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SYNTHESIS AND STUDY OF Ni-DOPED WILLEMITE CERAMIC PIGMENTS[1]

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Abstract: *In this study willemite ceramic pigments, doped with Ni were synthesized. The optimal parameters of the synthesis process have been determined. The willemite is a mineral (zinc silicate) with formula Zn_2SiO_4. For the production of willemite ceramic pigments in the system NiO-ZnO-SiO_2 we have used the following main materials: ZnO, NiO and $SiO_2.nH_2O$.*

The willemite ceramic pigments and rice husk ash were studied by X-ray analysis, FT-IR, and scanning electron microscopy (SEM). The color of the pigments was determined using a Lovibond Tintometer RT 100 Color. It has been found that the synthesized pigments are suitable and can be successfully applied in glaze tiles and sanitary ceramics.

Keywords: *pigments, colour, ceramic, willemite, CIELab*

INTRODUCTION

Ceramic pigments are inorganic colored finely dispersed powders which, when added to some medium, impart certain color and change some of its properties. Beside their coloring ability, the ceramic pigments are resistant to atmospheric and chemical influences, high temperatures, decomposing activity of silicate melts and the effects of light. The coloring of the pigment occurs due to the selective absorption of certain wavelengths of light by its crystal lattice. As a result, the pigments are colored in a color complementary to the absorbed one. Most often, the color carriers in the pigments are the chromophores. These are atoms and atomic agglomerates which have the ability to impart one or another color to the substances where they are present.

One of the most important classifications of ceramic pigments is that of Tumanov based on the crystal structure of the main phase. According to this classification, the pigments are spinel, garnet, zircon, willemite, mullite and others. (Maslennikova G.N., & Pishch I.V., 2009).

The ceramic pigments must have the following properties: high color intensity, resistance to high temperatures, resistance to the eroding effects of silicate melts at the temperatures of sintering, cover ability. Most of the compounds obeying these requirements are colorless. To make them play the role of pigment, they are artificially colored by introducing substances imparting the desired color. Such properties have the compounds of transition d- and f- elements, e.g. vanadium, iron, cobalt, manganese, nickel, chromium, copper, praseodymium, etc. (Eppler R., 1987).

Willemite is a mineral - zinc silicate. It has been discovered in the form of small brown

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crystals and in 1830 was named after the King of Holland Willem I (Willem Frederik). Willemite can be green, yellow, brown, red-brown, orange and blue. It can be found in nature as small prismatic or stubby crystals. It is one of not many silicates with trigonal singony which is more characteristic for the carbonates.

Researchers from different countries have worked on the synthesis and study of villemite ceramic pigments, studying the structure of these pigments and the possibility of partial replacement of ZnO with CoO (Ozel E., Yurdakul H., Turan S., & Dondi M., 2010)., (Chandrappa G. T., Ghosh S., & Patil K.C., 1999)., (Llusar M., Forés A., Badenes J., Calbo J., Tena M., & Monrós G., 2001)., NiO (Masslennikova G. N., & Fomina N.P., 1974)., FeO (Masslennikova G. N., Fomina N. P., & Glebicheva A. I., 1975). and MnO (Chandra Babu B., Vengla Ra, Ravi M., & Babu S., 2017).

In our earlier studies, we have proved the effect of CoO as an oxide imparting saturated blue color to the willemite pigments (Dimtrov Ts., Markovska I., & Ibreva Ts., 2018).

The aim of the present work is synthesis, investigation and characterization of Ni-containing willemite ceramic pigments.

EXPLANATION

Materials and method of synthesis

For the preparation of ceramic pigments in the system $NiO.ZnO.SiO_2$ the starting compositions are determined from the basic mineral willemite $xNiO.(2-x).ZnO.SiO_2$, where x = 0.125, 0.250, 0.375, 0.50, 0.625, 0.75, 0.875 and 1.00. Ceramics were syntesized via solid-state high temperature sintering. Starting materials used for the synthesis are NiO, ZnO and $SiO_2.nH_2O$ with particle size in the range of 2-7μm, which is much more reactive than conventionally used quartz sand as a source of SiO_2. NaF was used as a mineralizer. Calculated quantities of materials for 100 g batch are weighed with a precision, then mixed and dry homogenized in planetary mill Pulverizete-6 (Fritch). Synthesis was carried out in a laboratory muffle furnace in porcelain crucibles with a heating rate of 300-400°C/h in air with isothermal retention of 1 hour at the final temperature. The resulting powder mixtures were sintered at 800, 900, 1000, 1100 and 1200°C in order to obtain blue ceramic pigments.

STUDY OF SYNTHESIZED PIGMENTS

X-ray analysis of the resulting ceramic pigments.

X-ray analysis is a direct method for phase identification. The basis of the method lies in the X-ray diffraction. A major task in X-ray analysis is to identify different phases individually or in their mixtures based on the diffraction pattern given by the sample. The X-ray investigations were performed on an IRIS apparatus at Cu K_α irradiation with a nickel filter. X-ray diffraction patterns of the synthesized ceramic pigments are shown in fig. 1. and fig. 2.

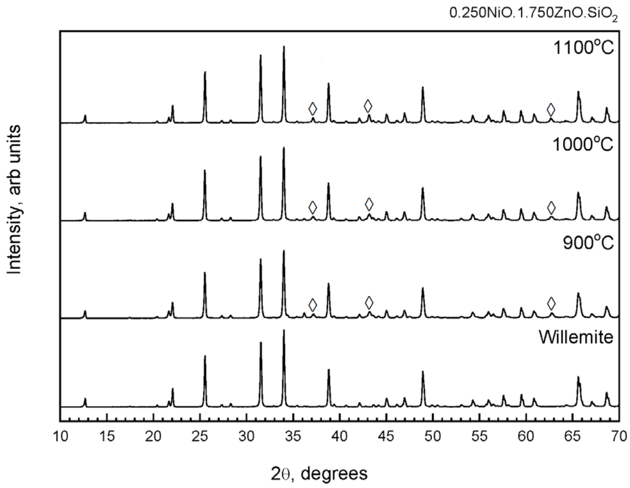

Fig. 1. XRD patterns of synthesized Ni-willemite pigments in the system $0,25NiO.1,75ZnO.SiO_2$: main phase - willemite - Zn_2SiO_4, ◊ - NiO PDF 652901

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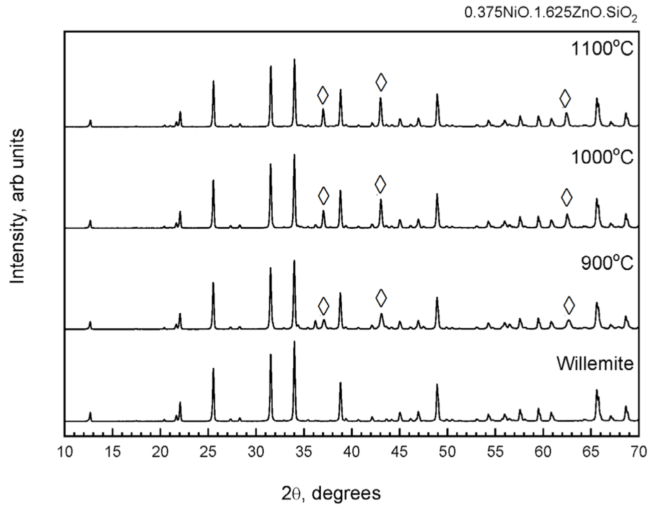

Fig. 2 XRD patterns of synthesized Ni-willemite pigments in the system 0,375NiO.1,625ZnO.SiO2: main phase - willemite - Zn_2SiO_4, ◊ - NiO PDF 652901

Fig. 1 and Fig. 2 shows the XRD patterns of willemite pigments synthesized at different temperatures. During the pigment synthesis, willemite appears as the main phase at temperatures lower than 900°C though there are still strong reflections corresponding to NiO.

The main mineral phase of the pigments synthesized at 900 ºC is willemite with the most intense absorption lines d, nm (I/I_1, %): 3.4846(72) - 2.8350(100) - 2.6344(86) - 2.3174(50), with content of 85% determined by the method of the internal standard. The coloring ion is introduced in it filling the gaps in the crystal lattice. Thus, it settles in a rigid crystal lattice in the structure of the main phase without affecting it except for the color.

Electronic paramagnetic resonance of the resulting ceramic pigments

EPR spectrum of the sample with composition $0.5NiO.1.5ZnO.SiO_2$ was recorded at 120 and 295K. (Fig. 3). At 295K, an asymmetric low intensity signal with g≈2.30 and Hpp≈95mT was detected. The low-temperature signal is expanded.

The signal is most likely derived from exchange-bound Ni^{2+} ions. The low intensity signal is due to the fact that Ni^{2+} ions have an overall spin quantum number S=1, making it difficult to observe them in the X-band at a frequency of 9.45GHz electromagnetic radiation.

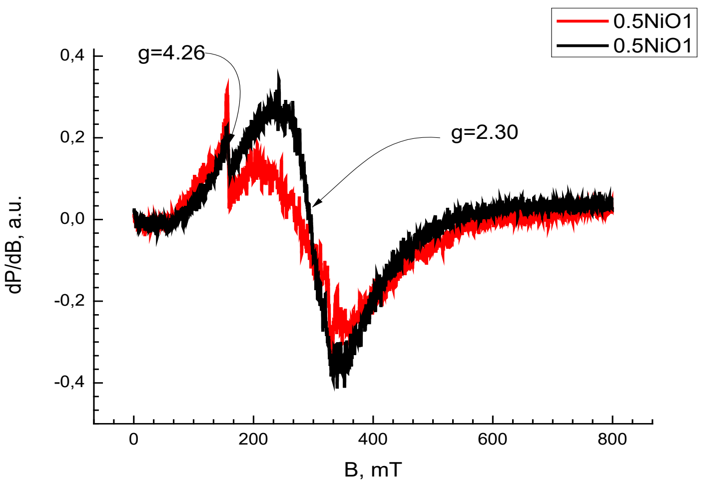

Fig.3. EPR sample spectrum $0.5NiO.1.5ZnO.SiO_2$ at 295K (black line) and 120K (red line)

Color Measurement

Color is one of the most important indicators of pigment quality. Colored substances absorb and convert light rays of a certain wavelength into the visible portion of the spectrum, due to their atomic structure. The CIELab system defines colors not only of ceramic pigments but also of other materials, which indicates that this system is universal and widely used.

In the CIELab system, the color coordinates are:

-L* (brightness), from absolute white L* = 100 to absolute black L*=0

-a* - green color (-) / red color (+)

-b* - blue color (-) / yellow color (+)

The color space of the CIELab system is shown in Figure. 4.

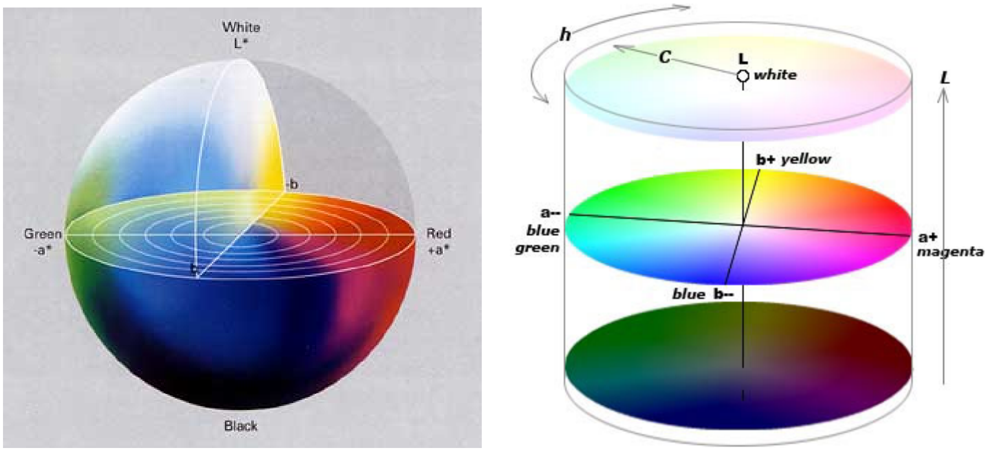

Fig. 4. The color space of CIELab system

The color determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color. The results obtained for color coordinates of the pigments are shown in Table 1.

№	Composition	Colour	L*	a *	b *
1	$0,125NiO.1,875ZnO.SiO_2$		67.1	-9,84	-21,18
2	$0,25NiO.1,75ZnO.SiO_2$		60.8	-10,5	-22,47
3	$0,375NiO.1,625ZnO.SiO_2$		58,2	-12,4	-17,54
4	$0,5NiO.1,5ZnO.SiO_2$		53,5	-12,5	-13,78
5	$0,625NiO.1,375ZnO.SiO_2$		52,0	-12,65	-8,49
6	$0,75NiO.1,25ZnO.SiO_2$		50,9	-12,45	-6,75
7	$0,875NiO.1,125ZnO.SiO_2$		49,8	-10,45	-5,17
8	$1,0NiO.1,0ZnO.SiO_2$		47,2	-9,01	-1,94

From the data presented, it can be seen that the most intense blue color is obtained with the pigment $CoO.ZnO.SiO_2$ synthesized at 1000 °C. After the introduction of additives from FeO, NiO, P_2O_5 there is a decrease in the blue color - the parameter -b *. As the synthesis temperature increases, the amount of blue color increases.

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Electron microscopic examination of pigments

Electronic microscopy is a method of directly studying the structure of the samples studied. To determine the topography of the test samples, Scanning Electron Spectroscopy was applied. Electron microscopic observations were performed with a TESCAN, SEM / FIB LYRA I XMU instrument at a 30 kV accelerating voltage of 30 kV. Observations were combined with an Energy Distributed X-Ray Spectroscopy conducted with Bruker's detector.

The synthesized pigments were observed in reflected electron mode at low (1500 times) and high (3000 times) magnifications. Electron microscopic observations at low magnifications were combined with a mapping EPCP to monitor the distribution of crystalline phase elements.

The particles are opaque to the electron beam, and from the photographs taken, only the shape and size of the crystals can be drawn, as well as their tendency to aggregation. Figure 5 presents the micrographs of the synthesized pigments.

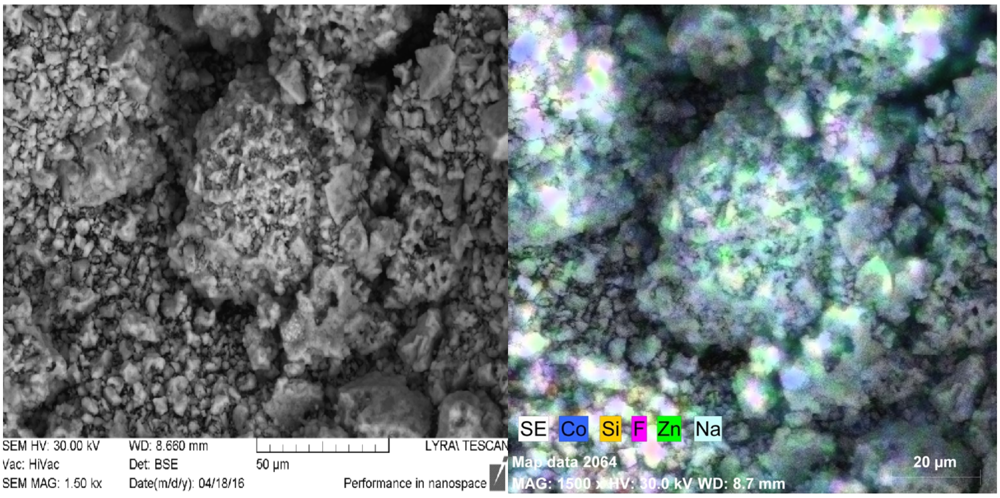

Fig. 5. Microfotographs of the synthesized valemithic ceramic pigments

The figure shows that the sample is polydispersed and two types of crystals are observed: particle size 3-5 μm and between 6 - 8 μm.

CONCLUSIONS

Willemite ceramic pigments containing NiO are synthesized and a technological scheme for their preparation is designed. Blue ceramic pigments based on solid phase sintering were synthesized. As main crystalline phase, willemite is formed at temperatures as low as 900°C. The optimal parameters of the synthesis process have been determined. Best results are obtained with the pigment synthesized at a firing temperature of 1000 °C. The synthesized pigments are suitable and can be successfully applied in glazing tiles and sanitary ceramics.

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