ANNUAL OF ASSEN ZLATAROV UNIVERSITY, BURGAS
BULGARIA, 2019, v. XLVIII (1)

SYNTHESIS AND STUDY OF Co-DOPED WILLEMITE CERAMIC PIGMENTS

Tsvetalina Ibreva, Tsvetan Dimitrov, Aleksander Karamanov, Georgi Avdeev
E-mail: cvetila@abv.bg

ABSTRACT

This study shows the possibility to synthesize Co-doped willemite ceramic pigments via solid-state high temperature sintering. The starting materials used for the synthesis of pigments were CoO, ZnO, Fe_2O_3, NiO, P_2O_5 and amorphous $Si_2O.H_2O$. In the synthesized pigments ZnO was substituted partially by CoO. The optimal parameters of the synthesis process were determined. The willemite ceramic pigments were studied mainly by X-ray analysis, scanning electron microscopy (SEM) as well as by the CIELab system of color measurement. It was found out that the synthesized pigments are suitable and can be successfully applied in glaze tiles and sanitary ceramics.

Key words: *willemite pigments, CIELab color measurement, oxide additives, solid-state sintering*

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, ceramic pigments are resistant to atmospheric and chemical influences, high temperatures, the decomposing activity of silicate melts and the effects of light [1 - 5]. These colored inorganic substances have a high coefficient of light refraction, they are insoluble in water, organic solvents and binding materials, but possess the ability to disperse in them and impart specific color.

In recent years, researchers from many countries work on the synthesis, characterization and properties of various kinds of willemite ceramic pigments prepared from both natural and waste materials [6, 7]. Willemite is a mineral, zinc silicate ($2ZnO.SiO_2$). It was discovered in the form of small brown crystals and named after the King of Holland Willem I (Willem Frederik) in 1830. Willemite can be green, yellow, brown, red-brown, orange, and blue. It can be found in nature as prismatic translucent and small needle crystals. It is one of the few silicates with orthogonal syngony, which is more characteristic of carbonates.

The ceramic pigments with structures of willemite $2ZnO.SiO_2$ which crystalize in the trigonal syngony have been known for some time. Such is the widely used cobalt silicate $2CoO.SiO_2$ with fine blue color. The color palette of willemite pigments today is quite large [8]. If zinc oxide is substituted with nickel oxide, blue pigments which successfully compete with the more expensive cobalt pigments can be obtained. The introduction of FeO results in yellow and brown pigments and MnO in pink, purple and grey [8]. Attempts have been made to substitute not only ZnO but also SiO_2 with other acidic oxides such as SnO_2, TiO_2, ZrO_2 [9].

The aim of the present paper is to study the possibilities to synthesize blue willemite ceramic pigments from pure materials with respect to their possible use as pigments in the silicate industry.

MATERIALS AND METHODS

1. *Materials*

The synthesis of pigments is carried out by a solid state reaction using the following chemically pure initial materials: CoO, ZnO, $SiO_2.2H_2O$, Fe_2O_3, NiO, P_2O_5 и NaF. Amourphous $Si_2O.H_2O$ was used as a source of SiO_2. In these synthesized pigments ZnO could be partially substituted by CoO.

The SiO_2 feedstock used in the system $SiO_2.nH_2O$ is considerably more reactive than conventional quartz sand and has a particle size in the range of 2-7 μm. The mineralizer of NaF is used to reduce the temperature of the synthesis and accelerate the processes of formation of the new phase.

2. *Methods*

The willemite ceramic pigments were studied mainly by X-ray analysis, scanning electron microscopy (SEM) as well as by the CIELab system of color measurement.

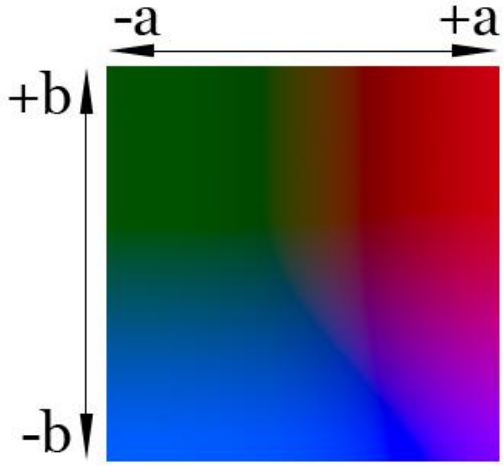
The X-ray analyses were carried out by the method of powder diffraction using X-ray apparatus equipped D2 PHASER AXS – Brueker, with Cu anode and K_α emission, (CuKα, λ=1.5406Å). The following operating regime was used during the experiments: current 10 mA and voltage 30 kV.

The morphology and microstructure of the piments were investigated by scanning electron microscopy (SEM). The electron microscope photographs were taken using a Philips SEM525M/EDAX9900 scanning electron microscope with attached X- ray microanalyst. The microphotographs were taken in a regime of secondary electrons at acceleration of 20 kV.

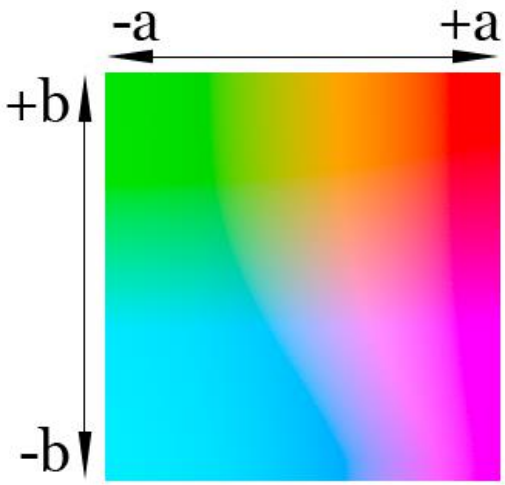
Color measurement. Color is one of the most important indicators of pigment quality. Colored substances absorb and convert light rays of a certain wavelength into the visible portion of the spectrum, due to their atomic structure. The CIELab system defines colors not only of ceramic pigments but also of other materials, which indicates that this system is universal and widely used. In the present paper the pigments color is determined spectrally with a Lovibond Tintometer RT 100 Color. The colour measurements were performed using the CIELab method. This method, which is the standard method in the ceramic industry, especially for ceramic pigments, allows to determine the whiteness and color degree of tiles by measuring the three parameters: *L**, *a** and *b**, where:

- *L** (brightness), from absolute white *L** = 100 to absolute black *L** = 0
- a* - green color (-) / red color (+)
- b* - blue color (-) / yellow color (+)

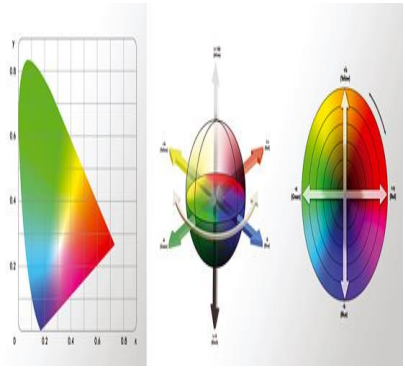
The color space of the CIELab system is shown in Fig. 1 (A-C).



A) brightness 25 %



B) brightness 75 %



C)

Fig. 1 (A, B, C) The colour space of CIELab system

EXPERIMENT

In order to obtain willemite ceramic pigments in the system $Co0.Zn0.SiO_2$ the composition of the blends was calculated. The following pigment compositions were prepared: $CoO.ZnO.SiO_2$,$CoO.ZnO.SiO_2.0.1Fe_20_3$,CoO.ZnO.SiO_2.0,1NiO and $CoO.ZnO.0.5SiO_2$. $0,5P_2O_5$. First, after calcination in a platinum crucible, the SiO_2 and H_2O content in SiO_2.nH2O was determined, as follows: SiO_2 – 76.3% and H2O – 23.7%. Quantities of the starting oxides, such as ZnO, CoO, Fe_2O_3, NiO, P_2O_5 and $Si_2O.H_2O$ in the 100 g batch recipe were weighed to the nearest 0.1 g, then mixed and homogenized in a FRITCH PULVERIZETE6 planetary mill.

The composition of the samples is shown in Table 1.

Table 1. Composition of the samples

No of sample	Composition
1	$CoO.ZnO.SiO_2$
2	$CoO.ZnO.SiO_2.0.1Fe_2O_3$
3	$CoO.ZnO.SiO_2.0,1NiO$
4	$CoO.ZnO.0.5SiO_2.0.5\ P_2O_5$

The synthesis of pigments was carried out by the method of solid state sintering. The sintering of the initial blends was performed in a laboratory muffle furnace at heating rate 6°C\min and 1 h isothermal period at the final temperature. The pigments were sintered at 900°C and 1000°C. After sintering, additional homogenization was carried out in a planetary mill PULVERIZETE6, a product of FRITCH Co.

RESULTS AND DISCUSSION

X – ray analysis of the pigments

Fig. 2 shows the results obtained from X-ray phase analyses of the pigments. The X-ray analyses carried out showed that cobalt – willemite ceramic pigments were synthesized in the system $x.CoO.(2-x).ZnO.SiO_2$, where x= 1,00.

It can be seen from the X-rays analyses that the main phase was a willemite and reflexes of the zinc silicate were also observed.

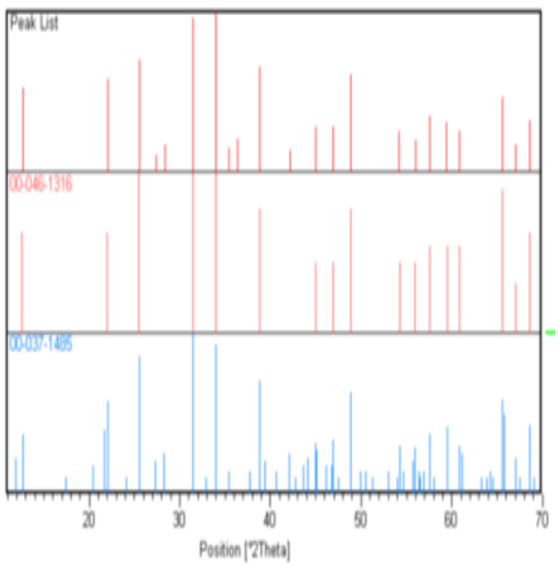


Fig. 2. XRD parents of Co – doped zinc silicate synthesized at 1000°C in the system CoO.ZnO.SiO2: 00-046-1316 - willemite – (Zn, Co) $_2SiO_4$: 00-037-1485 zinc silicate Zn_2SiO_4

Color Measurement

One of the most characteristic properties of pigments is their color. In this respect, one of the most important studies of pigments is connected with the determination of their color coordinates. The coloring of 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 in which they are present.

Table 2 shows the results obtained for color coordinates of the pigments synthesized, using the CIELab colour system. All pigments are blue, due to the cobalt ion. It can be seen from the data presented that the best results were obtained for Co-willemite pigment – k $CoO.ZnO.SiO_2$ synthesized at 1000°C-b*=-47.2. Good results are also obtained for the same composition synthesized at 900°C, b*=-31.4. After the introduction of additives such as FeO, NiO, P_2O_5 the blue color decreases, resp. parameter -b* decreases, too. As the temperature of the synthesis increases, the amount of blue color increases (Table 2).

Table 2. Color measurement of pigments synthesized at 900°C and 1000°C

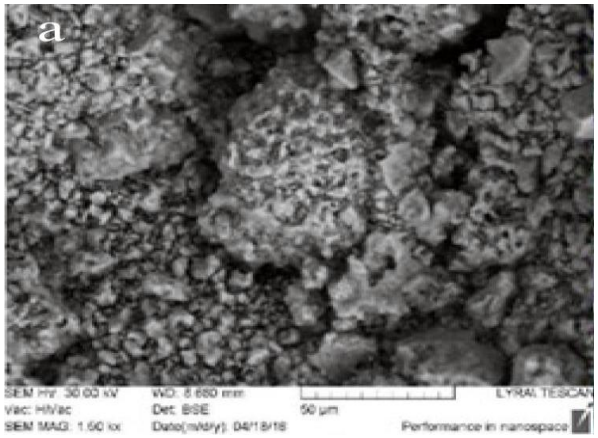
Pigment	Colour	L*	a*	b*
$CoO.ZnO.SiO_2$ 1 - 900°C		28,7	2,1	-31,4
$CoO.ZnO.SiO_2$ 1 - 1000°C		38,5	8,4	-47,2
$CoO.ZnO.SiO_2.0,1FeO$ 2 - 900°C		23,5	-3,2	-7,2
$CoO.ZnO.SiO_2.0,1FeO$ 2 - 1000°C		29,6	-0,1	-24,4
$CoO.ZnO.SiO_2.0,1NiO$ 3 - 900°C		29,3	1,3	-22,6
$CoO.ZnO.SiO_2.0,1NiO$ 3 - 1000°C		41,6	3,9	-37,5
$CoO.ZnO.0,5SiO_2.0,5P_2O_5$ 4 - 900°C		53,8	12,6	-24,3
$CoO.ZnO.0,5SiO_2.0,5P_2O_5$ 4 - 1000°C		62,3	10,5	-26,8

SEM analysis

To determine the topography of the samples, scanning electron spectroscopy was applied. Scanning electron microscopy (SEM) is a method for direct study of the structure of the samples. Observations were combined with Energy

Distributed X-ray Spectroscopy conducted with a Bruker detector. Fig. 3 (a, b) show micrographs of willemite pigments.

The synthesized pigments were observed in reflected electron mode at low (1500 times) and high (3000 times) increases. SEM observations at low magnifications were combined with a mapping EPCP to monitor the distribution of the elements in crystalline phase (Fig. 3b)



a)

b)

Fig.3 (a, b) Micrographs of Co – willemite pigment synthesized at 1000°C

The figure shows that the particles are opaque to the electron beam. In this aspect from the pictures taken, conclusions can only be drawn about the shape and size of the crystals as well as their tendency to aggregation. The crystal sizes were from 3 to 5 μm. In most cases, however, the tendency for aggregation was quite strong and the material began melting under the electron beam.

CONCLUSIONS

Willemite ceramic pigments were synthesized via solid-state high temperature sintering.

The optimal parameters for the process of synthesis of all initial mixtures were established.

The starting materials used for the synthesis were CoO, ZnO, CoO, Fe_2O_3, NiO and $SiO_2.H_2O$.

In the synthesized pigments ZnO was substituted partially by CoO.

It was found out that the pigment with composition $CoO.ZnO.SiO_2$ synthesized at 1000°C had the most saturated color. At this composition the amount of blue color measured by the system CIELab was b* =-41.24.

The introduction of oxide additives, such as FeO, NiO, P_2O_5, led to decrease of the intensity of blue color: the parameter (-b *) had lower values.

It was established that the synthesized pigments could successfully be used in glazes for wall tiles.

ACKNOWLEDGEMENT

This work was supported by the Bulgarian Ministry of Education and Science under the National Research Fund, grant agreement KP-06-H27/14 – 2018.

REFERENCES

1. Ozel, E. and H. Yurdakul, S. Turan, M. Ardit, G. Cruciani and M. Dondi. *J. Eur. Cer. Soc*., 30, (2010), p. 3319-3329.
2.Galindo, R., M. Llusar, A. Tena, G. Monros and J. Badenes. *J. Eur. Cer. Soc.*, 1, (2007), p. 199-205.
3. Alarcon, J., P. Escribamo and J. Gargallo. *Br. Ceram. Trans. J.*, 3, (1984), p. 81-83.
4. Carda, J., G. Monros, P. Escribano and J. Alarcon. *J. Am. Cer. Soc.*, 1, (1989) p.160-162.
5. Klemme, S., J. Miltenburg, P. Javorsky and F. Wastin. *Am. Miner.*, 90, (2005), p. 663-666.
6. Dimtrov, Ts., I. Markovska and Ts. Ibreva. *Eur. Un. Sci. (EUS),* 50, (2018) p. 55-58.
7. Ibreva, Ts., I Markovska and Ts. Dimitrov, *Annual of Assen Zlatarov University*, 2018, volume XLVII, book 1, p. 44- 49.
8. Masslennikova., G., A. Glebicheva and N. Fomina. *Glass and Ceram.,* 8, (1974), p. 23-25.
9. K. Kvjatkovskaj and A. Zazigin. *Glass and Ceram*., 2 (1986) 14-18.