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The effect of firing temperature on colour and structural properties of malayaites with Cr

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Abstract

Malayaites are calcium tin silicate compounds derived from natural occurring mineral the malayaite which has the chemical formula $CaSnSiO_5$. Malayaites are characterized by monoclinic crystal structure consisting of chains of distorted SnO_6 octahedra connected with tops of SiO_4 tetrahedra, forming a framework containing chains of CaO_7 polyhedra. This incurred structure is then stable for bond of metal ion and takes part in the final pigment colouring. In this contribution the compounds with the chemical formula of $Ca(SnCr)SiO_{5\pm\delta}$ (molar ratio of Cr/Sn = 0.015) were prepared. For the synthesis the classical ceramic method was used, *i.e.* procedures of calcination in an electric furnace at the temperatures 1200-1500°C for 4 h (one-step calcination) and multiple calcination (two-step calcination) for obtaining products with higher quality. Therefore, the objective of this work was to compare samples which were prepared by the one-step and also two-step calcination procedures. The two-step calcination procedure was carried out at two temperatures, during which the first calcination was always held at 1100°C for 4 hours. The second calcination was performed for 4 h at an appropriate temperature from the range 1200-1500°C. The colour properties were studied by a spectrophotometer ColorQuest XE (HunterLab, USA). The colour moved from pink to burgundy in dependence on temperature of calcination. The phase composition of tested compounds was verified by using X-ray diffraction analysis with using a diffractometer D8 Advance (Bruker, GB). A particle size distribution of heat treatment samples was measured by Mastersizer 2000/MU (Malvern Instruments, Ltd., GB). The signal was evaluated on the basis of Fraunhofer bending. Thermal stability was investigated by heating microscope EM201-12 (Hesse-Instruments, Germany).

Keywords: Malayaite, Colour properties, High temperature pigments, Burgundy, Pink

WPŁYW TEMPERATURY WYPALANIA NA BARWĘ I WŁAŚCIWOŚCI STRUKTURALNE MALAYAITÓW ZAWIERAJĄCYCH CHROM

Malayaity to związki krzemianowe wapnia i cyny otrzymane z naturalnie występującego minerału malayaitu o wzorze chemicznym $CaSnSiO_5$. Malayaity mają jednoskośną strukturę krystaliczną składającą się z łańcuchów zniekształconych oktaerów SnO_6 połączonych z wierzchołkami tetraedrów SiO_4, tworząc szkielet zawierający łańcuchy wielościanów CaO_7. Struktura ta stabilnie wiąże jony metalu i bierze udział w ostatecznym barwieniu pigmentu. W tym przyczynku przygotowano związki o wzorze chemicznym $Ca(SnCr)SiO_{5\pm\delta}$ i stosunku molowym Cr/Sn = 0,015. Do syntezy wykorzystano metodę klasyczną, tzn. procedury prażenia w piecu elektrycznym przez 4 h w temperaturach 1200-1500°C (kalcynacja jednoetapowa) i prażenia wielokrotnego (dwuetapowa kalcynacja) w celu otrzymania produktów o wyższej jakości. Dlatego, celem tej pracy było porównanie próbek, które przygotowano za pomocą procedur kalcynacji jedno- i dwuetapowej. Procedura dwuetapowa została przeprowadzona w dwóch temperaturach, w jej trakcie pierwsza temperatura prażenia była zawsze utrzymywana w 1100°C przez 4 h; drugie prażenie miało miejsce w odpowiedniej temperaturze z przedziału 1200-1500°C i trwało przez 4 h. Właściwości barwne badano za pomocą spektrofotometru ColorQuest XE (HunterLab, USA). Barwa przesunęła się od różowej do burgundu w zależności od temperatury prażenia. Skład fazowy badanych związków weryfikowano z użyciem dyfrakcyjnej analizy rentgenowskiej, stosując dyfraktometr D8 Advance (Bruker, GB). Rozkład wielkości cząstek zmierzono za pomocą analizatora Mastersizer 2000/MU (Malvern Instruments, Ltd., GB). Sygnał opracowano na podstawie przybliżenia Fraunhofera. Stabilność termiczną badano z użyciem mikroskopu EM201-12 (Hesse-Instruments, Germany).

Słowa kluczowe: malayait, właściwości barwne, pigmenty wysokotemperaturowe, burgund, róż

1. Introdution

The malayaites are calcium tin silicate compounds derived from natural occurring mineral malayaite which has the chemical formula $CaSnSiO_5$ or exactly $CaSnOSiO_4$. As the name of this mineral suggests, there are large deposits of malayaite compounds to be found in Malaysia as well as in Brazil, Madagascar, Russia, or Germany. Malayaites belong to a large family of sphene pigments and they are characterized by monoclinic crystal structure consisting of chains of distorted SnO_6 octahedra connected with tops of SiO_4 tetrahedra, forming a framework containing chains of CaO_7 polyhedra. Sphenes, more precisely nesosilicates, have many excellent properties, from which it can point on high specific density, high reflective index and high hardness. Malayaites have good thermal stability; therefore they are suitable candidate for a host lattice for preparation of high temperature pigments [1].

Many contributions are focused on research of sphene compounds. The attractiveness of the investigation of these compounds is directed in different areas. For example possibilities of new preparation of tin sphene pigments are reported in several works. The pigments were prepared by sol-gel [2], precipitation [3], the combustion [4], spray pyrolysis

[5], or freeze drying [6]. Works using the classical ceramic method are also mentioned. The method is based on a solid state reaction, and comprises calcination at one required temperature [5, 7-9], multi calcination procedure [10, 11], or utilization of mechanical activation as a pretreatment before the calcination [12].

Malayaite compounds doped by chromium are also very interesting from the viewpoint of determining the oxidation state of Cr because the chromium cation can be present in several states (II-VI). Recent studies devoted to Cr-doped malayaites point out on most chromium cations are in the tetravalent state and they substitute octahedral coordinate Sn(IV) places, but a very small amount of Cr(IV) is also presented substituting for tetrahedral Si(IV) position [7, 11, 13]. However, electrochemical work based on solid-state electrochemical data suggests that Cr(V) and Cr(IV) centres exist in chromium-doped cassiterite and sphene materials [14].

Pink chromium-doped malayaite belongs to the most important chromium pigments used in the ceramic industry for colouring glaze and they are the main alternative to the cadmium-containing pigments in the pottery industry [9]. Tin sphene with chromium is in the CPMA nomenclature well known under catalogue number 12-25-5 [15]. Various sources of chromium cation, *e.g.,* Cr_2O_3 [16], $K_2Cr_2O_7$ [7, 17], $PbCrO_4$ [10], $CrCl_3$ [18] can be used for preparation of this pigment. From ecological point of view the work of Hajjaji *et al.* is also very interesting, because the authors used wastes (Al-rich anodizing sludge, Cr/Ni galvanizing sludge, foundry sand, tionite and marble sawing mud) for preparation of inorganic pigments [8] which can be one of the possibilities of processing of dangerous wastes.

The above mentioned new methods for preparing sphene compounds namely bring a kind of improvement of the purity of the structure malayaite pigment, but the question remains whether this benefit will have an impact on the negative aspects of these methods. First, raw materials used in these alternative methods are expensive and for another, from the perspective of a technologist or producer of pigments, these methods are very complicated. Usually the simplest methods of production of inorganic pigments are used, because they consist in homogenization of the starting raw materials in the form of oxides, carbonates or other simple ingredients, and subsequent calcination at a desired temperature or several consecutive calcinations, even if the multi-calcination procedure generally increases production costs.

Cr-doped malayaite pigments have been prepared by solid state reaction in this work. For synthesis the one-step and two-step calcination procedures were used. The great attention was focused on assessment of an impact of the preparation methods and calcination temperatures on application-pigmentary properties. Therefore, the colour, optical and structural properties acquired for the pigments from both methods were compared together with respect to the best properties of the chromium malayaite pigment.

2. Experimental part

The pigment based on malayaite defined as $Ca(SnCr)SiO_{5\pm\delta}$ with the molar ratio of Cr/Sn = 0.015 was prepared using the solid-state reaction. The commercially available powder raw materials were used for the preparation: precipitated $CaCO_3$ (purity 98.5%, Merck Group KGaA, DE), SnO_2 (purity 99.9%, Alfa Aesar GmgH&KG, DE), SiO_2 (purity 99,6%, Sklopísek Střeleč, CZ) and Cr_2O_3 (purity 99%, Lachema Brno, CZ). A stoichiometric mixture of the raw materials was hand milled in an agate mortar and after that was inserted into corundum crucibles for firing procedure. The calcination process was performed in an electric furnace with a heating rate of 10 °C·min^{-1} and carried out at temperatures 1200-1500 °C with step 50 °C for 4 hours. This procedure was used for samples, which were prepared by the so called the one-step calcination (OSC).

The same quantity of the raw materials was used for preparation of the samples which have been synthesized by the multi-calcination process, concretely the two-step calcination (TSC) as a comparing method. In this case, the firing process was carried out at two calcinations; the first one was always at 1100 °C with 4 hours' duration, because in many works it is reported that the formation of tin sphene does not occur directly from the starting materials but calcium stannate is formed in the first, and after that malayaite is formed during the reaction between $CaSnO_3$ and SiO_2 [10, 19]. The samples were hand-pulverized in the agate mortar after cooling to room temperature, and subsequently calcined for 4 h at the same interval of temperatures (1200-1500°C) using a heating rate of 10 °C·min^{-1}.

The phase composition of powdered samples was studied by using the X-ray diffraction analysis with the help of a diffractometer D8 Advance (Bruker, GB) in the 2Θ range from 10° to 80°; Cu $K_{\alpha1}$ (λ = 0.15418 nm) for 2Θ < 35° and Cu $K_{\alpha2}$ (λ = 0.15405 nm) for 2Θ > 35°. A scintillation detector was used.

Particle size distribution was measured by a Mastersizer 2000/MU (Malvern Instruments, Ltd., BG). It is the highly integrated laser measuring system (a He-Ne laser, λ = 633 nm) for analysis of particle size distribution. The equipment uses scattering of the incident light on particles. The signal is evaluated on the basis of Mie theory or Fraunhofer bending.

For study of the thermal stability of powdered pigments a heating microscope with automatic image analysis EM201-12 (Hesse-Instruments, Germany) was used. This apparatus enables to monitor the thermal stability maximally until 1500 °C. The equipment has been calibrated using pure metallic Sn or In. Tablets in the shape of a cylinder of 3 mm in diameter and 6 mm in height were prepared. Area changes of the tablets were monitored. The conditions of this analysis were following: rate of temperature – 10 °C·min^{-1}, sensitivity conditions for taking a new image area change – 5%, shape factor change – 5%, corner angle change – 10%.

The main attention was devoted to determination of the colour properties of studied compounds. The colour properties of the powders and pigments applied into an inorganic binding system were measured in a visible region of light (400-700 nm) using a ColorQuest XE (HunterLab, USA). The measuring conditions were: illuminant D65 (6500 K), 10° complementary observed, geometry of measurements d/8°. The colour properties were described in terms of the CIE-L*a*b* system (1976). In this system *L** (darkness or

lightness of the colour) is described by numbers from 0 (black) to 100 (white). It means that L^* = 50 in this system corresponds to the grey colour. The colour hue is specified by the values a^* (the red-green axis) and b^* (the yellow-blue axis). For better description of the colour the next characteristic namely the chroma and the colour hue were used. The chroma C is calculated according to the following equation:

$$C = \sqrt{(a^{*2} + b^{*2})} \quad (1)$$

and represents a purity of the colour (C = 0 – grey colour, C = 100 – pure colour). The hue angle $H°$ is expressed in the degrees and ranges from 0° to 360°. It is defined by an angular position in the cylindrical colour space (for the red $H°$ = 35-350; for violet $H°$ = 285-350) and the value of hue angle is calculated from the formula:

$$H° = arctg\frac{b^*}{a^*} \quad (2)$$

3. Results and discussion

It has been found that for the formation of Cr-doped malayaite compound the temperature around 1300° C is necessary [19]. Therefore the samples calcinated at 1350 °C, 1400 °C and 1500 °C were chosen for the powder X-ray diffraction analysis. XRD patterns of malayaite pigments doped by Cr prepared of both methods under comparison are showed in Fig. 1. It is evident that both methods did not bring the information about the single-phase malayaite system. The XRD patterns of 1350 °C and 1400° C are very similar; the malayaite as a major phase and the cassiterite, cristobalite, and calcium tin oxide as minor phases were identified. A slight improvement in the phase composition was noticed for the TSC (Fig. 1b), consisting in the absence of cristobalite and also in decreasing intensities of the minor phases. An increase of firing temperature to 1500 °C considerable improved the quality of phase composition, where the malayaite and cassiterite compounds were found. The results of XRD analysis were consistent with the results of several contributions dealing with Cr-doped malayite pigments which were prepared by solid state reaction [8, 9, 16, 18], namely the occurrence of the cassiterite next to the malayaite.

Particle size and distribution rank among fundamental properties of the inorganic pigments and according to literature data [20] the mean particle sizes of inorganic pigment must be in the range of 0.1-10 μm. The recommended particle size is various and differs in application. For utilization into the ceramic glaze, the optimal particle size is moved between 5 μm and 15 μm, but for application into plastics it must be less than 2 μm. The obtained values of mean particle sizes for both compared methods are summarized in Table 1 and showed the increase of the median value d_{50} with growing calcination temperature in both cases. The values of mean particle size lay between 2.52 μm and 9.45 μm for the OSC and between 2.61 μm and 9.49 μm for the TSC. The growth is between 1 μm and 2 μm, only 3, respectively; 3.4 μm was detected for 1350 °C. A slight effect of the two-stage calcining process was recorded by a subtle increase of values d_{50}. Nevertheless the results of the particle size distribution showed that intensive grinding in the agate mortar is sufficient for application into the ceramic glaze and additional milling treatment is not necessary.

The colour characteristics of powders are also summarized in Table 1. The synthesized malayaite pigments doped by chromium can be characterized as pink or burgundy in dependence on the calcination temperature. The obvious influence of multi-calcination process was not visible. In both

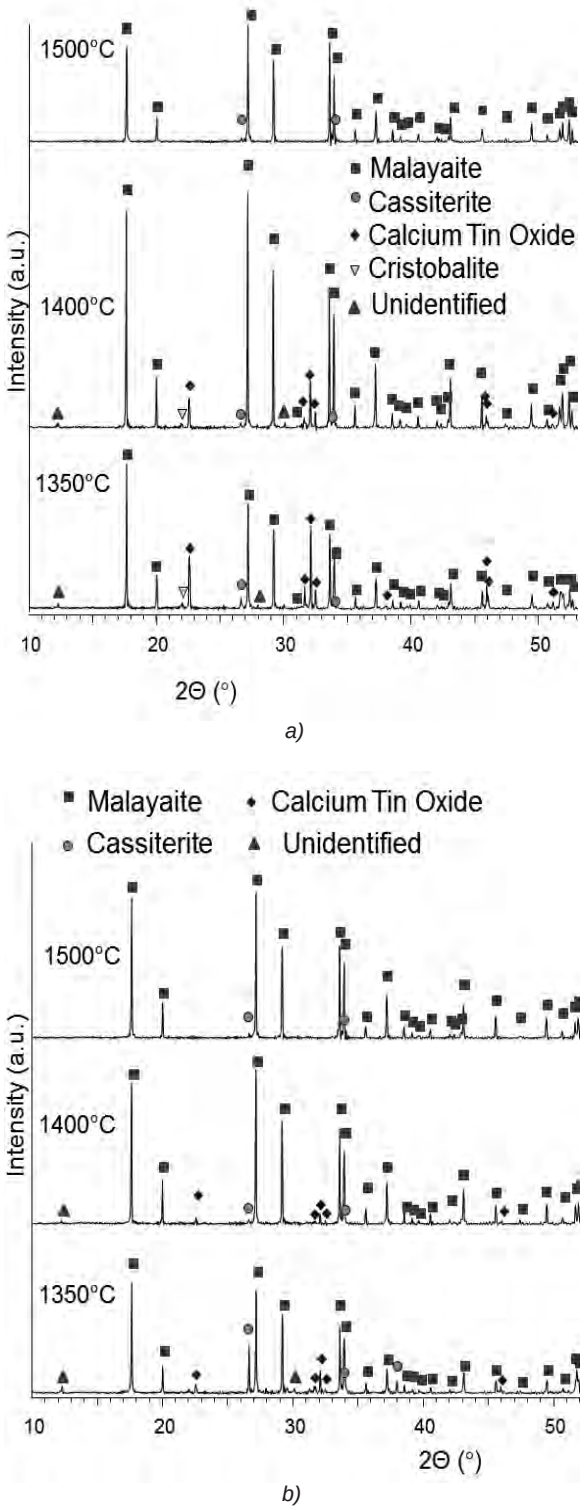


Fig. 1. XRD patterns of Cr-doped malayaite pigments prepared by: a) OSC, b) TSC.

cases, the values of *L** gradually decreased with increasing temperature. A slight jump was recorded for 1400 °C. The powdered pigments belong to hue values for the red area. A tendency to decrease with increasing temperature was for both assessed methods the same, *i.e.* a gradual shift toward blue-red. The shift from the temperature of 1350 °C was more uniform in case of the TSC process. Chroma slightly increased in both cases until the temperature of 1400 °C, thereafter diminution of values *C* occurred. Mildly higher values of chroma were recorded for the OSC.

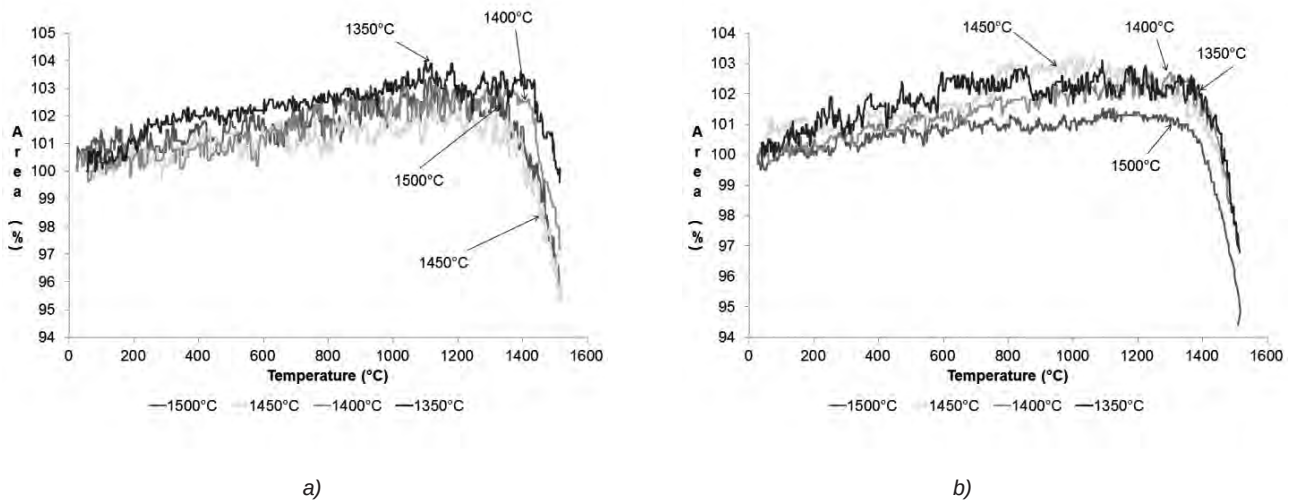
Since the malayaite pigments doped by chrome belong to the most important ceramic pigments, the main attention was concentrated on the study of colour properties after their application in the glaze. Based on literature data [8, 10] the transparent leadless borosilicate middle-temperature glaze with a glazing temperature of 1050 °C was chosen and the pigment was applied into the glaze in a mass of 10 wt.%. This bonding system was also choosen on the basis of the results of thermal analysis. The powdered pigments were heated up to 1500 °C and the results with detailed curves for temperatures of 1350-1500 °C are presented in Fig. 2.

The findings of this analysis confirmed that malayaite pigments with chromium have excellent thermal stability. Only temperatures of a start of sintering were detected and they moved between 1280-1360 °C for the OSC and 1320-1380 °C for the TSC process. Moreover detailed curves for the four highest calcination temperatures (1350-1500 °C) pointed to the fact that the decrease of area was minimal (2.7%-5.7% for the OSC and 0.5%-5.2% for the TSC). A slight improvement of thermal stability was observed for the TSC, the starts of sintering temperatures were shifted to higher values, loss area smaller and curves showed a smoother course than the OSC. The results of thermal analysis showed that application of the pigments into the middle-temperature glaze with the glazing temperature of 1050 °C is suitable.

Presentations of the colour properties and characteristics of the pigments applied to ceramic glazes for both compared methods are shown in Fig. 3 and Table 2. It is brightly visible a decreasing trend of values *a** and parallel growth of *b** up to the temperature of 1350 °C in case of the OSC. A slight decline in *b** values is recorded for further calcination temperatures. The negative values of the coordinate *b** (1200 °C and 1250 °C) indicated the contribution of the blue hue in the resultant colouring, which decreased with increasing temperature. The same trend of shifts of colour

Table 1. Comparison of particle size distribution and colour characteristics of the powdered samples.

T [°C]	OSC					TSC				
	*L**	*C*	*H*°	d_{50} [μm]	d_{10}-d_{90} [μm]	*L**	*C*	*H*°	d_{50} [μm]	d_{10}-d_{90} [μm]
1200	53.28	9.31	21.74	2.52	0.62-19.15	52.60	8.53	19.99	2.61	0.59-20.84
1250	52.15	9.24	19.67	2.83	0.58-16.86	53.66	7.99	19.25	3.50	0.58-23.15
1300	51.18	9.81	17.06	3.04	0.60-18.05	53.26	8.55	13.55	4.53	0.69-26.68
1350	50.40	10.20	13.86	4.15	0.84-22.57	52.76	9.76	8.06	5.09	0.78-26.26
1400	48.35	10.33	11.74	7.17	1.21-24.99	49.38	9.77	7.63	8.44	1.19-27.59
1450	48.00	9.56	7.31	8.21	0.98-25.29	48.10	9.40	5.82	8.81	1.04-28.40
1500	45.72	8.44	6.87	9.45	1.02-30.17	47.49	9.32	4.51	9.49	1.02-31.98



a) *b)*

Fig. 2. Comparison of thermal stability of Cr-doped malayaite` pigments prepared by: a) the one-step calcination (OSC), b) the two-step calcination (TSC).

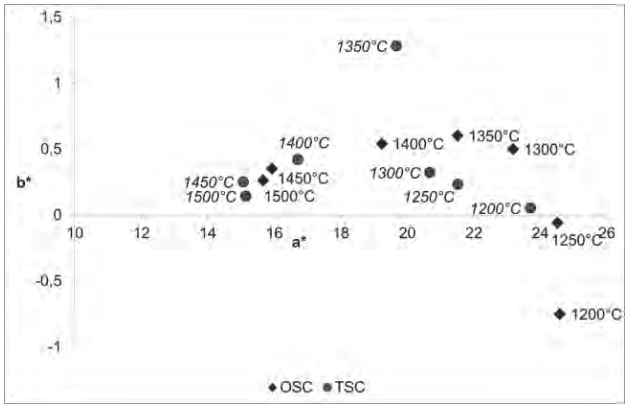


Fig. 3. The dependence of colour properties of Cr-doped malayaite pigments on calcination temperature prepared by OSC and TSC.

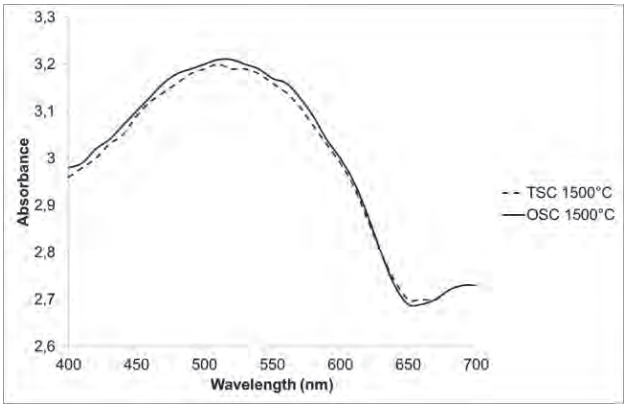


Fig. 4. The diffuse absorption spectrum of Cr-doped malayaite pigments prepared by OSC and TSC.

Table 2. Comparison of colour characteristics of the samples applied into ceramic glaze.

T [°C]	OSC			TSC		
	*L**	*C*	*H*°	*L**	*C*	*H*°
1200	53.19	24.61	358.25	54.67	23.71	0.12
1250	52.87	24.52	359.86	56.55	21.53	0.61
1300	48.89	23.20	1.24	51.86	20.69	0.89
1350	42.54	21.53	1.60	39.47	19.73	3.72
1400	38.61	19.25	1.61	37.41	16.73	1.44
1450	35.56	15.93	1.26	34.79	15.08	0.95
1500	34.05	15.67	0.95	34.52	15.15	0.53

coordinates was recorded for the TSC with the only difference that changes of coordinates *a** and *b** were very small in comparison with the OSC, and the samples prepared at lower investigated temperatures did not include the contribution of the blue hue in the final coloration. Fig. 3 also shows that very similar results, corresponding to the samples prepared at 1300-1400 °C by the OSC, were obtained for samples synthesized by the TSC at lower temperatures (1200-1300 °C). Colour coordinates of pigments, which were prepared by calcination at higher temperatures by both the compared methods, were very similar. The values of lightness *L** moved downwards with growing temperature as shown in Table 2, and it means darkening of the pigments. This shift towards lower values was more uniform in case of the OSC, but a large step change for 1350°C was detected for the TSC process. The chroma values also declined with increasing firing temperature. Marginally higher values of *C* were obtained for the OSC. According to the results of hue angle measurements, the pigments applied into the glaze were situated in the red region. The *H*° values shifted with increasing temperature from the blue-red to red area in case of the OSC. This movement was not visible at the TSC. The values of *H*° were very similar, and they indicated the stabilization of this property.

Although the oxidation state of the chromium ions incorporated into the lattice of malayaite pigments was not studied, the shape of a curve of the absorption spectrum may give clues about the possibilities of existence of oxidation state of Cr. The diffuse absorption spectrum of Cr-doped malayaite pigments prepared by both compared methods at 1500 °C is shown in Fig. 4, and the results are consistent with the works focused on the oxidation state of Cr ions in malayaite compounds with that the curves show a very broad maximum at around 516 nm (OSC) and 505 nm (TSC), and it most probably originates in the $^3A_2 \rightarrow {}^3T_1$ transition (under T_d) and if Cr^{4+} ions are indeed present in the lattice [7, 11].

4. Conclusion

The Cr-doped malayaite pigments were synthesized in this work by solid state reaction with using the one-step (OSC) and two-step calcination (TSC). By visual comparison it has been found that the pigments with a very attractive colour ranging from pink to dark burgundy, depending on the temperature of calcination, were prepared. Based on a careful comparison of the results it can be stated, although the TSC did not bring significant improvement of colour and optical properties, but powders prepared using the TSC showed improvement in the phase composition and thermal stability as the sintering temperatures of powders were shifted to higher values with lower loss of surface area. Therefore, in view of the obtained results it can be recommended to use the method based on double firing for the preparation of Cr-doped malayaite compounds.

Acknowledgements

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