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The effect of transition metals and rare-earth metals admixtures on the pigmentary properties of the cassiterite pigments

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This paper deals with the possibility to synthesise the SnO_2/Cr cassiterite violet pigments in which a part of stannic ions has been substituted by the transition-metal or rare-earth metal ions, respectively. Pigments with a general formula of $Sn_{0.99}Cr_{0.005}M_{0.005}O_2$ or $Sn_{0.99}Cr_{0.005}Ln_{0.005}O_2$ (where M = Ti, Zr and Ln = Tb, Ce) have been prepared by the solid state reactions at high calcination temperatures; namely, in a range from 1350 to 1500 °C. The aim was to develop the conditions for such a synthesis of this type of pigments and to determine the effect of admixed species on the colour properties of these compounds. Synthesised pigments were characterised in terms of colour properties after their application into ceramic glaze and organic binder. The compounds of interest have also been studied with respect to their phase composition, as well as the particle size distribution, finding that they may represent a potential extension of the range of violet shades applicable in practice; especially, when speaking about their use in ceramic industry.

Keywords: Cassiterite; Violet ceramic pigments; Solid state reaction; Colour

Introduction

Ceramic pigments belong to the group of special inorganic pigments. They are powdered crystalline materials with a high thermal and chemical resistance and, thus, exposable to a high temperature and the aggressive effect of molten glaze.

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These compounds have to be colour stable during the glazing process and they have to resist to furnace atmosphere. The base of ceramic pigments constitutes the hosting lattice derived from natural minerals [1]. Stannic pigments with structure of cassiterite mineral (SnO_2) rank among the most important inorganic pigments based on tin compounds. According to the CPMA classification [2], they belong — together with rutile pigments — to the eleventh group being based on tin dioxide crystallizing in the tetragonal structure and forming bipyramidal crystals which play a dominant role in the final compound [3].

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 the cassiterite mineral in which a suitable colourific admixture (chromophore) is doped [2,4]. By partial substitution of Sn(IV) ions for ions of suitable chromophores, a colour change in an originally colourless system can be achieved. In this case, the chromium ions are the matching admixture. With regard to a high shortage of violet ceramic pigments on the market, these pigments represent one of the few possible alternatives to ecologically unacceptable cadmium pigments [5]. The content of chromium in the compound affects the final colouration of the pigment, which can gain various colour shades – from light pink to deep violet [6,7]. According to the latest studies, the three types of chromium species exist in the Cr-doped cassiterite. The first of them consists of the Cr(III) oxide clusters, the next one of a small amount of the CrO_2 nanoparticles. The violet colour of the pigment is caused by the Cr(IV) atoms which substitute Sn(IV) species when being dissolved in the cassiterite lattice, thus forming a solid solution [8].

In previous studies, the positive effect of some rare-earth metals admixtures on the colour properties of these types of pigments has been already demonstrated [9]. The aim of the research presented herein was to investigate the effect of the transition metals (Ti, Zr) and lanthanides (Tb, Ce) as doping agents and the effect of the calcination temperature on the resultant colour properties of SnO_2/Cr pigments. The main emphasis was laid on the change of colour properties of these pigments in terms of their violet colour intensification allowing us to attain deeper and darker shades in the final pigment colouration; especially, when applied into ceramic glaze.

Materials and methods

Synthesis of cassiterite pigments

Both pigments $Sn_{0.99}Cr_{0.005}M_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Ln_{0.005}O_2$ (where M = Ti, Zr and Ln = Tb, Ce) were synthesised by classical ceramic route; i.e., via the solid state reaction method requiring the starting raw materials as homogenised powder oxides: SnO_2 (99% purity, Shepherd Color Company, Cincinnati, USA), Cr_2O_3

(99.8% purity, Lachema Brno, Czech Republic), TiO_2 AV-01 (>99% purity, Precheza Přerov, Czech Republic), ZrO_2 (>99% purity, Honeywell, Germany), Tb_4O_7 (99.9% purity), and CeO_2 (99.5% purity) both obtained from Indian Rare Earths, India. The reagents were weighed in suitable molar proportions and subsequently ground manually in a porcelain mortar to get a homogeneous reaction mixture. The corresponding mixtures were calcinated in corundum crucibles in electric resistance furnace with the heating rate of 10 °C min^{-1} at temperatures 1350, 1400, 1450 and 1500 °C and for firing time of 3 hrs. Samples of the synthesised pigments were assessed with respect to their colour properties, particle size distribution, and the structure analysed by X-ray diffraction.

Characterization of samples

All the synthesised pigments were applied into the organic matrix (dispersive acrylic paint Parketol Balakom Opava; Czech Republic) in mass tone and into medium-temperature ceramic glaze G07091 (Glazura 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 homogenised. Using a pestle and mortar, this system was converted into a dense "flowing" paste. Coloured coating films were prepared by deposition of the paste on the white non-absorbing glossy paper (size 7 × 8.5 cm). The coating layer of film was formed by dragging the Bird film applicator with typical thickness of the wet film of 100 μm. The coating films prepared by this procedure were kept to dry spontaneously in the open air for 1–2 hrs being then ready for an evaluation of colour properties of the pigments applied into organic matrix in mass tone. In case of applications into ceramic glazes, aqueous suspensions containing 10 wt. % of a pigment sample and 90 wt. % of the transparent ceramic glaze were prepared by manual grinding. This suspension was applied onto unglazed ceramic body by using a brush and, after a spontaneous drying in the open air, glazed at 1000 °C for 15 min. The colour properties of all the final applications were objectively evaluated via their colour change by measuring spectral reflectance in the visible region of light (400–700 nm) with the aid of a spectrophotometer (model "ColorQuest XE"; HunterLab, Reston, USA). This device can be operated with a wavelength interval of 10 nm and is equipped with a xenon lamp. Standard illuminant "D 65" was used as internationally recommended white daylight, measurement conditions being as follows: 10°supplementary standard observer and the measuring geometry of *d*/8°.

CIE $L^*a^*b^*$ colour system (1976) was used for description of colour properties, where the value L^* represents the lightness or darkness of the colour as related to the natural grey scale. The system can be described by numbers, where "0" represents black and "100" 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. Again, the values range from 0 (grey) to 100 (pure colour), showing the degree of difference between a colour and grey. The colour hue (otherwise a.k.a. shade) of pigments is also possible to express as a hue angle $H°$. It 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), and $H° = 285–350°$ (for violet). Chroma C and hue angle $H°$ of the samples analysed were calculated according to the Eq. (1) and (2).

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

$$H° = \text{arctg}\frac{b^*}{a^*} \tag{2}$$

The total colour difference ΔE^*_{CIE} in the CIE $L^*a^*b^*$ diagram, indicating the degree of colour difference between the two samples is defined by the following Eq. (3),

$$\Delta E^*_{\text{CIE}} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{3}$$

$0 \le \Delta E^*_{\text{CIE}} \le 0.5$	imperceptible colour difference
$0.5 \le \Delta E^*_{\text{CIE}} \le 1.5$	hardly perceptible colour difference
$1.5 \le \Delta E^*_{\text{CIE}} \le 3$	perceptible colour difference
$\Delta E^*_{\text{CIE}} > 3$	large colour difference

where ΔL^*, Δa^*, Δb^* are differences in L^*, a^* and b^* values between colour sample and colour of standard [10].

The distribution of particle sizes of the synthesised pigments was measured by using Mastersizer apparatus (model "2000/MU"; Malvern Instruments, Worcestershire, UK). This device provides volumetric distribution and uses the laser diffraction on particles dispersed in a liquid medium. The measured signal is then assessed by means of Mie scattering theory and Fraunhofer diffraction [11]. The particle size distribution was analysed by two lasers: (i) red light (He-Ne laser with wavelength 633 nm) and (ii) blue light (laser diode with wavelength 466 nm); the latter being used for wide-angle forward and back scattering in combination with the red light for forward, side and back scattering. Prior to measurement, the samples were gently ground in an agate mortar and subsequently dispersed in a solution with $Na_4P_2O_7$ (c = 0.15 g L^{-1}) by using an ultrasonic bath for 2 min. The signal was evaluated on the basis of Fraunhofer diffraction. The proper measurement was performed in three steps; the results being automatically calculated as the average and presented as d_{10}, d_{50}, d_{90} values.

The phase composition of the synthesised pigments was determined by using a diffractometer (model "D8 Advance"; Bruker AXS, Coventry, UK) equipped with a vertical θ–θ goniometer (radius 217.5 mm). Other accessories were: X-ray tube with Cu anode (U = 40 kV, I = 30 mA), secondary graphite monochromator, scintillation NaI(Tl) counter, and X-ray of copper. Wavelength of the X-ray applied is $K_{\alpha 1}$ = 0.15418 nm for angle $2\theta < 35°$ and $K_{\alpha 2}$ = 0.15405 nm for $2\theta > 35°$. The measuring range of 2θ was from 10 to 80° with a step 0.02° and step time 3 s at 25 °C.

Results and discussion

Colour characteristics

At first, the pure $Sn_{0.995}Cr_{0.005}O_2$ was prepared and used as a standard. Samples were heated in the temperature range of 1350–1500 °C (step 50 °C) and applied into the organic matrix and ceramic glaze. The results obtained have shown that the colour coordinates are changing in the dependence of the pigment composition and the calcination temperature.

In the case of both $Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$ pigments treated in this way (see Tab. 1 and Tab. 2, respectively), the rising calcination temperature caused a decrease of value L^* (lightness) and samples seemed darker. Furthermore, it is evident that the intensities of colour tones $+a^*$, $-b^*$ and value of C (chroma) have subsequently increased with the ascending temperature of calcination.

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

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	55.25	20.26	–15.74	25.66	322.16	2.15
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	53.20	19.60	–15.67	25.09	321.36	
1400	$Sn_{0.995}Cr_{0.005}O_2$	52.41	20.86	–16.88	26.83	321.02	2.04
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	50.42	21.28	–17.00	27.24	321.38	
1450	$Sn_{0.995}Cr_{0.005}O_2$	47.28	21.67	–18.10	28.23	320.13	0.89
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	48.09	21.81	–18.43	28.55	319.80	
1500	$Sn_{0.995}Cr_{0.005}O_2$	41.63	22.65	–19.69	30.01	319.00	3.08
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	44.70	22.70	–19.91	30.19	318.75	

Table 2 *The effect of calcination temperature on the colour properties of pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$ applied into the organic matrix in mass tone*

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	55.25	20.26	–15.74	25.66	322.16	0.87
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	54.38	20.18	–15.71	25.57	322.10	
1400	$Sn_{0.995}Cr_{0.005}O_2$	52.41	20.86	–16.88	26.83	321.02	2.62
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	50.01	21.73	–16.30	27.16	323.13	
1450	$Sn_{0.995}Cr_{0.005}O_2$	47.28	21.67	–18.10	28.23	320.13	1.17
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	47.44	22.80	–17.86	28.96	321.93	
1500	$Sn_{0.995}Cr_{0.005}O_2$	41.63	22.65	–19.69	30.01	319.00	2.11
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	43.12	23.62	–18.55	30.03	321.86	

The highest value C (30.19 or 30.03, respectively) was observed at temperature of 1500 °C, which means, that this pigment has provided the purest colour. The comparison of synthesised pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$ in terms of the colour properties acquired has shown that pigments with titanium atoms provide darker shades up to the temperature of 1400 °C. At higher temperatures (1450 and 1500 °C, respectively), the increase of pigments lightness was observed in comparison with that of the standard pigments. Also, in most cases, pigments doped by titanium provide slight increase in the chroma C. The comparison of the standard pigments with $Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$ has led to a similar situation, when darker pigments were obtained only at the lower temperatures of synthesis (1350 °C and 1400 °C). These pigments are typically characterised by slightly higher C values. In the case of pigments applied into the ceramic glaze, clearer shades according to the higher values of C were mostly achieved (see Tab. 3 and Tab. 4).

Table 3 *The effect of calcination temperature on the colour properties of pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$ applied into the ceramic glaze*

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	58.54	16.26	–7.75	18.01	334.52	2.83
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	60.94	17.64	–7.16	19.04	337.91	
1400	$Sn_{0.995}Cr_{0.005}O_2$	56.24	18.15	–9.23	20.36	333.04	1.71
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	57.62	18.62	–8.34	20.40	335.87	
1450	$Sn_{0.995}Cr_{0.005}O_2$	51.95	19.36	–9.68	21.65	333.43	2.88
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	54.77	19.49	–9.12	21.52	334.92	
1500	$Sn_{0.995}Cr_{0.005}O_2$	50.17	19.66	–10.42	22.25	332.08	2.71
	$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	52.69	20.28	–9.64	22.45	334.58	

Table 4 *The effect of calcination temperature on the colour properties of pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$ applied into the ceramic glaze*

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	58.54	16.26	–7.75	18.01	334.52	2.82
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	59.67	18.41	–6.31	19.46	341.08	
1400	$Sn_{0.995}Cr_{0.005}O_2$	56.24	18.15	–9.23	20.36	333.04	1.74
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	56.52	19.34	–7.99	20.93	337.55	
1450	$Sn_{0.995}Cr_{0.005}O_2$	51.95	19.36	–9.68	21.65	333.43	2.26
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	53.81	20.06	–8.61	21.83	336.77	
1500	$Sn_{0.995}Cr_{0.005}O_2$	50.17	19.66	–10.42	22.25	332.08	2.43
	$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	51.88	20.27	–8.80	22.10	336.53	

In comparison with the standard pigments, the higher colour purities are principally due to the increase of red tone (+a^*). On the other hand, the blue tone (–b^*) is decreasing in most cases. As seen in Table 4, the increase of red tone and decrease of blue tone intensity is more pronounced for pigments with zirconium. Therefore, the final colouration of these pigments applied into ceramic glaze is turned closer to the red-violet hues, which can be also confirmed from the higher values of $H°$. Generally speaking, the doping with Ti and Zr does not have a significant effect on colour properties with respect to C values. The occurence of lighter shades — especially, in ceramic glazes — seems to be a large deficiency of these admixtures. The assessment of $Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$ pigments in terms of their colour properties results in more significant colour changes. The values of ΔE^*_{CIE} characterise more pronounced colour differences between the synthesised pigments and standard pigments that are most noticeable at lower temperatures of synthesis (1350 °C and 1400 °C).

By considering the applications of pigments into organic matrix, both lanthanides admixtures lead to quite distinctly darker hues compared to $Sn_{0.995}Cr_{0.005}O_2$ pigments at all calcination temperatures (see Tab. 5 and Tab. 6). Regarding the C values as a parameter of the colour purity, significantly better results were obtained almost in all the cases. By using Tb admixture, the purest shades were reached at 1500 °C (31.42), in the case of Ce at 1400 °C (32.23). From a point of view of the pigments darkness, the best reaction conditions seem to be at the highest temperature of synthesis. Higher values of C are mostly caused due to a more pronounced contribution of the red tone meaning a shift in the $H°$ value towards red shades.

With respect to ceramic glazes, $Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$ pigments do not show such good results in this application (see Tab. 7). In terms of the pigment darkness, the positive effect of Tb atoms occurs only at the first two calcination temperatures.

Table 5 *The effect of calcination temperature on the colour properties of pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$ applied into the organic matrix in mass tone*

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	55.25	20.26	–15.74	25.66	322.16	7.05
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	48.21	19.93	–15.86	25.47	321.49	
1400	$Sn_{0.995}Cr_{0.005}O_2$	52.41	20.86	–16.88	26.83	321.02	3.04
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	49.39	21.20	–16.76	27.02	321.67	
1450	$Sn_{0.995}Cr_{0.005}O_2$	47.28	21.67	–18.10	28.23	320.13	4.24
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	43.66	23.86	–18.40	30.13	322.36	
1500	$Sn_{0.995}Cr_{0.005}O_2$	41.63	22.65	–19.69	30.01	319.00	2.20
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	40.56	24.57	–19.58	31.42	321.45	

Table 6 *The effect of calcination temperature on the colour properties of pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$ applied into the organic matrix in mass tone*

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	55.25	20.26	–15.74	25.66	322.16	7.22
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	48.37	21.31	–17.68	27.69	320.32	
1400	$Sn_{0.995}Cr_{0.005}O_2$	52.41	20.86	–16.88	26.83	321.02	8.07
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	46.42	25.08	–20.25	32.23	321.08	
1450	$Sn_{0.995}Cr_{0.005}O_2$	47.28	21.67	–18.10	28.23	320.13	5.43
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	42.32	23.66	–19.04	30.37	321.18	
1500	$Sn_{0.995}Cr_{0.005}O_2$	41.63	22.65	–19.69	30.01	319.00	4.04
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	38.01	23.93	–18.42	30.20	322.41	

In these cases, lower values of L^* were achieved compared to the standards. Slightly higher values of C caused mainly by the enhancing of red tone at the expense of the blue one, were determined at all the synthesis temperatures. According to the higher $H°$ values, colour of $Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$ pigments in ceramic glazes is turned to red shades, unlike the standard pigments, and this phenomenon is more pronounced at 1350 and 1400 °C.

The admixture of cerium ions has resulted in the best colour properties in the ceramic glaze of all dopants used. $Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$ pigments are characterised by a lower lightness at all temperatures of synthesis, as well as by gaining of higher colour purities according to higher values of C (see Tab. 8). Unlike all used admixtures, the loss of the blue tone was not observed. The most striking colour differences between the standards and pigment samples are obtained at the synthesis temperatures of 1350 and 1400 °C (ΔE^*_{CIE}). On the whole, the best colour properties were obtained with a pigment synthesised at 1500 °C – the darkest and the purest colour hue ($L^* = 49.81$, $C = 23.18$).

Table 7 *The effect of calcination temperature on the colour properties of pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$ applied into the ceramic glaze*

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	58.54	16.26	–7.75	18.01	334.52	2.59
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	57.76	17.89	–5.90	18.84	341.75	
1400	$Sn_{0.995}Cr_{0.005}O_2$	56.24	18.15	–9.23	20.36	333.04	2.23
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	54.56	19.12	–8.14	20.78	336.94	
1450	$Sn_{0.995}Cr_{0.005}O_2$	51.95	19.36	–9.68	21.65	333.43	1.15
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	52.52	20.36	–9.70	22.55	334.53	
1500	$Sn_{0.995}Cr_{0.005}O_2$	50.17	19.66	–10.42	22.25	332.08	0.86
	$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	50.37	20.46	–10.19	22.86	333.52	

Table 8 *The effect of calcination temperature on the colour properties of pigments $Sn_{0.995}Cr_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$ applied into the ceramic glaze*

T [°C]	Pigment	L^*	a^*	b^*	C	$H°$	ΔE^*_{CIE}
1350	$Sn_{0.995}Cr_{0.005}O_2$	58.54	16.26	–7.75	18.01	334.52	4.69
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	55.24	19.59	–7.92	21.13	337.99	
1400	$Sn_{0.995}Cr_{0.005}O_2$	56.24	18.15	–9.23	20.36	333.04	3.01
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	53.88	19.98	–9.61	22.17	334.31	
1450	$Sn_{0.995}Cr_{0.005}O_2$	51.95	19.36	–9.68	21.65	333.43	1.31
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	51.25	20.45	–9.84	22.69	334.30	
1500	$Sn_{0.995}Cr_{0.005}O_2$	50.17	19.66	–10.42	22.25	332.08	1.08
	$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	49.81	20.68	–10.48	23.18	333.13	

Particle size distribution

Composition of powdered materials and the temperature of calcination affect not only related colour properties, but also the particle size distribution. The particle size median of inorganic pigments must lie in the range of 0.1–15 μm. This fact originates from literature data [1]. In this work, the particle size distribution was analysed for unmilled samples that were ground manually in an agate mortar prior to each measurement. The most important value, characterising the particle size, is the value d_{50} (median). The results of the particle size distribution of powdered compounds are shown in Tab. 9. The respective data show that the growing synthesis temperature causes an increase of d_{50} values for all types of pigments. A comparison of standard pigments with Ti- and Zr-doped pigments leads to the following findings.

Pigments with both admixtures provide smaller particles with regard to d_{50} values, as well as particles with a narrower distribution. This can be caused by the fact that both admixtures pass through the changes in crystal modifications during calcination (in the case of TiO_2 this change is a modification of anatase into the rutile structure, in case of ZrO_2 a phase transformation of the monoclinic to tetragonal structure at 1175 °C), which may lead to some mineralization effects and a favourable influence on the pathway of the reaction [12,13]. The intervals of d_{50} values range of approx. 6–12 μm for Ti-doped samples, and 5–11 μm for Zr-doped samples, respectively.

The doping of $Sn_{0.995}Cr_{0.005}O_2$ compounds by the atoms of Tb and Ce cause the increase of d_{50} values, giving rise to a wider distribution of the particles. The values of d_{50} are in the range of approx. 8.5–16 μm for Tb-doped compounds and of approx. 7.5–15 μm for Ce-doped. The appropriate granulometric composition for application of pigments into the ceramic glaze is about 5–15 μm. In any case, the d_{50} value does not exceed significantly a limit of 15 μm and therefore these pigments are suitable for applications in ceramic glazes. For an eventual industrial use in painting coats, it would be necessary to treat the size mechanically up to the d_{50} value of about 2 μm.

Table 9 *The effect of calcination temperature and composition on the particle size distribution of synthesised powder compounds*

Pigment	T [°C]	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]
$Sn_{0.995}Cr_{0.005}O_2$	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
$Sn_{0.99}Cr_{0.005}Ti_{0.005}O_2$	1350	1.62	5.64	12.92
	1400	2.59	8.06	18.00
	1450	3.85	10.57	21.99
	1500	4.34	12.01	25.23
$Sn_{0.99}Cr_{0.005}Zr_{0.005}O_2$	1350	1.44	5.15	12.96
	1400	2.70	7.11	17.11
	1450	3.24	9.37	20.06
	1500	4.01	11.24	23.38
$Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$	1350	2.83	8.49	19.04
	1400	3.28	9.79	21.63
	1450	4.19	12.50	25.81
	1500	7.00	16.01	37.43
$Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$	1350	2.74	7.59	19.99
	1400	4.27	10.82	25.50
	1450	5.24	13.23	29.51
	1500	6.83	14.81	36.85

XRD analysis

The powdered materials were subjected to the study of their phase composition by means of X-ray diffraction analysis. The data obtained had shown that, for all the synthesised pigments, one phase composition with the only major crystalline phase corresponding to the tetragonal SnO_2 was formed at 1450 °C. The diagrams in Fig. 1 illustrates that, even at the lowest synthesis temperature, all the initial reagents were completely consumed in the respective reaction in the case of all the synthesised samples.

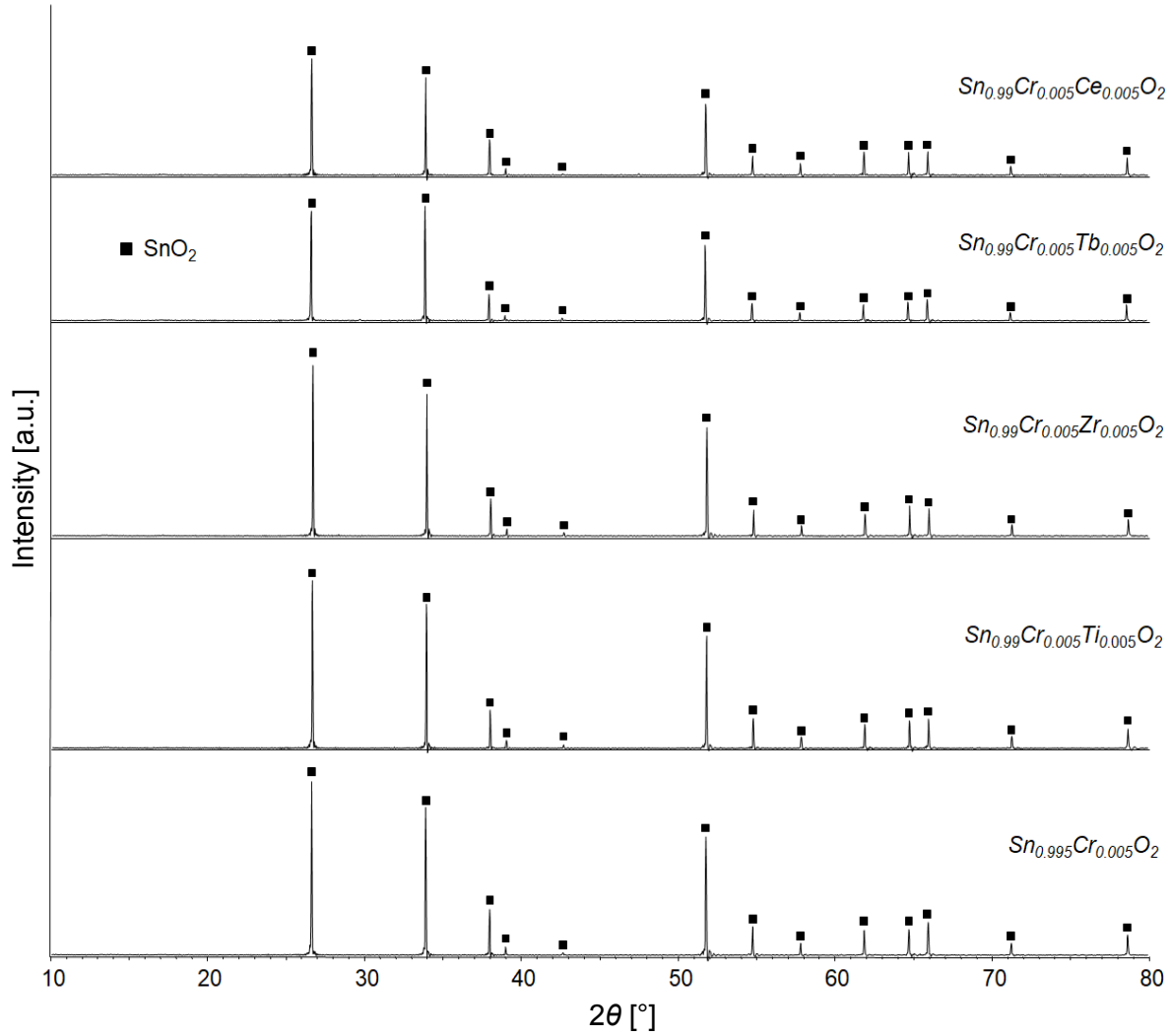

Fig. 1 *X-ray diffraction patterns of pigments synthesised at calcination temperature of 1350 °C*

At the highest synthesis temperature of 1500 °C (see Fig. 2), the secondary phase of the cubic $Tb_2Sn_2O_7$ in $Sn_{0.99}Cr_{0.005}Tb_{0.005}O_2$ pigment was also identified. The values of the lattice parameters for the prepared samples are summarised in

Tab. 10. As a result, the doping of SnO_2/Cr pigments by terbium and cerium atoms with larger ionic radii led to an expansion of the volume of the unit cell. Tb and Ce dopands substitute the stannic ions in their crystal lattice, when forming the substitution defects in the solid solution of $Sn_{1-2x}Cr_xTb_xO_2$ respectively $Sn_{1-2x}Cr_xCe_xO_2$.

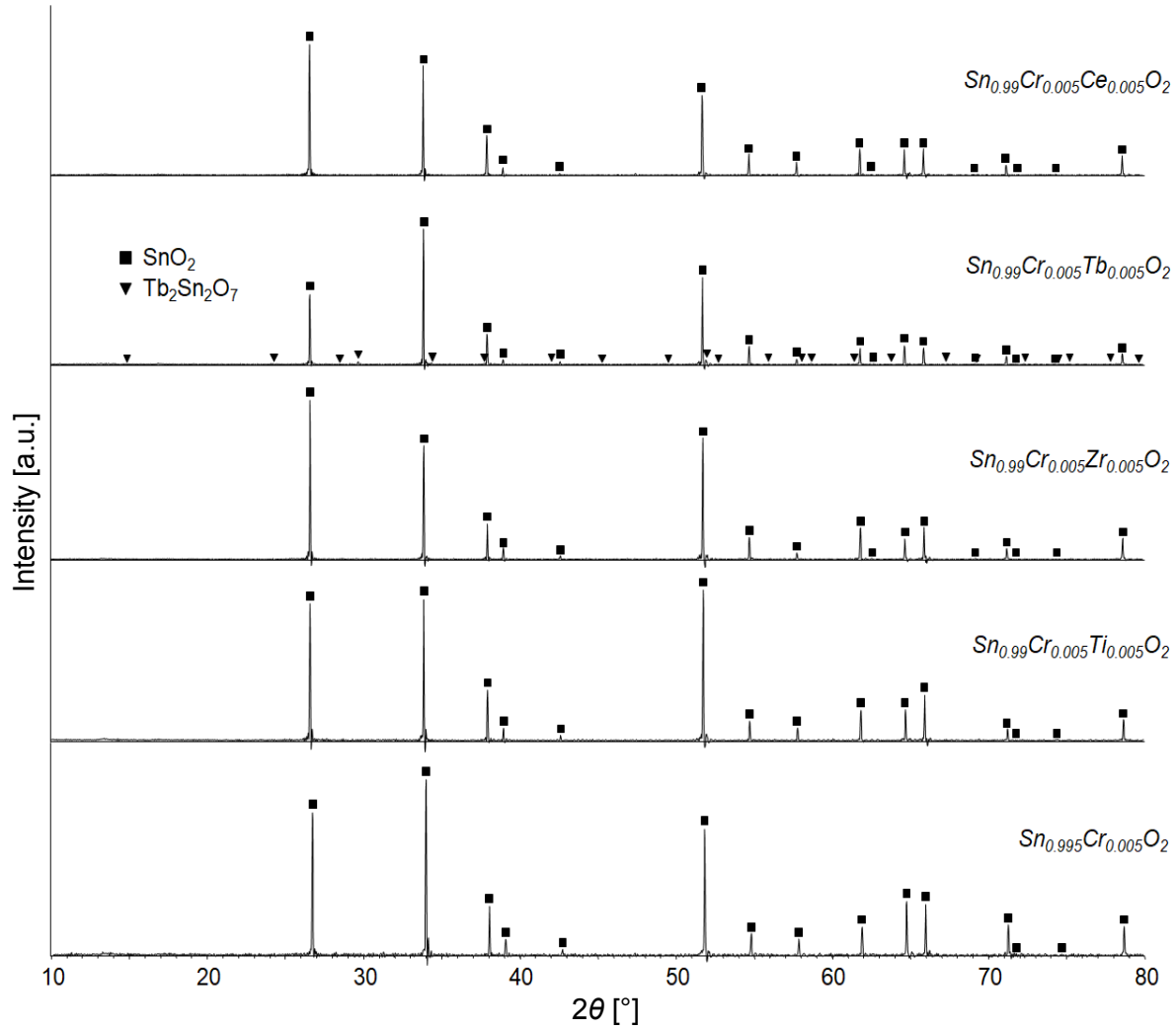

Fig. 2 *X-ray diffraction patterns of pigments synthesised at calcination temperature of 1500 °C*

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 corresponding Tb and Ce ions are characterised by larger ionic radii – Tb(IV) 0.076 nm; CN = 6, Ce(IV) 0.087 nm; CN = 6, whereas Sn(IV) occupies only 0.069 nm; with CN = 6 (see ref. [14]). On the other hand, the contraction of lattice constants using the admixtures of Ti and Zr has confirmed the embedding of these ions onto the SnO_2 hosting lattice.

It can be stated that the calcination at higher temperature has caused the increase of lattice parameters values, as well as the decrease of peaks intensity. This can be explained by the fact that the powdered material in the case of higher calcination temperatures consists of more coarse grains, which results in a certain loss of fine crystalline character.

Table 10 *Characterisation of the crystal structure of the prepared pigments*

Pigment	Detected phases	*T* [°C]	Lattice parameters			Volume of unit cell [nm^3]
			a	*b*	*c*	
Sn(Cr)O_2	SnO_2 – tetragonal	1350	0.473744	0.473744	0.318664	0.071519
		1500	0.473741	0.473741	0.318692	0.071524
Sn(Cr,Ti)O_2	SnO_2 – tetragonal	1350	0.473700	0.473700	0.318502	0.071469
		1500	0.473664	0.473664	0.318550	0.071469
Sn(Cr,Zr)O_2	SnO_2 – tetragonal	1350	0.473683	0.473683	0.318621	0.071491
		1500	0.473713	0.473713	0.318634	0.071503
Sn(Cr,Tb)O_2	SnO_2 – tetragonal	1350	0.473749	0.473749	0.318675	0.071523
		1500	0.473756	0.473756	0.318696	0.071530
	$Tb_2Sn_2O_7$ – cubic		1.041482	1.041482	1.041482	1.129680
Sn(Cr,Ce)O_2	SnO_2 – tetragonal	1350	0.473750	0.473750	0.318672	0.071522
		1500	0.473748	0.473748	0.318701	0.071528

Conclusions

The main aim of this research was to synthesise the SnO_2/Cr cassiterite violet pigments, in which a part of stannic ions was substituted by transition or rare-earth metals, respectively. The emphasis was laid on the change of SnO_2/Cr colour properties with respect to a colour enhancement enabling to attain deeper and darker shades in the final pigment colouration; primarily, when applied into the ceramic glaze. Pigments with the general formula $Sn_{0.99}Cr_{0.005}M_{0.005}O_2$ and $Sn_{0.99}Cr_{0.005}Ln_{0.005}O_2$ (where *M* = Ti, Zr and *Ln* = Tb, Ce) have been synthesised by classical ceramic method — i.e., via a solid-state reaction —, the calcination temperatures in the range of 1350–1500 °C were chosen.

The studies by X-ray diffraction showed that single-phased systems were prepared in the temperature range of 1350–1500 °C with the only exception being the pigment with the admixture of Tb prepared at the 1500 °C. The effect of the increasing synthesis temperature on the colour properties of pigments was positive. Thus, it can be concluded that higher synthesis temperature generally stimulates the formation of darker powders with higher values of chroma *C*. According to the highest values of *C* as a parameter characterising colour purity, the best pigment composition for both organic matrix and ceramic glaze applications appears to be $Sn_{0.99}Cr_{0.005}Ce_{0.005}O_2$.

The median of particle size d_{50} moved at pigments with Tb and Ce ions in the range of 8.5–16 μm and 7.5–15 μm, respectively, in dependence on the temperature of synthesis. When using transition elements admixtures, the corresponding values were 6–12 μm for Ti and 5–11 μm for Zr. Finally, the particle sizes of the synthesised pigments have been found convenient for potential industrial use in ceramic applications.

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