The Analysis about Synthesis, Structure and Properties of Willemite Ceramic Pigments Obtained by a Sol–Gel Method

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The Analysis about Synthesis, Structure and Properties of Willemite Ceramic Pigments Obtained by a Sol–Gel Method

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Abstract. This work focuses on the syntheses of willemite ceramic pigments doped with cobalt and nickel ions (Co^{2+}, Ni^{2+}). The pigments were prepared by the sol−gel process. The phase formation has been studied by X - ray diffraction analysis. The results showed that phase composition depends on sintering temperature, isothermal retention period as well as type of chromophore ion. The basic phase is obtained at even 900 - 1000^0C. Color characteristics of the pigments have been measured using the Lovibond Tintometer RT 100 Color – CIELab color measurement. Better results were obtained at pigments synthesized at 1100^0C. High temperature ceramic pigments representing solid solution with stable crystalline phase of Zn_2SiO_4 were obtained. The best pigments have been added to white faience glaze and sanitary ceramics.

1. Introduction

Willemite, Zn_2SiO_4 with phenakite structure is an orthosilicate with all atoms in general position and composed by a framework of tetrahedra accommodating zinc and silicon in three different fourfold crystallographic sites: two slightly different zinc sites Zn1(1.950Å) and Zn2 (1.961Å), and Si (1.635 Å), in rhombohedral symmetry with lattice parameters a = b ~13.948Å, and c ~9.315 [1-5].

Many other researchers [6-9] have devoted efforts on topics related not only the chemistry of the process but also to finding the main fields of application of the sol-gel technology. The sol-gel method is related to hydrolysis and polycondensation of metal alcoholates $Me(OR)_n$, where Me-metal with valence of n and R-alkyl radical C_XH_{2X+1}. At temperatures close to that of the environment, hydrolysis of the solution of the metal alcoholates is carried out and then polycondensation takes place which gives sol. As the reaction this sol transforms into gel which is heated to obtain the end product.

2. Experiment

2.1. Raw materials

The synthesis of pigments is carried by sol-gel method using raw materials as TEOS - $Si(OC_2H_5)_4$, $Zn(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ (pure grade).

For the preparation of willemite pigments by the sol-gel technology have been chosen the blends for which the best result were obtained with respect to color intensity after the solid state synthesis: $0.375CoO.1.625ZnO.SiO_2$ and $0.375NiO.1.625ZnO.SiO_2$. Due to the strong propensity of tetraethyl orthosilicate (TEOS) to hydrolysis, ethyl alcohol was added to it under continuous stirring. The nitrates of chlorides of the corresponding chromophore components were preliminarily dissolved in ethyl alcohol. After mixing the solutions, the mixture was intensely stirred with magnetic stirrer for 30 min for better homogenization.

2.2. Thermal treatment

The sol obtained transformed into gel-like mass after 48 h at 60°C and it was dried at temperature of 120°C, and then at 180°C, until complete separation of the nitrates. After the full drying, the samples were ground in agate mortar and subjected to thermal treatment at temperatures of 600°C, 700°C, 800°C, 900°C, 1000°C, 1100°C and 1200 °C with isothermal periods of 4 h.

2.3. Method of analysis

Phase composition of the synthesized ceramic pigments was determined using X-ray diffraction (XRD) with a Bruker D8 diffractometer operating at 40 kV and 40 mA with CuK_{α} radiation. FT-IR spectra were collected using a Tensor 37 spectrometer (Bruker) with a 4 cm^{-1} resolution on standard KBr pallets in the spectral region 400-4000 cm^{-1} at room temperature. The EPR spectra were taken with spectrophotometer Bruker EMX Premium X equipped with a system allowing varying the measurement temperature in the interval 120-450 K. The electron microscope photographs were taken using scanning electron microscope "JEOL 6390" with INCA Oxford analyst. The color determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Color.

3. Results and discussions

3.1. X-ray analyses

X-ray phase analysis is a direct method for phase identification. The method is based on X-ray diffraction. The main task of the XRD analysis is identification of the different phases separately or in mixtures on the basis of the diffraction pattern recorded with the sample studied.

The main method of phase analysis is with powdery sample which has been widely used due to its simplicity and universality. Diffraction patterns of the synthesized ceramic pigments are presented in figure 1 (A, B).

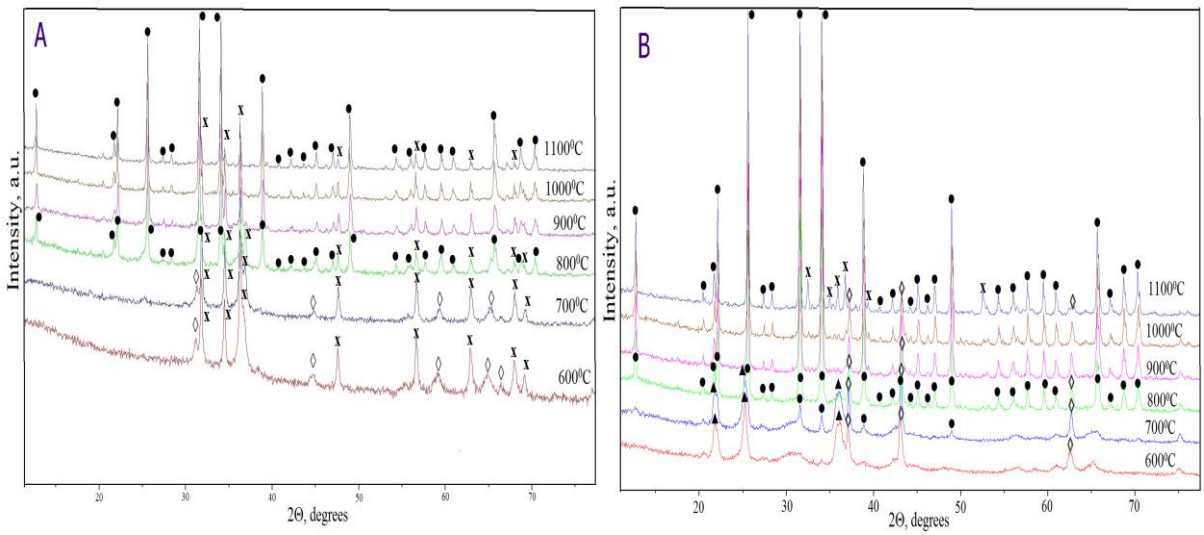

Figure 1. A) X – ray spectra of willemite pigments with composition 0,375CoO.1,625ZnO.SiO_2 synthesized at temperature: 600÷1000^{0}C, main phases: ● – Co willemite ; x - zincite ZnO; ◊ - Co_3O_4 B) X-ray spectra of pigments with composition 0,375NiO.1,625ZnO.SiO_2 synthesized at temperature: 600 ÷1000 ^{0}C, with main phases: ● – solid solution of Ni in willemite; x - Nickel Orthosilicate (Ni_2SiO_4); ◊ - bunsenit NiO; ▲-quartz SiO_2

Due to the size of ionic radii of Zn^{2+} - 0. 74 Å and Co^{2+} - 0.65 Å a solid solution is formed by incorporation of cobalt in the willemite lattice. Data for unit cell parameters presented by Ozel et al. [1] confirme that. It can be seen from the X-ray patterns shown in Figure 1 that the main phase Co-willemite was synthesized at temperature as low as 800°C and reflexes from cobalt oxide and zinc

oxide were also registered. With the increase of the temperature of thermal treatment, a tendency of increase of the intensities of the peaks for the main phase Co-willemite accompanied by decrease of the peak intensities for ZnO. Similar results were obtained in the system 0,375NiO.1,625ZnO.SiO_2. The X- ray data well correlated with the data from the FT-IR spectroscopy.

3.2. FT- IR spectra of pigments

The FT- IR spectra presented in Figure 2 shown the presence of absorption maxima characteristic for the pure willemite (Table 1): the symmetric valent vibration at 868 (869) cm^{-1} is due to the presence of Si-O bands, 900, 931 and 977 cm^{-1} – asymmetric valent of Si-O and deformation vibration at 459 cm^{-1}. The bands at 576 cm^{-1} are due to symmetric valent /614 cm^{-1} – asymmetric valent / vibrations of Zn-O in ZnO_4.

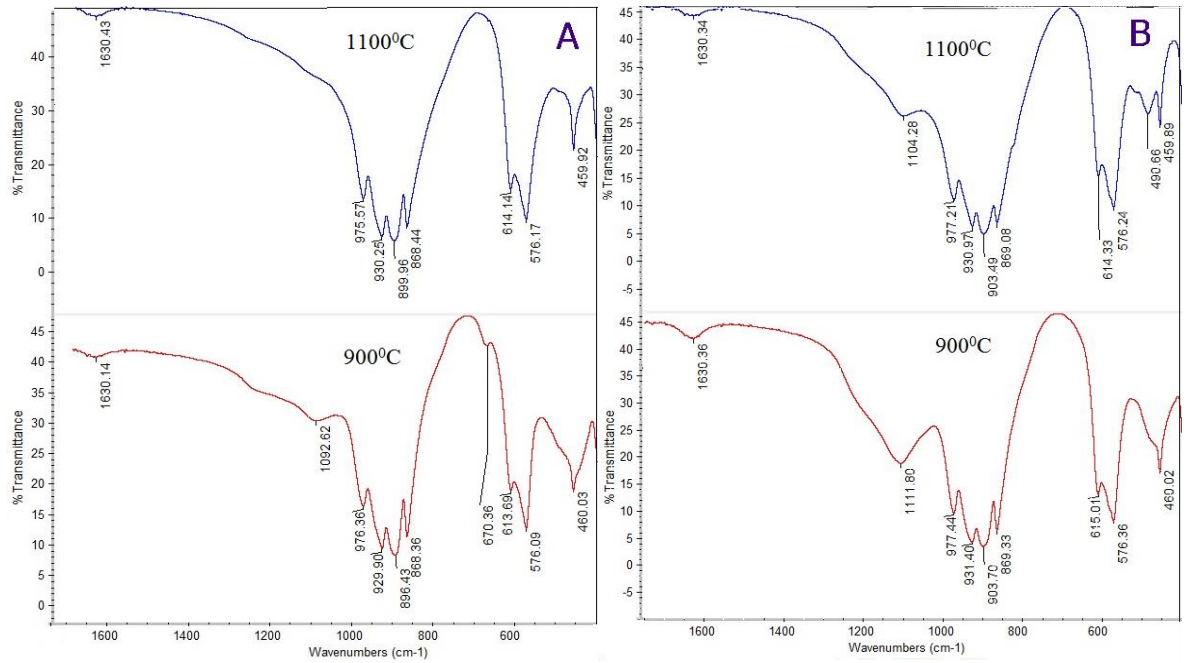

Figure 2. FT- IR spectra of pigments 0,375CoO.1,625ZnO.SiO_2(A) and 0,375NiO.1,625ZnO.SiO_2 (B)

Table 1. Basic IR - FT characteristic of willemite

Peak wave numbers (cm^{-1})	Type of oscillation, connection
977; 931; 900	(ν_3) Si-O antisymetric stretching vibration
868, 869	(ν_1) Si-O symmetric stretching
600-615	(ν_3) Zn-O antisymetric stretching in ZnO_4
575	(ν_1) Zn-O symmetric stretching in ZnO_4
459	(ν_4) SiO_4 bending

3.3. Electron paramagnetic resonance

The EPR spectrum of pigment 0.375CoO.1.625ZnO.SiO_2 (1100^{o}C) was registered in the temperature interval 100÷295 K (Figure 3).

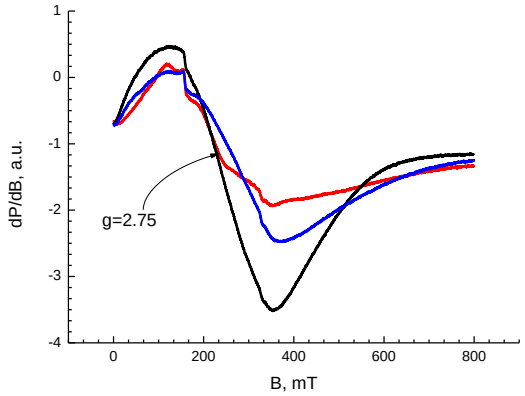

Figure 3. ESR spectrum of the sample $0.5CoO.1.5ZnO.SiO_2$ at 295 K (black curve), 210 K (blue curve) and 120 K (red curve).

The EPR spectra of sample $0.5CoO.1.5ZnO.SiO_2$ were registered in the temperature interval 120-295 K. A wide asymmetric signal with effective g-factor of 2.75 and width about 218 mT was observed at room temperature. With decrease of the temperature, this signal widens and at low temperatures, comparatively wider non-allowed overlapping signals were registered.

The single asymmetric signal observed at 295 K was attributed to electron exchange bonded Co^{2+} ions in field with octahedron distortion. The spectrum registered at 120 K contained lines of the Co^{2+} ions ultrafine structure (I=7/2) overlapping the wide signal which was attributed to exchange bonded Co^{2+} ions, as mentioned above. The ultrafine structure becomes visible at low temperatures due to the significant widening of the dominating signal at 295 K.

3.4. Color measuring

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. The colour measurements were performed using the CIELab method (Table 2). This method, which is the standard analysis in the ceramic industry, especially for the ceramic pigments allows to determine the whiteness and colour 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 (+).

Table 2. Results of color coordinate measurements of pigments

№	Composition	Colour	L*	a *	b *
1	**$0,375CoO.1,625ZnO.SiO_2$ - 900°C**		**47,67**	**-10,96**	**-9,67**
2	**$0,375CoO.1,625ZnO.SiO_2$ - 1000°C**		**44,08**	**-9,57**	**-22,02**
3	**$0,375CoO.1,625ZnO.SiO_2$ - 1100°C**		**42,34**	**-3,82**	**-45,44**
4	**$0,375CoO.1,625ZnO.SiO_2$ - 1200°C**		**41,65**	**-0,65**	**-37,56**
5	**$0,375NiO.1,625ZnO.SiO_2$ - 900°C**		**74,83**	**-4,69**	**4,05**
6	**$0,375NiO.1,625ZnO.SiO_2$ - 1000°C**		**72,52**	**-8,58**	**-0,52**

7	**0,375NiO.1,625ZnO.SiO_2 - 1100^{o}C**		**68,09**	**-14,40**	**-5,11**
8	**0,375NiO.1,625ZnO.SiO_2 - 1200^{o}C**		**64,56**	**-12,17**	**-4,75**

It can be seen from the data presented that the color of the pigments synthesized with cobalt and zinc is blue and blue - green. With the increase of the sintering temperature, their luminance L* was found to decrease. The amount of blue color (- b*) was the highest for the pigment with composition 0,375CoO.1,625ZnO.SiO_2 synthesized at 1100^{o}C, where (- b) = 45,44. This pigment (composition 3) is best suited for use in practice because it has the most intense blue color.

3.5. Scanning electron microscopy

The particle size of pigments can affect the final appearance of the coated surface. The morphology and microstructure of pigments were examined by scanning electron microscopy (SEM). As sputter coating material has been used gold, due to its high conductivity that enables high-resolution imaging. The ELMI Sputter installation was used for this purpose.

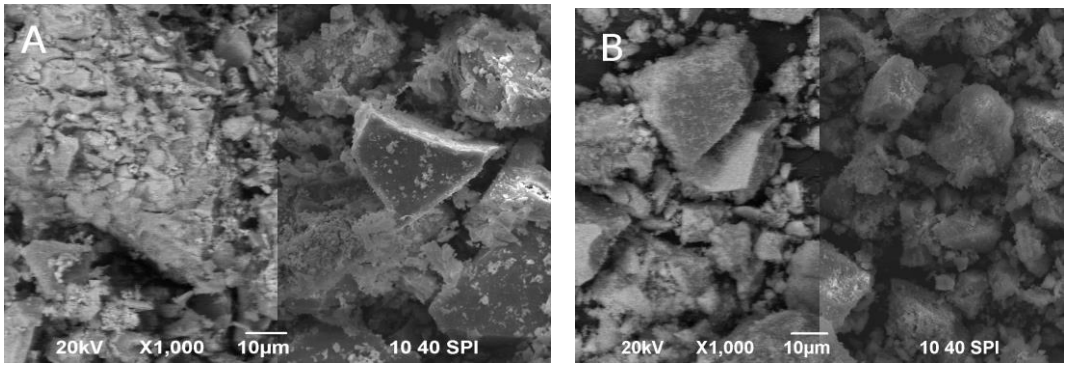

Figure 4. SEM of pigments with composition: A) 0,375CoO.1,625ZnO.SiO_2, B) 0,375NiO.1,625ZnO.SiO_2

The SEM micrographs of pigments containing Co^{2+}(composition 0,375CoO.1,625ZnO.SiO_2, 1100^{0}C) and Ni^{2+} (composition 0,375NiO.1,625ZnO.SiO_2, 1100^{0}C) are presented in Figure 4. Both pictures show that the pigments are monodispersed with unambiguous crystal habitus and crystal size of about 5-20 µm.

4. Conclusions

Colored ceramic pigments were synthesized with participation of two chromophore ions: Co^{2+} and Ni^{2+}. The color of all pigments is blue and blue-green. Sintering process was carry out by sol-gel method. The optimal parameters of the synthesis process have been established. Due to the very similar ionic radii of Zn^{2+} - 0.60 Å and Co^{2+} - 0.58 Å a solid solution of substitution is formed. The best results were obtained with pigments synthesized at a firing temperature of 1100C. SEM micrographs show that the pigments are monodispersed with unambiguous crystal habitus and crystal size of about 5-20 µm. The synthesized pigments are suitable and can be successfully applied in glazes for tiles and sanitary ceramics.

5. References

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