Synthesis of SnO₂/Cr pigments doped by praseodymium prepared by different methods and their pigmentary properties

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Abstract

The violet SnO_2/Cr pigments in which a part of tin ions was substituted by praseodymium ions were examined. 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. Pigments were characterised in terms of colour, they were also studied with respect to their phase composition as well as the particles size distribution. X-ray analysis confirmed that the synthesis temperature 1350 °C is sufficient to get mono-phase compounds in case of all ways of preparation. Mechanoactivation and two-step process can be suggested as the preferable method for acquirement of pigments with the most interesting colour.

1.   Introduction

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 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]. Nanocomposites derived from the mixture of SnO_2/Cr_2O_3 (in molar ratio 1:2) have been recently studied above all for their photocatalytic abilities [4]. 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 [5-7].

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, 8]. 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) [9], the chromophore ions can be comparatively easily implemented into crystal lattice of SnO_2 [10]. In this case the chromium ions are the matching admixture. With regard to high shortage of violet ceramic pigments on the market these pigments represent one of a few possible alternatives to ecologically unacceptable cadmium pigments [11]. 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 [12, 13]. 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 [14, 15].

Theory of colour properties of $Sn_{1-x}Cr_xO_2$ pigments originally came out from ideas of colloid Cr_2O_3 oxide deposited on the surface of SnO_2 grains [16]. Regardless of the degree of dispersity, chromium (III) oxide disposes of green colouration. According to Tumanov from pink up to violet colour should occur only in case of partial introduction of Cr (III) ions into interstitial positions of SnO_2 lattice [17]. Later a presumption was adopted according to which Cr (III) ions substitute Sn (IV) ions in cassiterite lattice to form a solid solution [8, 10]. Oxygen vacancies provide charge compensation [18]. However an opinion has been prevailing recently 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 [19, 20].

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) [9], this element was chosen with respect to the fact, that ions of Pr (IV) can be easily dispersed atomically in the crystals [21]. 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} ($4PrO_2·Pr_2O_3$). In the temperature range from 250 to 400 °C, mixed oxide is reduced to Pr_2O_3 [22]. From the previous thermoanalytical studies it was stated that process of reduction is represented by endothermal effect on the DTA curve. Oxidation of

trivalent praseodymium ions to tetravalent ions proceeds at an exothermal process at temperatures of around 1300 °C [23].

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. With the aim to achieve a one-phase compound, the composition of $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ was selected for the purpose of the work.

2. Experimental

2.1. *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, Cincinnati, USA), Cr_2O_3 (99.8% purity, Lachema, a.s. Brno, Czech Republic), Pr_6O_{11} (99.5% purity, Indian Rare Earths, Ltd. Mumbai, 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 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 Idar-Oberstein, 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. 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, Geel, Belgium) and urea (99.5% purity, PLIVA – Lachema a.s. Brno, 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, Cincinnati, USA), $Cr_2(SO_4)_3·6H_2O$ (99% purity, Lachema, a.s. Brno, Czech Republic), Na_2CO_3 (99% purity Lachema, a.s. Brno, Czech Republic) needed for the

neutralization of sulphate, eventually Pr_6O_{11} (99.5% purity, Indian Rare Earths, Ltd. Mumbai, India). The second step represents a classical calcination in an electric resistance furnace with a rate of temperature increase of 10 °C/min 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. Opava, Czech Republic) in mass tone and into medium-temperature ceramic glaze G07091 (Glazura, s.r.o. Roudnice nad Labem, 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 (size 7 x 8.5 cm). 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 5 wt% of a pigment sample and 95 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.

2.2. *Characterization of samples*

The phase composition of the synthesized pigments was determined by using Diffractometer D8 Advance (Bruker AXS, Ltd. Coventry, UK) equipped with a vertical θ-θ goniometer (radius 217.5 mm). X-ray tube with Cu anode (U = 40 kV, I = 30 mA), secondary graphite monochromator, scintillation NaI(Tl) counter, and X-ray of copper were used. Wavelength of the applied X-ray is $K\alpha1 = 0.15418$ nm for angle $2\theta < 35°$ and $K\alpha2 = 0.15405$ nm for angle $2\theta > 35°$. Measuring range of 2θ is from 10 to 80° with a step 0.02° and step time 3 s at 25 °C.

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. Reston, 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. 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 Eqs. (1) and (2) [24].

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

$$H° = \text{arctg } b*/a* \qquad (2)$$

The distribution of particle sizes of the synthesized pigments was measured by using apparatus Mastersizer 2000/MU (Malvern Instruments, Ltd. Worcestershire, UK). This device provides volumetric distribution and uses the laser diffraction on particles dispersed in a liquid medium. The measured signal is assessed by means of Mie scattering theory and Fraunhofer diffraction. The particle size distribution was analysed by two lasers - red light (He-Ne laser with wavelength 633 nm) and blue light (laser diode with wavelength 466 nm). The blue light was used for wide-angle forward and back scattering in combination with the red light for forward, side and back scattering. For the measurement pigments were dispersed in a solution with $Na_4P_2O_7$ (c = 0.15 g/L) by using an ultrasonic bath for 2 min. The signal was evaluated on the basis of Fraunhofer diffraction. The measurement is performed in three steps, results are automatically calculated as average and presented as d_{10}, d_{50}, d_{90} values. Prior to measurement, the samples were gently ground in agate mortar.

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, Inc. Peabody, USA) with an accelerating voltage of the primary electron beam 5 kV was used.

A heating microscope with automatic image analysis EM201-12 (Hesse-Instruments, Osterode am Harz, Germany) was used for study of the thermal stability of tested samples. This instrument enables to monitor the thermal stability of powdered materials maximally until 1600 °C into the furnace, with the guarantee of 100 °C delay on the sample, i.e. maximum 1500 °C on the sample and so to determine the characteristic temperatures. The equipment has been calibrated using Sn, In, Al, Zn and standard measurement uncertainty typically is ≤ 5 °C. For measurement of heat treatment samples, tablets in shape of cylinders a diameter of 3 mm and height of 6 mm were prepared. The conditions of this study were as follows: the temperature rate 20 °C/min until the temperature of 1000 °C and 10

°C/min up to the end temperature; end temperature – 1600 °C into the furnace, i.e. 1500 °C on the sample.

3.   Results and discussions

3.1.   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 $Sn_{0.995}Cr_{0.005}O_2$ (S1) and $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ (S2) 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. 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. 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).

Table 1 The effect of calcination temperature and way of preparation on colour properties of the pigments $Sn_{0.995}Cr_{0.005}O_2$ (S1) and $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ (S2) applied into organic matrix in mass tone

Method of preparation	T/°C	Sample name	L*	a*	b*	C	H°
CM	1350	S1	55.25	20.26	-15.74	25.66	322.16
		S2	51.01	21.52	-17.46	27.71	320.95
	1400	S1	52.41	20.86	-16.88	26.83	321.02
		S2	48.77	23.70	-18.93	30.33	321.38
	1450	S1	47.28	21.67	-18.10	28.23	320.13
		S2	45.80	23.99	-19.39	30.85	321.05
	1500	S1	41.63	22.65	-19.69	30.01	319.00
		S2	44.51	25.38	-20.81	32.82	320.65
MA	1350	S1	60.67	20.16	-15.97	25.72	321.62
		S2	56.73	21.64	-17.80	28.02	320.56
	1400	S1	57.94	21.21	-16.72	27.01	321.75
		S2	53.45	24.12	-19.05	30.74	321.70
	1450	S1	55.52	22.36	-18.97	29.32	319.69
		S2	51.18	24.53	-20.69	32.09	319.85
	1500	S1	49.74	24.82	-20.99	32.51	319.78
		S2	47.84	26.19	-22.85	34.76	318.90
MDR	1350	S1	52.04	20.95	-17.95	27.59	319.41
		S2	50.20	21.48	-18.25	28.19	319.65
	1400	S1	51.27	22.16	-18.35	28.77	320.37
		S2	47.21	23.08	-19.35	30.12	320.02
	1450	S1	49.95	22.54	-18.84	29.38	320.11
		S2	44.58	24.07	-20.01	31.30	320.26
	1500	S1	41.56	23.35	-20.32	30.95	318.97
		S2	40.68	25.25	-21.04	32.87	320.20

Table 2 The effect of calcination temperature and way of preparation on colour properties of the pigments $Sn_{0.995}Cr_{0.005}O_2$ (S1) and $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ (S2) applied into ceramic glaze

Method of preparation	T/°C	Sample name	L*	a*	b*	C	H°
CM	1350	S1	58.54	16.26	-7.75	18.01	334.52
		S2	53.56	18.35	-8.21	20.10	335.90
	1400	S1	56.24	18.15	-9.23	20.36	333.04
		S2	51.28	19.38	-9.97	21.79	332.78
	1450	S1	51.95	19.36	-9.68	21.65	333.43
		S2	49.47	20.24	-10.45	22.78	332.69
	1500	S1	50.17	19.66	-10.42	22.25	332.08
		S2	47.55	20.13	-11.54	23.20	330.18
MA	1350	S1	64.74	16.66	-7.87	18.34	334.71
		S2	60.24	18.75	-8.23	20.48	336.30
	1400	S1	61.31	18.57	-9.33	20.78	333.32
		S2	57.19	19.77	-9.98	22.15	333.22
	1450	S1	57.65	19.76	-9.80	22.06	333.62
		S2	53.20	20.75	-10.54	23.27	333.07
	1500	S1	54.16	20.16	-9.96	22.49	333.71
		S2	50.47	21.07	-11.30	23.91	331.80
MDR	1350	S1	56.47	16.48	-7.90	18.28	334.39
		S2	52.87	18.24	-8.42	20.09	335.22
	1400	S1	53.69	18.36	-9.52	20.68	332.59
		S2	50.45	19.66	-10.23	22.16	332.51
	1450	S1	49.32	19.21	-10.09	21.70	332.29
		S2	47.61	20.31	-10.89	23.05	331.80
	1500	S1	46.71	19.91	-10.62	22.57	331.92
		S2	46.29	20.38	-11.87	23.58	329.78

3.2. 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 0.01 – 15 μm. This fact originates from literature data [25]. 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. 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, the mean values of the pigment particles, which were prepared 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 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
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
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

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
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
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

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. 1a, 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. debond by ultrasonics. 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.
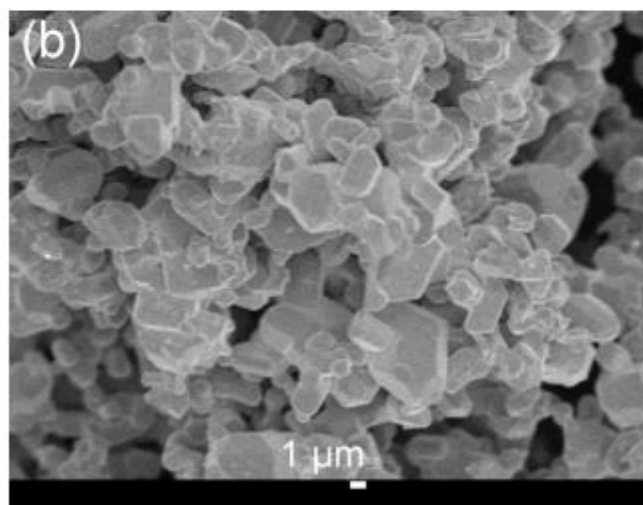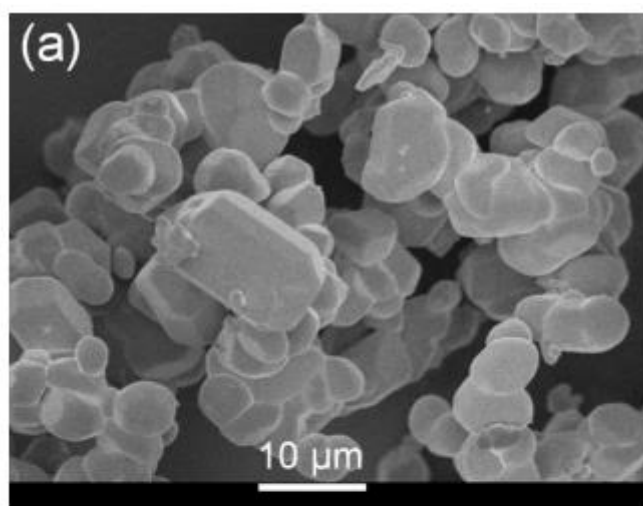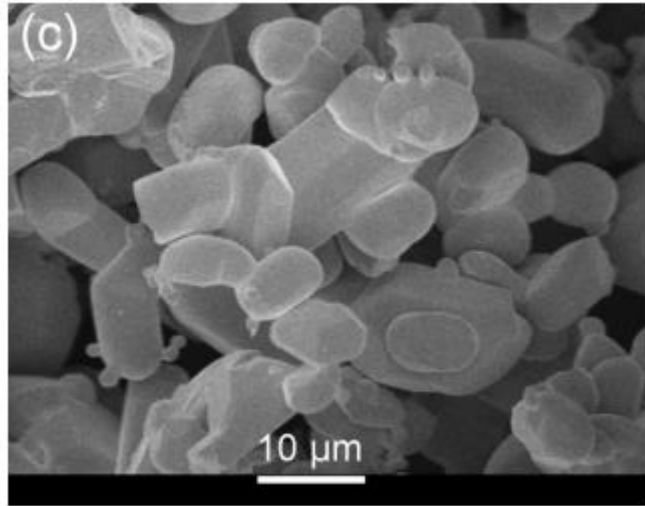
Fig. 1 SEM images of the $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ samples prepared by different methods: (a) CM, (b) MA and (c) MDR, acquired upon calcination at 1500 °C

3.3. *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) [9]. This fact indicates that solid solutions with cassiterite structure are formed [15].

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. 2 shows that even at the lowest synthesis temperature 1350 °C all the initial reagents were completely reacted in case of all preparation methods. 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.
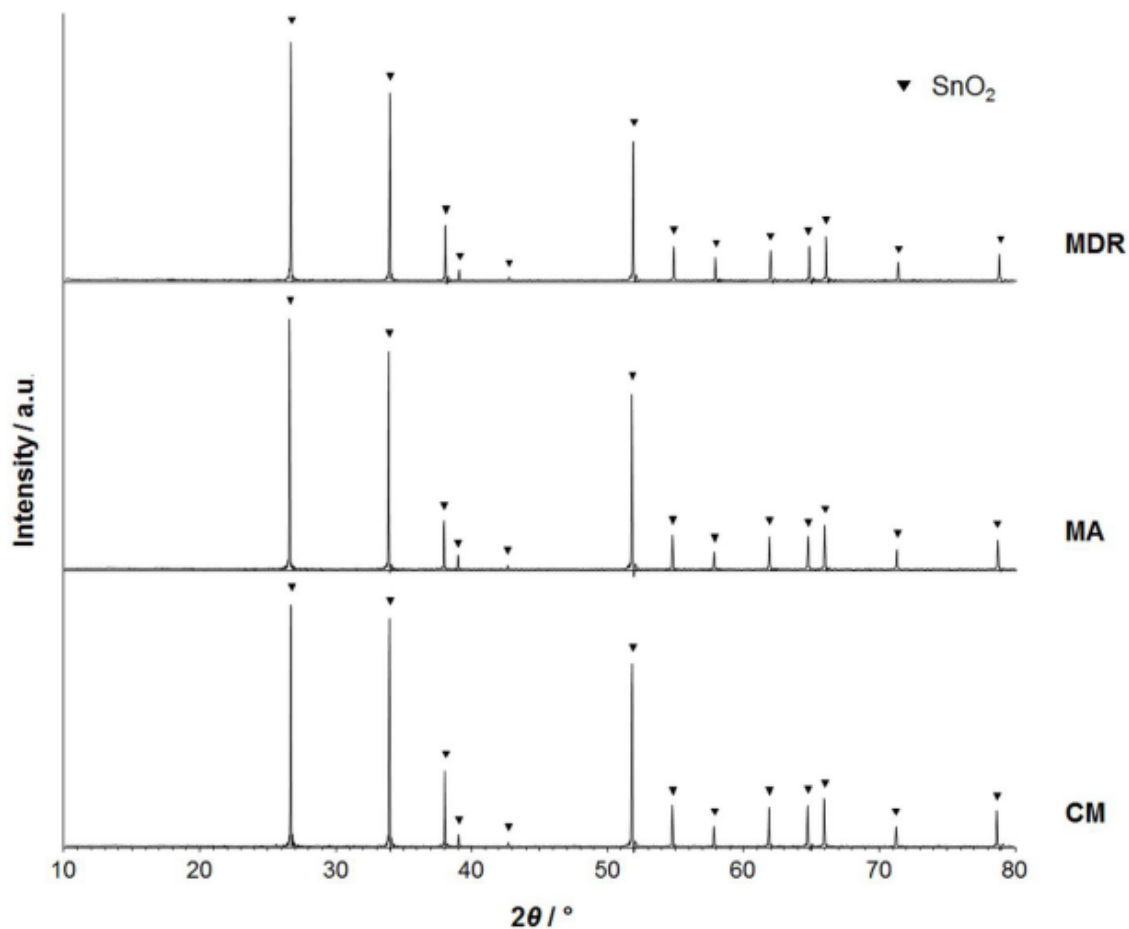
Fig. 2 X-ray diffraction patterns of samples $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ prepared by different ways, obtained upon calcination at the lowest temperature of 1350 °C

The 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 $Sn_{1-2x}Cr_xP_xO_2$. 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/nm³
			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/nm³
			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.

3.4. Thermal stability

Calcinated powder materials $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ were examined by using a heating microscope on the subject of their thermal stability in a temperature range of 20 – 1500 °C and the main aim was to compare all three methods. Obtained results are presented at Fig. 3. The curves represent the change of the sample area depending on the temperature. Accordingly, when sintering of the sample starts, a decrease of the sample area should appear. From thermal stability point of view the samples give very good results. There are no significant changes in area samples in the whole temperature range (there is a change in samples area maximally 1.8 % for MDR and 1.5 % for CCM, resp. 2.6 % for MA up to end temperature of 1500 °C). Images of samples captured at the beginning of the analysis and at the end are shown in Fig. 4. In mentioned temperature range in none of the samples was observed onset of the sintering and this piece of knowledge is very favourable.
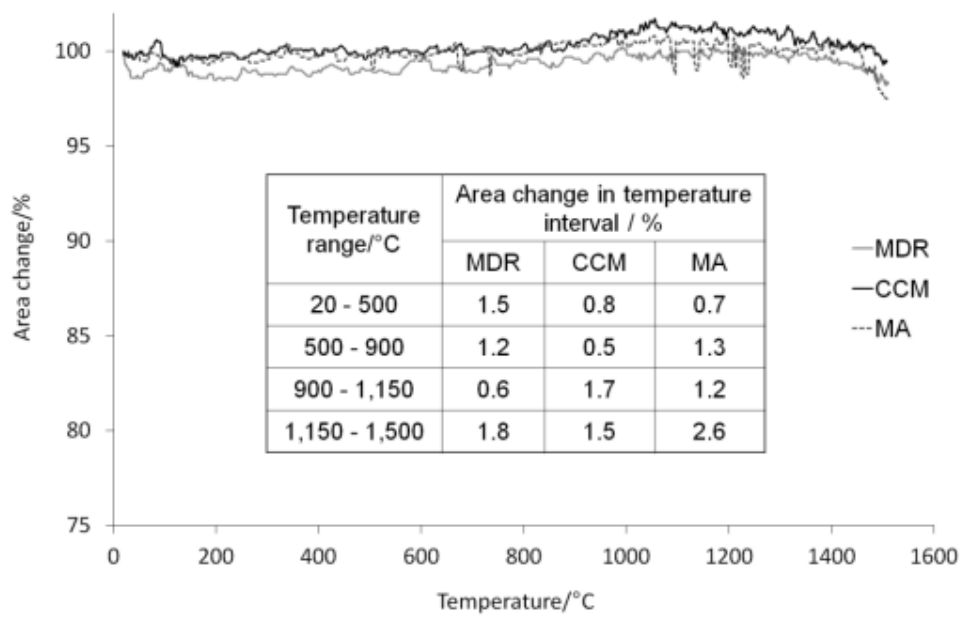
Temperature range/°C	Area change in temperature interval / %		
	MDR	CCM	MA
20 - 500	1.5	0.8	0.7
500 - 900	1.2	0.5	1.3
900 - 1,150	0.6	1.7	1.2
1,150 - 1,500	1.8	1.5	2.6

Fig. 3 Heating microscopy results of the $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ samples prepared by different methods representing the change of samples area with a temperature increase

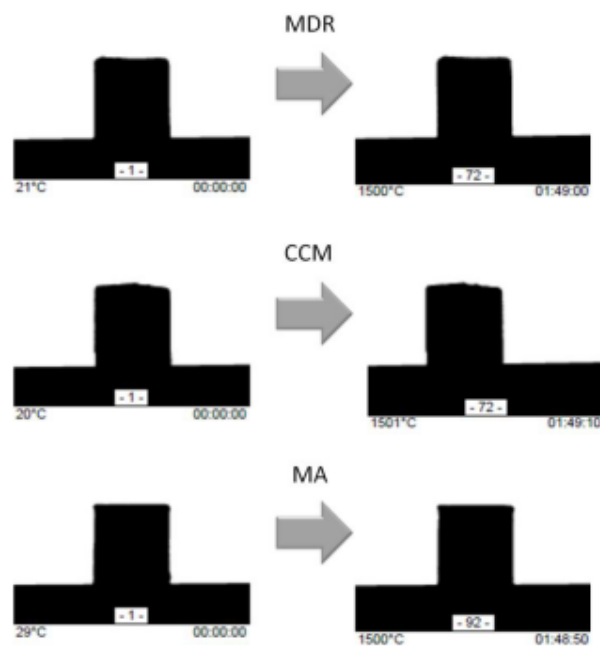Fig. 4 Pictures of the $Sn_{0.99}Cr_{0.005}Pr_{0.005}O_2$ samples prepared by different ways pressed into tablets at the start and at the end of the analysis (20 – 1500 °C

4.   Conclusion

The main aim of the present 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 values of C as a parameter characterizing 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.

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