerating voltage using an IEM11 microscope, Inovenso INC, (Turkey). SEM analysis (Figs. 10 and 11) shows that the particles in the pigments tend to form clusters larger in the pigments fired at a higher temperature - 1400 °C.

CONCLUSIONS

The main phases in the synthesized ceramic pigments were identified by X-ray diffraction (XRD): corundum (Al_2O_3), cristobalite (SiO_2), mullite ($3Al_2O_3.2SiO_2$), and nickel spinel ($NiAl_2O_4$). It is noteworthy that the main crystalline phase in all compositions is corundum, with nickel spinel also forming everywhere. These two phases are resistant and stable at high temperatures, which also determines the good properties of the synthesized pigments. This conclusion is also confirmed by the hot-stage analysis. The results of hot-stage microscopy of batches obtained from pure raw materials show that up to 1400 ℃, the shape of the samples remains constant, without visible changes. Extremely high thermal stability of the samples is observed. The size of the crystals in the main phases was determined. It varies from 13 nm (MR3-5) to 55 nm (PR3-5). The color characteristics of the synthesized pigments were determined spectrally, the pigment with composition M3-5 having the best indicators: (a) = -15.2 and (b) = -4.9.

Acknowledgement: *The financial support of this work by the Bulgarian Ministry of Education and Science, National Research Fund under contract number KP-06-N87/14 is gratefully acknowledged.*

REFERENCES

1. Ts. Ibreva, Ts. Dimitrov *et al*., *Bulg. Chem. Commun.*, **50**, 31 **(**2018).
2. F. A. Cotton, Modern Inorganic Chemistry, Moscow, 1979 (in Russian).
3. A. Wells, Structural Inorganic Chemistry, Mir, Moscow, 1987 (in Russian).
4. A. A. Grinberg, Introduction to the Chemistry of Complex Compounds, Chemistry, Leningrad, 1971 (in Russian).
5. Y. Wang *et al*., *Solid State Sci.*, **135**, 107088 (2023).
6. K. L. Patrocínio *et al*., *Ceramics International*, **50**, 31955 (2024).
7. F. Yovkova *et al*., *Annual of Assen Zlatarov University*, **XLVIII**, 2603 (2019).
8. M. Javanmardi *et al.*, *Trans. Nonferrous Met. Soc. China*, **26**, 2910 (2016).
9. R.M. Khattab *et al.*, *Materials Chemistry and Physics,* **281**, 125880 (2022).
10. B. S. Cherepanov *et al*., Glass and ceramics, 1983 (in Russian).
11. M. Troyan, Glass and Ceramics, 1988 (in Russian).