SYNTHESIS OF WILLEMITE PIGMENTS DOPED WITH DIFFERENT D-CHROMOPHORE ELEMENTS – Mn, Fe AND V (PART 2)

SYNTÉZA WILLEMITOVÝCH PIGMENTŮ DOTOVANÝCH RŮZNÝMI D-CHROMOFOROVÝMI PRVKY – Mn, Fe A V

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Summary

This work focuses on the syntheses of colored willemite ceramic pigments. The pigments were prepared by solid phase sintering technology. The paper reports experiments carried out on the synthesis of willemite pigments doped with ions of transition elements as well as iron, manganese and vanadium. The sintering temperatures were between 900 and 1 200 °C. Mainly methods of electron spin resonance spectroscopy, electron microscopy, X-ray analyses, hot stage microscopy, etc. were used to investigate the synthesized pigments. Hot stage microscope analysis of Mn, Fe and V –doped willemite pigments carry out show that all pigments are thermally stable up to 1 000 °C.

Keywords

Ceramic pigments, transition elements, ESR spectroscopy, Hot stage microscopy

Introduction

The research interest of ceramic pigments is based on the growing importance of ceramic materials, powders and pigments, as well as the diverse possibilities for obtaining them from both traditional and waste materials. They have potentially wide practical use in ceramic and glass industries, e.g. coloring of ceramic tiles and other articles, mosaic tiles, coloring of glass to obtain various types of colored glasses, etc. [1].

In recent years, researchers from many countries work on the synthesis, characterization and properties of various kinds of willemite ceramic pigments. Willemite is a mineral, zinc silicate with composition $2ZnO.SiO_2$. It was discovered in the form of small brown crystals and it was named in 1830 after the King of Holland Willem I (Willem Frederik). The color palette of willemite pigments today is quite large [2]. Willemite can be green, yellow, brown, red-brown, orange, blue colored. It can be found in nature as prismatic translucent and small needle crystals. It is one of the not many silicates with orthogonal syngony which is more characteristic for the carbonates. The ceramic pigments with structures of willemite $2ZnO.SiO_2$ and phenakite $2BeO.SiO_2$ crystalizeinthe trigonal syngony.

Researchers from different countries have long been working on the synthesis and characterization of the structure of willemite ceramic pigments and on the partial substitution of ZnO with CoO [3–5] with NiO [2], with FeO [6] and with MnO [7] as well.

Materials and methods

Materials

The determination of composition recipes for the production of willemite ceramic pigments is based on the main mineral willemite ($2ZnO.SiO_2$).

The chemical materials used in the synthesis are: MnO_2, Fe_2O_3, V_2O_5,ZnO, $SiO_2.nH_2O$ and NaF (as a mineralizer diminishing the temperature of synthesis and accelerating the processes of new phase formation).

The raw material used for introduction of SiO_2 in the system $SiO_2.nH_2O$ is significantly more reactive than the ordinary quartz sand. Its degree of dispersity of the particles is in the range of 2–7 °m. After annealing in a platinum crucible the initial SiO_2 and H_2O content in the $SiO_2.nH_2O$ compound was determined.

This is namely: SiO_2 – 76,3% and H_2O – 23,7%.

Methods

The resulting ceramic pigments were examinated mainly using X-ray analyses, electron microscopy, Hot stage microscopy. The color was determined spectrophotometrically using Lovibont Tintometer RT 100 Colour.

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 CuKα radiation.

An electron spin resonance spectroscopy (ESRS) study was performed on a spectrometer type B-ER-420 of Bruker-Physic, working in the X-range at a frequency of 9.8 GHz at room temperature.

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

The sintering behavior of the ceramic pigments under investigation was studied by means of optical hot stage microscopy (HSM) with an ESS HSM-1400 MISURA (Italy). This instrument allows measurements up to 1400 °C of the sample volume alterations.

All samples were measured non-isothermally by using a programmed constant linear thermal scan with a rate of 1 0 °C min^{-1} up to 1400 °C.

Experimental procedures

The following willemite pigment compositions have been prepared:

– Manganese-willemite pigments:x MnO. (2-x).ZnO.SiO_2,

– Iron-willemite pigments: x FeO. (2-x).ZnO.SiO_2,

– Vanadium-willemite pigments:xV_2O_5. (2-x).ZnO.SiO_2,

where x = 0.125, 0.250, 0.375, 0.50, 0.625, 0,75, 0.875 and 1,00.

The quantities of the materials in the recipe for a 100 g batch were weighted with the help of balances with a resolution of 0.1 g. Then the samples were mixed together and homogenized with a planetary mill FRITSCH Pulverisette–6 (Germany) in a dry environment.

The firing was carried out in a laboratory tube furnace with a heating rate of 300–400 °C h^{-1} in air environment and using porcelain crucibles. The firing regime consisted of an isothermal thermal scan at the final temperature with a holding time of 2 hours. All pigments were heat treated at temperatures of 800, 900, 1000, 1100 and 1200 °C.

Results and discussions

Mn – doped willemite pigments

Mn –doped willemite pigments were mainly studied by the methods of X-ray diffraction analysis, colour measurement, electron spin resonance spectroscopy (ESRS) and Hot stage microscopy.

Measurement of the colour

Table 1 shows the results of measurements of color characteristics made with Lovibont Tintometer RT 100 Color.

Table 1: Color characteristics of the synthesized Mn-willemite pigments

Composition	L*	a*	b*
0.125NiO.1.875ZnO.SiO_2	77.8	4.85	12.70
0.25NiO.1.750ZnO.SiO_2	64.94	8.60	20.39
0.375NiO.1.625ZnO.SiO_2	51.49	11.60	22.89
0.500NiO.1.500ZnO.SiO_2	54.74	10.71	17.05
0.625NiO.1.375ZnO.SiO_2	49.65	10.10	16.78
0.750NiO.1.250ZnO.SiO_2	42.42	9.87	15.82
0.875NiO.1.125ZnO.SiO_2	38.19	9.77	15.66
1.000NiO.1.000ZnO.SiO_2	35.72	9.02	15.17

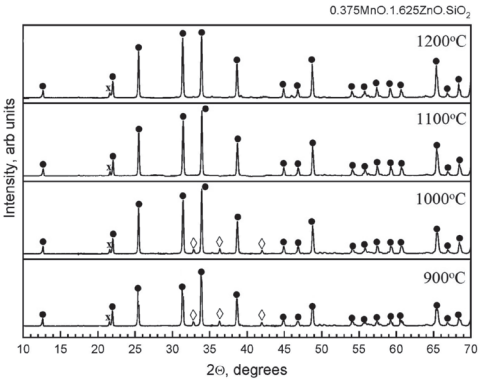
It can be seen from Table 1 that the colorof all synthesized pigments is brown. With increasing of MnO concentration, a parameter of light (L *) decreased. In the same time with increasing of MnO concentration the amount of red color (+ a *) initially increases and then decreases, being the highest in pigment with a composition of 0.375MnO.1.625ZnO.SiO_2.

X–ray diffraction analysis

Fig. 1 shows the results carry out of the X-ray analysis for a composition 0.375 MnO.1.625ZnO.SiO_2 synthesized at 900, 1 000, 1 100 and 1 200 °C. The main phases that occur are willemite and hetaerolite as well as a minor peak of α-SiO_2. It is a Zn–Mn oxide mineral with composition corresponding to the formula $ZnMn_2O_4$. Hetaerolite has a tetragonal spinel-type structure.

The major phases – willemite and $ZnMn_2O_4$ (hetaerolites) were observed as early as 900 °C. α-SiO_2 reflexes were also observed.

Fig. 1: X – ray patterns of pigments 0,375MnO.1,625ZnO.SiO_2 after treatmentat 900, 1 000, 1 100 and 1 200 °C: ●-willemite Zn_2SiO_4,◊ - hetaerolite $ZnMn_2O_4$, x - αSiO_2



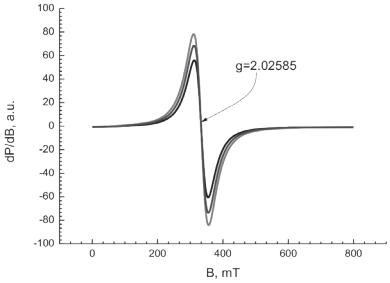
Electron spin resonance spectroscopy (ESRS)

The sample containing Mn^{2+} ions was measured in the temperature range 120–295 K. A symmetrical signal with a Lorenz shape is being observed within the whole measurement range. The bandwidth slightly increases with decreasing temperature – from 43.4mT up to 46.6mT. The G-factor remains almost unchanged – from 2.02583 at 295K up to 2.02691 at 120K.

This signal is characteristic for the Mn^{2+} ions bonded via magnetic exchange interactions.

In Figure 2 is presented the ESR spectrum of a pigment in the system $0.5MnO.1.5ZnO.SiO_2$

Fig. 2: ESR spectrum of sample $0.5MnO.1.5ZnO.SiO_2$at 295K (black curve), 210K (blue curve)and 120K (red curve)



Fe – doped willemite pigments

Fe –doped willemite pigments were mainly studied by the methods ofX-ray diffraction analysis, colour measurement, electron spin resonance spectroscopy (ESRS) and hot stage microscopy.

Table 2 shows the results of measurements of color characteristics made with Lovibont Tintometer RT 100 Color.

Color characteristics of Fe-willemite pigments

Table 2: Color characteristics of the synthesized Fe-willemite pigments

Composition	L*	a*	b*
$0.25FeO.1.75ZnO.SiO_2$ (–900 °C)	50.58	24.83	39.72
$0.25FeO.1.75ZnO.SiO_2$ (–1000 °C)	48.29	25.68	34.73
$0.25FeO.1.75ZnO.SiO_2$ (–1100 °C)	46.08	28.76	31.38
$0.25FeO.1.75ZnO.SiO_2$ (–1200 °C)	43.49	13.92	21.89
$0.50NiO.1.50ZnO.SiO_2$ (–900 °C)	48.76	20.36	35.27
$0.50NiO.1.50ZnO.SiO_2$ (–1000 °C)	45.35	22.67	29.65
$0.50NiO.1.50ZnO.SiO_2$ (–1100 °C)	42.78	24.73	25.05
$0.50NiO.1.50ZnO.SiO_2$ (–1200 °C)	41.16	16.39	21.11

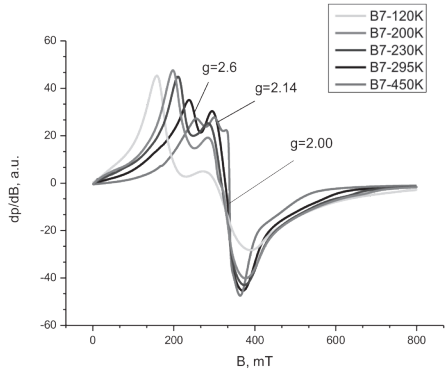
It can be seen from the data presented in table 2 that the color of the synthesized pigments is red-brown. With increasing the heating temperature, a decreasing of parameter of light (L *) is observed. The amount of red color (+ a *) with increasing of FeO concentration decreases, being highest with the pigment having a composition of 0.25FeO.1,75ZnO.SiO_2 at 1100 °C.

Electron spin resonance spectroscopy (ESRS) results

In Figure 3 is presented the ESR spectrum of a pigment in the system 0.5FeO.1.5ZnO.SiO_2 which is relatively complicated and can be rather separated into three signals with the following EPR parameters: 1) g≈2.6; ΔHpp≈30mT; 2) g≈2.14; ΔHpp≈30mT; 3) g≈2.00; ΔHpp≈12mT.

The analysis of the temperature dependence of the signals reveals the following features: signals 1 and 2 are being shifted toward a weaker magnetic field and become wider with decreasing temperature as well, while signal 3 is being most clearly distinguished at 450 K. Its intensity is decreasing with decreasing temperature and at 120 K it cannot be measured any further. The shape of the first two signals (1 and 2) and their temperature dependence represent a proof for the presence of super-magnetic interactions.

Fig. 3: ESR spectrum of sample 0.5FeO.1.5ZnO.SiO_2 recorded at 120, 200, 230, 295 and 450K (the specified g-factors describe the observed signals of the EPR spectrum measured at 295K)



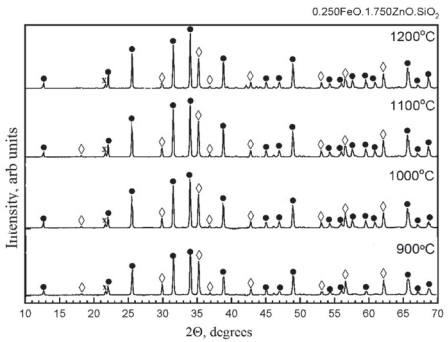
With the temperature increase is being initiated a destruction of the super-magnetic interactions. Latter has been proved by the appearance of a paramagnetic signal at 200 K with g≈2.00 (signal 3) and by the increasing of its intensity in the temperature range 200–450K.

The analysis of the spectrum of this pigment reveals the presence of nano-sized areas built with clusters containing Fe-O particles. Among them are being realized effective exchange interactions which are getting weaker with a temperature increase from 120 K up to 450 K but still dominating over the ESR spectrum. The appearance of a signal with g≈2.00 characterized by an increasing intensity in the range 200–450K can be contributed to the paramagnetic Fe^{3+} ions.

X-ray diffraction analysis

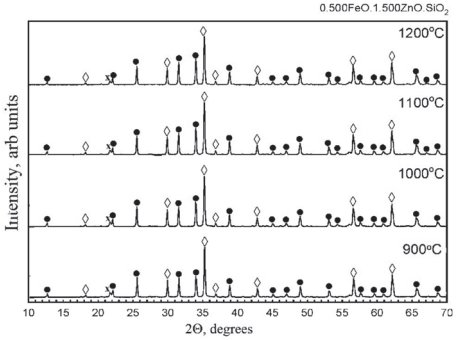
Figures 4 and 5 show the results of the X-ray diffraction analysis of composition 0.25FeO.1.75ZnO.SiO_2 and composition 0.50 FeO.1.50ZnO.SiO_2, both synthesizedat 900, 1000, 1 100 and 1 200 °C.

Fig. 4: X-ray patterns of pigments 0,25FeO.1,75ZnO.SiO_2 after treatment at different temperature: ● – Zn_2SiO_4, ◊ –$ZnFe_2O_4$



The diffraction patterns shown the presence of a main crystalline phases of willemite and zinc ferrite. The formation of the wilemite phase is almost completeat 900 °C (fig. 4).

Fig. 5: X-ray patterns of pigments 0,50FeO.1,50ZnO.SiO_2 after treatment at different temperature: ● – Zn_2SiO_4, ◊ –$ZnFe_2O_4$



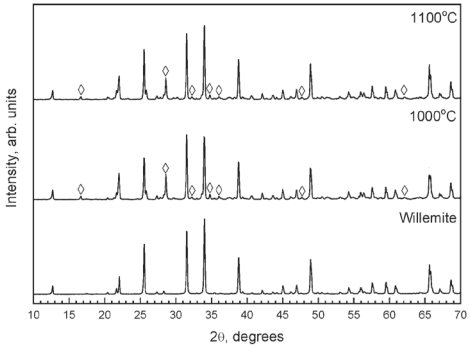
V-doped willemite pigments

V-doped willemite pigments were studied mainly by the methods of X-ray analyses and electron spin resonance spectroscopy (ESRS) and Hot stage microscopy.

X-ray diffraction analysis

The X-ray diffraction spectra of the synthesized V-doped willemite pigmentsare presented in Figure 6.

Fig. 6: X-ray spectra of the synthesized V-willemite pigments in the system 0,375V_2O_5.1,625ZnO.SiO_2: main phase, willemite – Zn_2SiO_4, ◊ - Zn_2VO_7 (PDF 291396)

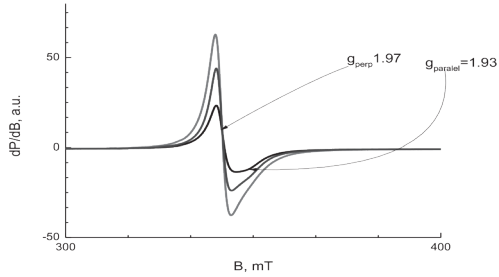


In the presented results it is obvious that even at 1 000 °C peaks of the main phase willemite, Zn_2SiO_4, are already observed. The diffraction pattern reveals well defined peaks with peak positions corresponding to the standard model JSPDS PDF 46-1316 with a willemite structure. At all sintering temperatures are being observed insignificant peaks of Zn_2VO_7 where the tendency of the decrease of the peak intensity with increasing temperature is present. According to XRD data the optimal synthesis temperature of these pigments is 1 100 °C.

Electron spin resonance spectroscopy (ESRS) results

In Figure 7 is presented the EPR spectrum of a pigment in the system $0.5V_2O_5.1.5ZnO.SiO_2$.

Fig. 7: ESR spectrum of sample $0.5V_2O_5.1.5ZnO.SiO_2$ at 295K (black curve), 210K (blue curve) and 120K (red curve)



The analysis of the sample has been carried out in the temperature range of 120–295K. The EPR spectrum consists of an anti-symmetrical signal with an axial symmetry. Clearly distinguished are a perpendicular and a parallel component of the EPR spectrum with the following respective g-factors: g∥≈1.97 and g⊥≈1.93. The intensity of the signal increases with decreasing temperature according to the Currie law.

The observed signal is related to V^{4+} ions (most probably an oxovanadium (IV) cation – VO^{2+}) [8], being found in an octahedral symmetry together with a tetragonal distortion due to the Jahn–Teller effect.

Hot stage analysis of Mn, Fe and V –doped willemite pigments

Figures 8 and 9 show sintering curves of willemite pigments obtained by hot stage microscopy (HSM).

Fig. 8: Sintering curves of willemite pigments 0,5.MnO.1,5ZnO.SiO_2, 0,25Fe_2O_3.1,75ZnO.SiO_2 and 0,375$V_2O_3$1,625ZnO.SiO_2 by hot stage microscopy (HSM) at 10 °C/min.

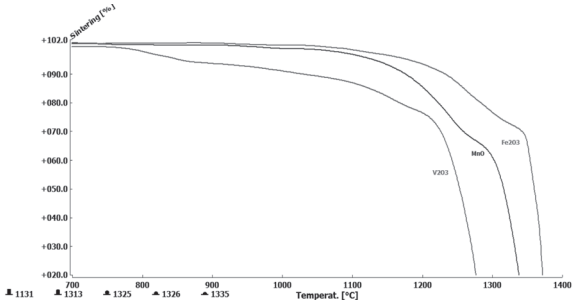
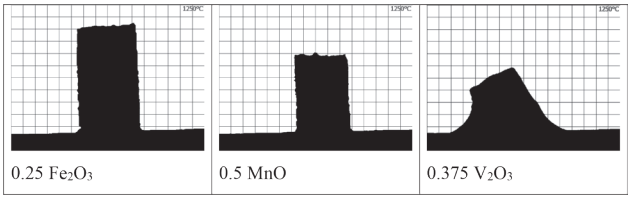


Fig. 9: Images at 1 250 °C by HSM of willemite pigments 0,5.MnO.1,5ZnO.SiO_2, 0,25Fe_2O_3.1,75ZnO.SiO_2 and 0,375V_2O_3.1,625ZnO.SiO_2



All pigments are thermally stable up to 1 000 °C. At higher temperatures however the samples reveal different behavior of densification and melting in terms of rate of change and respective characteristic temperature.

The pigment with Fe_2O_3 sinters in the interval 1 200–1 350 °C and then rapidly melt. At the same time the densification for compositions with MnO takes place in the interval 1 100–1 250 °C and at 1 350 °C it is totally melted. Finally, the pigment 0,375V_2O_3.1,625ZnO.SiO_2 show unusual behavior, because yet at 800 °C are observed some volume variations. The sintering interval is very large (between 900 and 1 200 °C) but the melting completes bellow 1300 °C.

The comparison of the images at 1 250 °C elucidates the begging of the densification in 0,25Fe_2O_3.1,75ZnO.SiO_2, an completed sintering in 0,5.MnO.1,5ZnO.SiO_2 and partial melting in 0,375V_2O_3.1,625ZnO.SiO_2.

It can be concluded that only the pigment, based on iron oxides, is appropriated for high temperature application, while when V_2O_3 is used the glazing temperature can be significantly lower.

Cconclusions

The synthesis of willemite ceramic pigments with added three chromophore elements: Mn, Fe and V was studied. Ceramic pigments were prepared using solid phase sintering technology. Amorphous SiO_2 was used as the source of SiO_2.nH_2O. The determination of composition recipes for the production of willemite ceramic pigments is based on the main mineral willemite. The optimal parameters of the synthesis process have been established. In-depth studies with Electron spin resonance spectroscopy (ESRS) have been performed. From the Hot Stage analysis date can be concluded that only pigment based on iron oxides is suitable for high temperature application, while when V_2O_3 is used the glazing temperature can be significantly lower.

Acknowledgements

The financial support of this work by the Bulgarian Ministry of Education and Science, National Research Fund under the contract number KP-06-H27/14 – 2018 is gratefully acknowledged.

References

[1] Maslennikova G.N., Pisch I.V., *Keramicheskie pigmentyi* (Ceramic pigments), Moscow, Stroymaterialyi, 2009, 224p. (in Russian)

[2] G.N. Masslennikova., A.I. Glebicheva, N.P. Fomina, Willemite pigments with NiO addition, *Glass and Ceramics*,1974, 8, 23–25

[3] Ozel E., Yurdakul H., Turan S., Ardit M., Cruciani G., Dondi M. Co-doped willemite ceramic pigments: Technological behaviour, crystal structure and optical properties, *Journal of the European Ceramic Society*, 2010, Vol. 30, no 16, 3319–3329.

[4] G.T. Chandrappa, S. Ghosh, K.C. Patil, Synthesis and Properties of Willemite, Zn_2SiO_4, and M^{2+}:Zn_2SiO_4 (M = Co and Ni), *Journal of Materials Synthesis and Processing*, 1999, 7(5), 273–279

[5] M. Lusar,A. Forés, J. Badenes, J. Calbo, M. Tena, G. Monrós, Colour analysis of some cobalt--based blue pigments, *Journal of the European Ceramic Society*, 2001, 21(8), 1121–1126

[6] G.N. Masslennikova, N.P.Fomina, A.I. Glebicheva, Synthesis of iron-containing Willemite pigments, *Glass and Ceramics*, 1975, 4, 26–28

[7] B. Chandra Babu, B. Vengla Ra, M.Ravi, S.Babu, Structural, microstructural, optical and dielectric properties of Mn^{2+}: Willemite Zn_2SiO_4 nanocomposites obtained by a sol-gelmethod, *J. Mol. Struct.*, 2017, 1127(5), 6–14

[8] V.N. Shevchuk, A.P. Luchechko, Yu.N. Usatenko, I.V. Kayun and D.Yu. Sugak, Optical properties of V_2O_5 crystals, Conference paper, *Oxide Materials for Electronic Engineering*, 2012, 223–224.