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Ts.I. Dimitrov [a], Ts.H. Ibreva [b], A.V. Zaichuk [c], I.G. Markovska [b], A.A. Amelina [c], E.V. Karasik [c]

SYNTHESIS AND STUDY OF LOW-TEMPERATURE FERRUM-WILLEMITE CERAMIC PIGMENTS

[a] University of Ruse, Razgrad Branch, Razgrad, Bulgaria
[b] Assen Zlatarov University, Burgas, Bulgaria
[c] Ukrainian State University of Chemical Technology, Dnipro, Ukraine

The synthesis of ferrum-willemite ceramic pigments in the system $xFeO\cdot(2-x)ZnO\cdot SiO_2$ (where x=0.125–1.00) was investigated in this work. The results of colorimetric measurements (in the system $CIEL^*a^*b^*$) showed that the concentration of iron(II) oxide in the composition of 0.25 mol is sufficient for preparation of ceramic pigments of red-brown color. An increase in the content of iron(II) oxide in the composition of ceramic pigments from 0.125 to 0.25 mol causes the growth of values of color coordinates a^* (up to +26.68) and b^* (up to +36.73) as well as lightness L^* (up to 48.51). A further increase in the concentration of FeO in pigments to 1.0 mol results in a decrease in the amount of red color: the value of red color coordinate a^* falls to +21,87. An effective role of hydrate of silicon(IV) oxide introduced as a quartz-containing component of experimental pigments is also shown. It allows reducing the temperature of their synthesis to 900–1000^{0}C. Moreover, the growth of the firing temperature from 900 to 1000^{0}C leads to a slight increase in the amount of red color of the developed red-brown pigments (value of color coordinate a^* increases from +25.38 to +26.68). By means of the methods of X-ray phase analysis and electron paramagnetic resonance, it was found that willemite solid solution and spinel (zinc ferrite) act as a carrier of color in these ceramic pigments. Formation of the above crystal phases is completed already at the firing temperature of 1000^{0}C. The synthesized pigments can be successfully used for coloring of glaze coatings on ceramics as well as glass-enamel coatings for metals.

Keywords: ceramic pigments, willemite, mineral composition, crystal lattice, colorimetric indices.

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Introduction

Ceramic pigments are widely used for decoration of ceramic products, coloring of glaze, glass-enamel and engobe coatings. They are mainly obtained by the method of solid-phase synthesis from chemically pure reagents [1] or various industrial wastes [2–6] at high temperatures.

The study of the processes of synthesis of the ceramic pigments, their structure and conditions of their formation is of great scientific and practical importance. Development of new competitive pigments is based now on the concept that takes into account the modern crystal-chemical ideas of the structural changes in the pigments' crystal lattices. The principle of using stable crystal lattices as acceptors to synthesize ceramic pigments is the most effective one. It allows creating the wide range of dyes capable of withstanding high temperatures and action of chemical reagents.

In order to expand the range of ceramic pigments, one can use non-deficient natural raw materials as the primary components and reduce the temperature of their synthesis. A peculiar feature of the synthesis of these pigments is a relatively low temperature of solid-phase reactions. As a result, the ions of transition metals are incorporated in the crystal structure of silicates to form the specified color-bearing phase [1,7–9].

By using the crystal lattices of silicates with the isolated single tetrahedra $[SiO_4]^{4-}$, pigments of forsterite, garnet, sphene and willemite structures [1] are obtained. Willemite dyes are among the most brightly colored ceramic pigments. Willemite mineral ($2ZnO \cdot SiO_2$) is crystallized in the rhombic system. With the partial replacement of ZnO by oxides of transition elements, the colored compounds with the willemite structure can be produced. They are characterized by high resistance to dissolving action of glazes and fluxes, as well as the impact of temperatures of up to 1200^0C.

The works [10–12] reported the synthesis of cobalt-containing pigments of the willemite series. Such pigments are used for making blue overglaze and underglaze paints of high intensity and purity of color. Willemite pigments containing nickel oxide as the dying components [12] are known as well.

Maslennikova et al. [13] studied the processes of the fabrication of ceramic pigments based on willemite in the structure of which zinc oxide was replaced by iron(II) oxide in the amount of 0.1–1.0 mol. Color of these pigments varied from light-yellow to yellowish-brown. According to the data of X-ray phase analysis, the beginning of formation of willemite phase was registered at the temperature of 1000^0C. However, high-temperature firing at 1200^0C is required for the completion of this process.

The aim of this work was to establish physical-chemical patterns and process parameters for fabrication of the crystal-phase composition of low-temperature ferrum-willemite ceramic pigments.

Experimental

Chemically pure iron and zinc oxides were used for preparation of the experimental ceramic pigments. Silicon(IV) oxide was introduced with the use of amorphous hydrate of silicon(IV) oxide ($SiO_2 \cdot nH_2O$). The choice of this component was determined by its high reactivity in the process of solid-phase sintering compared with quartz sand. Chemically pure sodium fluoride was used as a mineralizer. Pigment batches were prepared by the method of joint wet grinding of the initial raw materials components in the planetary mill Pulverizete 6 («FRITCH» company). Blends dried to residual moisture of 1% were fired in the electric furnace in the range of temperatures of 900–1200^0C (with an increment of 100^0C) with hold up time of 1 h. Synthesized pigments were finely ground to the degree of dispersion characterized by residue on the control sieve No. 0056 (not more than 0.4%). After that, they were dried to the moisture content of 0.8% at most.

Crystal-phase composition of ceramic pigments was studied by means of X-ray diffractometer Philips APD-15 (1030) in Cu-K_α radiation in the range of $10^0<2\theta<70^0$. Spectra of electron paramagnetic resonance (EPR) were measured using EPR-spectrometer BRUKER EMX. Color coordinates in the system CIEL*a*b* were taken using spectral tintometer Lovibont Tintometer RT100.

Results and discussion

We studied the ceramic pigments in the system $xFeO \cdot (2-x)ZnO \cdot SiO_2$, where x=0.125–1.00 (with the increment of 0.125 mol).

Color coordinates of synthesized pigments were determined in the system CIEL*a*b* (Fig. 1):

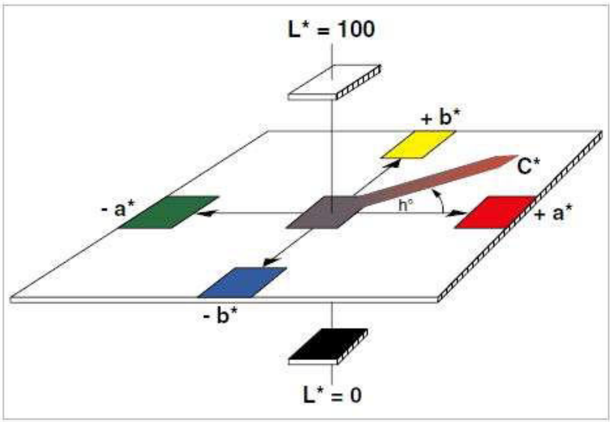

Fig. 1. Color diagram in the system CIELab:
L* – lightness; L*=0 (black color); L*=100 (white color);
a* – green color (–)/ red color (+);
b* – blue color (–)/ yellow color (+)

The results of color measurements of the experimental ceramic pigments are given in Table 1.

The experiments showed that the enhancement of red-brown coloring occurs with an increase in the content of iron(II) oxide in the composition of ceramic pigments from 0.125 to 0.25 mol. The growth of the values of color coordinates a* (up to +26.68) and b* (up to +36.73) as well as lightness L* (up to 48.51) was detected.

A further increase in the concentration of FeO in pigments to 1.0 mol causes a decrease in the amount of red color. The value of color coordinate a* falls to +21,87. A tendency to the reduction of lightness (to 39.63) is also observed (Table 1).

Therefore, the concentration of iron(II) oxide in thei composition equal to 0.25 mol is sufficient for obtaining ceramic pigments of red-brown color in the system $FeO-ZnO-SiO_2$. In this regard, the relationships between the firing temperature for the pigment of composition $0.25FeO \cdot 1.75ZnO \cdot SiO_2$, its color indices and crystal-phase composition were further studied.

It is shown (Table 2) that the amount of red

Table 1

Results of determination of color characteristics of ceramic pigments fired at the temperature of 1000⁰C

The composition of the pigment, mole	Color	L^*	a^*	b^*
$0.125FeO \cdot 1.875ZnO \cdot SiO_2$		47.45	23.74	33.57
$0.25FeO \cdot 1.75ZnO \cdot SiO_2$		48.51	26.68	36.73
$0.375FeO \cdot 1.625ZnO \cdot SiO_2$		44.35	24.12	32.49
$0.5FeO \cdot 1.5ZnO \cdot SiO_2$		42.36	23.05	30.25
$0.625FeO \cdot 1.375ZnO \cdot SiO_2$		41.72	22.08	29.87
$0.75FeO \cdot 1.25ZnO \cdot SiO_2$		41.66	22.03	29.14
$0.875FeO \cdot 1.125ZnO \cdot SiO_2$		40.57	21.94	28.67
$FeO \cdot ZnO \cdot SiO_2$		39.63	21.87	27.45

color increases insignificantly (value a^* grows from +25.38 to +26.68) with the rise in temperature of firing of such a pigment from 900 to 1000⁰C. Color of willemite pigment synthesized at 1000⁰C is characterized by the value of dominating wavelength λ=675 nm (red spectral region), and color purity is 20%.

A subsequent increase in the firing temperature to 1200⁰C causes a significant drop in the values of color coordinate a^* to +13.92. A gradual decrease in the values of other color indices of the experimental pigments is observed throughout the firing temperature range.

The results of X-ray phase analysis (Fig. 2) showed the presence of crystal phases of willemite ($2ZnO \cdot SiO_2$) and zinc ferrite ($ZnO \cdot Fe_2O_3$) in the structure of the experimental pigment. Furthermore, the willemite phase is actively formed at the temperature of 900⁰C, and the process is already completed at 1000⁰C. It is evidenced by the intensity of the main reflexes in X-ray diffraction patterns of the pigment which correspond to willemite.

EPR-spectrum of the ceramic pigment of composition $0.25FeO \cdot 1.75ZnO \cdot SiO_2$ fired at 1000⁰C was recorded in the temperature interval of 120–490 K (Fig. 3). At the temperature of 120 K, the asymmetric signal with g≈2.15 and ΔHpp≈160mT prevailed. When the temperatures rises to 295 K, the basic signal shifts towards stronger magnetic field (g=2.05), gets narrower (ΔHpp=80 mT) and its intensity decreases. At the temperatures of above 400 K, the signal completely disappeared, while new weak asymmetric signal with EPR parameters (g=2.006, ΔHpp=122 mT) was recorded at the temperatures of 460 K and 490 K. In the range of magnetic field of 100–250 mT, partially resolved lines of lower intensity are observed as well. The position and width of these lines show the temperature dependence similar to that of the basic signal. Their intensity gradually decreases and

Table 2

Results of determination of color characteristics of the ceramic pigment with the composition $0.25FeO \cdot 1.75ZnO \cdot SiO_2$ fired in the temperature range of 900–1200⁰C

Firing temperature, ⁰C	Color	L^*	a^*	b^*
900		51.28	25.38	40.28
1000		48.51	26.68	36.73
1100		47.78	23.69	32.39
1200		43.49	13.92	21.89

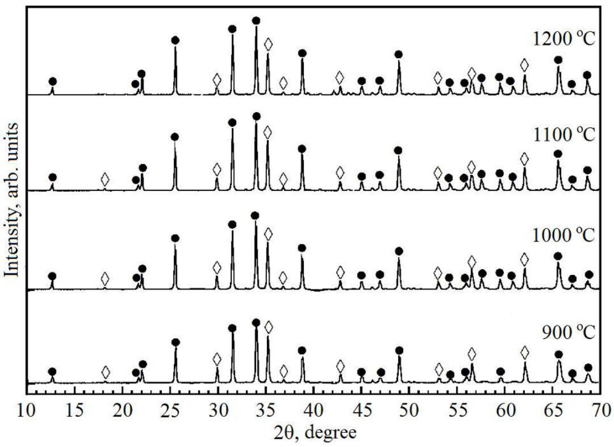

Fig. 2. X-ray diffraction patterns of pigment $0.25FeO \cdot 1.75ZnO \cdot SiO_2$ synthesized at various temperatures: ● – $2ZnO \cdot SiO_2$, ◇ – $ZnO \cdot Fe_2O_3$

disappears completely at 350 K.

Based on EPR parameters and their temperature dependence, it can be concluded that the observed basic signal as well as partially resolved lines of weak magnetic fields are associated with the efficient exchange magnetic interaction between Fe^{3+} ions. These interactions increase with an increase in temperature and cease to act in the interval of 350–400 K. Appearance of weak asymmetric signal at the temperatures of 460 K and 490 K is due to the presence of paramagnetic ions of iron. It proves the presence of ferrite phase in the structure of the experimental pigment and correlates with the results of X-ray phase analysis.

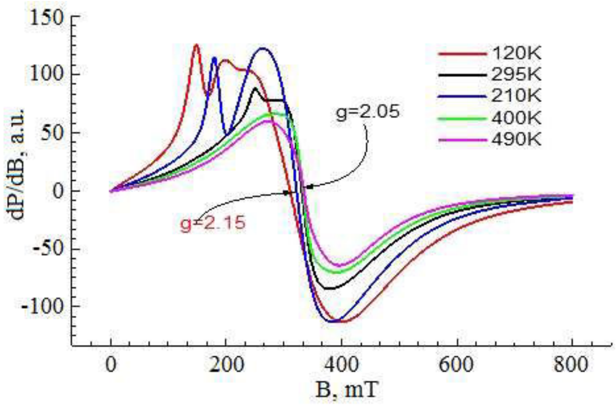

Fig. 3. EPR spectrum of the pigment of composition $0.25FeO{\cdot}1.75ZnO{\cdot}SiO_2$ (firing temperature of 1000^{0}C) at 120, 295, 210, 400 and 490 K

Conclusions

Experimental study showed the efficiency of introduction of hydrate of silicon (IV) oxide as a quartz-containing component of willemite ceramic pigments. Low-temperature ferrum-willemite pigments of brown series were synthesized. An increase in their firing temperature from 900 to 1000^{0}C led to an increase of the amount of red color (the value of color coordinate a^* increased from +25.38 to +26.68). The methods of X-ray phase analysis and electron paramagnetic resonance revealed that willemite solid solution and spinel (zinc ferrite) acted as a carrier of color in such pigments. Formation of the above crystal phases was completed at the temperature of 1000^{0}C. The synthesized pigments can be used for coloring of glaze coatings on ceramics as well as glass-enamel coatings for metals.

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СИНТЕЗ І ДОСЛІДЖЕННЯ НИЗЬКОТЕМПЕРАТУРНИХ ФЕРУМ-ВІЛЛЕМІТОВИХ КЕРАМІЧНИХ ПІГМЕНТІВ

Ц.І. Димитров, Ц.Х. Ібрева, О.В. Зайчук, І.Г. Марковська, О.А. Амеліна, О.В. Карасик

Вивчена можливість синтезу ферум-віллемітових керамічних пігментів в системі $xFeO{\cdot}(2-x)ZnO{\cdot}SiO_2$, де x=0,125–1,00. Результати колориметричних вимірювань (в системі $CIEL^*a^*b^*$) показали, що для одержання керамічних пігментів червоно-коричневого кольору достатньою є концентрація ферум(ІІ) оксиду в їх складі 0,25 моль. Збільшення вмісту ферум(ІІ) оксиду в складі керамічних пігментів від 0,125 до 0,25 моль викликає зростання значень координат кольору a^* (до +26,68) і b^* (до +36,73), а також світлоти L^* (до 48,51). Подальше збільшення концентрації FeO в пігментах до 1,0 моль призводить до зменшення кількості червоного кольору: значення координати кольору a^* падає до +21,87. Також показана ефективна роль гідрату силіцій(IV) оксиду, введеного в якості кварцової складової дослідних пігментів. Це дозволяє знизити температуру їх синтезу до 900–1000^{0}C. Підвищення температури випалу від 900 до 1000^{0}C приводить до незначного збільшення кількості червоного кольору розроблених червоно-коричневих пігментів (значення координати кольору a зростає від +25,38 до +26,68). Методами рентгенофазового аналізу і електронного парамагнітного резонансу встановлено, що як носій кольору в таких пігментах виступає віллемітовий твердий розчин і шпінель (цинк ферит). Формування зазначених кристалічних фаз повністю закінчується вже при температурі випалу 1000^{0}C. Синтезовані пігменти можуть успішно застосовуватись для забарвлення глазурних покриттів на кераміці, а також склоемалевих покриттів на металах.*

Ключові слова: керамічні пігменти, віллеміт, мінералогічний склад, кристалічна решітка, колориметричні показники.

SYNTHESIS AND STUDY OF LOW-TEMPERATURE FERRUM-WILLEMITE CERAMIC PIGMENTS

Ts.I. Dimitrov [a]***, Ts.H. Ibreva*** [b]***, A.V. Zaichuk*** [c, *]***, I.G. Markovska*** [b]***, A.A. Amelina*** [c]***, E.V. Karasik*** [c]

[a] **University of Ruse, Razgrad Branch, Razgrad, Bulgaria**

[b] **Assen Zlatarov University, Burgas, Bulgaria**

[c] **Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

[*] **e-mail: zaychuk_av@ukr.net**

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