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Mixed metal oxide pigments

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Abstract

The presented dissertation thesis deals with the possibility of synthesis of blue-violet cassiterite pigments in which a part of tin ions was substituted by cobalt ions and ions of other admixtures. In this case, phosphorous ions were used as charge-compensating elements. The compounds of formula $Sn_{1-(x+y)}Co_xP_yO_2$ and $Sn_{1-(x+y+z)}Co_xP_yZ_zO_2$ (Z = Ce, Pr, Tb, Ti, Zr, Si, Mn) were prepared by solid state reaction using the classical ceramic method and also by the method of mechanical activation. The goal was to develop conditions for synthesis and the most suitable preparation method of these pigments. On the basis of results of thermal analysis the temperature range from 1350 to 1500 °C for synthesis was chosen. The synthesised pigments were characterised in terms of colour properties after their application into the transparent ceramic glaze and into the organic binder. They were also studied with respect to their phase composition as well as the particle size distribution. In the final part of this thesis, the effect of mineralizers on the properies of synthetized pigments was studied. These pigments were prepred by ceramic method in the temperature range 1200 – 1450 °C and $Na_2B_4O_7$. $10H_2O$, Li_2CO_3, $CaCl_2.2H_2O$, $MgO\text{-}MgCl_2.6H_2O$ (1:1) a LiF were used as mineralizers.

Abstrakt

Předkládaná disertační práce se zabývá možnostmi přípravy modrofialových kasiteritových pigmentů, u kterých byla část cíničitých iontů nahrazena ionty kobaltu a ionty dalších příměsí. Jako nábojově-kompenzační prvky byly použity ionty fosforu. Sloučeniny $Sn_{1-(x+y)}Co_xP_yO_2$ and $Sn_{1-(x+y+z)}Co_xP_yZ_zO_2$ (Z = Ce, Pr, Tb, Ti, Zr, Si, Mn) byly připraveny reakcemi v tuhé fázi – tradiční keramickou metodou a metodou mechanické aktivace. Cílem bylo nalézt optimální metodu pro přípravu pigmentů a rozpracovat podmínky pro jejich syntézu. Výsledky termické analýzy prokázaly, že nejvhodnější je tyto pigmenty kalcinovat v rozmezí teplot 1350 – 1500 °C. Připravené pigmenty byly po aplikaci do organického pojivého systému a po aplikaci do

transparentní keramické glazury hodnoceny z hlediska barevných vlastností. Rovněž byly studovány z hlediska jejich fázového složení a také z hlediska distribuce velikosti pigmentových částic. V poslední části této práce, byl posuzován vliv mineralizátorů na pigmentově-aplikační vlastnosti připravených pigmentů. Tyto pigmenty byly syntetizovány keramickou metodou v rozmezí teplot 1200 – 1450 °C. Jako mineralizační přísady byly použity – $Na_2B_4O_7$. $10H_2O$, Li_2CO_3, $CaCl_2.2H_2O$, MgO-$MgCl_2.6H_2O$ (1:1) a LiF.

Keywords

Inorganic pigments, cassiterite, colour properties, solid state reaction, particle size distribution, mineralizer, ceramic pigments, violet pigment

Klíčová slova

Anorganické pigmenty, kasiterit, barevné vlastnosti, reakce v pevné fázi, distribuce velikosti částic, mineralizátor, keramické pigmenty, fialový pigment

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INTRODUCTION

The ceramic pigments are special inorganic pigments of crystallic character with high thermal stability and chemical restistance against molten glass. They are used above all for the colouring of ceramic glazes and enamels and for the production of colours for tiles, glass, porcelain and ceramics also. The pigments are composed by high thermal stable structure, to which it is properly integrated the definite chromophore component. Theirs colour stability depends on a great extent on the type of theirs crystallic structure, firing temperature and the firing rate, on the chemical composition of dyed material, the grinding method and the character of furnace atmosphere. The important ceramic pigments are based on baddeleyite, rutile, zirconium, sphene, spinel or cassiterite structure.

THE AIM OF THESIS

The aim of this thesis was to prepare high temperature cassiterite pigments and to evaluate their pigmentary-application properties. The main attention was focused on the development of conditions for the synthesis of these pigments, which use cobalt ions as chromophore components and phosphorus ions as charge-compensating element. The main goal was primarily to strengthen the red colour component in the resulting coloration and achieve a blue-violet or violet shades, especially after application to the ceramic glaze. For this purpose, a process has been proposed utilizing the incorporation of additional chromophore components into the pigment structure. Therefore the possibilities and conditions of pigment synthesis of general formula $Sn_{1-(x+y)}Co_xP_yO_2$ and $Sn_{1-(x+y+z)}Co_xP_yZ_zO_2$ (where Z = Ce, Pr, Tb, Ti, Zr, Si and Mn) were studied. The synthesis of cassiterite pigments is more effective at high calcination temperatures (1350 - 1600 ° C) and therefore their production is demanding in terms of economy and energy. In order to lower the synthesis temperature and to support the solid state reaction, substances with a mineralizing effect (mineralizers) were added to the chosen reaction mixtures before calcination. The effect of mineralizers addition on the phase composition of the resulting powder materials and on their pigmentary-application properties was also investigated.

1 THEORETICAL PART

Ceramics pigments are inorganic compounds, which provide colour and they are insloluble in a medium, with which the 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].

Cassiterite pigments are based on tin dioxide respectively they are mixed oxides, where tin dioxide is the main component. These pigments belong to the group of ceramic pigments with high thermal and chemical stability and they are based on tetragonal mineral cassiterite SnO_2 (a = 0.4737 nm and c = 0.3185 nm) [2, 3]. Their crystal structure is modified by doping elements (chromophores), which can change the cell parameters. The structure of the host lattice is preserved, but it can be disordered. The advantage of cassiterite pigment si their easy preparation and great availability of raw materials [4]. Tin dioxide is used as a host lattice for important ceramic pigments, e.g. Chrome tin orchid cassiterite, Tin vanadium yellow cassiterite and Tin antimony grey cassiterite [5].

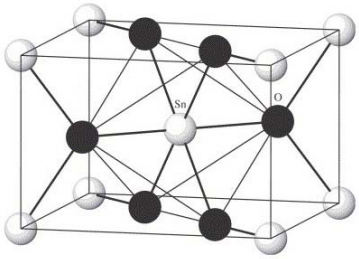

Fig. 1: Tetragonal structure of tin dioxide [6]

In this part of research, the ions of cobalt and terbium as chromophores were chosen. 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 [5, 7]. However, the colour performance of cobalt pigment depends on their thermal stability, chemical reactivity towards the glaze components, as well as on the coordination of Co^{2+} ions (tetrahedral coordination is preferred to octahedral). Due to Co ions (II) have oxidation state lower than (IV), the second element with oxidation

state higher than (IV) is always added in order to fulfil the electroneutrality of the structure. In this case, P (V) ions are used as charge-compensating elements [8].

In this presented part of work, the synthesis of terbium doped cassiterite pigments is studied. The compounds of formula $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ were prepared by the classical ceramic method. This method involves homogenisation of the mixture of the corresponding compounds and their subsequent calcination at high temperatures. The main aim of this research was to prepare blue-violet or violet high temperature pigments that would be suitable for application into the ceramic glazes.

2 EXPERIMENTAL PART

2.1 Synthesis of cassiterite pigments

The powder synthesis was carried out by ceramic method, based on the solid state reaction. The starting materials used for preparation of $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ pigments were SnO_2 (>99.9%, Alfa Aesar, Germany), $Co(OH)_2$ (99%, Shepherd Color Company, USA), $NH_4H_2PO_4$ (99.5%, Lachema a.s., Czech Republic) and Tb_4O_7 (>99.9%, Alfa Aesar, Germany) weighed in suitable molar proportion and subsequently ground manually in a porcelain mortar to obtain a homogenous reaction mixture. 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 °C.min^{-1} and the calcination temperature of 1200 – 1450 °C was maintained for three hours. All samples were gradually cooled to room temperature and ground in an agate mortar.

2.2 Application pigments into the binder

The calcinated powder samples were applied into an organic matrix in mass tone and into medium temperature transparent ceramic glaze with amount of a pigment sample 10 wt%. For testing in organic binder, suspension containing 1 g of the sample and 1.5 cm^3 of binder was homogenized. 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 into organic binder in mass tone. In the case of application into 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 brush on unglazed ceramic tile and after drying in air was glazed at 1050 °C for 15 min.

2.3 Method of thermal analysis

The formation of $Sn_{0.76}Co_{0.08}P_{0.16}O_2$ and $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ was followed by thermal analysis using STA 449C Jupiter (Netzsch, Germany) which allows the simultaneous registration of the thermoanalytical curves TG and DTA. Powder specimens (300–400 mg) in corundum crucibles were heated up to a temperature of 1400 °C with a heating rate of 10 °C min^{-1} in air. α-Al_2O_3 was used as a reference material.

2.4 Measuring of colour properties

The optical properties of pigments and their applications were measured by spectrophotometer ColourQuest XE (HunterLab, USA). The measurement conditions were the following: an illuminant D65, 10°complementary observer and measuring geometry d/8°. 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; $H°$ = 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) [9].

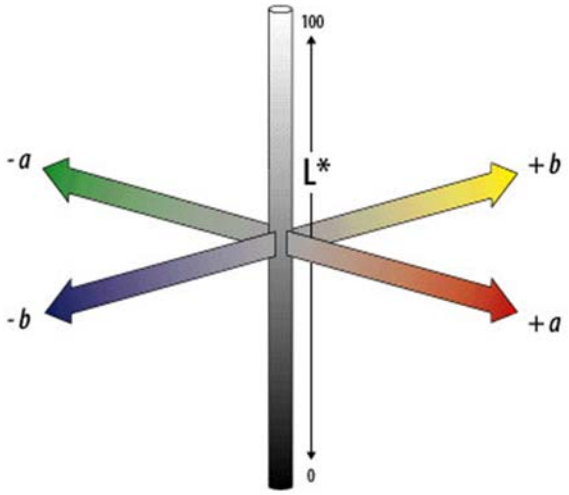

Fig. 2: CIE L*a*b* colour space [10]

2.5 XRD analysis

The crystal structures of the powdered materials were studied by X-ray diffraction analysis. The phase composition was determined using diffractometer D8 Advance (Bruker AXS, GB) with a goniometer of 17 cm in the range 2 Θ of 10-80°. CuKα1 (λ = 0.15418 nm) radiation was used for angular range of 2 Θ < 35° and Cu Kα2 (λ = 0.15405 nm) for the range of 2 Θ > 35. A scintillation detector was used.

2.6 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 pigments were ultrasonically homogenized in solution of $Na_4P_2O_7$ (c = 0.15 mol dm^{-3}) for 120 s. The signal was evaluated on the basis of Fraunhofer diffraction. The measurement is performed in three steps, the results are automatically calculated as average and presented as d_{10}, d_{50}, d_{90} and *span* values.

3 RESULTS AND DISSCUSION

3.1 Thermal analysis of cassiterite pigments

Thermal behaviour of reaction mixtures containing SnO_2, $Co(OH)_2$, $NH_4H_2PO_4$ and (eventuelly) Tb_4O_7 was followed by methods of thermal analysis.

The TG and DTA curves of compound $Sn_{0.760}Co_{0.08}P_{0.16}O_2$ (mass sample 367.70 mg) are shown in Fig. 3. The DTA curve shows the three endothermic effects and four exothermic effects. The first endothermic peak with the minimum at 110 °C is attributed to the loss of physisorbed water [11]. The sharp and strong endothermic peak with the minimum at 230 °C is connected with melting process and decomposition of $NH_4H_2PO_4$ [12]. The third endothermic peak at 280 °C is connected with the formation of Co_3O_4 [11, 13]. The exothermic peaks with maximum the at 507, 615 and 732 °C could be related to the reaction of phosphorus compound with SnO_2 and with the incorporation of P^{5+} ions into the lattice of SnO_2 [14]. The exothermic peak with a maximum at 1055 ° C is probably associated with the formation of the $Co_3(PO_4)_2$ structure [13]. This fact is confirmed by the results of XRD analysis of samples synthesized in the temperature range 900 – 1100 ° C. 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.

Table 1 Thermal decomposition of reaction mixture containing Sn, Co, P precursors for preparation of $Sn_{0.760}Co_{0.008}P_{0.16}O_2$

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

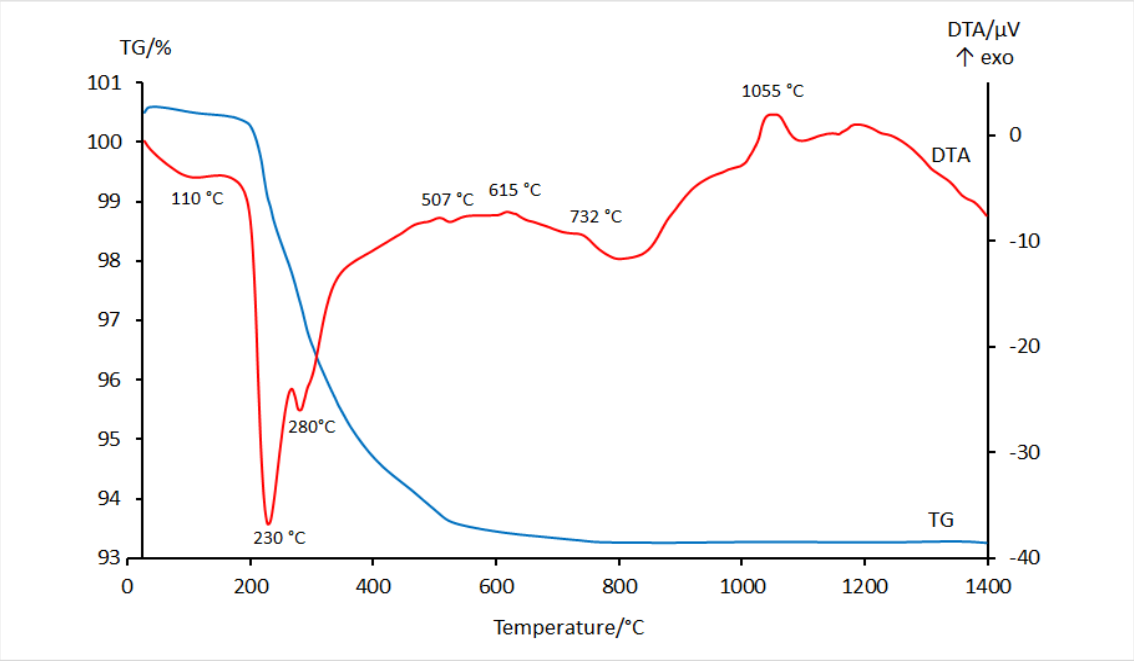

Fig. 3: The DTA/ TG curve of the reaction mixture containing SnO_2, $Co(OH)_2$ and $NH_4H_2PO_4$ (367.70 mg)

The Figure 4 describes the thermal behaviour of the reaction mixture for the preparation of sample $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ (mass sample 320.01 mg). The endothermic peak detected at 99 °C is connected with the loss of physisorbed and chemically bound water and the second endothermic peak detected at 228 °C corresponding to melting of $NH_4H_2PO_4$ [11, 12]. The next endothermic peak with the minimum at temperature 273 °C corresponds to the formation of Co_3O_4 [13]. The exothermic peaks with maximum the at 464, 616 and 754 °C could be related to the reaction of phosphorus compound with SnO_2 and with the incorporation of P^{5+} ions into the lattice of SnO_2 [12, 14]. The endothermic peak with the minimum at 1142 °C corresponds to the phase transformation from $TbPO_4$ (monoclinic) to $TbPO_4$ (tetragonal) [15] and the exothermic peak with the maximum at 1248 °C is probably connected with oxidation of Tb^{3+} ions to Tb^{4+} ions. These ions are then incorporated into the matrix of tin dioxide. The total mass loss which is showed on TG curve was 5.58 % and it was 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 – 1500 °C.

Table 2 Thermal decomposition of reaction mixture containing Sn, Co, P and Tb precursors for preparation of $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$

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

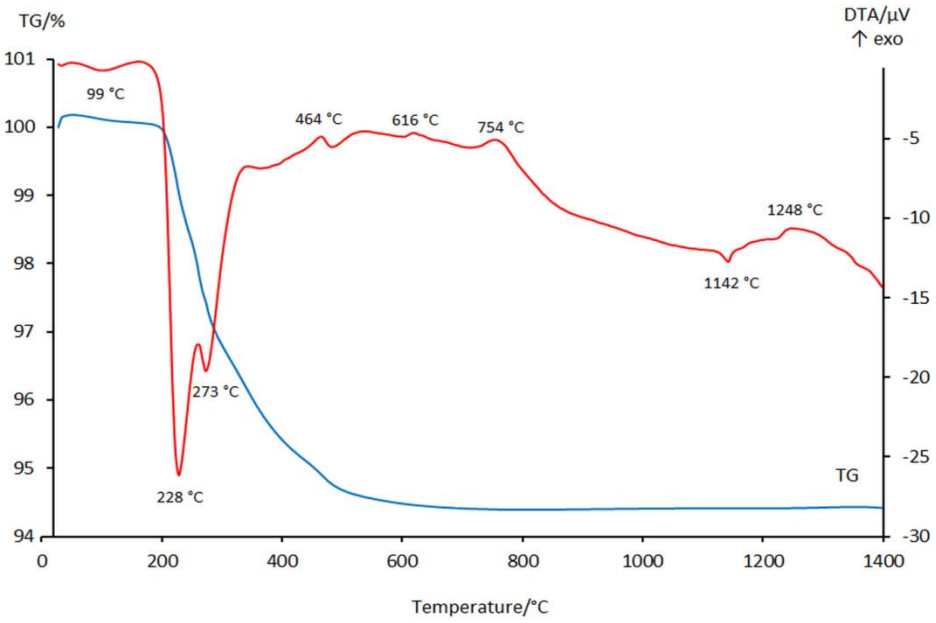

Fig. 4: The DTA/TG curve of the reaction mixture containing SnO_2, $Co(OH)_2$, $NH_4H_2PO_4$ and Tb_4O_7 (320.01 mg)

3.2 XRD analysis of cassiterite pigments

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, monoclinic structure of $Co_2P_2O_7$, was observed at all samples, which were prepared in the temperature range 900 – 1200 °C. The sample of $Sn_{0.760}Co_{0.08}P_{0.16}O_2$ provided tertiary crystalline phase corresponding with monoclinic $Co_3(PO_4)_2$ in the temperature range 1100 – 1200 °C and the sample of $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ 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.

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
$Sn_{0.760}Co_{0.08}P_{0.16}O_2$	900	SnO_2 (tetragonal)	01-071-0652
		$Co_2P_2O_7$ (monoclinic)	01-070-1491
		Unknown	-
	1100	SnO_2 (tetragonal)	01-071-0652
		$Co_2P_2O_7$ (monoclinic)	01-070-1491
		$Co_3(PO_4)_2$ (monoclinic)	01-070-1795
	1200	SnO_2 (tetragonal)	01-071-0652
		$Co_2P_2O_7$ (monoclinic)	01-070-1491
		$Co_3(PO_4)_2$ (monoclinic)	01-070-1795
$Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$	900	SnO_2 (tetragonal)	01-071-0652
		$Co_2P_2O_7$ (monoclinic)	01-070-1491
		$TbPO_4$ (monoclinic)	01-077-0224
	1100	SnO_2 (tetragonal)	01-071-0652
		$Co_2P_2O_7$ (monoclinic)	01-070-1491
		$TbPO_4$ (monoclinic)	01-077-0224
	1200	SnO_2 (tetragonal)	01-071-0652
		$Co_2P_2O_7$ (monoclinic)	01-070-1491
		$TbPO_4$ (tetragonal)	01-079-6618

The calcination of reaction mixtures at temperature higher than 1200 °C brought synthesis of single phase products. The only major crystalline phase corresponding to tetragonal cassiterite structure of SnO_2 with $P4_2/mnm$ 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 means that the peaks were the sharpest and the most intense at 1450 °C. The intensity of diffraction lines of $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ pigment rapidly decreased at 1500° C (Fig. 5) however the intensity of $Sn_{0.760}Co_{0.08}P_{0.16}O_2$ remained the same at this calcination temperature. The XRD analysis confirmed that the synthesis temperature of 1350 °C is sufficient to get a single-phase compound. The contraction of lattice constants confirmed the incorporation of Co and Tb ions in SnO_2 host lattice.

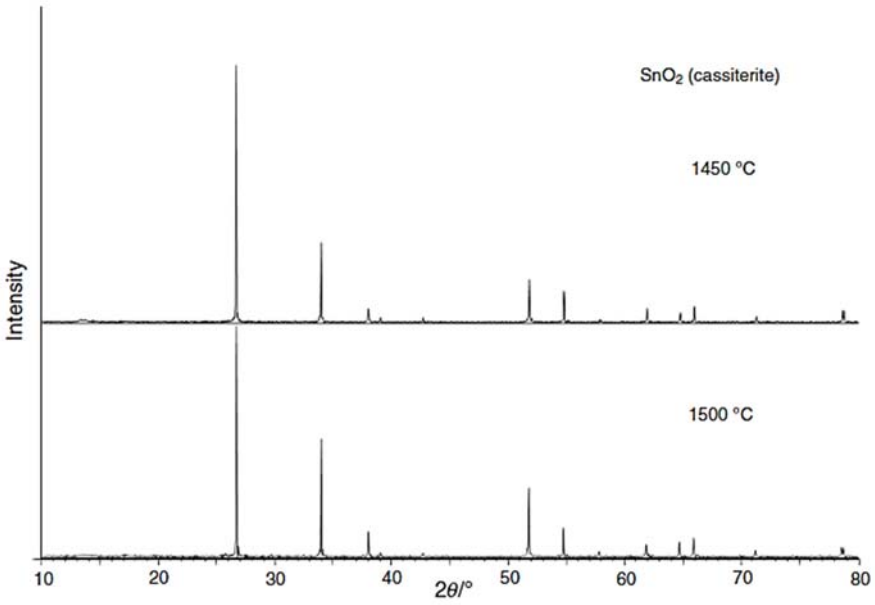

Fig. 5 X-ray diffraction patterns of $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ synthesized at calcination temperature 1450 °C and 1500 °C

3.3 Colour properties of prepared pigment

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 it is evident that the values of colour coordinates *a**, *b** and value *C* (chroma) subsequently increase with ascending temperature of calcination up to 1450 °C. 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 297.4 to 307.3°. The admixture of terbium ions has a positive effect on colour properties. The comparison of synthesised pigments $Sn_{0.760}Co_{0.08}P_{0.16}O_2$ and $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ 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 hue angle *H° (Figure 6)*. It means that $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ pigments in comparison with $Sn_{0.760}Co_{0.08}P_{0.16}O_2$ are shifted closer toward blue-violet shades. The best results are obtained with ions of terbium as admixture at the calcination temperature 1450 °C. In

this case, the sample acquires the highest value of colour coordinate a^* (22.0), the highest value of chroma (36.3) and the highest value of hue angle (307.3°). This sample is characterised by violet colour.

Table 4: CIE L*a*b* parameters of $Sn_{0.76}Co_{0.08}P_{0.16}O_2$ pigments applied into the organic matrix and into the ceramic glaze

T [°C]	Organic binder					Ceramic glaze				
	L*	a*	b*	C	H°	L*	a*	b*	C	H°
1350	56.2	7.9	-15.3	17.2	297.2	46.6	8.1	-25.2	26.5	288.9
1400	57.0	4.6	-10.0	11.1	294.7	45.8	8.8	-26.6	28.0	288.2
1450	59.1	6.9	-13.3	14.9	297.1	47.7	6.4	-23.4	24.2	285.3
1500	49.3	12.3	-17.3	21.2	305.3	45.4	9.1	-24.4	26.0	290.5

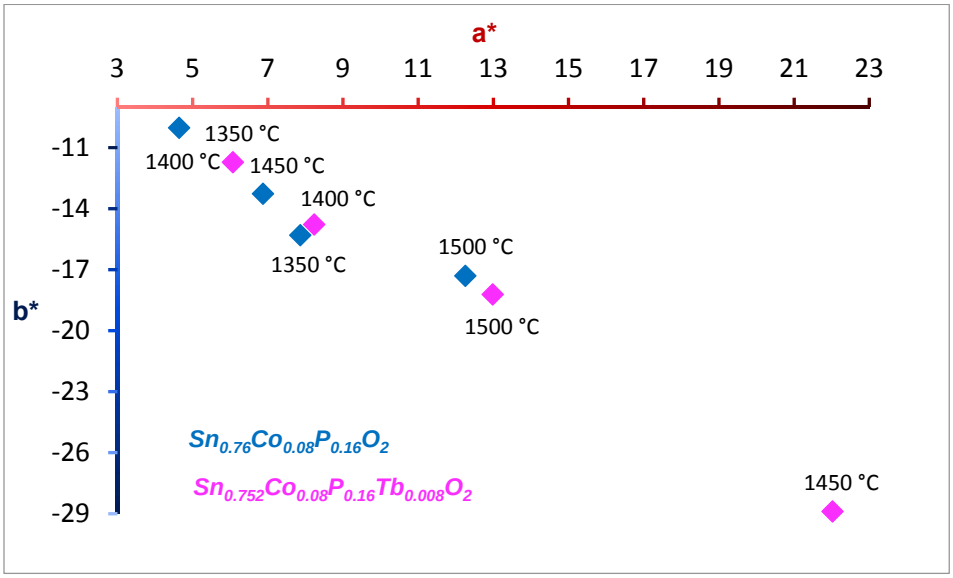

Fig. 6: The comparison of colour properties of $Sn_{0.760}Co_{0.008}P_{0.16}O_2$ and $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ pigments applied into organic matrix

The second system represents 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. 4 and Tab. 5. In the case of the $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ 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** (10.0) and also the highest value of chroma (29.0) is achieved. The comparison of synthesised pigments $Sn_{0.760}Co_{0.08}P_{0.16}O_2$ and $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ 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 $Sn_{0.76}Co_{0.08}P_{0.16}O_2$ 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 $Sn_{0.760}Co_{0.08}P_{0.16}O_2$.

Table 5: CIE L*a*b* parameters of $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ pigments applied into the organic matrix and into the ceramic glaze

T [°C]	Organic binder					Ceramic glaze				
	L*	a*	b*	C	H°	L*	a*	b*	C	H°
1350	61.5	6.1	-11.7	13.2	297.4	45.5	7.4	-23.4	24.6	287.6
1400	58.3	8.2	-14.8	16.9	299.1	46.6	8.0	-25.3	26.6	287.6
1450	45.3	22.0	-28.9	36.3	307.3	43.7	9.1	-26.8	28.3	288.8
1500	54.9	13.0	-18.2	22.4	305.5	40.4	10.0	-27.2	29.0	290.0

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 $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ pigments provided in both applications (organic matrix, ceramic glaze) required blue or blue-violet colouration.

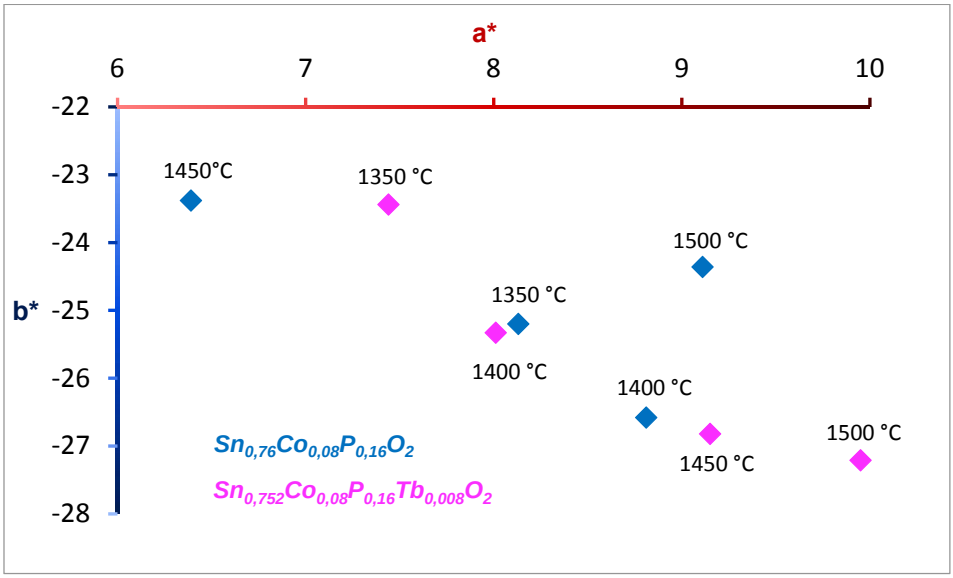

Fig. 7: The comparison of colour properties of $Sn_{0.760}Co_{0.008}P_{0.16}O_2$ and $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ pigments applied into the ceramic glaze

3.4 Particle size distribution of prepared pigments

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 6 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 6: Particle size distribution of the samples $Sn_{0.760}Co_{0.008}P_{0.16}O_2$ and $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$

Sample	T /°C	d_{10} /μm	d_{50} /μm	d_{90} /μm
$Sn_{0.760}Co_{0.08}P_{0.16}O_2$	1350	0.9	7.7	36.9
	1400	1.0	8.3	41.6
	1450	1.2	10.5	63.2
	1500	1.2	13.7	75.6
$Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$	1350	0.9	6.4	40.1
	1400	0.9	6.9	38.2
	1450	0.8	7.0	43.9
	1500	1.0	9.0	59.6

4 CONCLUSION

The main aim of this part of dissertation thesis was to prepare blue-violet $Sn_{0.76}Co_{0.08}P_{0.16}O_2$ and $Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O_2$ ceramic pigments. The samples were synthesised by ceramic method. 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. The results of XRD analysis 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 $Sn_{0.760}Co_{0.008}P_{0.16}O_2$ 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 6.4 – 13.7 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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