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Synthesis and characterization of willemite ceramic pigments in the system xCoO. (2–x)ZnO. SiO_2

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Zinc silicate α-willemite (Zn_2SiO_4) is an orthosilicate with rhombohedral symmetry. Cobalt doped willemite is a pigment with application in high-temperature ceramics and glaze production. A full series of cobalt containing willemite ceramic pigments with composition xCoO. (2–x)ZnO. SiO_2, where x = 0.125, 0.250, 0.375, 0.50, 0.625, 0,75, 0.875 and 1, were syntesized via solid-state high temperature sintering. The resulting ceramic pigments were examined by powder X-ray diffraction analysis, electron microscopy, infrared spectroscopy and the color was determined spectrophotometrically. It was found that the pigmentwith composition 0,375CoO.1,625ZnO.SiO_2 sintered at 1000 °C has the brightest blue color as defined after spectrophotometric measurments of the coloring efficience. The results confirmed that the synthesized pigments are suitable for application in sanitary ceramics and glaze tiles.

Keywords: willemite, color, pigments, ceramic.

INTRODUCTION

Ceramic pigments are inorganic substances consisting of crystalline ceramic matrix and a chromophore element that provides the color [1]. These ceramic materials should exhibit certain properties such as thermal stability, insolubility in the glazes, high resistance to chemical and physical agents, high color intensity, cover ability, light stability and have to be acceptable in production technology. Most often, materials produced for ceramics are mixed oxides such as spinels, zirconium oxides and silicates. Zinc silicate (Zn_2SiO_4) known as natural ore mineral willemite is orthosilicate with trigonal symmetry (space group $R\bar{3}$). Zn_2SiO_4 is suitable host matrix for many rare earth and transition metal ions that cause efficient luminescence. For this reason, doped zinc silicate has been extensively studied to produce materials for various applications [2–8].

Cobalt doped willemite is blue pigment promising for application in high-temperature ceramics and glaze production as an alternative of ceramics based on spinel and olivine. The advantage of willemite pigments is that saturated blue color can be achieved with much lower cobalt concentrations than ceramics based on spinel and olivine matrix [3].

In our previous studies, we have proven the effect of CoO as an oxide that gives a saturated blue color in the synthesis of willemite pigments [9, 10]. In the present work, our efforts have focused on a detailed study of the effect of cobalt concentration and temperature on the characteristics and properties of synthesized blue ceramic pigments.

The aim of this study is to obtain single phase Co-doped willemite ceramic pigments with various concentration of cobalt in order to determine the optimal composition and temperature of sintering to produce a pigment with the most intense blue color and good mechanical performance.

EXPERIMENTAL DETAILS

Synthesis

For the preparation of ceramic pigments in the system CoO.ZnO.SiO_2 the starting compositions are determined from the basic mineral willemite fol-

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lowing the expression xCoO (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 synthesized via solid-state high temperature sintering. Starting materials used for the synthesis are CoO, ZnO and $SiO_2.nH_2O$ as a source of SiO_2. The used $SiO_2.nH_2O$ with particle size in the range 2–7 μm is much more reactive than conventionally used quartz sand. 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. The compositions of the synthesized pigments are presented in Table 1.

Characterization

The resulting ceramic pigments were examined by powder X-ray diffraction (XRD) analysis, electron microscopy, infrared spectroscopy and the color was determined spectrophotometrically.

Phase composition of the synthesized ceramic pigments was determined using XRD with a Bruker D8 diffractometer operating at 40 kV and 40 mA with CuKα radiation.

FT-IR spectra were collected using a Tensor 37 spectrometer (Bruker) with 4 cm^{-1} resolution after averaging 72 scans on standard KBr pallets in the spectral region 400–4000 cm^{-1} at room temperature.

Electron probe microanalyses (EPMA) and secondary electron (SE) images of the materials were carried out on ZEISS SEM EVO 25 LS – EDAX Trident (IMC-BAS) at acceleration voltage of 20 kV and beam current of 500 pA. The standard less quantification results were performed through automatic background subtraction, matrix correction, and normalization to 100% for all of the elements in the peak identification list.

The color of pigments is determined by tintometer (Lovibont Tintometer RT 100 Colour) and presented in the CIELab color space as defined by the International Commission on Illumination (CIE).

RESULTS AND DISCUSSION

A series of Co-doped ceramics with various concentration of CoO were prepared successively at 800, 900, 1000 and 1100 °C and characterized.

X-ray diffraction (XRD) analysis

The crystal structure of a- Zn_2SiO_4 polymorph is phenakite type, space group *R–3,* where both Zn^{2+} and Si^{4+} ions are coordinated by four oxygen atoms [11]. The powder XRD revealed that cobalt doped willemite ceramics were successfully synthesized even at 800 °C. XRD patterns for two compositions sintered at different temperatures are presented on Figure 1.

At 800 °C no peaks of β-Zn_2SiO_4 phase are observed, pointing to formation of willemite α- Zn_2SiO_4 phase. The XRD patterns show well defined sharp peaks with peak positions corresponding to the standard pattern of willemite PDF 46-1316 (Powder Diffraction File of the International Centre for Diffraction Data – ICDD. Some of the low intensity peaks, marked in Figure 1 with asterisk, reveal presence of minor amount of ZnO in samples sintered at 800 and 900 °C. Such impure phases disappeared at higher temperature of sintering. According to the XRD data the optimal temperature of sintering is 1000 °C as no other impurity peaks are detected.

Figure 2 presents the XRD patterns for the pigments with various concentration of CoO sintered at 1000 °C. Calculated crystallite sizes vary in

Table 1. Compositions of the synthesized pigments

№	Willemite pigment	CoO [g]	ZnO [g]	$SiO_2.nH_2O$ [g]	NaF [g]
1	0.125.CoO.1.875.ZnO.SiO_2	0.2	6.86	3.52	0.2
2	0.250.CoO.1.750.ZnO.SiO_2	0.86	6.42	3.54	0.2
3	0.375.CoO.1.625.ZnO.SiO_2	1.28	5.98	3.56	0.2
4	0.500.CoO.1.500.ZnO.SiO_2	1.71	5.55	3.58	0.2
5	0.625.CoO.1.375.ZnO.SiO_2	2.15	5.10	3.60	0.2
6	0.750.CoO.1.250.ZnO.SiO_2	2.59	4.66	3.62	0.2
7	0.875.CoO.1.125.ZnO.SiO_2	3.03	4.23	3.64	0.2
8	1.000.CoO.1.000.ZnO.SiO_2	3.52	3.81	3.66	0.2

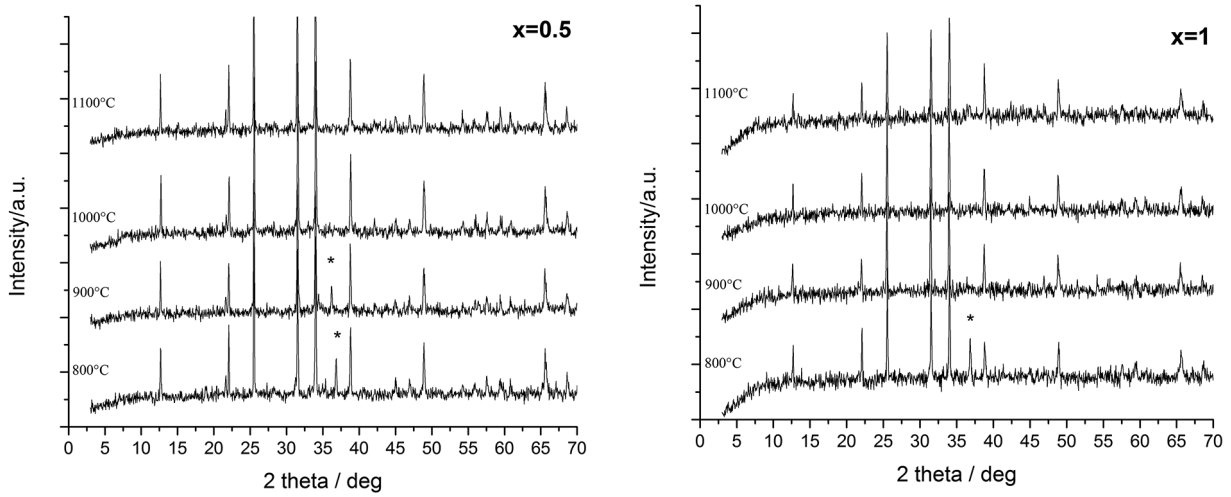

Fig. 1. XRD patterns: *a*) 0.5CoO 1.5ZnO.SiO_2 and *b*) 1.0 CoO 1.0ZnO.SiO_2 at 800, 900, 1000 and 1100 °C. The presence of ZnO is marked with asterisks.

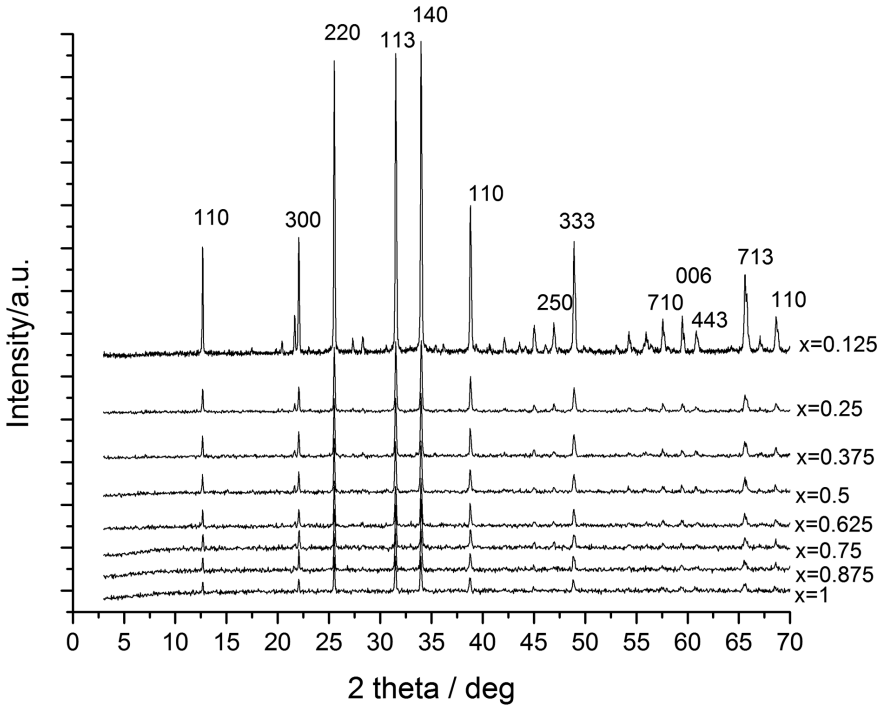

Fig. 2. XRD patterns of full series Co-doped ceramics at 1000 °C.

close range between 80–100 nm. Lattice parameters (Table 2) do not revealed significant differences due to Co for Zn substitution because of close ionic radii in tetrahedral coordination (Zn^{2+} 0.60 Å, Co^{2+} 0.58 Å).

Morphological analysis

Figure 3 presents SEM micrograph of pigment with composition 1.0CoO1.0ZnO.SiO_2 sintered at different temperatures. It is seen that idiomorphic crystals are formed at 800 °C with average size of about 3–5 μm in length. More dense and compact texture is formed with increase of temperature.

FT-IR analysis

FT-IR spectra of Co doped willemite reveal intensive absorption at 900, 930 and 973 cm^{-1} due to

Table 2. Cell parameters of full series Co-doped ceramic pigments sintered at 1000 °C

№	Sample	a (Å)	c (Å)	V (Å^3)
1	0.125.CoO.1.875.ZnO.SiO_2	13.934(5)	9.338(3)	1570(1)
2	0.250.CoO.1.750.ZnO.SiO_2	13.940(4)	9.337(2)	1571(1)
3	0.375.CoO.1.625.ZnO.SiO_2	13.940(4)	9.329(2)	1570(1)
4	0.500.CoO.1.500.ZnO.SiO_2	13.942(5)	9.329(2)	1570(2)
5	0.625.CoO.1.375.ZnO.SiO_2	13.941(5)	9.329(2)	1570(2)
6	0.750.CoO.1.250.ZnO.SiO_2	13.925(3)	9.331(2)	1567(1)
7	0.875.CoO.1.125.ZnO.SiO_2	13.943(5)	9.328(3)	1570(1)
8	1.000.CoO.1.000.ZnO.SiO_2	13.942(4)	9.330(2)	1570(1)
Ref.	$(Zn, Co)_2SiO_4$ PDF 46-1316	13.950	9.336	1574

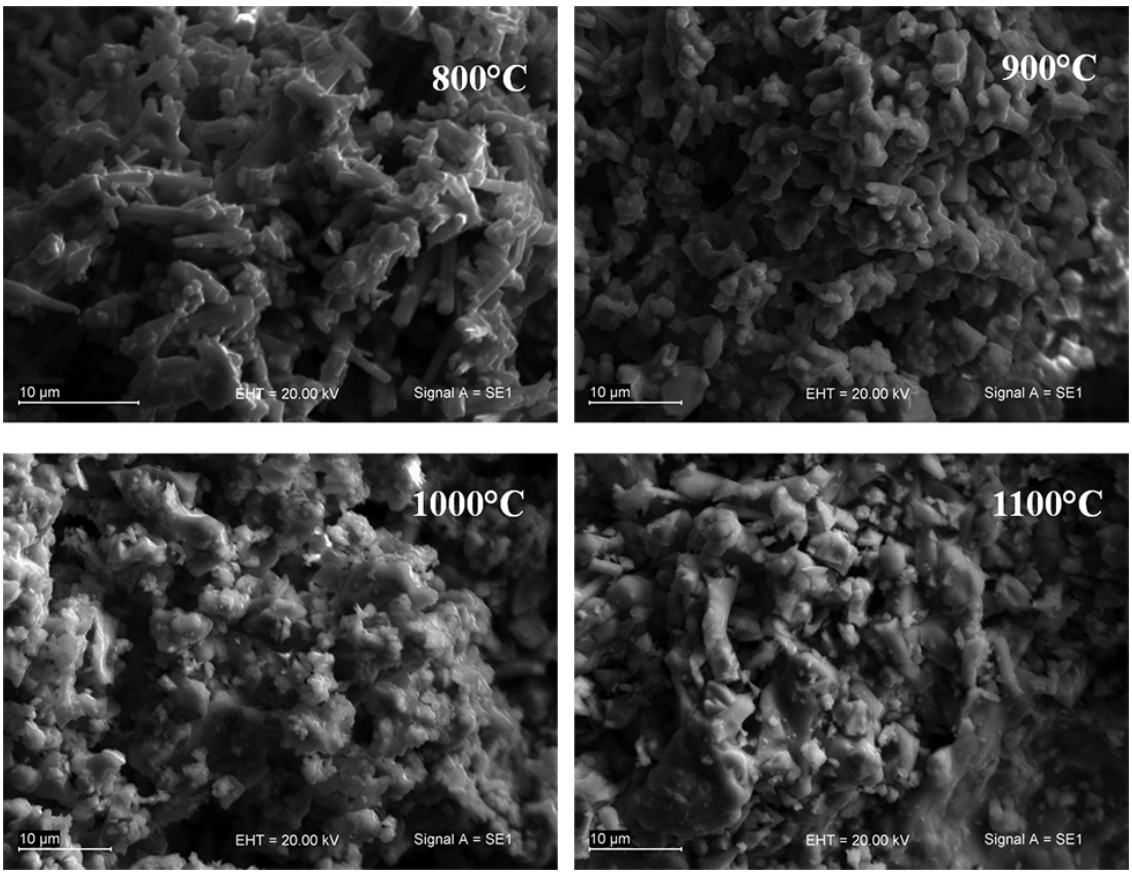

Fig. 3. SEM images of 1.0CoO1.0ZnO.SiO_2 at 800, 900, 1000 and 1100 °C.

Si–O antisymmetric and near 865 cm^{-1} due to the symmetrical stretching mode of SiO_4 tetrahedra. The absorption peak at 460 cm^{-1} is attributed to the Si–O antisymmetric bending mode. The peak at 580 cm^{-1} is assigned to Zn–O totally symmetric stretching mode and the band at 614 cm^{-1} to antisymmetric stretching mode of Zn–O [12]. The presence of these characteristic peaks confirms that crystalline willemite is formed.

Probably, part of the amorphous SiO_2 has not reacted with ZnO, which is visible from the broad absorption band at 1100 cm^{-1}, characteristic for amorphous silica.

It is seen that temperature (Fig. 4) and cobalt concentration (Fig. 5) have a similar effect on the spectral characteristics, namely, their increase leads to a shift to lower wave numbers (Table 3). In the range of Si-O stretching a systematic shift of the

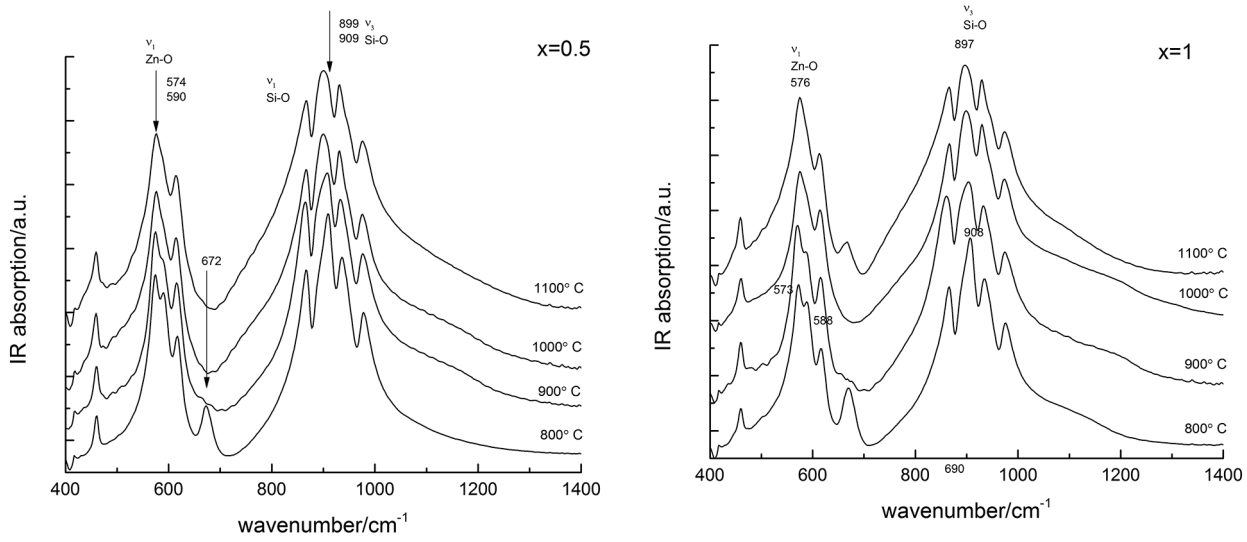

Fig. 4. IR spectra of 0.5CoO 1.5ZnO.SiO_2 and 1.0 CoO 1.0ZnO.SiO_2 synthesized at different temperatures.

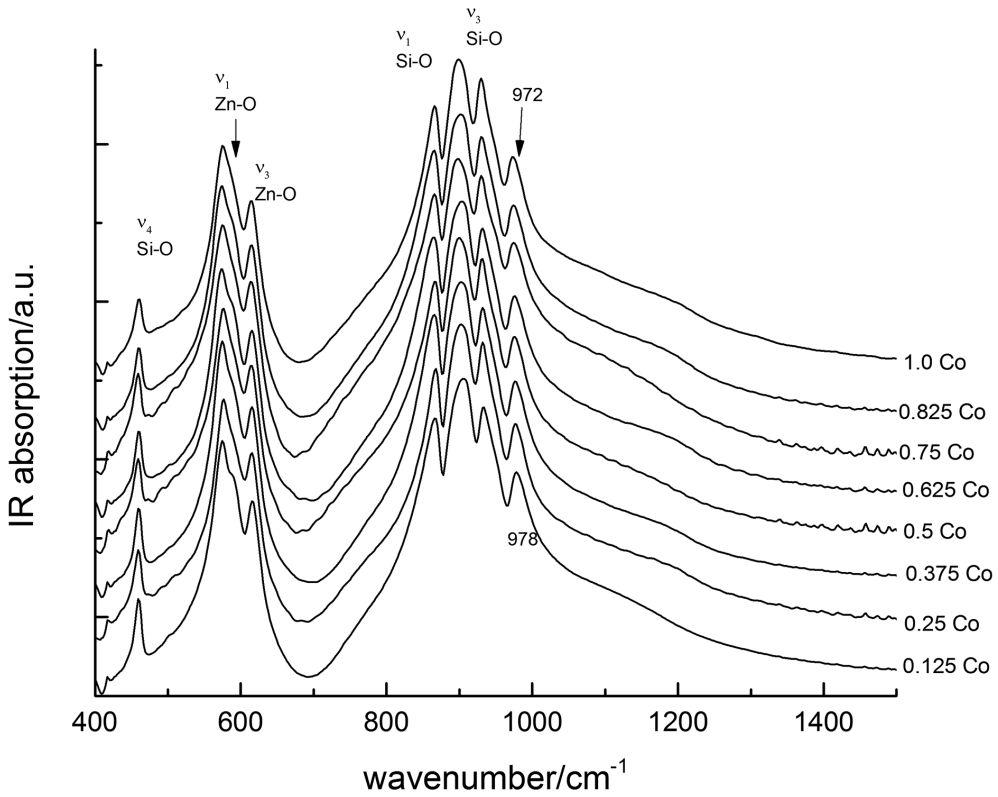

Fig. 5. IR spectra of full series Co-doped ceramics at 1000 °C.

peak at 978 cm^{-1} to low frequency is observed with increase of Co concentration, pointing that cobalt is structurally incorporated. In the range of Zn-O stretching a shoulder at 589 cm^{-1} is visible in the spectra of samples with low Co concentration. This peak disappeared at higher concentration of cobalt.

At low temperature, additional peak near 670 cm^{-1} points to a presence of another mineral phase, probably Co_3O_4 (Fig. 5). The band at 456 cm^{-1} could arise from ZnO presence. Infrared spectra confirmed that residual phases could be detected at low temperatures of sintering.

Table 3. IR peak positions of samples with different Co concentration at 900 and 1000 °C

Sample	ν_4 Si-O [cm^{-1}]		ν_1 Zn-O[cm^{-1}]		ν_3 Zn-O[cm^{-1}]		ν_1 Si-O [cm^{-1}]		ν_3 Si-O [cm^{-1}]	
	900 °C	1000 °C	900 °C		1000 °C	900 °C	1000 °C	900 °C	1000 °C	900 °C	1000 °C
0.25CoO. 1.75ZnO. SiO_2	460	459	576	589	576	616	615	867	867	907 933 977	902 932 976
0.5CoO. 1.5ZnO. SiO_2	460	459	574	590	575	615	615	865	866	907 933 976	900 931 975
0.75CoO. 1.25ZnO. SiO_2	459	459	572	590	574	615	614	864	965	906 932 975	898 930 974

Color measurements

Color is one of the most important indicators of the 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 space expresses color with three numerical values, where ***L**** is a lightness; ***a**** defines the green–red and ***b**** defines the blue–yellow color components. The value of lightness (*L**), represents black at *L** = 0, and white at *L** = 100. The color channels, *a** and *b**, represent true neutral gray values at *a** = 0 and *b** = 0. The *a** axis represents the green–red component, with green in the negative direction and red in the positive direction. The *b** axis represents the blue–yellow component, with blue in the negative direction and yellow in the positive direction. The scaling and limits of the *a** and *b** axes run in the range of ±100 or −128 to +127 (signed 8-bit integer). The CIELab system defines colors not only for the ceramic pigments but also of other materials, indicating that this system is universal and has a wide application. The color space of the CIELab space is presented in Figure 6 and the results for the ceramics sintered at 1000 °C are presented in Table 4.

Increasing the amount of the CoO the parameter b* reaches the highest negative value at x = 0.375, after which the amount of blue color begins to decrease. Generally, as the x increases, L* decreases and the pigments become darker. It can be seen that the most intense blue color is obtained with the pigment 0.375.CoO.1.625.ZnO.SiO_2 synthesized at 1000 °C, with the value of blue color being –b* = –52.85.

A tendency of decrease of lightness L* was observed for all the pigments (they became darker) with increase of the sintering temperature.

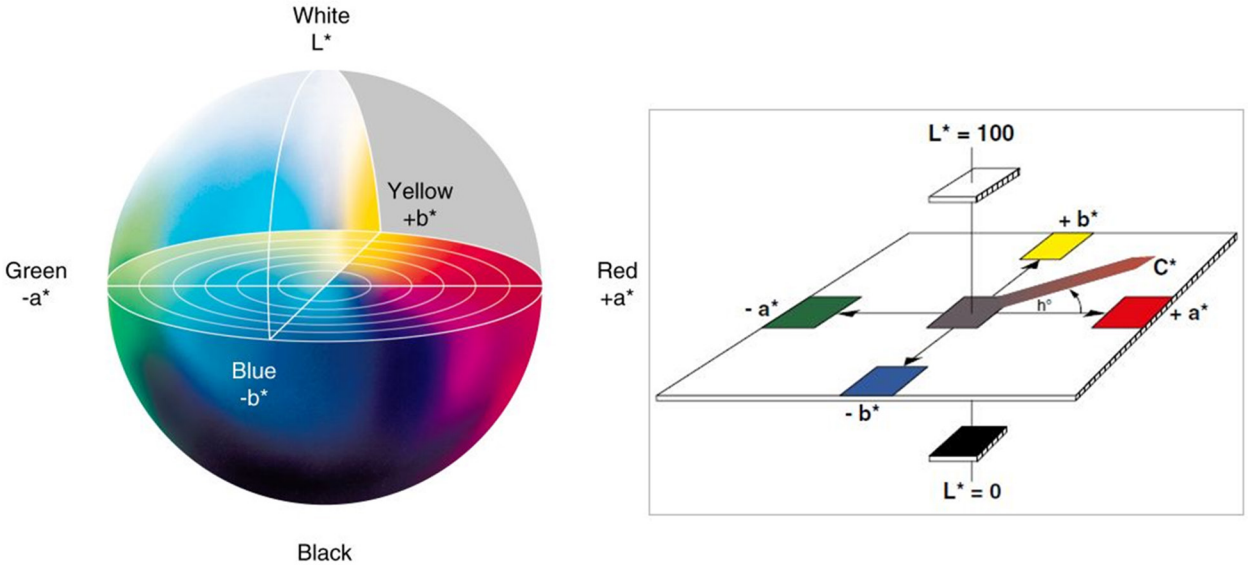

Fig. 6. CIELab model.

Table 4. Results of color coordinates measurements using CIELabe system

Pigment – 1000 °C	L*	a*	b*
0.125.CoO 1.875.ZnO.SiO_2	45.55	2.33	–45.25
0.250.CoO 1.750.ZnO.SiO_2	46.93	6.52	–48.26
0.375.CoO 1.625.ZnO.SiO_2	37.56	13.18	–52.85
0.500.CoO 1.500.ZnO.SiO_2	36.09	9.68	–47.22
0.625.CoO 1.375.ZnO.SiO_2	32.73	8.75	–44.42
0.750.CoO 1.250.ZnO.SiO_2	30.56	5.35	–33.10
0.875.CoO 1.125.ZnO.SiO_2	30.44	3.65	–28.27

CONCLUSIONS

The synthesis of Co-doped willemite pigments was successfully performed and the optimal parameters for the process of synthesis of all the initial mixtures were established. It was found that the best results were obtained with composition 0.375CoO.1.625ZnO.SiO_2 synthesized at 1000 °C. In this case no residual phases are detected and the measured color coordinates in the system CIELab revealed highest value of the blue color (b* = –52.85). The same composition showed also highest luminance (L* = 37,56) and saturation of the color. The synthesized pigments are suitable and can be successfully applied in glaze tiles and sanitary ceramics.

REFERENCES

1. Г. Н. Масленникова, И. В. Пищ, Керамические пигменты, Стройматериалы, Москва, 2009.
2. R. Eppler, *J. Am. Ceram. Soc. Bull.*, **66**, 1600 (1987).
3. E. Ozel, H. Yurdakul, S. Turan, M. Ardit, G. Cruciani, M. Dondi, *Journal of the European Ceramic Society*, **30**(16), 3319 (2010).
4. G. T. Chandrappa, S. Ghosh, K. C. Patil, *Journal of Materials Synthesis and Processing*, **7**(5), 273 (1999).
5. M. Lusar, A. Forés, J. Badenes, J. Calbo, M. Tena, G. Monrós, *Journal of the European Ceramic Society*, **21**(8), 1121 (2001).
6. G. N. Masslennikova., A. I. Glebicheva, N. P. Fomina, *Glass and Ceramics*, **8**, 23 (1974).
7. G. N. Masslennikova, N. P. Fomina, A. I. Glebicheva, *Glass and Ceramics*, **4**, 26 (1975).
8. B. Chandra Babu, B. Vengla Ra, M. Ravi, S. Babu, *J. Mol. Struct*., **1127**(5), 6 (2017).
9. Ts. Dimtrov, I. Markovska, Ts. Ibreva, *Eurasian Union of Scientists (EUS)*, **5**(50), 55 (2018).
10. Ts. Dimitrov, *Proc. of Universit of Ruse Angel Kanchev*, **55** (10.1), 102 (2016).
11. H. McMurdie, M. Morris, E. Evans, B. Paretzkin, W. Wong-Ng, C. Hubbard, *Powder Diffr.*, **1**, 274 (1986).
12. C. C. Lin, P. Shen, *Journal of non-crystalline solids*, **171**, 281 (1994).