

SYNTHESIS AND CHARACTERIZATION OF MIXED OXIDE PIGMENT $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$

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Abstract

The novel environmentally friendly inorganic yellow pigment based on bismuth oxide, $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$, was successfully synthesized. The influence of synthesis conditions on the product properties was examined. Samples of the pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ were obtained by solid-state reaction and various homogenisation methods of initial components were employed (hand-milling, dry and wet ball-milling). Focusing on the pigmentary application, specific properties of the samples were evaluated, such as particle size distribution and colour parameters. The homogenization by hand-milling can be rated as the best method of preparation for this composition, which provides saturated yellow and yellow-orange hues in an organic matrix and ceramic glaze. The lowest value of the mean particle size was achieved by wet ball-milling ($d_{50} = 1.49\text{-}5.72 \mu\text{m}$). Based on obtained results, $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ could be considered as a perspective high-performance pigment which has a potential to be alternative yellow-orange colourant for paint, plastics, ceramics and building materials.

Introduction

Inorganic pigments are applied in a wide range of products such as paints, ceramics, porcelains, plastics, enamels and glasses, due to their high thermal and ultraviolet stability compared to organic pigments¹. One of the first synthetic yellow pigments is called Naples yellow $\text{Pb}_2\text{Sb}_2\text{O}_7$. This pigment represents sulphur-yellow up to orange-yellow tint depending on the mass ratio of lead and antimony². Typical modern yellow inorganic pigments include chromate compounds of lead, cadmium sulphides and bismuth vanadates³.

There is a strong incentive to develop new yellow-coloured inorganic materials to substitute for industrial pigments that are based on toxic metals hazardous to human health and the environment. Nowadays, the industrial utilization of lanthanides is rapidly growing because of their known low toxicity^{4,5}. The compounds on the base of Bi_2O_3 belong to pigments of oxide types and seem to be interesting, because they provide interesting colour hues from yellow to orange. Intense colours of these pigments are based on the incorporation of doped Ln ions into the host lattice of Bi_2O_3 ⁶. Among several earth-based nontoxic yellow pigments, CeO_2 , and related materials have come to the forefront because of their opacity, low toxicity and high thermal stability^{7,8}. From this point of view, the studied compound can be described by the pyrochlore structure with the general composition $\text{A}_2\text{B}_2\text{O}_7$. Composition electroneutrality can be achieved with several combinations of different valences for cation species A and B⁹. The pyrochlore structure is closely related to fluorite and can be considered as an ordered defective fluorite. It exhibits space group $\text{Fd}\bar{3}\text{m}$ with eight formula units within the cubic unit cell¹⁰. Pyrochlore oxides display a remarkable range of physical properties, including metallic, semiconducting or ionic electrical behaviour that can be controlled by doping. The bismuth-based pyrochlores can be used for applications including high-frequency multilayer capacitors, catalysts, thin film resistors and other¹¹.

In our research, we have employed solid-state reaction in combination with different homogenisation method of initial compounds (hand-milling, dry and wet ball-milling) in order to reveal the best method of preparation of pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ in relation to its important characteristics for the pigmentary application.

Experimental

$\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ samples were synthesized by methods which are based on classical ceramic route, i.e. solid state reaction. For this purpose, hand-milling, dry ball-milling and wet ball-milling were applied. For hand- and ball-milling methods, initial compounds Bi_2O_3 (99.9 % purity, ML-Chemica, CZ), ZnO (>99 % purity, The Shepherd Color Company, USA), CeO_2 (99.9% purity, ML-Chemica, CZ) and Nb_2O_5 (99.8% purity, Bochemie, a.s., CZ) were used. Reaction mixtures were thoroughly homogenised in an agate mortar with a pestle by hand grinding or in an agate form by ball-milling in a planetary mill (Pulverisette 5, Fritsch, Germany). Wet ball-milling of the samples was performed in ethanol-water media (volume ratio 1:1). For dry and wet ball-milling, rotation speed of 200 rpm was employed and the homogenisation time was 2 h. The resulting homogeneous liquid mixture was dried at 100 °C during 2 h. In case of hand-milling, raw materials were

blended and homogenised in a porcelain mortar for 15 min. After the hand- and ball-milling, the homogenous mixtures were calcined in corundum crucibles in an electric furnace at temperatures from 850 °C to 1050 °C. The samples were maintained for 2 h with the heating rate of 10 °C/min. The synthesized samples were left to cool at ambient temperature and subsequently ground in a porcelain mortar.

All prepared pigments were applied to an organic matrix (dispersive acrylic paint Parketol, Balakom, a.s., CZ) in mass tone. The suspension containing 1 g of the pigment and approx. 2 cm³ of a binder were homogenised. Colour paints were prepared by deposition of the slurries on the white nonabsorbing paper. Layers of paint film were created by a pulling of the Bird applicator slit width of 100 µm. Coating films were allowed to dry in the air for 1-2 h. For testing in the ceramic glaze, the pigments were also applied into medium-temperature borate-silicate ceramic glaze G 070 91 (Glazura, s.r.o., Roudnice nad Labem, CZ). The aqueous suspension containing 10 mass% of a pigment and 90 mass% of the glaze was applied by a brush to ceramic fragments, which were dried at room temperature and then calcined in an electric furnace at 1000 °C at a heating rate of 10 °C/min for 15 min.

Particle size distribution was measured using a laser scattering system based on Fraunhofer bending (Mastersizer 2000/MU, Malvern Instruments, GB). Used granulometer is highly integrated laser measuring device for analysis of particle size in the range from 2x10⁻⁵ to 2 mm. Results were automatically calculated as average and presented as a parameters d_{10} , d_{50} , d_{90} and span.

The colour properties of the samples were evaluated by measurement of spectral reflectance in the visible region of light (400-700 nm) using a ColorQuest XE (HunterLab, USA). The measurement conditions for colour change were following: an illuminant D65, 10° complementary observer and measuring geometry $d/8^\circ$. The colour properties are described in terms of CIE $L^*a^*b^*$ system (1976), where the values a^* (the axis red-green) and b^* (the axis yellow-blue) indicate the colour hue, the value L^* represents the lightness or darkness of the colour in relation to a neutral grey scale. The value C (chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The colour of pigment is also expressed by the hue angle H° defined by an angular position in the cylindrical colour space (for the orange $H^\circ = 35-70^\circ$ and for the yellow $H^\circ = 70-105^\circ$).

Results and discussion

The colour parameters of the obtained samples that were prepared by hand-grinded are stated in Table I. The colour tone of studied pigments after their application in organic matrix is characterized as yellow and orange. Increasing calcination temperature leads to a considerable shift in tones and primarily to weakening of the yellow to yellow-orange tone in all analysed pigments. The values of lightness L^* and hue angle H° are declining with an ascending temperature of calcination. The values H° of these samples lie approx. from 73° to 92°. On the other hand, the colour coordinates a^* and b^* and chroma C are increasing. The negative value of colour coordinate a^* (-1.85) was achieved at a temperature 900 °C and therefore in the final colour shade is small representation of green tone. Based on the investigation and evaluation of colour properties of the samples, the temperature 1050 °C is the best for preparation of dark yellow-orange colour, because the coordinate L^* has the lowest value (74.14) and the value of the hue angle H° (72.50) approximates the area that is represented by an orange shade. This sample also disposes by the highest value of the colour coordinate b^* (56.32), which corresponds to the contribution of yellow. Table I also demonstrates the influence of calcination temperature on the colour properties of pigments, which were applied into ceramic glaze. The samples can be characterized by lighter yellow colour shades. In this case, the colour coordinate b^* and chroma C have a growing tendency. The colour coordinate a^* achieves low values, which lie in narrow interval approx. 1-4. An increasing calcination temperature decreases values of lightness L^* and hue angle H° . For this application is the best highest calcination temperature, which was achieved darkest yellow shade. Generally, both types of application provide a dark yellow and yellow-orange shades, which correspond to the high values of chroma C .

Table I

An effect of calcination temperature on colour properties of pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ prepared by solid state reaction (hand-milling) and applied into organic matrix in mass tone and into ceramic glaze

T [°C]	Organic matrix					Ceramic glaze				
	L^*	a^*	b^*	C	H°	L^*	a^*	b^*	C	H°
850	86.49	1.87	41.50	41.54	87.42	86.11	1.47	41.91	41.94	87.99
900	89.28	-1.85	45.07	45.11	92.35	85.87	1.80	46.49	46.52	87.78
950	87.37	3.14	51.35	51.45	86.50	84.80	3.08	48.91	49.01	86.40
1000	78.08	12.54	50.21	51.75	75.98	84.76	2.84	50.41	50.49	86.78
1050	74.14	17.76	56.32	59.05	72.50	82.54	4.35	53.45	53.63	85.35

Results from samples which were homogenised by dry ball-milling are noticed in Table II. The pigments applied into organic matrix provided higher values of colour coordinates a^* , which correspond to the contribution of red colour. The growing temperature of calcination leads to a decrease of lightness L^* and hue angle H° . The opposite trend with increasing calcination temperature records the colour coordinate b^* and chroma C . These values increase up to 1000 °C and then come to the decline. Based on the lowest value of the lightness L^* (72.09) and hue angle H° (71.63) was evaluated as the most interesting yellow-orange the temperature 1050 °C. The second system for application was transparent glaze with glazing temperature 1000 °C. The pigments applied to ceramic glaze provided lower values of colour coordinates a^* and b^* and chroma C in comparison with the previous manner of homogenisation of the pigment. For these pigments, an application in ceramic glaze caused the small increase in the lightness L^* , which is in range approx. from 84 to 87. The samples are characterized by lighter yellow shade. This fact is confirmed by the values of angle H° that are located in the interval 86.61-88.95. The temperature 1050 °C is the most suitable for the application of the pigment into ceramic glaze, because the maximum values of the colour coordinate b^* (49.68) and chroma C (49.77) were obtained. Finally, this type of homogenisation provides lighter yellow and yellow-orange shades.

Table II

An effect of calcination temperature on colour properties of pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ prepared by solid state reaction (dry ball-milling) and applied into organic matrix in mass tone and into ceramic glaze

T [°C]	Organic matrix					Ceramic glaze				
	L^*	a^*	b^*	C	H°	L^*	a^*	b^*	C	H°
850	84.17	7.32	43.28	43.89	80.40	87.36	0.78	42.76	42.77	88.95
900	83.70	8.01	44.40	45.12	79.77	87.14	1.00	43.44	43.45	88.68
950	80.82	10.59	46.72	47.91	77.23	86.53	1.12	44.52	44.53	88.56
1000	78.19	14.03	50.58	52.49	74.50	85.97	1.52	47.21	47.23	88.16
1050	72.09	15.17	45.67	48.12	71.63	83.78	2.94	49.68	49.77	86.61

The last process for preparing of pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ (wet ball-milling) provided yellow and orange shades after the application of samples into the organic binder (Table III). From the table it follows that increasing calcination temperature decreases values of L^* and H° . Dark orange shade was achieved at the temperature 1050°C based on the lowest value of lightness L^* (71.79) and angle H° (69.90). On the other hand values of colour coordinates are growing. The negative colour coordinate a^* (at 850 °C) is in final colour shade in a small representation of green tone. The highest saturation C was obtained by temperature 1000 °C. The colour properties of pigments applied into ceramic glaze are very similar as at the previous method of preparation. These applications are characterized by low values of colour coordinate a^* and narrow interval of hue H° (86.29-89.37). While calcination temperature grows, the colour coordinate b^* and chroma C increase. The lightness L^* lies in the very narrow interval at the calcination temperature from 850 to 1000 °C. The sample calcinated at 1050 °C provides the darkest yellow shade in ceramic glaze.

Table III

An effect of calcination temperature on colour properties of pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ prepared by solid state reaction (wet ball-milling) and applied into organic matrix in mass tone and into ceramic glaze

T [°C]	Organic matrix					Ceramic glaze				
	L^*	a^*	b^*	C	H°	L^*	a^*	b^*	C	H°
850	89.86	-0.33	40.43	40.43	90.47	86.72	0.59	43.32	43.32	89.22
900	86.61	3.57	44.16	44.30	85.38	86.84	0.48	43.62	43.62	89.37
950	82.67	8.47	47.73	48.48	79.94	86.53	1.55	45.39	45.42	88.04
1000	78.66	11.64	50.18	51.51	76.94	86.04	1.10	48.85	48.86	88.71
1050	71.79	17.60	48.10	51.22	69.90	83.97	3.24	49.94	50.04	86.29

The particle size distribution of the samples depending on the method of preparation and calcination temperature was analysed using a laser scattering technique. Obtained results are presented in Table IV. The particle size values d_{10} , d_{50} and d_{90} correspond to the volume size limits of 10, 50 (median value) and 90% of the particles. The parameter span is the width of the distribution [$\text{span} = (d_{90} - d_{10})/d_{50}$]. Important to note, that particle size influences many properties of the pigments and is a valuable indicator of quality and performance. As it follows from the Table IV, the samples prepared by hand-milling can be characterized as very uniform with a narrow width of size distribution. Mean particle size d_{50} of samples calcinated at temperature 850-1000 °C lies in range from 3.08 to 4.64 μm . At the highest temperature, this value increases to 9.15 μm . The lowest value of parameter span was achieved at calcination temperature 1000 °C. Results from samples prepared by ball-milling are noticed in Table IV. The mean particle size d_{50} decreased at the whole temperature range (2.04-6.81 μm). From the values presented in Table IV it is visible that the mean particle size of prepared samples homogenised by ball-milling is rising with an ascending temperature of calcination. Specifically, the value d_{50} is in interval from 1.49 to 5.72 μm . In this case, the lowest value of span was achieved at 850 °C.

Table IV

An effect of calcination temperature on particle size distribution of pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$

T [°C]	Hand-milling				Dry ball-milling				Wet ball-milling			
	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]	span	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]	span	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]	span
850	0.51	3.08	9.92	3.06	0.47	2.04	15.10	7.17	0.38	1.49	3.88	2.36
900	0.60	3.48	11.73	3.20	0.47	2.08	14.61	6.79	0.42	1.89	5.07	2.46
950	0.66	3.75	12.33	3.11	0.51	2.36	15.86	6.50	0.44	2.11	5.83	2.55
1000	1.00	4.64	15.11	3.04	0.62	3.83	20.03	5.07	0.53	3.01	10.22	3.22
1050	1.99	9.15	29.85	3.05	0.77	6.81	27.75	3.96	0.65	5.72	31.83	5.45

Conclusion

In our research, the influence of synthesis conditions on the formation of pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$ was examined. Obtained results indicate that the different ways of homogenisation of initial compounds are possible to employ for the synthesis of dark yellow and orange shades in an organic binder and ceramic glaze. The most important properties of prepared samples were evaluated in relation to its application in the pigmentary field. Homogenisation via hand-milling can be rated as the best method of preparation for the composition $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$. This way of homogenisation in terms of colour properties provides the satisfactory dark yellow-orange shade (1050 °C) in an organic binder in mass tone. This pigment exhibits the highest value of saturation C (59.05) and yellowness value b^* (56.32). The colour shade of sample approximates orange area due to the measured value of hue H° (72.50). The formation of dark yellow hue in the ceramic glaze is the most appropriate homogenisation by hand-grinded. On this case, it was achieved dark yellow shade at temperature 1050 °C ($H^\circ = 85.35^\circ$ and $C = 53.63$). The shift of hue into the pure orange area in organic matrix caused the method of wet ball-milling at the highest temperature ($H^\circ = 69.90^\circ$). The dry ball-milling process provided less saturated yellow and yellow-orange shades. It could be summarised that hand-milling homogenisation is more suitable for the development of yellow-orange pigment $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{CeNbO}_7$. In case of particle size distribution, the value of d_{50} grows with increasing temperature in all cases. The mean size of particles (at 1050 °C) is consistent with the requirements for use of pigment for ceramic purposes. The lowest value of mean particle size was achieved by wet ball-milling ($d_{50} = 1.49\text{-}5.72 \mu\text{m}$). Since the present

pigment consists of non-toxic elements, it should be an effective alternative to the commercially available yellow and orange pigments (chromate and cadmium pigments).

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