UNIVERSITY OF PARDUBICE

FACULTY OF CHEMICAL TECHNOLOGY

Department of Inorganic Technology

Jakub Trojan

Cassiterite pigments

Theses of the Doctoral Dissertation

Pardubice 2020

Study program: **Chemistry and Chemical Technology**

Study field: **Inorganic Technology**

Author: **Jakub Trojan**

Supervisor: **prof. Ing. Petra Šulcová, Ph.D.**

Year of the defence: 2020

References

TROJAN, Jakub. *Cassiterite pigments.* Pardubice, 2020. 121 pages. Dissertation thesis (PhD.). University of Pardubice, Faculty of Chemical Technology, Department of Inorganic Technology. Supervisor prof. Ing. Petra Šulcová, Ph.D.

Abstract

The violet SnO_2/Cr pigments in which a part of tin ions was substituted by praseodymium ions were examined within this dissertation thesis. The compounds $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ may represent a potential extension of the range of violet shades, especially in their use in ceramics. Pigments have been prepared by classical ceramic route i.e. solid state reaction method, also by the method of mechanoactivation and finally by a two-step process based on the suspension mixing of the initial reagents. The temperature range for the reaction was from 1350 to 1500 °C. The goal was to develop conditions for synthesis and the most suitable preparation method of these pigments. Pigments were characterised in terms of colour after their application into organic matrix and transparent ceramic glaze, they were also studied with respect to their phase composition as well as the particles size distribution. The sample of chosen starting reaction mixture has been subjected to thermal analysis. Using electron microscopy (SEM), the morphology of the pigment prepared by different methods was assessed.

Abstrakt

V rámci této disertační práce byly zkoumány fialové SnO_2/Cr pigmenty, ve kterých byla část iontů cínu substituována ionty praseodymu. Sloučeniny o složení $Sn_{0,99}Cr_{0,005}Pr_{0,005}O_2$ mohou potenciálně rozšiřovat škálu fialových odstínů, zejména pokud jde o jejich použití v keramice. Pigmenty byly připravovány reakcí v tuhé fázi tedy klasickou keramickou metodou, mechanickou aktivací a dvoustupňovým procesem založeným na suspenzním mísení surovin. Teplota, při níž reakce probíhaly, byla zvolena v rozsahu od 1350 do 1500 °C. Cílem bylo nalézt optimální metodu pro přípravu pigmentů a rozpracovat podmínky pro jejich syntézu. Z hlediska barevných vlastností byly pigmenty charakterizovány po jejich aplikaci do organického pojivového systému a transparentní keramické glazury, byly rovněž studovány s ohledem na jejich fázové složení a distribuci velikosti částic. Vybraný vzorek výchozí

reakční směsi byl podroben termické analýze. Pomocí elektronové mikroskopie (SEM) byla sledována morfologie pigmentů připravených různými metodami.

Keywords

Cassiterite, Violet ceramic pigments, Chromium, Praseodymium, Solid state reaction, Colour

Klíčová slova

Kasiterit, Fialové keramické pigmenty, Chróm, Praseodym, Reakce v tuhé fázi, Barva

TABLE OF CONTENT

1 INTRODUCTION

In this work, the main focus is devoted to synthesis of SnO_2/Cr pigments. These compounds represent essentially the only possibility to achieve violet shades among ceramic pigments. The colouring admixture is chromium oxide in various molar ratios (according to the desired shade). The research dealt with the assessment of the effect of other possible colouring admixtures from the group of rare earth elements.

One of the main efforts was to attained deeper and darker violet shades and thus bring the colour shades of cassiterite SnO_2/Cr pigments, prepared in laboratory conditions, closer toward shades of industrially produce pigments, which often use the ecologically problematic $K_2Cr_2O_7$ as a source of chromium.

2 THEORETICAL PART

Stannic pigments with structure of cassiterite mineral rank among the most important inorganic pigments based on tin compounds. According to the CPMA (Classifiacation and Chemicals Descriptions of the Complex Inorganic Color Pigments) they belong, together with rutile pigments, to eleventh group [1]. They are based on tin dioxide which crystallizes in tetragonal structure to form bipyramidal crystals (Fig. 1) and which plays a dominant role in the final compound [2]. Owing to their various material and surface qualities, compounds on the basis of SnO_2 offer a wide range of applications in the field of catalysis, semiconductor techniques or as gas sensors [3]. Also with regard to their high both thermal and chemical stability they find use in ceramic industry (for making glaze and enamel opacity) and owing to their relatively high refractive index it is also find suitability in paint application or textile dyeing [4-6].

Chrome Tin Orchid Cassiterite of general formula $Sn_{1-x}Cr_xO_2$ (according to the CPMA classification with numerical designation 11-23-5) contains basic crystal matrix of cassiterite mineral in which a suitable colourific admixture (chromophore) is doped [2, 7]. By partial substitution of Sn (IV) ions for ions of suited chromophores, a colour change in an originally colourless system is achieved. Owing to a relatively high ionic radius of Sn (IV) ions (0.069 nm) [8], the chromophore ions can be comparatively easily implemented into crystal lattice of SnO_2 [3]. In this case the chromium ions are the matching admixture. Chrome Tin Orchid Cassiterite is most frequently prepared by a high-temperature calcination of homogenized mixture of SnO_2 and a small amount of Cr_2O_3 [9, 10]. The content of chromium in the compound effects the final colouration of pigment, which can gain various colour shades from light pink to deep violet [11, 12].

In the theory of colour properties of $Sn_{1-x}Cr_xO_2$ pigments prevails recently an opinion according to which the three types of chromium species exist in the Cr-doped cassiterite. The first of them is consisting of Cr (III) oxide clusters, the next one of a small amount of CrO_2 nanoparticles. The violet colour of the pigment is caused by Cr (IV) ions that are dissolved in cassiterite lattice to form solid solution. Nevertheless this shade is achieved in a relatively narrow concentration range of chromium in SnO_2

system and gradually disappears when w ≥ 1.6 wt% Cr_2O_3. The solubility limit of chromium in SnO_2 lattice is 0.8 wt% Cr_2O_3 [13, 14].

The aim of this research was to try different ways of preparation combined with suitable chromophore agents to effect colour properties of SnO_2/Cr pigments in terms of their violet colour intensification to reach higher contribution of the desired blue shade in the final pigment colouration, especially when applied into ceramic glaze. Binary praseodymium oxide Pr_6O_{11} was chosen as the admixture because of the presumption of Pr (IV) ions substitution in cassiterite lattice instead of Sn (IV). The formation of SnO_2/Cr pigments doped by praseodymium is based on the possibility of partial substitution of Sn ions by Pr. Regardless the difference between ionic radii of Sn (IV) (0.069 nm; CN = 6) and Pr (IV) (0.085 nm; CN = 6) [8], this element was chosen with respect to the fact, that ions of Pr (IV) can be easily dispersed atomically in the crystals [15]. This fact provides a possible formation of compounds, composition of which is described by formula $Sn_{1-2x}Cr_xPr_xO_2$. The raw material for the preparation of the mentioned system was mixed oxide Pr_6O_{11}. Praseodymium ions are available in two oxidation states in this mixed oxide Pr_6O_{11} ($4PrO_2 \cdot Pr_2O_3$). In the temperature range from 260 to 300 °C the mixed Pr_6O_{11} is reduced to Pr_2O_3 according to the equation:

$$Pr_6O_{11} \rightarrow 3\ Pr_2O_3 + O_2 \qquad (1)$$

In the range of temperature 300 - 400 °C in an oxygen atmosphere, oxidation occurs according to the equation [16]:

$$Pr_2O_3 + ½\ O_2 \rightarrow 2\ PrO_2 \qquad (2)$$

Synthesized pigment $Sn_{1-2x}Cr_xPr_xO_2$ was always compared with concurrently prepared pigment $Sn_{1-x}Cr_xO_2$ in dependence of the used method of preparation and calcination temperature with respect to colour properties in CIE *L*a*b** colour system, furthermore from the point of particle size distribution and phase composition by means of X-ray diffraction analysis. The amount of Pr admixture was chosen to be equimolar to the amount of Cr.

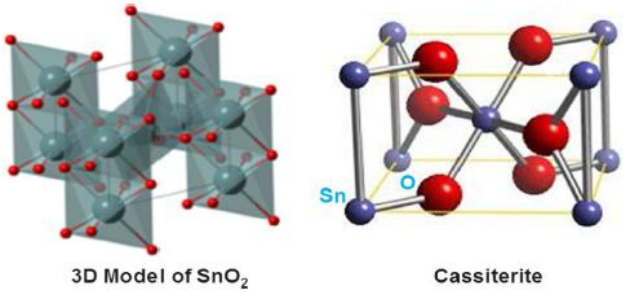

Fig. 1: Tetragonal structure of tin dioxide [17]

3 EXPERIMENTAL PART

3.1 Material and samples preparation

Pigments $Sn_{1-2x}Cr_xPr_xO_2$ (x = 0.005) were synthesized by three methods of preparation. The first two methods of the synthesis were based on the classical ceramic route, i.e. solid state reaction. The first of them was the classical method (CM) which makes use of homogenization of starting raw materials presented in a form of powder oxides: SnO_2 (99% purity, Shepherd Color Company, USA), Cr_2O_3 (99.8% purity, Lachema, a.s., Czech Republic), Pr_6O_{11} (99.5% purity, Indian Rare Earths, Ltd., India). The reagents were weighed in suitable molar proportions and subsequently ground manually in a porcelain mortar to get a homogeneous reaction mixture. These mixtures were calcinated in corundum crucibles in an electric resistance furnace at temperatures 1350, 1400, 1450 and 1500 °C with the rate of temperature increase 10 °C.min^{-1} and the total duration of 3 hrs.

The other method of solid state reaction (MA) was innovated by the mechano-chemical activation prior to calcination. The high energy milling process was carried out in a planetary mill Pulverisette 5 (Fritsch GmbH, Germany). The reaction mixtures were ground with agate balls (Ø10 mm) in a ball-to-powder weight ratio of 10:1. The milling was carried out for 5 hours at a rotational velocity of 500 rev.min^{-1}. The activated reaction mixtures were transferred into corundum crucibles and exposed to the same calcining process as in the previous method.

The third method represents a simulation of ´Mixer Dryer Reactor´ (MDR) under laboratory conditions. This two-step method is based on suspension mixing of the initial reagents. The first step represents the formation of semi-product at medium

temperature. The semi-product was obtained by mixing of raw materials and foaming agents, i.e. fumaric acid (99% purity Acros Organics, USA) and urea (pure, PENTA s.r.o., Czech Republic) in aqueous suspension (approx. 70%) in a porcelain mortar. This suspension was subsequently thermally treated at 400 °C on an alloy steel plate. The reaction mixture contained equimolar amounts of SnO_2 (99% purity, Shepherd Color Company, USA), $Cr_2(SO_4)_3 \cdot 6H_2O$ (99% purity, Lachema, a.s., Czech Republic), Na_2CO_3 (99,9% purity Merck Chemicals GmbH, Germany) needed for the neutralization of sulphate, eventually Pr_6O_{11} (99.5% purity, Indian Rare Earths, Ltd., India). The second step represents a classical calcination in an electric resistance furnace with a rate of temperature increase of 10 °C.min^{-1} and the heating at 1350 - 1500 °C (for 3 hrs).

All samples synthesized by the three methods of preparation were allowed to cool to room temperature after each heating stage and subsequently ground in an agate mortar. Samples of synthesized pigments of formula $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ were assessed with respect to their colour properties, particle size distribution and by X-ray diffraction analysis. To assess the influence of the pigments preparation on their morphological properties, the pigments were also analysed by using a scanning electron microscopy (SEM). The prepared samples were always compared with the concurrently prepared standard sample of $Sn_{0.995}Cr_{0.005}O_2$.

All synthesized pigments were applied into the organic matrix (dispersive acrylic paint Parketol, Balakom, a.s., Czech Republic) in mass tone and into medium-temperature ceramic glaze G07091 (Glazura, s.r.o., Czech Republic). For testing in an organic matrix, suspensions containing 1 g of the sample and 1.5 cm^3 of a binder were homogenized. This system was converted by a pestle to a dense paste able to a flowing. Coloured coating films were prepared by deposition of the paste on the white non-absorbing glossy paper. The coating layer of film was created by dragging the Bird film applicator. Thickness of the wet film was 100 μm. Coating films prepared by this procedure were kept to dry spontaneously in the open air for 1 - 2 hrs. Then they were ready for an evaluation of colour properties of the pigments into organic matrix in mass tone. In the case of applications into ceramic glazes, an aqueous suspension containing 10 wt% of a pigment sample and 90 wt% of the

transparent ceramic glaze was prepared by manual grinding. This suspension was applied on unglazed ceramic body by using a brush and after a spontaneous drying in the open air it was glazed at 1000 °C for 15 min.

3.2 Characterization of samples

The phase composition of the synthesized pigments was determined by using Diffractometer D8 Advance (Bruker AXS, Ltd., UK).

The colour properties of all final applications were objectively evaluated for their colour change by measuring spectral reflectance in the visible region of light (400 - 700 nm) by using a spectrophotometer ColorQuest XE (HunterLab, Inc., USA). This device operates with a wavelength interval 10 nm and is equipped with a xenon lamp. Standard illuminant D 65 was used as internationally recommended white daylight, measurement conditions are as follows: 10° supplementary standard observer, measuring geometry d/8°. CIE $L^*a^*b^*$ colour system (1976) was used for description of colour properties (Fig. 2). The value L^* represents the lightness or darkness of the colour as related to the natural grey scale. There is description by numbers where zero represents black and hundred represents white. The values of a^* and b^* indicate colour tones from $+a^*$ to $-a^*$ (the red - green axis) and from $+b^*$ to $-b^*$ (the yellow - blue axis). C (Chroma) represents saturation of the colour and determines colour purity. The values range from 0 (grey) to 100 (pure colour) and shows the degree of difference between a colour and grey. The colour hue (otherwise also shade) of pigments is also possible to express as a hue angle $H°$. Hue angle $H°$ is defined as starting at the $+a^*$ axis and indicates the position of the sample in a^*, b^* diagram. It is expressed in degrees; $H° = 350 – 35°$ (for red), $H° = 35 – 70°$ (for orange), $H° = 70 – 105°$ (for yellow), $H° = 105 – 195°$ (for green), $H° = 195 – 285°$ (for blue), $H° = 285 – 350°$ (for violet). Chroma C and hue angle $H°$ of samples were calculated according to the equations (a) and (b) [18].

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

$$H° = \text{arctg } b^*/a^* \quad \text{(b)}$$

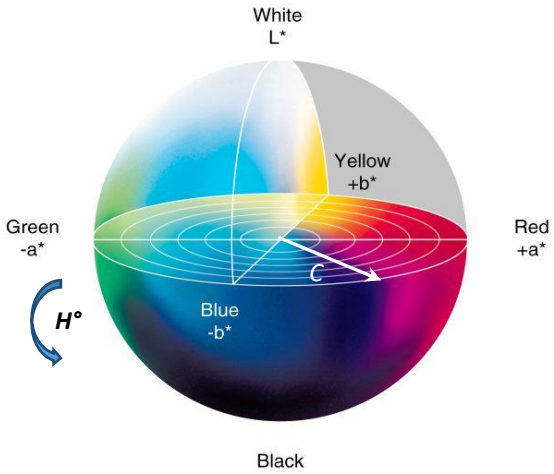

Fig. 2: CIE L*a*b* colour space [19]

The particle size distribution of the synthesised pigments was measured using an equipment Mastersizer 2000/MU (Malvern Instruments, Ltd., UK). This device provides volumetric distribution and uses the laser diffraction on particles dispersed in a liquid medium. The pigments were ultrasonically homogenized in solution of $Na_4P_2O_7$ (c = 0.15 mol.dm^{-3}) for 120 s. The signal was evaluated on the basis of Fraunhofer diffraction. The measurement is performed in three steps, the results are automatically calculated as average and presented as d_{10}, d_{50}, d_{90} values.

In order to examine the morphology of the synthesized pigments with respect to preparation method used, the scanning electron micrographs of powder materials were taken by means of high-resolution scanning electron microscopy (SEM). The apparatus JEOL JSM-7500F (JEOL GmbH, Germany) with an accelerating voltage of the primary electron beam 5 kV was used.

To obtain more information about $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$, the formation was followed by thermal analysis using STA 449C Jupiter (Netzsch GmbH, Germany) which allows the simultaneous registration of the thermoanalytical curves TG and DTA.

4 RESULTS AND DISSCUSION

4.1 Colour characteristics

The effects of the preparation method as well as the calcination temperature on the colour properties of synthesized pigments after their application into an organic matrix and ceramic glaze are shown in Table 1 and Table 2. The obtained results show that the colour coordinates are changing in the dependence of the pigment composition, the calcination temperature (*T*) and the way of preparation. For both applications of pigments, the increasing calcination temperature decreases value *L** (lightness) for all methods of preparation and pigments become darker. The growing calcination temperature causes the increase of the saturation *C* (Chroma). For all three methods the highest value of *C* occurs at temperature of 1500 °C. The comparison of the synthesized pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ in terms of the acquired colour properties shows that when using praseodymium as admixture in SnO_2/Cr pigments the better results were achieved in case of all synthesized samples. This fact can be derived from the obtained higher values of saturation caused, above all in ceramic glazes, by the increase of the desired blue shade as well as in most cases the acquirement of darker pigments with lower value of lightness *L**.

A comparison of the three used ways shows that the obtained colour purities *C* differ. When using MA and MDR method, the obtained values are higher than those obtained in case of CM method. Speaking of MA method it is obvious that the increasing value of *C* in case of organic matrix results from the increase of both colour coordinates (+*a**, -*b**). The growth of *C* value is more considerable at pigments synthesized at higher temperatures (1450, 1500 °C) and the increasing contribution of blue colour (at 1500 °C; *b** = -20.99, resp. -22.85, *C* = 32.51, resp. 34.76) has positive effect as well. Nearly in case of most pigments applied into organic matrix, a higher share of blue colour is gained when using MA method compared with CM. This fact is confirmed by mostly decreasing values of angle *H*° which means a shift closer toward blue-violet shades. However pigments of higher values of lightness *L** are obtained which is a drawback of this method. The situation is changing when the pigments are applied into ceramic glaze. In case of all calcination temperatures the higher saturations *C* (the highest at 1500 °C; *C* = 22.49, resp. 23.91) are obtained in

comparison with pigments prepared by CM method. However the red colour has a bigger share in the increasing of *C*, values of which at the *a** axis are increasing with temperature. On the other hand the blue shade in comparison with CM method shows just a slight increase. At the highest temperature of synthesis its share compared with this method even slightly dropped (*b** = -9.96, resp. -11.30 unlike *b** = -10.42, resp. -11.54). It is proved with slightly higher values of *H*° indicating a shift rather toward red-violet shades. At all temperatures the lighter colour shades (of higher *L** values) are attained in ceramic glazes as well as in organic matrix.

Table 1 The effect of calcination temperature and way of preparation on colour properties of the pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ applied into organic matrix in mass tone

Method of preparation	*T/°C*	*Pigment*	*L**	*a**	*b**	*C*	*H°*
CM	1350	$Sn_{0.995}Cr_{0.005}O_2$	55.25	20.26	-15.74	25.66	322.16
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	51.01	21.52	-17.46	27.71	320.95
	1400	$Sn_{0.995}Cr_{0.005}O_2$	52.41	20.86	-16.88	26.83	321.02
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	48.77	23.70	-18.93	30.33	321.38
	1450	$Sn_{0.995}Cr_{0.005}O_2$	47.28	21.67	-18.10	28.23	320.13
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	45.80	23.99	-19.39	30.85	321.05
	1500	$Sn_{0.995}Cr_{0.005}O_2$	41.63	22.65	-19.69	30.01	319.00
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	44.51	25.38	-20.81	32.82	320.65
MA	1350	$Sn_{0.995}Cr_{0.005}O_2$	60.67	20.16	-15.97	25.72	321.62
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	56.73	21.64	-17.80	28.02	320.56
	1400	$Sn_{0.995}Cr_{0.005}O_2$	57.94	21.21	-16.72	27.01	321.75
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	53.45	24.12	-19.05	30.74	321.70
	1450	$Sn_{0.995}Cr_{0.005}O_2$	55.52	22.36	-18.97	29.32	319.69
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	51.18	24.53	-20.69	32.09	319.85
	1500	$Sn_{0.995}Cr_{0.005}O_2$	49.74	24.82	-20.99	32.51	319.78
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	47.84	26.19	-22.85	34.76	318.90
MDR	1350	$Sn_{0.995}Cr_{0.005}O_2$	52.04	20.95	-17.95	27.59	319.41
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	50.20	21.48	-18.25	28.19	319.65
	1400	$Sn_{0.995}Cr_{0.005}O_2$	51.27	22.16	-18.35	28.77	320.37
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	47.21	23.08	-19.35	30.12	320.02
	1450	$Sn_{0.995}Cr_{0.005}O_2$	49.95	22.54	-18.84	29.38	320.11
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	44.58	24.07	-20.01	31.30	320.26
	1500	$Sn_{0.995}Cr_{0.005}O_2$	41.56	23.35	-20.32	30.95	318.97
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	40.68	25.25	-21.04	32.87	320.20

When the pigments are prepared by MDR method, then in comparison with pigments of the same composition but prepared via CM method and applied into organic matrix,

it can be stated that through the change of the preparation method the slight increase of *C* and blue colour (to the detriment of red colour) were attained nearly at all synthesis temperatures. The values of *b** are shifting more distinctly toward to blue colour with the growing temperature (at 1500 °C; *b** = -20.32, resp. -21.04, *C* = 30.95, resp. 32.87). Lightness *L** of pigments synthesized by MDR method is decreasing with the increasing synthesis temperature and is subtly lower than in case of pigments prepared by CM method and considerably lower than in case of MA method.

Table 2 The effect of calcination temperature and way of preparation on colour properties of the pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ applied into ceramic glaze

Method of preparation	*T/°C*	*Pigment*	*L**	*a**	*b**	*C*	*H°*
CM	1350	$Sn_{0.995}Cr_{0.005}O_2$	58.54	16.26	-7.75	18.01	334.52
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	53.56	18.35	-8.21	20.10	335.90
	1400	$Sn_{0.995}Cr_{0.005}O_2$	56.24	18.15	-9.23	20.36	333.04
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	51.28	19.38	-9.97	21.79	332.78
	1450	$Sn_{0.995}Cr_{0.005}O_2$	51.95	19.36	-9.68	21.65	333.43
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	49.47	20.24	-10.45	22.78	332.69
	1500	$Sn_{0.995}Cr_{0.005}O_2$	50.17	19.66	-10.42	22.25	332.08
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	47.55	20.13	-11.54	23.20	330.18
MA	1350	$Sn_{0.995}Cr_{0.005}O_2$	64.74	16.66	-7.87	18.34	334.71
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	60.24	18.75	-8.23	20.48	336.30
	1400	$Sn_{0.995}Cr_{0.005}O_2$	61.31	18.57	-9.33	20.78	333.32
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	57.19	19.77	-9.98	22.15	333.22
	1450	$Sn_{0.995}Cr_{0.005}O_2$	57.65	19.76	-9.80	22.06	333.62
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	53.20	20.75	-10.54	23.27	333.07
	1500	$Sn_{0.995}Cr_{0.005}O_2$	54.16	20.16	-9.96	22.49	333.71
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	50.47	21.07	-11.30	23.91	331.80
MDR	1350	$Sn_{0.995}Cr_{0.005}O_2$	56.47	16.48	-7.90	18.28	334.39
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	52.87	18.24	-8.42	20.09	335.22
	1400	$Sn_{0.995}Cr_{0.005}O_2$	53.69	18.36	-9.52	20.68	332.59
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	50.45	19.66	-10.23	22.16	332.51
	1450	$Sn_{0.995}Cr_{0.005}O_2$	49.32	19.21	-10.09	21.70	332.29
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	47.61	20.31	-10.89	23.05	331.80
	1500	$Sn_{0.995}Cr_{0.005}O_2$	46.71	19.91	-10.62	22.57	331.92
		$Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$	46.29	20.38	-11.87	23.58	329.78

When the pigments are applied into ceramic glaze the colour change is very similar. At all pigments prepared by MDR method a slight increase of blue shade in the final colour occurs in comparison with both previous methods. The share of blue shade is growing with the increasing calcination temperature (at 1500 °C; *b** = -10.62,

resp. -11.87, C = 22.57, resp. 23.58). This trend is apparent also from the slightly decreasing values of angle $H°$ which indicates a shift closer toward blue-violet colour. The colours of higher colour purity C in comparison with CM method were acquired. Compared with MA method the similar values of C or slightly lower were observed. In terms of lightness L^* the MDR method provides pigments of the darkest colouration of all used methods (the darkest at the highest temperature of 1500 °C; L^* = 46.71, resp. 46.29).

4.2 Size of pigment particles and their morphology

The preparation method, pigment composition and the calcination temperature affect not only related colour properties, but also particle size distribution. The mean particle size of inorganic pigments must lie in the range of 0.1 – 15 μm. This fact originates from literature data [20]. Values of mean particle size (d_{50}) of the powder compounds are presented in Table 3 (for $Sn_{0.995}Cr_{0.005}O_2$ pigments) and Table 4 (for $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ pigments). The results show that the growing synthesis temperature causes an increase of values d_{50} for all three ways of preparation. Pr-doped pigments are mostly characterized by slightly higher values of d_{50}. In case of CM method the mean values range from approx. 6 to 14 μm, resp. from approx. 8 to 15 μm.

Table 3 The effect of calcination temperature and way of preparation on particle size distribution of $Sn_{0.995}Cr_{0.005}O_2$ pigments

Method of preparation	*Calcination temperature/°C*	*Particle size/μm*		
		d_{10}	d_{50}	d_{90}
CM	1350	1.93	6.02	16.11
	1400	2.21	7.52	17.81
	1450	3.84	10.44	27.81
	1500	4.51	13.69	31.81
MA	1350	1.13	5.34	27.08
	1400	1.40	7.36	31.32
	1450	1.79	8.96	33.54
	1500	1.84	9.02	34.17
MDR	1350	2.51	8.54	25.04
	1400	3.68	10.82	29.24
	1450	4.26	12.43	30.07
	1500	5.19	14.68	33.23

Lower values of mean particle size were obtained by MA method. Their interval ranges from approx. 5 to 9 μm, resp. 6 to 10 μm. However, this way of preparation caused wider distribution of pigment particles. The mean values of the pigment particle sizes, which were gained by the MDR method, are in number interval from approx. 8 to 15 μm, respectively 8 to 16 μm. The appropriate granulometric composition for application of pigments into ceramic glaze is about 5 - 15 μm. These values were attained for pigments prepared by all three ways. For their potential use in painting coats it would be necessary to treat the size mechanically, especially for pigments synthesized at higher temperatures (1450 and 1500 °C).

Table 4 The effect of calcination temperature and way of preparation on particle size distribution of $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ pigments

Method of preparation	*Calcination temperature/°C*	*Particle size/μm*		
		d_{10}	d_{50}	d_{90}
CM	1350	3.56	8.73	20.88
	1400	4.78	10.52	25.15
	1450	5.05	12.54	26.50
	1500	6.43	14.70	33.31
MA	1350	1.15	5.91	27.68
	1400	1.64	8.31	32.24
	1450	1.87	9.27	36.82
	1500	2.58	10.22	38.95
MDR	1350	2.22	7.99	19.90
	1400	3.90	10.89	29.54
	1450	4.71	12.65	31.56
	1500	5.79	15.95	37.19

To obtain more information about surface morphology, about grain size and about homogeneity of the powder materials, the SEM characterization was carried out. SEM micrographs of $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ samples prepared by the CM, MA and MDR method are shown in Fig. 3a, b, c. Figures show the tetragonal symmetry of pigments particle and indicate the existence of agglomerates and aggregates depending on the way of preparation. In case of mechano-chemical activation is apparent that this way provides agglomerates and aggregates of individual particles. In this case it would be appropriate to use grinding to disconnection of the individual particles. On the other hand both remaining methods resulted in addition to the agglomerates also to the

formation of individual grains of pigments and therefore in these cases it is not necessary to modify the pigments by grinding, but e.g. deagglomerate them by ultrasonic. The particles that were obtained by the MA method are smaller than particles obtained by the CM and MDR method. This fact confirms the results of the measured particle size distribution. It is also obvious that MA method provides more finely granular product with tighter particles arrangement, but these pigments have a high tendency to aggregate.

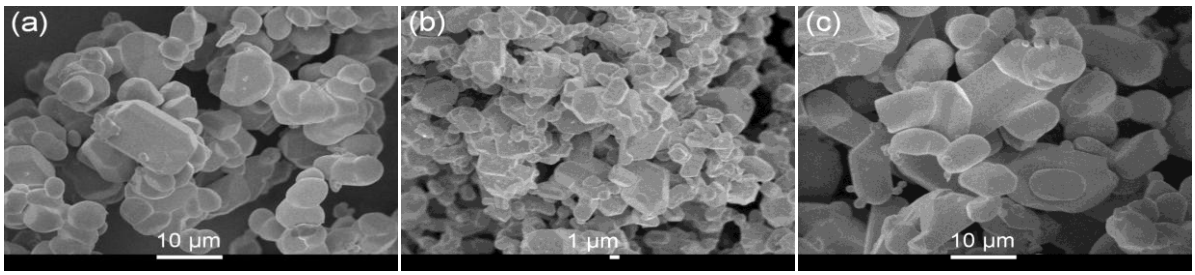

Fig. 3 SEM images of the $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ samples prepared by different methods: (a) CM, (b) MA and (c) MDR, acquired upon calcination at 1500 °C

4.3 Phase composition

The effect of reaction conditions as well as the amount of Cr_2O_3 introduced in SnO_2/Cr pigments as admixture on the phase composition and first of all on the colour properties were put to the test already in the past. Generally it can be stated that the one-phase composition of $Sn_{1-x}Cr_xO_2$ pigments with the single crystalline phase as tetragonal tin dioxide is achieved at amount of chromium $x \leq 0.01$. By the correction of the reaction conditions (e.g. firing time, alternatively by increase the synthesis temperature up to 1600 °C) the limit can be moved up to $0.01 < x \leq 0.03$. Beyond this boundary values the phase of Cr_2O_3 is detected together with cassiterite. This residual phase hides the violet colour in ceramic glazes and final colouration passes then over from grey to green depending on the amount of chromium.

The slight decrease of lattice parameters is occurred by the replacement of Sn (IV) ions with Cr (IV) ions (which is in compliance with values of ionic radii: 0.069 nm, CN = 6; instead of 0.055 nm, CN = 6) [8]. This fact indicates that solid solutions with cassiterite structure are formed [14].

The structure of powder compound $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ prepared by three methods mentioned above was studied by powder X-ray diffraction analysis for the purposes of this work. Fig. 4 shows that even at the lowest synthesis temperature 1350 °C all the initial reagents were completely reacted in case of all preparation methods.

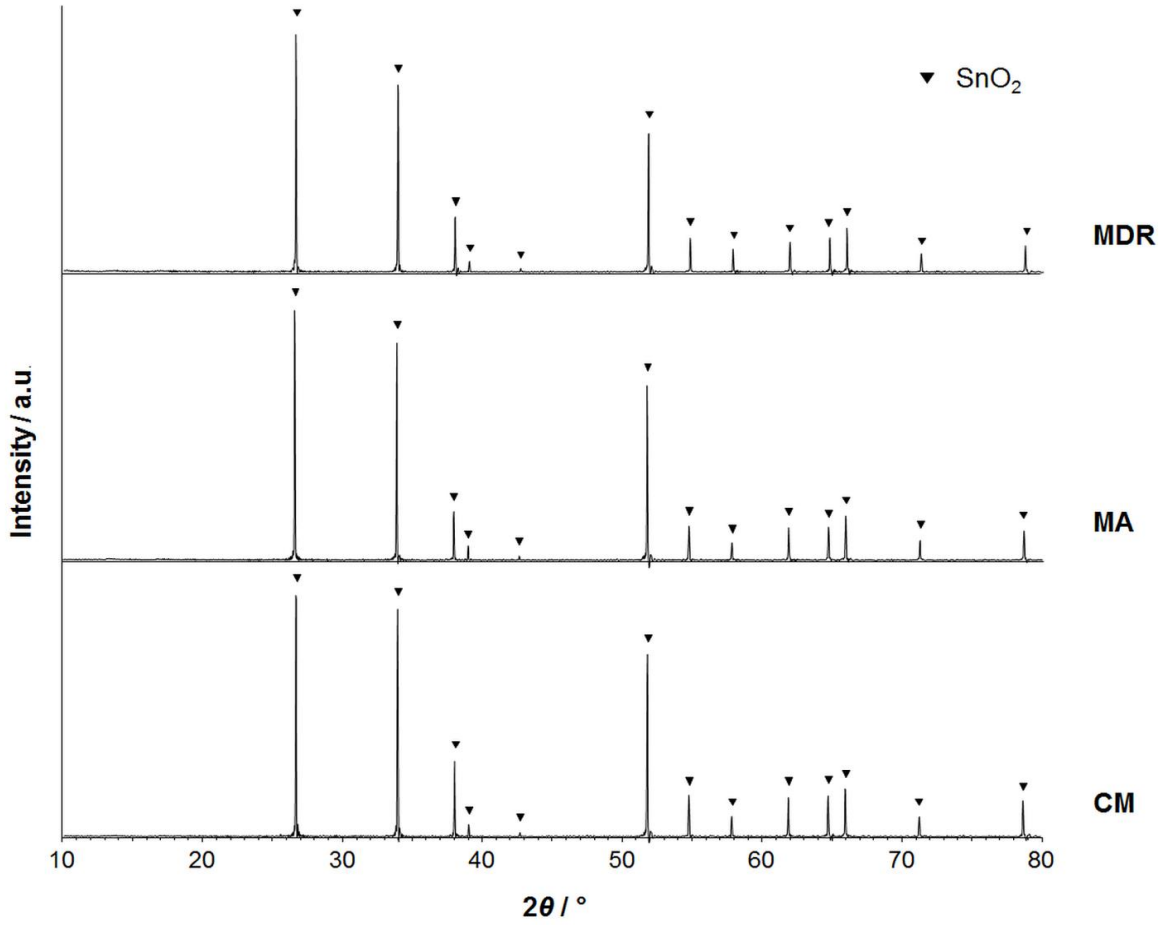

Fig. 4 X-ray diffraction patterns of samples $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ prepared by different ways, obtained upon calcination at the lowest temperature of 1350 °C

The only major crystalline phase corresponding to SnO_2 with tetragonal symmetry was identified. By comparison of all methods it is proved that MA method provides slightly higher intensity of peaks than the remaining methods. This fact can be explained by the reason that the powder material in case of CM and MDR method is consisting of more coarse grains which results in a certain loss of fine crystalline character. This trend can be observed at all single methods with the increasing calcination temperature and increasing size of grains.

The values of the lattice parameters for both prepared samples are summarized in Table 5 and Table 6. The results show that the doping of SnO_2/Cr pigments by praseodymium ions with larger ionic radii resulted in an expansion of the volume of the unit cell. Calcination at higher temperature caused the increase of lattice parameters values. Praseodymium ions substitute stannic ions in their crystal lattice forming substitutional defects in the solid solution $Sn_{1-2x}Cr_xPr_xO_2$. The formation of these defects is associated with the increase of the volume of the elementary cell of $Sn_{1-x}Cr_xO_2$. The measured parameters for CM method at the temperature of 1500 °C were: $a = b = 0.473795$ nm; $c = 0.318665$ nm, for MA method: $a = b = 0.473798$ nm; $c = 0.318663$ nm and for the method of MDR: $a = b = 0.473813$ nm; $c = 0.318685$ nm. It is obvious that MDR method provides the highest values of lattice parameters at the highest temperature of synthesis.

Table 5 Summary of results from XRD analysis of $Sn_{0.995}Cr_{0.005}O_2$ pigments prepared by different ways at chosen temperatures

Method of preparation	*Detected phases*	*T/°C*	*Lattice parameters/nm*			*Volume of unit cell/nm^3*
			a	*b*	*c*	
CM	SnO_2-tetragonal	1350	0.473744	0.473744	0.318664	0.071519
		1500	0.473741	0.473741	0.318692	0.071524
MA	SnO_2-tetragonal	1350	0.473742	0.473742	0.318665	0.071518
		1500	0.473781	0.473781	0.318657	0.071528
MDR	SnO_2-tetragonal	1350	0.473735	0.473735	0.318661	0.071515
		1500	0.473742	0.473742	0.318700	0.071526

Table 6 Summary of results from XRD analysis of $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ pigments prepared by different ways at chosen temperatures

Method of preparation	*Detected phases*	*T/°C*	*Lattice parameters/nm*			*Volume of unit cell/nm^3*
			a	*b*	*c*	
CM	SnO_2-tetragonal	1350	0.473758	0.473758	0.318656	0.071521
		1500	0.473795	0.473795	0.318665	0.071534
MA	SnO_2-tetragonal	1350	0.473771	0.473771	0.318659	0.071526
		1500	0.473798	0.473798	0.318663	0.071535
MDR	SnO_2-tetragonal	1350	0.473772	0.473772	0.318655	0.071525
		1500	0.473813	0.473813	0.318685	0.071544

The results of X-ray diffraction analysis approve the possibility of the formation of the single-phase SnO_2/Cr system doped by praseodymium.

4.4 Thermal analysis

The intermediate of pigment prepared by MDR process was subjected to simultaneous thermal analysis. The aim of the analysis was to find out which processes take place during the heating of the prepared powdered intermediate. The measurement was carried out in the temperature range from 30 °C to 1400 °C in a protective atmosphere of argon with a heating rate 10 °C.min^{-1}.

The first endothermic peak with a minimum of 106 °C (Fig. 5) is associated with the loss of residual moisture. Mixed oxide Pr_6O_{11} ($4PrO_2.Pr_2O_3$) was used to incorporate Pr (IV) ions into the SnO_2 crystal lattice. This compound is reduced to Pr_2O_3 in the temperature range of 260 - 300 °C and subsequently oxidized to PrO_2 according to the previously mentioned equations (1) and (2) [16]. These endothermic events are represented in the thermogram only by slight hints of peaks. Thus, the mentioned reactions of Pr_6O_{11} probably occur to a greater extent already in the preparation of the intermediate product, where the mixture is processed at a temperature of ≈ 400 °C. Higher, but not very significant weight loss in the temperature range of 30 - 600 °C (-0.356%) can be attributed to the loss of moisture and decomposition of residual organic compounds. The endothermic peak detected at 793.5 °C presumably corresponds to the decomposition of $Cr_2(SO_4)_3$. This sulphate is stable up to 300 °C and it decomposes slowly beyond this temperature. The detailed decomposition process is not defined accurately, but it can be expressed by equations [21]:

$$Cr_2(SO_4)_3 \rightarrow Cr_2O_3 + 3\ SO_2 + 3/2\ O_2 \qquad (3)$$

$$Cr_2(SO_4)_3 \rightarrow Cr_2O_3 + 3\ SO_3 \qquad (4)$$

The complete decomposition of $Cr_2(SO_4)_3$ to Cr_2O_3 thus occurs only in the range of temperature 700 - 800 °C [21]. Both exothermic effects, the more pronounced one at 1041.1 °C and the second one at 1195 °C, correspond to the onset of cassiterite pigment formation. Studies have confirmed, that the first colour changes are evident from a temperature of 800 °C, but the first distinct pink shades are achieved only at temperatures beyond 1000 °C. Higher temperatures are necessary to overcome the

lattice energy to make the diffusion of ions into the tin dioxide lattice more efficient. For this reason, higher calcination temperatures (>1300 °C) are used for the synthesis of deeper cassiterite pigments [14]. The slight exothermic peak detected at 1379 °C appears to be related to the formation of a small amount of cubic $Pr_2Sn_2O_7$ [22].

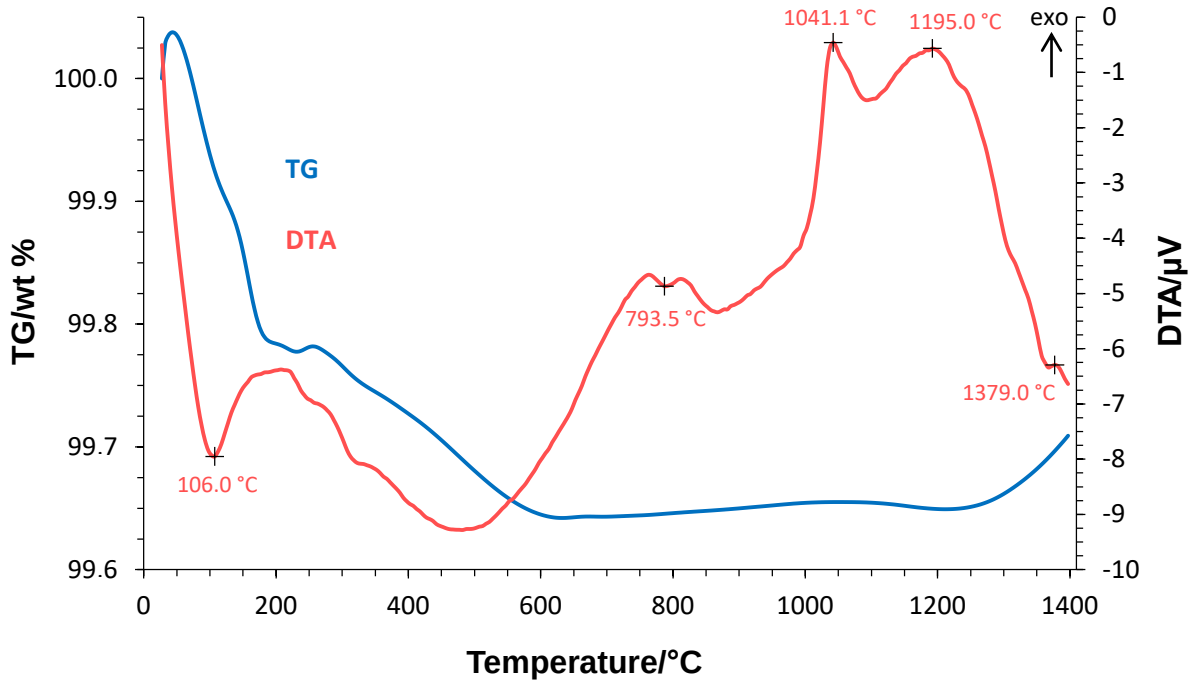

Fig. 5 TG/DTA curve of pigment intermediate $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ gained by MDR process of initial reaction mixture (605.10 mg)

Nevertheless the presence of this minority phase was not confirmed by X-ray diffraction analysis, arguably because of its low detection limit.

The total mass loss recorded on the TG curve was 0.29%. This insignificant decrease is primarily caused owing to the loss of moisture and the thermal decomposition of the organic compounds residues in the temperature range of 30 - 600 °C.

Table 7 Thermal behaviour of intermediate gained by MDR process in $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ pigment preparation

Temperature range/°C	*Maximum/minimum of peak/°C*	*Mass change/%*
30 - 600	106.0 (endo)	-0.356
600 - 800	793.5 (endo)	+0.002
800 - 1200	1041.1; 1195.0 (exo)	+0.003
1200 - 1400	1379.0 (exo)	+0.060

5 CONLUSIONS

The main aim of the presented work was to synthesize SnO_2/Cr compounds doped by praseodymium ions and to find out whether the presence of Pr can affect the colour properties, phase composition and other main pigmentary properties. The compounds $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ were synthesized by using the classical ceramic method (CM) based on the solid state reaction. Furthermore the solid state reaction was innovated by an activation of the precursors by mechano-chemical treatment prior to calcination (MA). The third method makes use of a suspension mixing of the initial reagents and represents a simulation of ´Mixer Dryer Reactor´ (MDR) under laboratory conditions. The X-ray analysis confirmed that the synthesis temperature of 1350 °C is sufficient to get a single-phase compound for all three methods of preparation. The use of praseodymium ions as dopant results in the expansion of the tetragonal unit cell of cassiterite.

From the point of view colour properties a positive effect of praseodymium presence in the final compound was proved. In case of all three methods of preparation the higher colour purities (higher values of *C*) were obtained at pigments of $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ in comparison with $Sn_{0.995}Cr_{0.005}O_2$ pigments prepared in the same way. The best results of all used methods were achieved at MA and MDR methods. By these two methods the higher values of *C* were gained than in case of CM method. However the acquirement of higher lightness of colours seems to be a disadvantage of MA method. The biggest abundance of the desired blue shade and an overall shift closer toward blue-violet colour in ceramic glazes were observed at MDR method. This method also provided the darkest colouration (the lowest L^* values). The positive influence of the increasing synthesis temperature on the colour properties of pigments was confirmed as well. According to the highest colour purity, the best temperature for synthesis of these pigments is 1500 °C. The resulting SnO_2/Cr compounds doped by praseodymium allow an extension of the scale of the attainable violet colours that are in shortage in the field of high-temperature ceramic pigments. They can be convenient for colouring of organic binders and above all decorative ceramic glazes.

6 LIST OF REFERENCES

[1] *Classification and Chemical Description of the Complex Inorganic Pigments*. 4th ed. Alexandria: Color Pigments Manufacturers Associations, 2013.

[2] SWILER, D.R. *Inorganic pigments.* Kirk-Othmer encyclopedia of chemical technology. 5th ed. New York: John Wiley, 2006, ISBN 9780471484974.

[3] BATZILL, M. and U. DIEBOLD. The surface and materials science of tin oxide. *Progress in Surface Science* [online]. 2005, **79**(2–4), 47–154 [cit. 2019-11-20]. Available: https://www.sciencedirect.com/science/article/pii/S007968160500050X. ISSN 00796816.

[4] EPPLER, D.R. and R.A. EPPLER. The Relative Stability of Ceramic Pigments. In 98th Annual Meeting and the Ceramic Manufacturing Council's Workshop and Exposition: Materials & Equipment/Whitewares: *Ceramic Engineering and Science Proceedings* [online]. 1997, **18**, 139-149 [cit. 2020-04-11]. Available: https://ceramics.onlinelibrary.wiley.com/doi/10.1002/9780470294420.ch14. ISBN 9780470375471.

[5] DOSTA, S., M. TORREL, I.G. CANO and J.M. GUILEMANY. Functional Colored Ceramic Coatings Obtained by Thermal Spray for Decorative Applications. *Journal of the European Ceramic Society* [online]. 2012, **32**(14), 3685-3692 [cit. 2020-04-11]. Available: https://www.sciencedirect.com/science/article/abs/pii/S0955221912002245. ISSN 0955-2219.

[6] CASTRO, R.H.R., J. RUFNER, P. HIDALGO, D. GOUVÊA, J.A.H. COAQUIRA, and K. van BENTHEM. Surface Segregation in Chromium-Doped Nanocrystalline Tin Dioxide Pigments. *Journal of the American Ceramic Society* [online]. 2012, **95**(1), 170-176 [cit. 2020-04-11]. Available: https://ceramics.onlinelibrary.wiley.com/doi/abs/10.1111/j.1551-2916.2011.04868.x.

[7] TCHEICHVILI, L., and W. A. WEYL. Synthesis of Ceramic Pigments. *The glass industry*. 1963, **44**(11), 234. ISSN 0017-1026.

[8] SHANNON, R. D.*: Database of Ionic Radii* [online]. London: Materials Department of Imperial College London, c2008 [cit. 2020-04-11]. Available: http://abulafia.mt.ic.ac.uk/shannon/ptable.php.

[9] ŠOLC, Z., M. TROJAN and K. KUCHLER. Formation of Ceramic Pigments of Sn-Cr Type. A Study Using Thermal Analysis Method. *Thermochimica Acta* [online]. 1985, **88**(2), 421-424 [cit. 2020-04-11]. Available: https://www.sciencedirect.com/science/article/abs/pii/0040603185854642. ISSN 0040-6031.

[10] HURD, B. M. Chrome-tin pinks and maroons. *Ceramic Bulletin*. 1961, **40**(1), 11–12. ISSN 0002-7812.

[11] BEATRIZ, J., H. BELTRÁN, E. CORDONCILLO, P. ESCRIBANO, J.V. FOLGADO, M. VALLET-REGÍ and R.P. del REAL. A Study of The Method of Synthesis and Chromatic Properties of the Cr-SnO_2 Pigment. *European Journal of Inorganic Chemistry* [online]. 2002, **2002**(10), 2694-2700 [cit. 2020-04-11]. Available: https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/1099-0682%28200210%292002%3A10%3C2694%3A%3AAID-EJIC2694%3E3.0.CO%3B2-N.

[12] TENA, M. A., S. MESEGUER, C. GARGORI, A. FORÉS, J. A. BADENES and G. MONRÓS. Study of Cr-SnO_2 ceramic pigment and of Ti/Sn ratio on formation and coloration of these materials. *Journal of the European Ceramic Society* [online]. 2007, **27**(1), 215-221 [cit. 2020-04-11]. Available: https://www.sciencedirect.com/science/article/pii/S0955221906004043. ISSN 0955-2219.

[13] KATO, M., H. UNUMA, and M. TAKAHASHI. Color Modification of Chromium-tin Pink Pigment of Ti for Sn. *Journal of the Ceramic Society of Japan*. 2000, **108**(5), 478-481. ISSN 0914-5400.

[14] LÓPEZ-NAVARRETE, E., A. R. GONZÁLEZ-ELIPE and M. OCAÑA. Non-conventional synthesis of Cr-doped SnO_2 pigments. *Ceramics International* [online]. 2003, **29**(4), 385-392 [cit. 2020-04-11]. Available: https://www.sciencedirect.com/science/article/pii/S0272884202001499?via%3Dihub. ISSN 02728842.

[15] ADACHI, G. and N. IMANAKA. The Binary Rare Earth Oxides. *Chemical Reviews*. 1998, **98**(4), 1479-1514.

[16] ŠULCOVÁ, P. and M. TROJAN. Thermal Analysis of Pigments Based on CeO_2. *Journal of Thermal Analysis and Calorimetry* [online]. 2001, **65**(2), 399-403 [cit. 2020-04-11]. Available: http://link.springer.com/10.1023/A:1012404432433. ISSN 14182874.

[17] KANNAN, S., N. P. SUBIRAMANIYAM and M. SATHISHKUMAR. Synthesis and Characterization of Tin Oxide: A Review. *International Journal for Research in Applied Science & Engineering Technology*. [online]. 2017, **5**(11), 47–154 [cit. 2020-04-11]. Available: https://www.ijraset.com/fileserve.php?FID=11593. ISSN 2321-9653.

[18] VÖLZ, H.G. *Industrial color testing: Fundamentals and techniques*. 2nd ed. Weinham: Wiley-VCH, 2003, 17-36, ISBN 9783527600489.

[19] PLOUMIDIS, Dimitris. Salmon Creek Publishing.*Color Perception* [online]. c2018 [cit. 2019-12-04]. Available: https://www.flexoglobal.com/flexomag/08-September/flexomag-ploumidis.htm.

[20] BUXBAUM, Gunter. *Industrial inorganic pigments*. 3rd ed. Weinheim: Wiley-VCH, 2005, ISBN 3527303634.

[21] STERN, Kurt B. *High temperature properties and thermal decomposition of inorganic salts with oxyanions*. Boca Raton: CRC Press, 2001. ISBN 0849302560.

[22] LIU, Q., M. XU, Z. LOW, W. ZHANG, F. TAO, F. LIU and N. LIU. Controlled synthesis of pyrochlore $Pr_2Sn_2O_7$ nanospheres with enhanced gas sensing performance. *RSC Advances* [online]. 2016, **6**(26), 21564-21570 [cit. 2020-03-11]. Available: http://xlink.rsc.org/?DOI=C5RA26028K. ISSN 2046-2069.

7 LIST OF STUDENTS' PUBLISHED WORK

J. Trojan, L. Karolová, J. Luxová, M. Trojan: *Synthesis of SnO_2/Cr pigments doped by praseodymium prepared by different methods and their pigmentary properties*. Ceramics-Silikáty, 60 (3) (2016) 234-242.

J. Trojan, J. Luxová, P. Šulcová: *The effect of transition metals and rare-earth metals admixtures on the pigmentary properties of the cassiterite pigments*. Scientific Papers of the University of Pardubice, Series A; Faculty of Chemical Technology, 24 (2018) 119-132.

J. Trojan, P. Luňáková, L. Karolová, J. Luxová, M. Trojan: *Kasiteritové pigmenty s příměsemi* **(poster)**. 21. Chemicko-technologická konference s mezinárodní účastí Aprochem 2012, Kouty nad Desnou, Czech Republic, 2012, p. 650-654.

J. Trojan, J. Luxová, M. Trojan, P. Luňáková: *Číničité kasiteritové pigmenty s příměsemi Cu a Co* **(poster)**. 64. sjezd chemických společností, Olomouc, Czech Republic, 2012, Chemické listy, p. 541.

J. Trojan, M. Zvonková, J. Luxová, M. Trojan, P. Luňáková: *Kasiteritové pigmenty s příměsí zinku* **(poster)**. 14. Konference o speciálních anorganických pigmentech a práškových materiálech, Pardubice, Czech Republic, 2012, p. 140-143.

J. Trojan, M. Trojan, M. Zvonková, J. Luxová, P. Luňáková: *Cassiterite pigments* **(poster)**. International Days of Materials Science 2012, Pardubice, Czech Republic, 2012, p. 53.

J. Trojan, P. Luňáková, M. Trojan, J. Luxová: *Yellow Cassiterite pigments* **(poster)**. 10th International Conference Solid State Chemistry 2012, Pardubice, Czech Republic, 2012, p. 199.

J. Trojan, M. Zvonková, J. Luxová, M. Trojan, P. Luňáková: *Cassiterite pigments with rare earth metals* **(poster)**. International Masaryk Conference for Ph.D. Students and Young Researchers 2012, Hradec Králové, Czech Republic, 2012, p. 3598-3603.

J. Trojan, J. Luxová, M. Trojan, M. Zvonková, P. Luňáková: *Cassiterite pigments with Cr* **(poster)**. International Days of Materials Science - ReAdMat 2013, Pardubice, Czech Republic, 2013, p. 60.

J. Trojan, J. Luxová, M. Trojan, P. Luňáková, M. Zvonková: *Kasiteritová šeď s příměsemi lanthanoidů* **(poster)**. International Conference On Chemical Technology - ICCT 2013, Mikulov, Czech Republic, 2013, p. 41.

J. Trojan, L. Karolová, J. Luxová, P. Luňáková, M. Zvonková: *Kasiteritová violeť* **(poster)**. 65. zjazd chemikov, Tatranské Matliare, Slovak Republic, 2013, ChemZi p. 185.

J. Trojan, L. Karolová, J. Luxová, M. Trojan, M. Zvonková, P. Luňáková: *Kasiteritové pigmenty s příměsí chromu* **(poster)**. 15. Konference o speciálních anorganických pigmentech a práškových materiálech, Pardubice, Czech Republic, 2013, p. 112-115.

J. Trojan, L. Karolová, J. Luxová, M. Trojan, P. Luňáková: *Cassiterite pigments with chromium and rare earth metals* **(poster)**. 11th Conference on Solid State Chemistry, Trenčianske Teplice, Slovak Republic, 2014, p. 145.

J. Trojan, L. Karolová, J. Luxová, M. Trojan, P. Luňáková: *Pigmenty typu kasiteritové violeti s příměsemi* **(poster)**. International Conference On Chemical Technology - ICCT 2014, Mikulov, Czech Republic, 2014, electronic proceedings, P012, p. 1-5.

J. Trojan, L. Karolová, J. Luxová, P. Luňáková, M. Zvonková: *Vliv způsobu přípravy na barevné vlastnosti kasiteritových pigmentů* **(poster)**. 4. ročník konference Moderní TRENDY v anorganických technologiích 2014, Praha, Czech Republic, 2014, p. 120-123.

J. Trojan, L. Karolová, J. Luxová, M. Trojan, P. Luňáková: *Colour properties of Sn-Cr doped pigments prepared by different methods* **(poster)**. International Days of Materials Science 2014 - ReAdMat, Pardubice, Czech Republic, 2014, p. 62.

J. Trojan, L. Karolová, J. Luxová, M. Trojan, P. Luňáková: *Vliv způsobu přípravy na pigmentově aplikační vlastnosti Sn-Cr pigmentů* **(poster)**. 16. Konference o speciálních anorganických pigmentech a práškových materiálech, Pardubice, Czech Republic, 2014, p. 102-106.

J. Trojan, L. Karolová, J. Luxová, M. Trojan: *Synthesis of Sn-Cr pigments doped by praseodymium and their pigmentary properties* **(lecture)**. 4th Electronic International Interdisciplinary Conference 2015, Žilina, Slovak Republic, 2015, p. 179-182.

J. Trojan, L. Karolová, J. Luxová, M. Trojan: *Syntéza a studium fialových kasiteritových pigmentů dopovaných příměsemi* **(poster)**. 17. Konference o speciálních anorganických pigmentech a práškových materiálech, Pardubice, Czech Republic, 2015, p. 122-125.