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Phase analysis and color characteristics of Co-, Cu-, and Ni-doped ceramic pigments

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Applying a solid-phase synthesis method, ceramic materials of the $Al_2O_3 – SiO_2$ system were obtained by using pure raw materials. Cobalt, copper, and nickel were added as coloring ions, in an amount of 20%. Qualitative and quantitative analysis of the synthesized pigments was performed using X-ray diffraction. In the $Al_2O_3 – SiO_2$ system, the most important compound formed is mullite ($3Al_2O_3 \cdot 2SiO_2$). However, the results of the conducted studies show that with such a large amount of chromophore (20%), mullite is formed only with the addition of cobalt oxide. When adding nickel oxide, a tendency is observed to form predominantly nickel-aluminum spinel, and with the chromophore copper, the introduced CuO does not bind to Al_2O_3 but part of it passes into Cu_2O, so that in the system $Al_2O_3 – SiO_2 – CuO$ the two copper oxides– CuO and Cu_2O are formed.

Keywords: ceramic pigments, solid-state sintering, CIELab system

INTRODUCTION

The most common carriers of color in pigments are the chromophores. These are atoms or atomic groups that have the ability to impart a certain color to the substances in which they are found. One of the most complete classifications is based on the crystal structure of the main phase. According to this classification of pigments, they can be spinel, willemite, garnet, zircon, etc. In the chemical technology of spinel pigments, various methods are currently used to obtain the final product. The main ones are ceramic and sol-gel methods. Sol-gel methods are associated with the presence of a stage of co-precipitation of divalent and trivalent metal ions with the formation of poorly soluble precipitates and the need to grind the agglomerate to a finely dispersed state. The color of pigments depends not only on the chemical nature of the introduced chromophore ion but also on the coordination in which it is located, as well as on the level of symmetry of the coordination polyhedron. The most stable and bright colors are those of the spinel series which have a cubic structure [1–3]. They are obtained mainly by solid-phase synthesis at high temperatures from chemically pure reagents or waste. Many scientists from all over the world are conducting research on the synthesis and study of various types of spinel pigments [4–8]. The developed compositions and technological regimes for obtaining cobalt- and nickel-containing spinel-type pigments using a solid-phase method ensure the production of pigments in a finely dispersed state with a particle size ≤50 μm [9]. In this connection, it is of interest to carry out the synthesis in a way that would allow the production of pigments with good color characteristics in a finely dispersed state. Therefore, the study of the processes of solid-phase synthesis of ceramic pigments, the conditions of their formation a spinel structure, and their influence on color is of great scientific and practical importance.

The purpose of the present work is the production of ceramic materials of the system Al_2O_3 - SiO_2 by the method of solid-phase synthesis.

EXPERIMENTAL

Methods

- *X-ray diffraction* – The phase composition was determined using a Philips X-ray diffractometer, 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 HighScore Plus program, using the ICSD (Inorganic Crystal Structure Database).
- *Color measurement* – The color of the pigments is determined spectrally by the Lovibond Tintometer RT 100 Color.

Materials

As initial raw materials, pure Al_2O_3 and $SiO_2 \cdot nH_2O$ with 20% chromophore introduced as Co_2O_3, NiO, and CuO were used. The most important operation, on which the reliability of the

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technology and the stability in the quality of the finished pigment depend, is the preparation of the batch. In the case of poorly prepared batches, the coloring effect of the baked pigment may be reduced even when using chemically pure raw materials and optimal compositions.

The raw materials used for the synthesis of pigments by the solid-phase sintering method are dry and non-hygroscopic, which is why the dry method for preparing the batch was chosen. A crucial aspect in pigment synthesis is the precise dosing of the different components and adherence to the specified formulation.

The quantities of materials according to the recipe for 100 g of the batch are weighed on scales with an accuracy of 0.1 g, then mixed and homogenized in a planetary mill Pulverisette–6 of the company "Fritch" (Germany) in dry conditions.

The firing of the batches was carried out in a high-temperature furnace NaberTherm with a heating rate of 300 ÷ 400°C/h in air atmosphere in corundum crucibles with isothermal retention at the final temperature of 1 h. The pigments were fired at final temperatures of 1400°C.

Table 1 gives the compositions of the prepared pigments.

Table 1. Compositions of the pigments

Sample №	Composition		Chromophore
P1-20	Al_2O_3	$SiO_2{\cdot}nH_2O$	Co
P2-20	Al_2O_3	$SiO_2{\cdot}nH_2O$	Cu
P3-20	Al_2O_3	$SiO_2{\cdot}nH_2O$	Ni

Figure 1 shows the scheme by which the pigments are made.

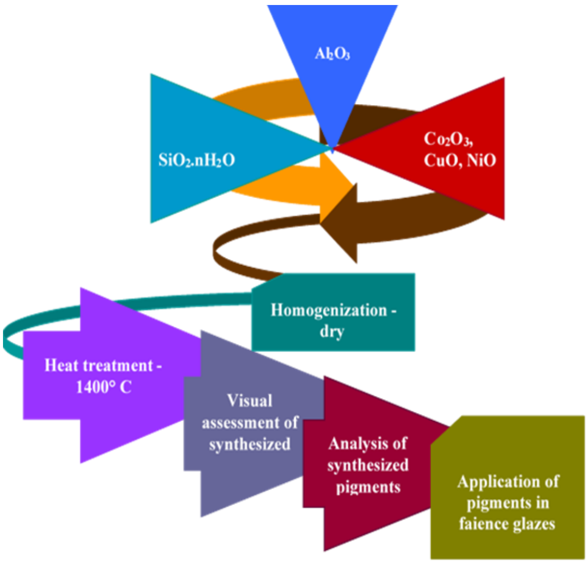


Figure 1. Scheme of pigment preparation

Photographs of the prepared batches are shown in Figure 2.

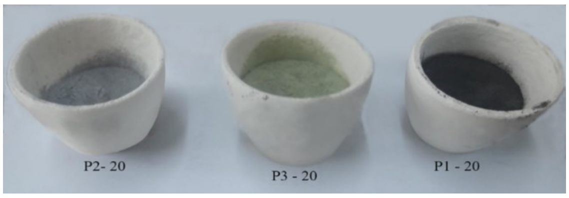


Figure 2. Photos of mixtures

RESULTS AND DISCUSSION

After firing and free cooling to room temperature of the synthesized pigments, a photograph was taken (Figure 3).

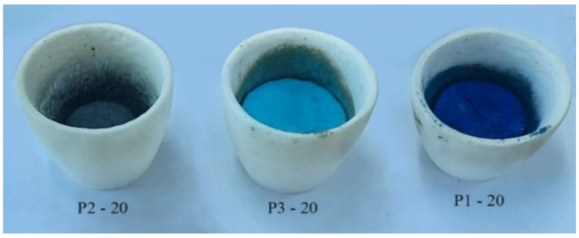


Figure 3. Photos of pigments

Color measurement

The color of the pigments was determined with a Lovibond Tintometer RT 100 Color in a spectral way, where:

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

The results of the measurements are presented in Table 2.

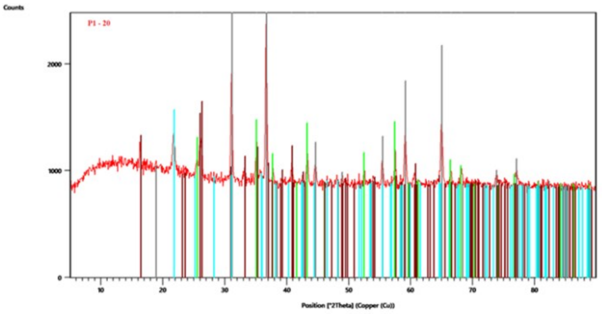
Table 2. Color coordinates of samples with compositions P1-20 ÷ P3-20

Sample №	T, °C	Color	L*	a*	b*
P1-20	1400		35.1	–0.5	–35.2
P2-20	1400		42.2	9.2	16.4
P3-20	1400		65.5	–24.7	–18.5

For composition P1-20 of the system Al_2O_3 – SiO_2 – CoO, the color characteristics are: green color a* = –0.5, blue color b* = –35.2. In the system Al_2O_3 – SiO_2 – CuO, brown-colored pigments were obtained, with an amount of red color a* = 9.2, and yellow color b* = 16.4. In the system Al_2O_3 – SiO_2 – NiO, pigments with a beautiful blue-green color were obtained, whose spectral indicators are: green color a* = –24.7 and blue color b* = –18.5.

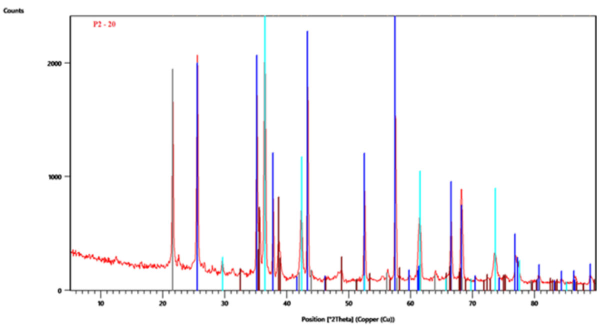
X-ray analysis

- *Qualitative analysis.* Using X-ray diffraction (XRD), qualitative and quantitative analysis of the finished pigments was performed. Figures 4, 5, and 6 present the results of the qualitative analysis of the pigments synthesized at 1400°C for 1 h, with cobalt, copper, and nickel chromophores.



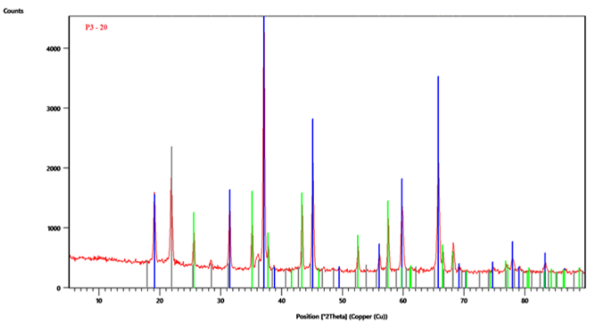
No.	Visi...	Ref. Code	Compound Name	Chemical Formula
1	✓	ICSD 98-003-0024	Corundum (Cr-dop...	Al2 O3
2	✓	ICSD 98-007-8404	Spinel-(Co)	Al2 Co1 O4
3	✓	ICSD 98-009-9327	Mullite	Al4.44 O9.78 Si1.56
4	✓	ICSD 98-003-4933	Cristobalite low	O2 Si1

Figure 4. X-ray diffraction pattern for composition P1-20 (with chromophore cobalt)



No.	Visi...	Ref. Code	Compound Name	Chemical Formula
1	✓	ICSD 98-003-3639	Corundum	Al2 O3
2	✓	ICSD 98-016-2660	Cristobalite beta	O2 Si1
3	✓	ICSD 98-004-3179	Tenorite	Cu1 O1
4	✓	ICSD 98-002-6963	Cuprite	Cu2 O1

Figure 5. X-ray diffraction pattern for composition P2-20 (with chromophore copper)



No.	Visi...	Ref. Code	Compound Name	Chemical Formula
1	✓	ICSD 98-024-7085	Nickel Aluminium T...	Al2 Ni1 O4
2	✓	ICSD 98-008-5137	Aluminium Oxide - ...	Al2 O3
3	✓	ICSD 98-005-2371	Cristobalite low	O2 Si1

Figure 6. X-ray diffraction pattern for composition P3-20 (with chromophore nickel)

Due to the large amount of chromophore, in addition to mullite (Fig. 4), a very large amount of spinel (Al_2CoO_4), residual cristobalite – the high-temperature modification of SiO_2, and corundum (Al_2O_3) is formed. That is, at 20% of chromophore, mullite-spinel pigments are obtained.

In Fig. 5, no mullite formation is observed. The main phases are – corundum, cristobalite, and 2 copper oxides – tenorite and cuprite. That is, in the case of chromophore copper, the introduced CuO does not bind to Al_2O_3, and in the system, Al_2O_3 – SiO_2 – CuO, the two copper oxides – CuO and Cu_2O – are formed.

In Fig. 6 again no mullite phase is observed. Due to the large amount of the chromophore, it has bonded preferentially to aluminum oxide and the formed spinel. The main phases formed are corundum, nickel-aluminum tetroxide (nickel-aluminum spinel), and cristobalite.

- *Quantitative analysis.* The percent content of the main phases in the pigments with compositions P1-20 ÷ P3-20 is given in Figures 7 ÷ 9.

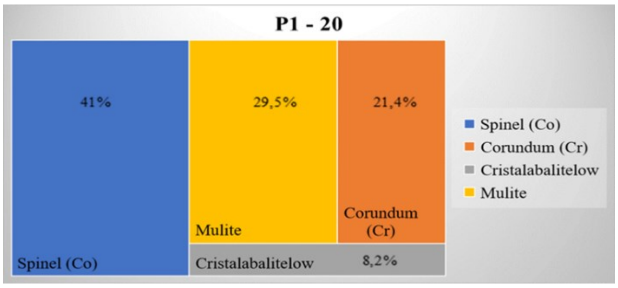


Figure 7. Quantities of the main phases in composition P1-20

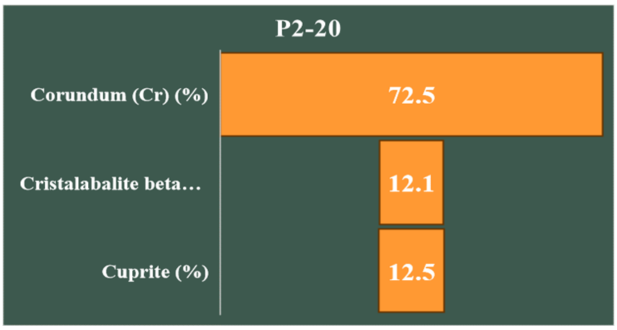


Figure 8. Quantities of the main phases in composition P2-20

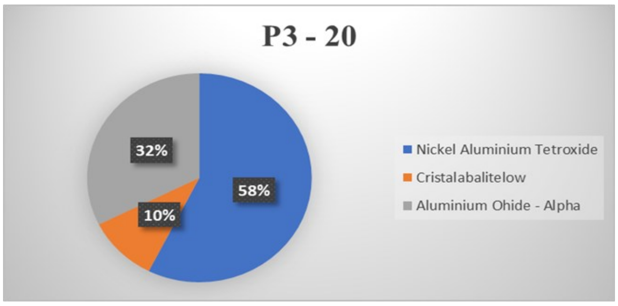


Figure 9. Quantities of the main phases in composition P3-20

CONCLUSIONS

Ceramic materials from the Al_2O_3 – SiO_2 system were obtained by a solid-phase synthesis method. Pure starting materials and chromophores in an amount of 20% were used. The optimal conditions for their preparation were determined.

The main phases and their amounts in the individual compositions were established by X-ray qualitative and quantitative analysis. Mullite is observed only in compositions P1-20. This is because the amount of the chromophore is large and spinels are predominantly formed. In compositions P1-20, aluminum-cobalt spinel (Al_2CoO_4) is found, and in compositions P3-20, nickel-aluminum spinel (Al_2NiO_4). Corundum and cristobalite are also observed in all compositions.

The influence of coloring ions and their quantity on the formation of the main mineral by solid-phase synthesis from chemically pure raw materials was studied, and it was found that pigments with saturated colors are obtained, with the best color characteristics being the pigments with composition P1-20 (a^* = –0.5, and b^* = –35.2) of the system Al_2O_3 – SiO_2 – CoO.

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