

THE EFFECT OF PREPARATION METHOD ON COLOUR PROPERTIES OF TERBIUM DOPED CASSITERITE PIGMENTS

Karolová L., Luxová J., Dohnalová Ž.

*University of Pardubice, Faculty of Chemical Technology, Department of Inorganic Technology, Studentská 95, 532 10, Pardubice, Czech Republic
lucie.karolova@student.upce.cz*

Abstract

The presented work deals with the possibility of synthesis of blue-violet cassiterite pigments in which a part of tin ions was substituted by cobalt and terbium ions. In this case, phosphorous ions are used as charge-compensating elements. The compounds of formula $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ were prepared by solid state reaction using the classical ceramic method and also by the method of dry mechanical activation. The goal was to develop conditions for synthesis and the most suitable preparation method of these pigments. The temperature range was chosen from 1,350 to 1,500 °C. The synthesised pigments were characterised in terms of colour properties after their application into the transparent ceramic glaze P 074 91 and into the organic binder. They were also studied with respect to their phase composition as well as the particles size distribution.

INTRODUCTION

Inorganic pigments are a fundamental part of many decorative and protective coatings. They are widely used in ceramic industry as a colourant for glazes. Therefore, ceramic pigments must possess superior colouring force in the molten glaze and high thermal stability¹. As known, ceramic pigments are composed of metal oxide or metal oxide compounds². Stannic pigments with the structure of cassiterite mineral are classified as the important ceramic pigments based on tin compounds³. Cassiterite pigments are based on tin dioxide respectively they are mixed oxides, where tin dioxide is the main component. 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)⁴⁻⁷. By partial substitution of Sn (IV) ions (0.069 nm) for ions of suited chromophores, a colour change in originally colourless system is achieved⁸. In this research the ions of cobalt and terbium as chromophores were chosen. 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)⁹. Due to Co ions (II) 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 P (V) ions are used as charge-compensating elements. In the presented work, the effect of preparation method on pigmentary properties of cassiterite pigments with formula $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ was studied. Moreover, the goal was to develop conditions (especially calcination temperature) for the synthesis 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 from the standpoint of their structure, colour properties and particle size distribution.

EXPERIMENTAL

Synthesis of cassiterite pigments

Pigments $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ were synthesised by two methods of preparation. The both methods of the synthesis were based on the classical ceramic route, i.e. solid state reaction. The first of them was the classical method (CM) which makes use of homogenization of starting raw materials presented in a form of powder compounds: SnO_2 (>99.9%, Alfa Aesar, Germany), $\text{Co}(\text{OH})_2$ (>99%, 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%, Indian Rare Earths Ltd., India). Above mentioned compounds were weighed in the required stoichiometric amounts and then were homogenized 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 $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and the calcination temperature of 1,350 - 1,500 °C was maintained for three hours. All samples were gradually cooled to room temperature and ground in an agate mortar. The other method of solid state reaction (MA) was innovated by

the mechano-chemical activation prior to calcination. The high energy milling process was carried out in a planetary mill Pulverisette 5 (Fritsch, GmbH Idar-Oberstein, Germany). The reaction mixtures were ground with agate balls ($\varnothing 10$ mm) in a ball-to-powder weight ratio of 18:1. The milling was carried out for 5 hours at a rotational velocity of 200 rps. The activated reaction mixtures were transferred into corundum crucibles and exposed to the same calcining process as in the previous method.

Application of the pigments into organic matrix and ceramic glaze

The calcinated powder samples were applied into an 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 amount of a pigment sample 10 wt%. For testing in organic binder, suspension containing 1 g of the sample and 1.5 cm³ 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 1,050 °C for 15 min.

The XRD analysis

The phase analysis of the powdered materials was studied by X-ray diffraction analysis. The phase composition was determined using diffractometer D8 Advance (Bruker AXS, UK) equipped with a vertical goniometer of 17 cm in 2θ range of 10-80°. X-ray tube with Cu anode ($U = 40$ kV, $I = 30$ mA), secondary graphite monochromator, scintillation NaI(Tl) counter, and X-ray of copper were used. Wavelength of the applied X-ray is $K\alpha_1 = 0.15418$ 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°. 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; $H^\circ = 350-35^\circ$ (for red), $H^\circ = 35-70^\circ$ (for orange), $H^\circ = 70-105^\circ$ (for yellow), $H^\circ = 105-195^\circ$ (for green), $H^\circ = 195-285^\circ$ (for blue), $H^\circ = 285-350^\circ$ (for violet). Chroma C and hue angle H° of samples were calculated according to the Eqs. (1) and (2)¹⁰.

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

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

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 homogenized in solution of Na₄P₂O₇ ($c = 0.15$ mol dm⁻³) for 120 s. The

signal was evaluated on the basis of Fraunhofer diffraction. The measurement is performed in three steps, results are automatically calculated as average and presented as d_{10} , d_{50} , d_{90} and $span$ values Eqs.(3).

$$span = \frac{d_{90}-d_{10}}{d_{50}} \quad (3)$$

DISCUSSION AND RESULT ANALYSIS

XRD analysis

The synthesised powder compounds were studied by XRD analysis. The diffractograms of the samples, which were prepared by classical ceramic method, were single-phase at all synthesis temperatures. The only major crystalline phase corresponding to tetragonal cassiterite structure of SnO₂ (JCPDS No. 77-0452) with P4₂/mm symmetry was confirmed. No other phases were detected in the XRD patterns. The intensities of peaks increase with calcination temperature, which means that the peaks are the sharpest and the most intense at 1,450 °C. The highest calcination temperature (1,500 °C) caused a slight decrease of the peak intensity of cassiterite phase. The contraction of lattice constants confirmed the incorporation of Co (II) and Tb (IV) ions in SnO₂ host lattice (lattice parameters of pure SnO₂: $a = 0.473700$ nm and $c = 0.318500$ nm). The phase composition was also evaluated at pigments, which were prepared by dry mechanical activation. From the presented results follows, that second minor phase was observed. This phase corresponds to cubic SnP₂O₇ (JCPDS No. 29-1352) with Pa-3 symmetry was identified in the temperature range from 1,350 to 1450 °C. The intensities of peaks increase with calcination temperature and at the temperature of 1,500 °C slightly decrease as in the case of pigments, which were prepared by the classical ceramic method.

Table I

The effect preparation method and calcination temperature on the phase composition of powder Sn_{0.752}Co_{0.08}P_{0.16}Tb_{0.008}O₂

Method of preparation	Temperature [°C]	Structure	a [nm]	c [nm]
Classical ceramic method	1,350	tetragonal SnO ₂	0.473662	0.318631
	1,400		0.473674	0.318639
	1,450		0.473694	0.318645
	1,500		0.473700	0.318550
Dry mechanical activation	1,350	tetragonal SnO ₂	0.473595	0.318629
		cubic SnP ₂ O ₇	0.739601	
	1,400	tetragonal SnO ₂	0.473690	0.318638
		cubic SnP ₂ O ₇	0.793512	
	1,450	tetragonal SnO ₂	0.473693	0.318665
		cubic SnP ₂ O ₇	0.793180	
1,500	tetragonal SnO ₂	0.473721	0.318549	

Colour properties

In this part, the effect of growing calcination temperature and the effect of preparation method on colour properties of the cassiterite pigments were investigated. At first, the powder materials were prepared by the classical ceramic method and they were applied into the organic matrix in mass tone. From Table II is evident that the values of colour coordinates a^* , b^* and value of C (chroma) gradually increase up to 1,450 °C. On the other hand, the values of coordinates L^* (lightness) decline – pigments seem darker. All pigments produced blue-violet hue because the value H° lay in range from 297° to 308°. After application into the organic binder, these samples provided violet colour. The best results were obtained at calcination temperature 1,450°C. In this case, the prepared sample disposes 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 intensive violet colour.

Table II

The effect of calcination temperature on colour properties and particle size distribution of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments prepared by classical ceramic method and applied into organic binder

$T [^\circ\text{C}]$	L^*	a^*	b^*	C	H°	$d_{50} [\mu\text{m}]$	span
1,350	61.55	6.07	-11.72	13.20	297.38	6.44	5.49
1,400	58.31	8.23	-14.78	16.92	299.11	6.87	5.43
1,450	45.37	22.02	-28.83	36.33	307.31	7.05	6.10
1,500	54.86	12.98	-18.22	22.37	305.47	9.04	6.48

The comparison of synthesised pigments by dry mechanical activation (*Table III*) in terms of acquired colour properties showed that pigments which were synthesised by the classical ceramic method provided better results. The pigments prepared using mechanical activation had rather a dark grey than violet colouration. It was caused by very low values of chroma C (from 3.48 to 10.07) and very low values of both colour coordinates a^* , b^* . The negative changes of colour properties were probably caused by presence of secondary phase – cubic SnP_2O_7 . The growth of the calcination temperature had not a positive effect on colour properties and therefore the best results were achieved at lowest calcination temperature (1,350 °C). This compound is characterised by grey-blue colour after application into the organic binder.

Table III

The effect of calcination temperature on colour properties and particle size distribution of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments prepared by dry mechanical activation and applied into organic binder

$T [^\circ\text{C}]$	L^*	a^*	b^*	C	H°	$d_{50} [\mu\text{m}]$	span
1,350	58.73	4.45	-9.03	10.07	296.23	6.51	5.81
1,400	56.11	1.44	-5.02	5.22	286.00	6.86	4.03
1,450	55.14	1.22	-3.26	3.48	290.50	5.38	5.50
1,500	58.28	2.47	-5.87	6.37	292.81	7.71	5.50

The prepared powder materials were applied into the transparent ceramic glaze as well. The colour properties of the samples were different in comparison with the organic binder. First, pigments which were prepared by the classical ceramic method. From *Table IV* is apparent that the values of colour coordinate b^* and value C (chroma) moderately increase up to 1,500 °C. The values of coordinate L^* (lightness) started to decline markedly in the temperature range of 1,450-1,500 °C. All pigments produced blue-violet hue with higher contribution of blue. The best results were obtained at calcination temperature 1,500°C. In point of fact, the sample disposes of the highest value of colour coordinate a^* (9.95), the highest value of chroma (28.97) and the highest value of hue angle (290.09°).

Table IV

The effect of calcination temperature on colour properties and particle size distribution of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments prepared by classical ceramic method and applied into ceramic glaze

$T [^\circ\text{C}]$	L^*	a^*	b^*	C	H°	$d_{50} [\mu\text{m}]$	span
1,350	46.54	7.44	-23.44	24.59	287.61	6.44	5.49
1,400	46.61	8.01	-25.33	26.57	287.55	6.87	5.43
1,450	43.65	9.15	-26.82	28.34	288.84	7.05	6.10
1,500	40.43	9.95	-27.21	28.97	290.09	9.04	6.48

If we are talking about the application of prepared powder pigments using mechanical activation into ceramic glaze, we can say that in comparison with pigments prepared by classical ceramic method were obtained pigments with lower values of lightness L^* (*Table V*). The colour coordinate a^* had not the obvious trend according to the growing temperature and colour coordinate b^* did not change significantly. At prepared pigments, decreasing values of angle H° were achieved. It means that final colour was shifted closer toward blue shades than blue-violet. As in the case of application into the organic binder, the best results were achieved at temperature of 1,350 °C. This sample had a higher value of coordinate a^* (8.73) and chroma C .

Table V

The effect of calcination temperature on colour properties and particle size distribution of $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ pigments prepared by dry mechanical activation and applied into ceramic glaze.

$T [^\circ\text{C}]$	L^*	a^*	b^*	C	H°	$d_{50} [\mu\text{m}]$	span
1,350	47.08	8.73	-26.97	28.35	287.14	6.51	4.03
1,400	50.58	7.88	-26.34	27.49	286.66	6.86	5.50
1,450	53.13	7.15	-25.96	26.93	285.40	5.38	5.50
1,500	49.77	7.99	-26.48	27.66	286.79	7.71	5.81

Particle size distribution

The particle size distribution of pigments was also measured. It belongs to the one of the most significant measured properties of synthesised powders and it can affect optical properties (final colour of pigments) and opacity. The most important value, which characterises particle size, is the value of d_{50} . The samples of pigments which were prepared by the classic ceramic method are characterised by higher mean values d_{50} of particles in the interval from approx. 6–10 μm . In the case of dry mechanical activation, where the reaction mixture were milled for 5 hours before the calcination, was the mean of particle size in the interval approx. 5–8 μm . The increasing calcination temperature made the increase of values d_{50} for both ways of preparation. The size range of 5–10 μm predicts the effective utilisation of the pigments for the colouring of ceramic glaze. For their applications into organic binders, it would be appropriate to treat the d_{50} to a value of about of 2 μm .

CONCLUSION

The main aim of the research was to prepare blue-violet $\text{Sn}_{0.752}\text{Co}_{0.08}\text{P}_{0.16}\text{Tb}_{0.008}\text{O}_2$ ceramic pigments. The samples were synthesised by the classical ceramic method and by dry mechanical activation, which are based on solid state reaction. The calcination temperatures were chosen in the range of 1,350–1,500 $^\circ\text{C}$. Studies of X-ray diffraction showed that single-phased samples were prepared by the classical ceramic method at all calcination temperatures. In the case of using dry mechanical activation, the presence of secondary phase – cubic SnP_2O_7 , was observed at calcination temperatures 1,350, 1400 and 1,450 $^\circ\text{C}$. The preferable method for preparation of cassiterite pigment is the classical ceramic method. In this method, 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 1,450 $^\circ\text{C}$ for application into the organic binder and 1,500 $^\circ\text{C}$ for application into the ceramic glaze. For pigments prepared using dry mechanical activation was found to be the best calcination temperature 1,350 $^\circ\text{C}$ in both applications. However neither at this calcination temperature was obtained such interesting colour shades as in the case using classical ceramic method. Cassiterite pigments doped by ions of terbium provided violet (classical ceramic method) and grey (dry mechanical activation) shades in the organic binder and blue-violet shades in the ceramic glaze. The mean of particle size d_{50} moved in range 5.38–9.04 μm in dependence on synthesis temperature (the predominantly increasing character with increasing calcination temperature), and this particle size is appropriate for the potential using in ceramic glazes.

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References

1. Buxbaum G., Pfaff G., Industrial Inorganic Pigments. Wiley, Weinheim, 2005.
2. Eppler D.R., Eppler R.A.: Ceram. Eng. Sci. Proc. 18, 139 (1997).

3. Batzill M., Diebold U.: *Prog. Surf. Sci.* 79, 47 (2005).
4. CPMA, Classification and chemical description of the complex inorganic color pigments. Color Pigments Manufacturers Association, 2010.
5. Beatriz J., Beltrán H., Cordoncillo E., Escribano P., Folgado J.V., Vallet-Regí M., del Real R.P.: *Eur. J. Inorg. Chem.* 10, 2694 (2002).
6. Fujiyoshi K., Yokoyama H.: *J. Am. Ceram. Soc.* 76, 981(1993).
7. Tena M.A., Sorlí S., Llusar M., Badenes J.A., Forés A., Monrós G.: *Z. Anorg. Alleg. Chem.* 631, 2188(2005).
8. Shannon R.D.: *Acta Cryst.* A32, 751 (1976).
9. Monari G., Manfredini T.: *Ceram. Eng. Sci. Proc.* 17, 109 (1996).
10. Völz H.G.: *Industrial Color Testing: Fundamentals and Techniques.* Wiley, Weinheim, 2002.