

Synthesis and colour properties of blue-violet cassiterite pigments doped by terbium ions

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Abstract

This research was focused on the preparation of mixed metal oxide pigments doped with terbium ions with the general formula of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$. These pigments were synthesised by solid state reactions at high calcination temperatures. The temperature range was chosen from 1350 to 1500 °C. The goal was to develop conditions for the synthesis of this type of pigments and to determine the influence of terbium ions on the colour properties of these compounds. All prepared pigments were applied into the organic matrix and into the ceramic glaze. Thermal behaviours of the reaction mixtures were investigated using differential thermal and thermogravimetric analysis. Synthesised $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments were compared with concurrently prepared pigment $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ depending on the calcination temperature with respect to the colour properties in CIE $L^*a^*b^*$ colour space, furthermore from the point of particle size distribution and phase composition. All compounds provided blue-violet hues that are stable in ceramic glazes.

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Keywords:

Solid state reaction, colour properties, thermal properties, cassiterite

Introduction

Ceramic pigments are inorganic chemical compounds, which provide colour and they are insoluble in a medium, with which they do not interact physically or chemically. They are characterised by high thermal and chemical stability. Structures of ceramic pigments contain chromophore ions, which impart colour to the originally colourless system [1]. All blue ceramic pigments known currently (except the vanadium-zirconium blue, CPMA 14-42-2) are based on doping of thermally stable crystal lattice by ions of cobalt [2–3]. The colour of cobalt pigments depends on their thermal stability, chemical reactivity towards the glaze components. For cobalt based pigments, Co (II) ions can be incorporated as colouring agents, where commonly they adopt a tetrahedral coordination, though octahedral coordination is also possible. In this regard, an evaluation from octahedral $[\text{Co}^{\text{II}}\text{O}_6]$ to the most stable tetrahedral $[\text{Co}^{\text{II}}\text{O}_4]$ coordination has been observed with an increase in the alkalinity and also with the increase in the calcination temperature of the material [4–5].

Cassiterite pigments are based on tin dioxide respectively they are mixed oxides, where tin dioxide is the main component. Tin dioxide (SnO_2) is an n-type semiconductor with tetragonal rutile structure that possesses superior properties, such as transparency, remarkable chemical and thermal stabilities [6]. It has been widely used as electrode materials, optoelectronic devices, gas sensors, catalysts and as colouring agents in the ceramic industry [7–11]. Cassiterite pigments contain crystal lattice of tin dioxide, which is suitable for doping by coloured admixtures (chromophores). By partial substitution of Sn (IV) ions (0.069 nm), the chromophore ions can be comparatively easily implemented into the crystal lattice of tin dioxide [12–14]. The advantage of cassiterite pigments is their easy preparation and great availability of raw materials [15]. These pigments are based on tin dioxide which crystallises in tetragonal structure to form bipyramidal crystals and which plays the dominant role in the final compound [16]. Tin dioxide is used as a host lattice for important ceramic pigments, e.g. Chrome Tin Orchid Cassiterite (CPMA No. 11–23–5), Tin Vanadium Yellow Cassiterite (CPMA No. 11–22–4) and Tin Antimony Grey Cassiterite (CPMA No. 11–24–8) [2, 17–19].

The solubility limit of Co (II) ions in SnO_2 is up to $x = 0.08$ (for temperatures up to 1150 °C). On the other hand, the solubility limit is just $x = 0.02$ at low temperature [20]. The presence of the second phase – cubic Co_2SnO_4 is usually observed when the solid solution limit is exceeded. Co (II) ions were reported as one of the most effective dopants for the densification of SnO_2 , because Co (II) ions behave as acceptors and create oxygen vacancies in the SnO_2 lattice. The doping of Co (II) ions in SnO_2 brought significant changes in the physical properties of the samples. Mehraj et al. observed that average crystallite size, lattice constant and porosity decreased with Co doping. The Co-doped samples are paramagnetic at room temperature [21–25].

In the present work, the synthesis of pigments with general formula $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ was studied. Because of Co ions have oxidation state lower than (IV), a second element with oxidation state higher than (IV) is always added in order to fulfill the electroneutrality of the structure. In this case are P (V) ions used as charge-compensating elements. The goal was to develop conditions (especially calcination temperature) for the synthesis of these pigments and to determine the influence of terbium ions on the colour properties of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments. Synthesised $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ compounds were compared with concurrently prepared pigments $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ from the standpoint of their structure, colour properties and particle size distribution.

Experimental

Synthesis of cassiterite pigments

The starting raw materials used for preparation of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments were SnO_2 (>99.9%, Alfa Aesar, Germany), $\text{Co}(\text{OH})_2$ (98%, Shepherd Color Company, USA), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.5%, Lachema a.s., Czech Republic) and Tb_4O_7 (99.9%, Indian Rare Earths Ltd., India). Above mentioned compounds were weighed in the required stoichiometric amounts and then were homogenised in an agate mortar. The mixtures were calcinated in corundum crucibles in an electric resistance furnace. The heating of furnace was programmed with increasing temperature at a rate $10^\circ\text{C}\cdot\text{min}^{-1}$ and the calcination temperature of 1350–1500 °C was maintained for three hours. All samples were gradually cooled to room temperature and ground in an agate mortar.

Application of the pigments into organic matrix and ceramic glaze

The calcinated powder samples were applied into the organic matrix (dispersive acrylic paint Parketol, Balakom a.s., Czech Republic) in mass tone and into medium temperature ceramic glaze P 074 91 (Glazura, s.r.o., Czech Republic), with the amount of a pigment sample 10 wt%. For testing in the organic matrix, the suspension containing 1 g of the sample and 1.5 cm³ of the binder was homogenised. This suspension was converted by a pestle to dense paste able to flowing. Coloured coating films were prepared by application of the paste on white nonabsorbing glossy paper. The coating layer of film was created by dragging the Bird's applicator. Prepared coating films were kept to dry spontaneously in the open air. Then they were ready for an evaluation of colour properties of pigments in the organic matrix in mass tone. In the case of application in the ceramic glaze, an aqueous suspension containing 10 wt% of pigment and 90 wt% of transparent ceramic glaze with an appropriate amount of distilled water was prepared by hand-grinding. The suspension was applied by using the brush on unglazed ceramic tile and after drying in the air was glazed at 1050 °C for 15 min.

Simultaneous TG-DTA analysis

The methods of thermal analysis can provide the first information about the temperature area of the formation of inorganic pigments. The formation of these pigments was followed by thermal analysis using STA 449C Jupiter (Netzsch, Germany) which allows the simultaneous registration of the thermoanalytical curves TG and DTA. The thermoanalyzer determines small changes in mass and thermal effects with high accuracy (weighing accuracy 10^{-8} g; error in measuring thermal effects 1 mV). The starting raw materials – SnO_2 , $\text{Co}(\text{OH})_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ (or eventually Tb_4O_7) and the prepared starting mixtures were studied by thermal analysis in corundum crucible in the air in temperature area from 30 to 1400 °C. The increase of temperature was $10^\circ\text{C}\cdot\text{min}^{-1}$. $\alpha\text{-Al}_2\text{O}_3$ was used as reference material.

XRD analysis

The phase analysis of the powdered materials was studied by X-ray diffraction analysis. The phase composition was determined using diffractometer MiniFlex 600 (Rigaku, JPN) equipped with a vertical goniometer of 15 cm in the 2Θ range of 10–80°. The accuracy of goniometer was $\pm 0.02^\circ$. X-ray tube with Cu anode ($U = 40$ kV, $I = 15$ mA), secondary graphite monochromator, scintillation NaI(Tl) counter, and X-ray of copper were used. Wavelength of the applied X-ray is $K_{\alpha 1} = 0.15418$ nm for angle $2\Theta < 35^\circ$ and $K_{\alpha 2} = 0.15405$ nm for angle $2\Theta > 35^\circ$.

Measurement of colour properties of applied cassiterite pigments

The colour properties of all final applications were objectively evaluated by measuring of spectral reflectance in the visible region of light (400–700 nm) by using a spectrophotometer ColorQuest XE (HunterLab, USA). Standard illuminant D65 was used as internationally recommended white daylight, measurement conditions were as follows: 10° supplementary standard observer, measuring geometry $d/8^\circ$. The colour properties are

described in terms of CIE $L^*a^*b^*$ system (1976). The value a^* (the red–green axis) and b^* (the yellow–blue axis) indicate the colour hue. The value L^* represents the lightness or darkness of the colour as related to the natural grey scale. In the $L^*a^*b^*$ system, it is described by numbers from 0 (black) to 100 (white). The value C (Chroma) represents saturation of the colour and determines colour purity. The colour hue 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; $H^\circ = 350\text{--}35^\circ$ (for red), $H^\circ = 35\text{--}70^\circ$ (for orange), $H^\circ = 70\text{--}105^\circ$ (for yellow), $H^\circ = 105\text{--}195^\circ$ (for green), $H^\circ = 195\text{--}285^\circ$ (for blue), $H^\circ = 285\text{--}350^\circ$ (for violet). Chroma C and hue angle H° of samples were calculated according to the Eqs. (1) and (2).

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

$$H^\circ = \arctg(b^*/a^*) \quad (2)$$

The total colour difference ΔE^*_{CIE} in the CIE $L^*a^*b^*$ diagram, which indicates the degree of colour difference between the two samples, is defined by the following equation (3), where ΔL^* , Δa^* , Δb^* are differences in L^* , a^* and b^* values between colour sample and colour of standard.

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

Measuring of particle size distribution

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 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 pigments were ultrasonically homogenised in the solution of $\text{Na}_4\text{P}_2\text{O}_7$ ($c = 0.15 \text{ mol dm}^{-3}$) for 120 s. 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.

Results and discussion

Thermal analysis

Thermal behaviour of reaction mixtures containing SnO_2 , $\text{Co}(\text{OH})_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ (eventually Tb_4O_7) was followed by methods of thermal analysis.

The TG and DTA curves of compound $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ (mass sample 367.70 mg) are shown in Fig.1. The DTA curve shows the three endothermic effects and one exothermic effect. The first endothermic peak with the minimum at 110 °C is attributed to the loss of physisorbed water. The sharp and strong endothermic peak with the minimum at 230 °C is connected melting process and decomposition of $\text{NH}_4\text{H}_2\text{PO}_4$. The melting and decomposition processes are very close to each other. The ammonium dihydrogen phosphate decomposed to orthophosphoric acid H_3PO_4 , with the evolution of ammonia. The small amounts of $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ and $\text{H}_4\text{P}_2\text{O}_7$ were probably also formed. Then in the temperature range 230–400 °C the orthophosphoric acid is transformed to pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$. The pyrophosphoric acid is liquid in this temperature range ($T_m = 61 \text{ }^\circ\text{C}$) and the subsequent heating of the sample led to the dehydration of $\text{H}_4\text{P}_2\text{O}_7$, which was transformed to metaphosphoric acid HPO_3 . At the same time, this heating process resulted in polycondensation reaction and formation of the polyphosphate acids. The TG data show a continuous weight loss up in the temperature range 230–780 °C without any constant segment, indicating that the above reactions take place continuously in a very complex manner, and cannot be separated as individual reactions [26–29]. The third endothermic peak at 280 °C is connected with the formation of Co_3O_4 [30–31]. The minor exothermic peaks with the maximum at 507, 615 and 732 °C could be related with the decomposition of $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$ and HPO_3 to P_2O_5 and with the reaction of phosphorus compound with SnO_2 and subsequent incorporation of P (V) ions into the lattice of SnO_2 as well [32]. The exothermic peak with the maximum at 1055 °C is probably connected with the start of formation of $\text{Co}_3(\text{PO}_4)_2$ structure. The total mass loss which is showed on TG curve was 7.24 %. It is mainly caused by thermal decomposition of cobalt and phosphorous compounds and elimination of water in the temperature interval 220–780 °C.

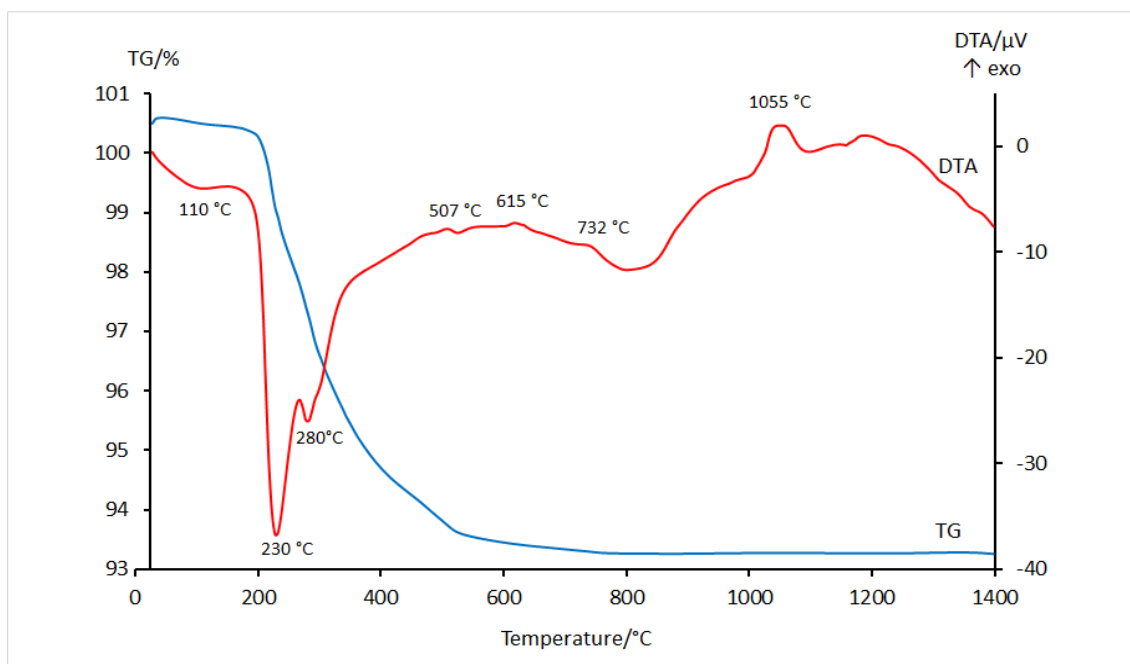


Fig. 1 The DTA/ TG curve of the reaction mixture containing SnO_2 , $\text{Co}(\text{OH})_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (367.70 mg)

Table 1 Thermal decomposition of reaction mixture containing Sn, Co, P precursors for preparation of $\text{Sn}_{0.760}\text{Co}_{0.008}\text{P}_{0.16}\text{O}_2$

Temperature range /°C	Peak temperature /°C	Mass change /%
30–230	110, 230 (endo)	-1.59
230–400	280 (endo)	-4.24
400–770	507, 615, 732 (exo)	-1.40
770–1400	1055 (exo)	-0.01

Figure 2 describes the thermal behaviour of the reaction mixture for preparation of sample $\text{Sn}_{0.752}\text{Co}_{0.008}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ (mass sample 320.01 mg). The endothermic peaks in the temperature range 99–228 °C are connected with the loss of physisorbed and chemically bound water. The next endothermic peak with the minimum at temperature 273 °C corresponds with the formation of Co_3O_4 . The exothermic peaks with maximum the at 464, 616 and 754 °C (as in the case of $\text{Sn}_{0.760}\text{Co}_{0.008}\text{P}_{0.16}\text{O}_2$) could be related to the reaction of phosphorus compound with SnO_2 and with the incorporation of P (V) ions into the lattice of SnO_2 . The terbium ions were available in two oxidation states in the raw material mixed oxide Tb_4O_7 ($\text{Tb}_2\text{O}_3 \cdot \text{TbO}_2$). During the heat treatment, this mixed oxide changes to Tb_2O_3 at the temperature about 950 °C and the temperature above 1400 °C occurs to the oxidation of Tb (III) ions to the Tb (IV) ions [33]. These effects were not detected on the DTA-TG curve perhaps because the mixed oxide Tb_4O_7 was used in the very low quantities. The endothermic peak with the minimum at 1142 °C corresponds to the phase transformation from TbPO_4 (monoclinic) to TbPO_4 (tetragonal) [34]. The exothermic peak with the maximum at 1248 °C is connected with the start of formation of final structure. The total mass loss which is showed on TG curve was 5.58 % and it is mainly caused by thermal decomposition of cobalt and phosphorous compounds and elimination of water in the temperature interval 220–760 °C.

On the basis of results of thermal analysis, the reaction mixture containing rare earth oxides were calcinated in the temperature range 1350–1550 °C.

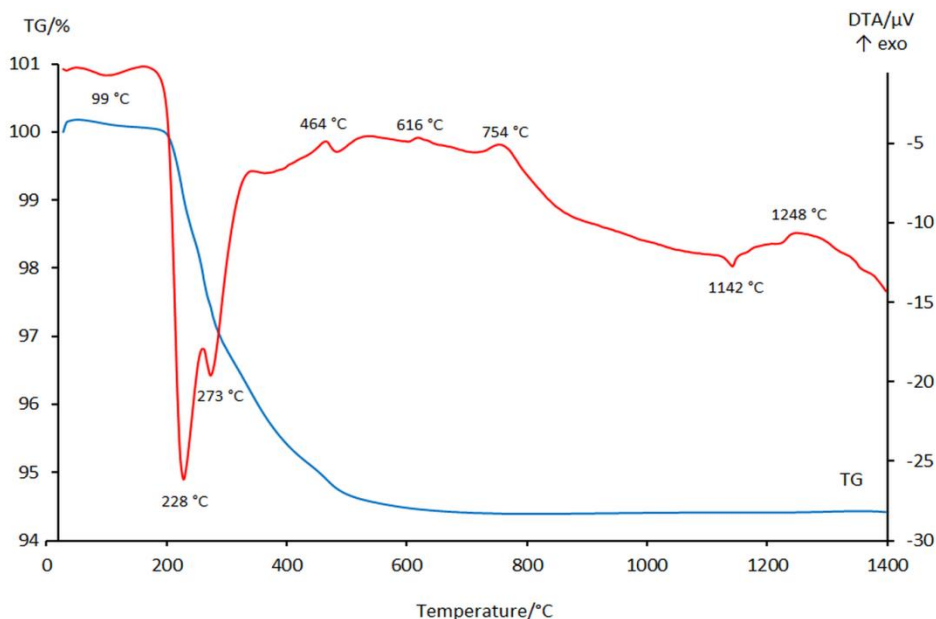


Fig. 2 The DTA/ TG curve of the reaction mixture containing SnO_2 , $\text{Co}(\text{OH})_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ and Tb_4O_7 (320.01 mg)

Table 2 Thermal decomposition of reaction mixture containing Sn, Co, P and Tb precursors for preparation of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$

Temperature range /°C	Peak temperature /°C	Mass change /%
30–233	99, 228 (endo)	-1.15
233–403	273 (endo)	-3.46
403–773	464, 616, 754 (exo)	-1.00
773–1398	1142 (endo), 1248(exo)	+0.03

XRD analysis

The powder pigments were studied by XRD analysis. The diffractograms of the samples were single-phased at higher synthesis temperatures. Due to results of thermal analysis the analysis of the phase composition of the reaction mixture fired at 900 °C, 1100 °C and 1200 °C was also performed (Table 3). The secondary phase, corresponded with monoclinic structure of $\text{Co}_2\text{P}_2\text{O}_7$ was observed at all samples, which were prepared in the temperature range 900 – 1200 °C. The sample of $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ provided tertiary crystalline phase corresponding with monoclinic $\text{Co}_3(\text{PO}_4)_2$ in the temperature range 1100 – 1200 °C and the sample of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ provided tertiary crystalline phase corresponding with TbPO_4 in the temperature range 900 – 1200 °C, when the phase transformation from monoclinic TbPO_4 to tetragonal TbPO_4 occurred at 1142 °C.

At prepared pigments, the only major crystalline phase corresponding to tetragonal cassiterite structure of SnO_2 with $\text{P4}_2/\text{mnm}$ symmetry (JPDF No. 04-003-0649), was confirmed. No other phases were detected in the XRD patterns. The intensities of peaks increased with calcination temperature, which meant that the peaks were the sharpest and the most intense at 1450 °C. The intensity of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigment rapidly decreased at 1500 °C (Fig. 3) however the intensity of $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ remained the same at this calcination temperature (Fig. 4). The XRD analysis confirmed that the synthesis temperature of 1350 °C is sufficient to get a single-phase compound (Table 4). The contraction of lattice constants confirmed the incorporation of Co and Tb ions in SnO_2 host lattice.

Table 3 Characterization of the crystal structure of the samples prepared at calcination temperature 900, 1100 and 1200 °C

Pigment	Temperature /°C	Obtained phases	JPDF card number
$\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$	900	SnO_2 (tetragonal)	01-071-0652
		$\text{Co}_2\text{P}_2\text{O}_7$ (monoclinic)	01-070-1491
		Unknown	-
	1100	SnO_2 (tetragonal)	01-071-0652
		$\text{Co}_2\text{P}_2\text{O}_7$ (monoclinic)	01-070-1491
		$\text{Co}_3(\text{PO}_4)_2$ (monoclinic)	01-070-1795
	1200	SnO_2 (tetragonal)	01-071-0652
		$\text{Co}_2\text{P}_2\text{O}_7$ (monoclinic)	01-070-1491
		$\text{Co}_3(\text{PO}_4)_2$ (monoclinic)	01-070-1795
$\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$	900	SnO_2 (tetragonal)	01-071-0652
		$\text{Co}_2\text{P}_2\text{O}_7$ (monoclinic)	01-070-1491
		TbPO_4 (monoclinic)	01-077-0224
	1100	SnO_2 (tetragonal)	01-071-0652
		$\text{Co}_2\text{P}_2\text{O}_7$ (monoclinic)	01-070-1491
		TbPO_4 (monoclinic)	01-077-0224
	1200	SnO_2 (tetragonal)	01-071-0652
		$\text{Co}_2\text{P}_2\text{O}_7$ (monoclinic)	01-070-1491
		TbPO_4 (tetragonal)	01-079-6618

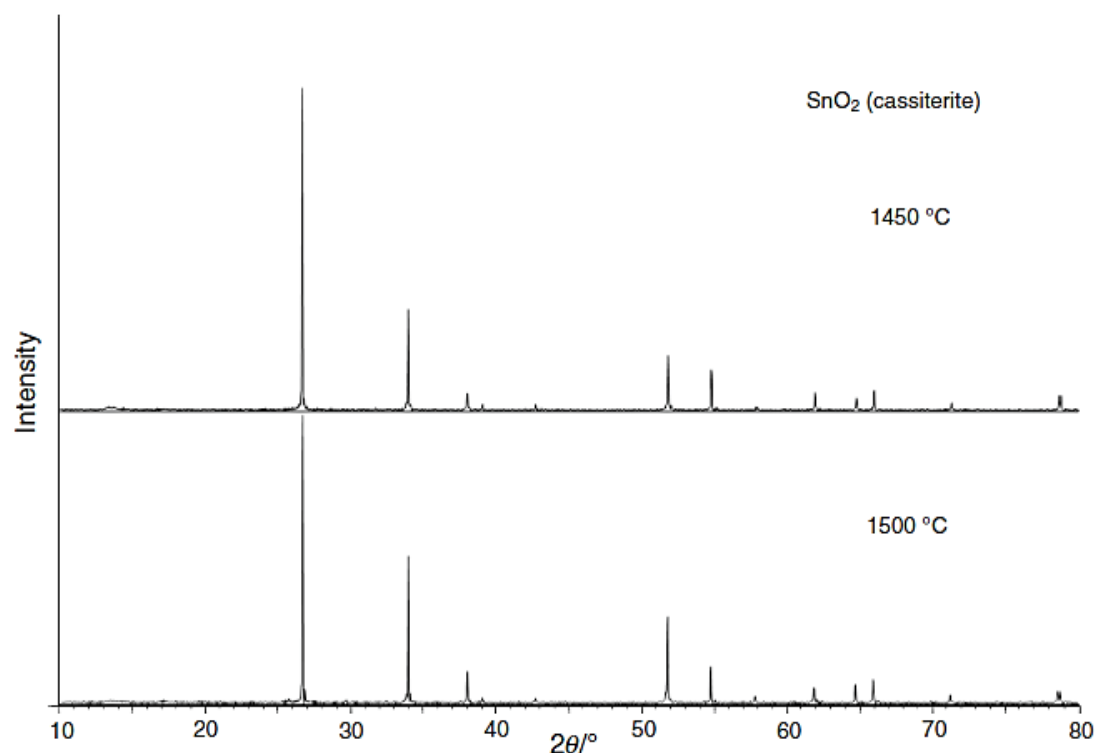
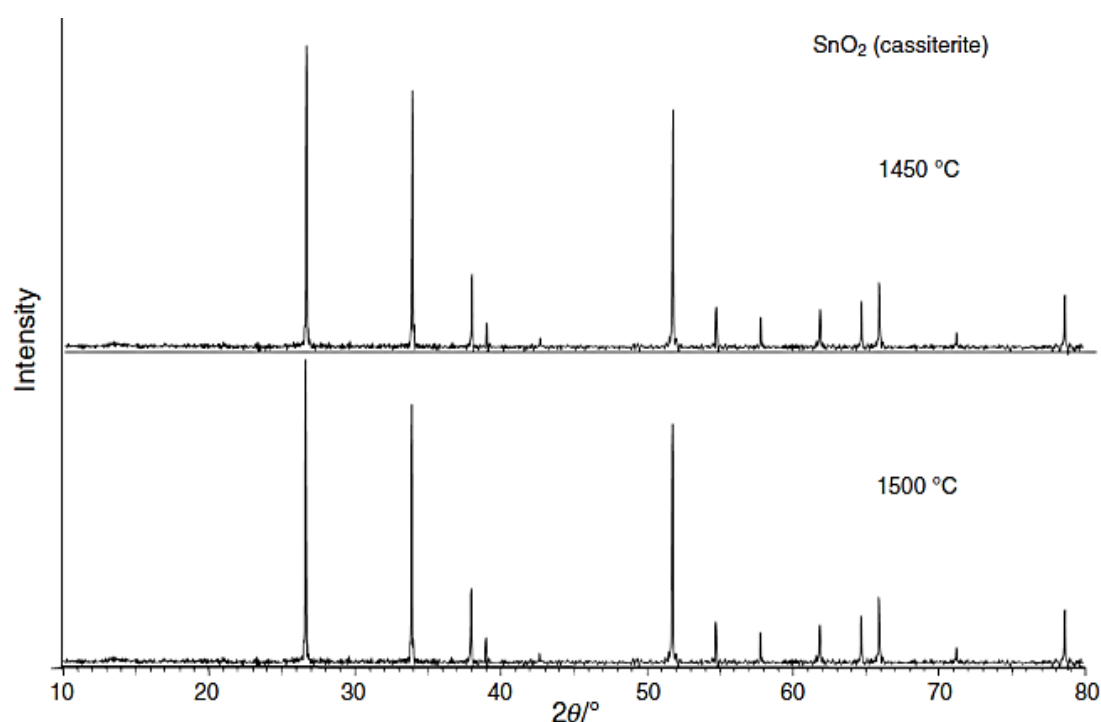


Fig. 3 X-ray diffraction patterns of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ synthesized at calcination temperature 1450 °C and 1500 °C.

Table 4 Characterization of the crystal structure of the prepared pigments

Pigment	Temperature /°C	Obtained phases	<i>a</i> /nm	<i>c</i> /nm
Sn _{0.760} Co _{0.08} P _{0.16} O ₂	1350		0.473662	0.318631
	1400	SnO ₂	0.473674	0.318639
	1450	tetragonal	0.473694	0.318645
	1500		0.473700	0.318550
Sn _{0.752} Co _{0.08} P _{0.16} Tb _{0.008} O ₂	1350		0.473595	0.318629
	1400	SnO ₂	0.473675	0.318638
	1450	tetragonal	0.473763	0.318696
	1500		0.473776	0.318686

**Fig. 4** X-ray diffraction patterns of Sn_{0.760}Co_{0.08}P_{0.16}O₂ synthesized at calcination temperature 1450 °C and 1500 °C.

Colour properties

Currently, the lack of violet pigments shades is on the market. Therefore, the effect of terbium ions on the colour properties of Sn_{0.760}Co_{0.08}P_{0.16}O₂ was investigated. The aim of the research was to intensify red shade in the final colouration of prepared pigments and to obtain violet or blue violet colour.

The effect of growing calcination temperature and the effect of terbium ions on colour properties of the cassiterite pigments were investigated. At first, the prepared powder materials were applied into the organic matrix in mass tone. From Tab. 5 and Tab. 6 it is evident that the values of colour coordinates *a**, *b** and value *C* (chroma) subsequently increase with ascending temperature of calcination. On the other hand the values of coordinates *L** (lightness) decline. All pigments produce blue-violet hue. This fact is obvious in view of the value *H*°, which lies in range of 294.74° to 307.31°. The admixture of terbium ions a positive effect on colour properties. The comparison of synthesised pigments Sn_{0.760}Co_{0.08}P_{0.16}O₂ and Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O₂ in terms of acquired colour properties showed that pigments with terbium ions provide lower values of lightness *L**. Furthermore, pigments doped by terbium ions provide the increase of chroma *C*. All of the prepared terbium doped pigments have higher values of both colour coordinates (+*a**, -*b**). This fact is also confirmed by mostly increasing values of angle *H*°. It means that Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O₂ pigments in comparison with Sn_{0.760}Co_{0.08}P_{0.16}O₂ are shifted closer toward blue-violet

shades. The best results are obtained with ions of terbium as admixture at the firing temperature 1450 °C. In this case, the sample acquires the highest value of colour coordinate a^* (22.02), the highest value of chroma (36.33) and the highest value of hue angle (307.31°). This sample is characterised by violet colour. The values of total colour difference describe colour differences between samples ($\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$) and standard ($\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$). The pigment synthesised at 1450 °C disposes of the highest value of the total colour difference (25.81). It is mainly caused by the decrease of lightness and increase of coordinate $+a^*$.

Table 5 CIE $L^*a^*b^*$ parameters of $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ powders applied into the organic matrix

T /°C	L*	a*	b*	C	H°
1350	56.19	7.86	-15.31	17.21	297.18
1400	56.99	4.64	-10.07	11.09	294.74
1450	59.16	6.78	-13.27	14.90	297.06
1500	45.38	9.11	-24.36	26.00	290.50

Table 6 CIE $L^*a^*b^*$ parameters of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ powders applied into the organic matrix

T /°C	L*	a*	b*	C	H°	ΔE^*_{CIE}
1350	61.55	6.07	-11.72	13.20	297.38	5.06
1400	58.31	8.23	-14.78	16.92	299.11	2.22
1450	45.37	22.02	-28.89	36.33	307.31	25.81
1500	54.86	12.98	-18.22	22.37	305.47	5.63

The second system was pigment applied into the transparent ceramic glaze with glazing temperature 1050 °C. The tested cassiterite pigments belong to the group of the high-temperature pigments, and therefore the glaze with the middle temperature of glazing for the study of colour properties was selected. The colour properties of synthesised pigments applied into transparent ceramic glaze are showed in Tab. 7 and Tab. 8. In the case of the $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments, growing synthesis temperature causes a drop of value L^* (approx. from 47 to 40). For these types of pigments, rising temperature caused the slight increase of the chroma C . However the blue colour has a bigger impact on the increasing of C and values of a^* increase with temperature. On the other hand, the red shade shows the insignificant increase. The values of coordinate a^* ranged between 7 to 10 and coordinate b^* reached values from -23 to -28. This trend is apparent also from slight increasing values of angle H° within a very narrow range (approx. from 287° to 290°) and these pigments provide blue-violet colour shades. The good results are obtained with ions of terbium as admixture at the firing temperature 1500 °C. In this case, the highest value of the colour coordinate a^* (9.95) and also the highest value of chroma (28.97) is achieved. The comparison of synthesised pigments $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ and $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ in terms of acquired colour properties demonstrates that pigments with ions of terbium provided lower values of lightness L^* from the temperature of 1450 °C. The chroma (in comparison with $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ pigments) decreases at 1400 °C from approx. 28 to 24 and subsequently grows from approx. 24 to 30, when firing temperature increases. The highest effect on the increase of chroma C at 1500 °C has a distinct increase of value b^* compared with standard pigments $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$. The values of total colour difference are low for samples synthesised in temperature range of 1350–1400 °C. It means that colour differences ΔE^*_{CIE} between standard ($\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$) and samples ($\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$) are imperceptible to the human eye. The highest value of total colour difference ΔE^*_{CIE} (5.77) is observed in case of pigment synthesised at 1500 °C. This fact is mainly caused by the decrease of lightness and increase of coordinate $-b^*$.

In this case, the best results provided pigments synthesised at higher calcination temperatures (1450 and 1500 °C). At calcination temperature 1450 °C, great results were obtained thanks to the high intensity of crystalline phase as well. The prepared $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments provided in both applications (organic matrix, ceramic glaze) required blue or blue-violet colouration.

Table 7 CIE $L^*a^*b^*$ parameters of $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ powders applied into the ceramic glaze P 074 91

T /°C	L*	a*	b*	C	H°
1350	46.59	8.13	-25.20	26.48	287.88
1400	45.75	8.81	-26.58	28.00	288.34

1450	47.67	6.39	-23.38	24.24	285.29
1500	45.38	9.11	-24.36	26.00	290.50

Table 8 CIE $L^*a^*b^*$ parameters of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ powders applied into the ceramic glaze P 074 91

T / °C	L*	a*	b*	C	H°	ΔE^*_{CIE}
1350	46.54	7.44	-23.44	24.59	287.61	0.69
1400	46.61	8.01	-25.33	26.57	287.55	1.17
1450	43.65	9.15	-26.82	28.34	288.84	3.82
1500	40.43	9.95	-27.21	28.97	290.09	5.77

The Kubelka–Munk absorption spectra of samples $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ and $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ shown on Fig. 5 present the characteristic spectrum of Co (II) ion in tetrahedral coordination [35], with a triple absorption peak centred in the visible region of light at approximately 560 nm (green region), 580 nm (yellow–orange region) and 610 nm (red region), and with a multiple reflection valley between 400–450 nm (blue region), which gives rise to the blue–violet colour.

Substitution of part Sn^{4+} ions by terbium ions in pigment $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ caused origin of significant absorption band centred at 490 nm. The absorption edge of this sample is shift from 625 nm $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ to 650 nm.

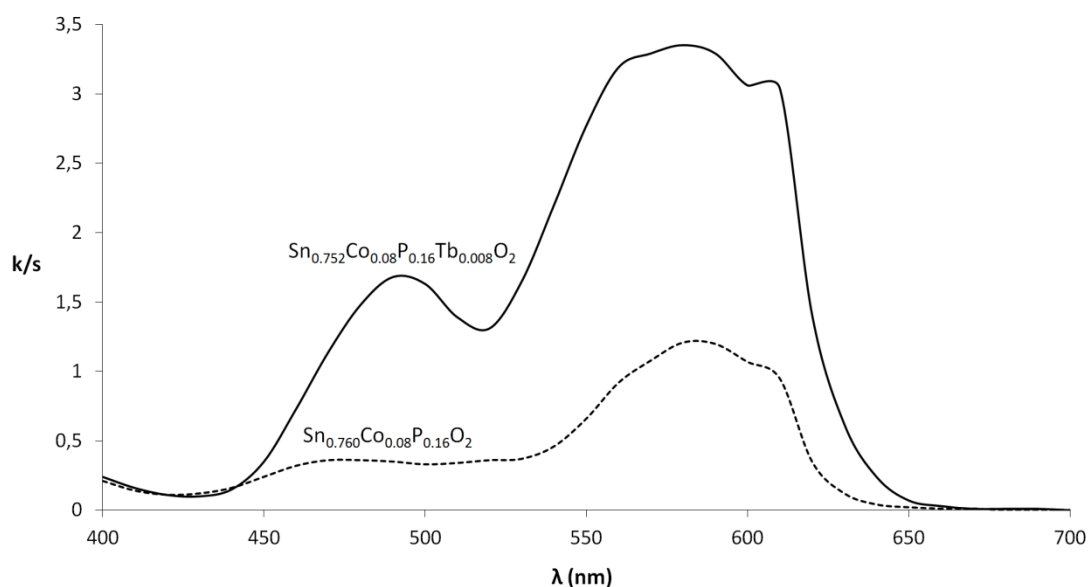


Fig. 5 Kubelka-Munk absorption spectra of $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ and $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ powders (synthesis temperature of 1450 °C) applied into the organic matrix

Particle size distribution

All prepared pigments were characterised by measuring of the particle size distribution. The most important value, which characterises particle size, is the value d_{50} (median). From Table 9 is evident, that with the increase of calcination temperature, the main particle size grows too. Terbium doped pigments are characterised by lower values of d_{50} in comparison with the standard pigments. Their values lie in range of 6 to 14 μm . A suitable granulometric composition for application of pigments into ceramic glaze is about 5–15 μm . These values were attained for all prepared pigments. For their potential use in painting coats, it would be necessary to decrease their size mechanically.

Table 9 Particle size distribution of the samples $\text{Sn}_{0.760}\text{Co}_{0.08}\text{P}_{0.16}\text{O}_2$ and $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$

Sample	T /°C	d ₁₀ /μm	d ₅₀ /μm	d ₉₀ /μm
Sn _{0.760} Co _{0.08} P _{0.16} O ₂	1350	0.85	7.68	36.93
	1400	1.02	8.31	41.62
	1450	1.16	10.48	63.15
	1500	1.21	13.73	75.63
Sn _{0.752} Co _{0.08} P _{0.16} Tb _{0.008} O ₂	1350	0.90	6.44	40.06
	1400	0.88	6.87	38.17
	1450	0.83	7.05	43.86
	1500	1.03	9.04	59.61

Conclusions

The main aim of the research was to prepare blue-violet Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O₂ ceramic pigments. The samples were synthesised by classical ceramic method (solid state reaction). Methods of thermal analysis were used for assigning the optimal heating temperature necessary for the formation of a cassiterite structure. From the simultaneous TG–DTA analysis, it was found that the formation of the cassiterite compounds starts in the temperature range of 1250–1350 °C. On the basis of results of thermal analysis, the calcination temperatures in the range of 1350–1500 °C were chosen. Studies of X–ray diffraction showed that single-phased samples were prepared in the temperature range of 1350–1500 °C. The positive effect of the increasing synthesis temperature on the colour properties of pigments was found. From the obtained results it can be concluded, that higher calcination temperature generally stimulates the formation of darker powders with higher values of chroma *C* and with higher values of hue angle *H*[°]. According to the highest values of *C* as a parameter characterising colour purity, the best temperature for synthesis of these pigments is 1450 °C for application into the organic matrix and 1500 °C for application into the ceramic glaze. The effect of terbium ions on pigmentary properties was also investigated. In comparison with Sn_{0.760}Co_{0.08}P_{0.16}O₂ pigments were obtained pigments with higher value of saturation and with the higher contribution of red and blue shade. The cassiterite pigments doped by ions of terbium provided violet shades in the organic matrix and blue–violet shades in the ceramic glaze. The median of particle size *d*₅₀ moved in range of 6.44–13.73 μm in dependence on synthesis temperature (increasing character with increasing temperature), and this particle size is sufficient for the potential using in ceramic glazes.

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