Sol-gel synthesis and crystal chemical properties of the pigment Zn$_{1.9}$Cu$_{0.1}$SiO$_4$

The pigment Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ was obtained by the method of sol-gel synthesis. The crystallization temperature was set at 776 °C, $\Delta H \approx -16.3$ kJ/mol. Thermal expansion of the individual Zn$_2$SiO$_4$ and Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ solid solutions was studied by in situ high-temperature X-ray diffraction. It is shown that the substitution of Zn$^{2+}$ → Cu$^{2+}$ does not lead to significant changes in the lattice parameters; in the range from room temperature to 800 °C the structure expands monotonically when heated. The coefficients of volumetric thermal expansion for Zn$_2$SiO$_4$ and Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ are $\alpha_V = 8.05 \cdot 10^{-6}$ and $8.81 \cdot 10^{-6}$ 1/K, respectively. The colorimetric coordinates in the RGB system are 71.8% red, 72.9% green and 79.6% blue, which corresponds to the gray-blue pigment.

Keywords: pigment; willemite; sol-gel synthesis; thermal expansion.

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Introduction

Divalent metal silicates are widely used as luminescent, corrosion protecting, electrical insulating materials, catalysts, pigments. Thus, the emergence of the chemical manufacturing of synthetic pigments began with the production of dyed double silicates, known as egyptian blue CaCuSi$_4$O$_{10}$, han blue BaCuSi$_4$O$_{10}$ [1–3]. The continued interest to the silicate pigments is caused due to the pure intense color, as well as by their high thermal and chemical resistance. Therefore, it is possible to use them for dyeing ceramic products that exposed to high temperature calcination in the manufacturing process. Transition metal orthosilicates containing copper, nickel, and cobalt ions are well known as blue pigments. Dopant M$^{2+}$ ions (M = Cu, Ni, Co) in Zn$_{2-2x}$M$_{2x}$SiO$_4$ solid solutions are coordinated by four oxygen atoms, which causes the blue color of the compounds due to the splitting of electron levels of M$^{2+}$ ions in the crystal field. Since the information about Zn$_{2-2x}$M$_{2x}$SiO$_4$ (M = Cu, Ni, Co) is limited, the purpose of this work is a disclosure of sol-gel synthesis mechanism for Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ and determination of main pigment characteristics, such as colorimetric parameters and thermal expansion coefficient.
**Experimental**

The precursors used in the sol-gel synthesis of Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ were zinc acetate Zn(CH$_3$COO)$_2$·2H$_2$O, copper acetate Cu(CH$_3$COO)$_2$·H$_2$O, and tetraethyl orthosilicate (TEOS) Si(OC$_2$H$_5$)$_4$. The phase composition within the range from room temperature up to 800 °C was controlled in situ by the X-ray powder diffraction (XRPD) method (Shimadzu diffractometer, CuKa$_1$ radiation, $\theta$ angle interval from 10 to 60° with a step of 0.02°), comparing the XRD data with the X-ray characteristics of the possible impurity oxides and zinc silicates (PDF2 database, ICDD, USA, Release 2009). The temperature was controlled using an Anton Paar TTK-450 attachment. The unit cell parameters were refined by the Rietveld method using the Fullprof 2010 software. Thermogravimetric (TG) analysis together with differential thermal analysis (DTA) were performed using a Setsys Evolution thermal analyzer (Setaram) in air at a temperature scan rate of 10 °/min in the temperature range 20–1100 °C, with alumina as a reference substance. Colorimetric analysis was performed using an SLR Olympus e-420 (light source temperature of 5400 K; ISO = 200; light camera parameters L×W×H = 35×25×32 cm) Photo Impact 12 program, through a calibrator monitor One-Eye Pro. The colorimetry results are given in the RGB color coordinates system.

**Results and discussion**

The synthesis method used in our work allowed us to obtain the Cu$^{2+}$ dopant concentration equal to 5 at.%. Hydrolysis of [Si(C$_2$H$_5$O)$_4$] in the mixture with the ratio H$_2$O:TEOS = 1:1 took place within 30 min. The alcohol solutions of metal acetates and hydrolized TEOS were mixed. After the solutions were poured together the mixture was stirred on a magnetic stirrer for 1 h. The precursor for the final stage of synthesis was obtained by evaporation of the mixture for 2 hours at 65 °C. The gel was formed after 2 days at room temperature.

In order to determine the temperature range of Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ formation, thermogravimetric and differential thermal analyses of the obtained precursor were carried out (Fig. 1).

The mass loss of 2–3%, accompanied by a small endothermic effect at 100 °C, corresponds to the removal of water and ethanol residual. The weight loss of about 20% with a simultaneous exothermic signal on the DTA curve within the region of 250–410 °C is caused by the decomposition of organic components. The DTA curve shows the sharp exothermic effect ($\Delta H \approx -16.3$ kJ/mol) with a maximum at 776 °C, while the mass of the sample remains constant. The assignment of this effect was determined by the thermal analysis of Zn$_2$SiO$_4$ precursor, prepared from zinc acetate and TEOS (Fig. 2). The exothermic effect recorded on the DTA curve in the temperature range 320–500 °C with simultaneous mass loss on the TG curve corresponded to the decomposition of organic components. The exothermic effect at 786 °C ($\Delta H \approx -15.5$ kJ/mol) with a constant sample mass is similar to that observed on the DTA curve for the precursor with the nominal composition Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ (Fig. 1). Consequently, one can conclude that the exothermal effects on the compared DTA curves for the Zn$_2$SiO$_4$ and Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ precursors are of the same nature, and both are related.
to the process of a phase with the willemite structure formation. Thus, a comparative analysis of the thermal behavior of these samples showed that at temperatures above 776 °C the process of forming a long-range order at sol-gel synthesis of Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ was completed.

XRD data of the Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ precursor annealed at 800 °C does indicate the formation of the phase with the willemite structure; however, an insignificant admixture of copper (II) oxide is present in the sample (Fig. 3). The single-phase product was obtained by firing the precursor sample at 900 °C (Fig. 3).

X-ray pattern of the single phase Zn$_{1.9}$Cu$_{0.1}$SiO$_4$ sample taken at room temperature was indexed in the willemite type structure with the trigonal space group $R\overline{3}$. The refined unit cell parameters, unit cell volume and number of formula units are: $a = 13.927(1)$ Å, $c = 9.305(3)$ Å, $V = 1563.03(8)$ Å$^3$, $Z = 18$.

One of the most important characteristics of the pigment is the volumetric thermal expansion coefficient (VTEC), which should be comparable to the thermal expansion of the coated material. Colored zinc orthosilicate doped with copper may be suitable as a pigment for ceramics made of porcelain, earthenware, majolica. Manufacturing and operation proceeds in wide temperature range, therefore, the coincidence VTEC of the matrix and the pigment will allow to avoid cracking of the coating.
The values of VTEC were calculated from the experimental results for the Zn_{2-2x}Cu_{2x}SiO_{4} unit cell parameters (x = 0; 0.05) in the range from room temperature up to 800 °С (Fig. 4). It was shown that the sizes of the unit cell for the zinc orthosilicate Zn_{2}SiO_{4} and Zn_{1.9}Cu_{0.1}SiO_{4} solid solution monotonically expanded with increasing temperature. Doping of zinc orthosilicate with the cations with similar size, like Cu^{2+} (for c.n. = 4 \( r_{Zn^{2+}} = 0.74 \text{ Å}, \ r_{Cu^{2+}} = 0.71 \text{ Å} \)) does not lead to significant differences in the polyterms of unit cell parameters. A comparison of VTEC for Zn_{2-2x}Cu_{2x}SiO_{4} (x = 0; 0.05) with that for the ceramic substrate [4], most often used as a coated material (Table 1), shows their proximity.

Colorimetric coordinates of blue-gray Zn_{1.9}Cu_{0.1}SiO_{4} in the RGB color space consists of 71.8% red, 72.9% green and 79.6% blue (the percentages are relative to pure color), the color saturation is 16.1%.

**Conclusion**

The gray-blue pigment Zn_{1.9}Cu_{0.1}SiO_{4} was obtained by the sol-gel synthesis method. The consequence of phase transformations during the synthesis of the Zn_{1.9}Cu_{0.1}SiO_{4} solid solution was disclosed with the help of X-ray diffraction and thermal analysis. In situ high-temperature X-ray study for Zn_{2-2x}Cu_{2x}SiO_{4} (x = 0; 0.05) in the range of 25–800 °С showed that the volume thermal expansion of the ceramic pigment reveals monotonic character. The calculated VTEC value for Zn_{2-2x}Cu_{2x}SiO_{4} is close to VTEC reported for porcelain, earthenware, majolica.

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**References**

1. Berke H. The invention of blue and purple pigments in ancient times. *Chem. Soc. Rev.* 2007;36:15–30. DOI: 10.1039/B606268G.
2. Pozza G., Ajo’ D., Chiari G., De Zuane F., Favaro M. Photoluminescence of the inorganic pigments Egyptian blue, Han blue and Han purple. *J. Cultural Heritage*. 2000;1:393–8. DOI: 10.1016/S1296-2074(00)01095–5.

3. Sidorov V.I., Malayvskyi N.I., Pokid’ko B.V. Poluchenie nizkoosnovnikh silikatov nekotorikh perekhodnikh metallov metodom osadzenizya. *Vestnik MGSU*. 2007;1:163–6. Russian.

4. Khleborodova O. A. Tablica sootvetstviya keramicheskikh mass I bazovikh glazurei [Internet]. 2017. Russian. Available from: https://www.ceramistam.ru/blog/Keramicheskie_massy/tablitsa-sootvetstviya-keramicheskikh-mass-i-bazovykh-glazurey/.