

THE MIXED OXIDE IN Bi₂O₃-ZnO-CeO₂ SYSTEM PREPARED BY SOLID STATE REACTION

TěšitelováK., ŠulcováP.

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

Abstract

Present work contains results related to the synthesis of mixed oxide inorganic pigments based on Bi₂O₃-ZnO-CeO₂. The sample with composition Bi_{1.5}Zn_{0.5}Ce₂O₇ was synthesized by solid state reaction. The prepared samples were characterized by X-ray diffraction analysis. XRD analysis indicates that mixed oxide pigments are multiphase. Colourimetric parameters were evaluated by measuring of the reflectance in the visible region of light. Studied powder materials with defect structure of CeO₂ are characterized by dark yellow and yellow-orange hues, depending on the calcination temperature. The mixed oxide pigments were also evaluated from the standpoint of their particle size distribution. A technological use of the prepared samples was tested by application into an organic matrix and middle temperature ceramic glaze.

Introduction

In the field of inorganic pigments is a current need to develop environmentally friendly inorganic materials without content of heavy metals (Pb, Cd, Sb, Se, Mo and Cr^{VI+}), which are unsuitable in terms of health and environmental protection¹. This fact opens the great necessity for development and investigation of new ecological pigments. For this reason, the main attention has been directed to the preparation of new material of oxide type which would be found useful as a colour pigment.

Numerous ternary oxides with the formula A₂B₂O₇, where A is a 3⁺ ion and B a 4⁺ ion adopt the pyrochlore structure. This cubic crystal, related to the fluorite structure, can accommodate a wide range of solid solution between BO₂ and A₂O₃ compounds. Elemental versatility ensures that pyrochlore compounds display a variety of interesting properties². Pyrochlore exhibits high chemical stability and catalytic activity at high temperatures in an oxidative coupling of methane³. They are of particular interest to the nuclear energy community as they have been proposed as a potential crystalline waste form for the immobilization of fission products and actinides⁴. Further, pyrochlores are an important class of fast ion conductors⁵. The pyrochlore structure is a superstructure of fluorite-type structure AO₂ (Fm-3m). In general, the introduction of trivalent B₂O₃ in fluorite-type AO₂ will lead to the formation of a defect fluorite. The pyrochlore structure is observed when r_A/r_B lies between 1.46 and 1.75, known as the radius ratio rule for pyrochlores. For the radius ratio lower than 1.46, defect fluorite is observed while for radius ratios higher than 1.75 a monoclinic structure is obtained. It could also simply be understood as follows – the closer are the ionic radii of A and B cations, the higher would be their tendency to randomize and they would crystallize as defect fluorite⁶.

In this research, we focused on the study of mixed oxide from Bi₂O₃-ZnO-CeO₂ as a new yellow inorganic pigment without toxic elements. The sample Bi_{1.5}Zn_{0.5}Ce₂O₇ was synthesized by solid state reaction. The introduction of smaller Zn²⁺ ions with ionic radii 0.074 nm into the Bi³⁺ (0.117 nm) sites of Bi₂Ce₂O₇ generates a defect fluorite structure. The goal was to develop conditions for the synthesis of this type of pigment and to determine the phase composition of prepared samples. The colour properties and particle size distribution of prepared samples were characterized.

Experimental

The mixed oxide inorganic pigment with composition Bi_{1.5}Zn_{0.5}Ce₂O₇ was prepared by solid state reaction. Bi₂O₃ (99.8 % purity, LachemaPliva, a.s., CZE), ZnO (98 % purity, SlovZink, a.s., SVK) and CeO₂ (99.9 % purity, ML-Chemica, CZE) were used for the sample preparation. The reagents were weighted in suitable molar proportions and ground manually in a porcelain mortar. The prepared mixture was calcined in corundum crucibles in an electric resistance furnace at temperatures from 800 to 1000 °C with the step 50 °C for 20 hours. All samples were gently ground in a porcelain mortar before characterization.

The phase composition of all powder samples was studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using X-ray diffractometer (Empyrean, PANalytical, NLD).

All prepared samples were applied to an organic matrix (dispersive acrylic paint Parketol, Balakom, a.s., CZE) in mass tone and evaluated for colour change by measuring of spectral reflectance in the visible region of light (400-700 nm) using a ColorQuest XE (HunterLab, USA). For testing in an organic matrix, suspensions containing 1 g of the pigment and 1.5 cm³ of a matrix were homogenized. Coloured paints were prepared by deposition of the slurries on the white not absorbing paper. The thickness of the wet film was 100 μm. The prepared samples (10 wt.% of mixed oxide pigment) were also applied into a middle temperature borate-silicate transparent glaze G 07016 (Glazura, s.r.o., CZE). The slurries were deposited using a brush on wall tile bodies. The temperature of glazing was 1000 °C during the time of 15 min. The measurements conditions for colour change were following: an illuminant D65, 10° complementary observer and measuring geometry d/8°. The colour properties are described in terms of CIE $L^*a^*b^*$ (1976)⁷.

The distribution of particle sizes of the calcined powders was obtained by laser scattering using Mastersizer 2000/MU (Malvern Instruments, Ltd., GBR). The equipment employs a scattering of incident light on particles. The samples were ultrasonically homogenized in Na₄P₂O₇ solution ($c = 0.15 \text{ mol/dm}^3$) for 120 s and measured. The signal was evaluated on the basis of Fraunhofer bending.

Results and discussion

Incorporation of the zinc ions into lattice Bi₂Ce₂O₇ was studied by X-ray diffraction analysis. From previous scientific studies, the structure of Bi₂Ce₂O₇ can be viewed as a disorder CeO₂ structure with the Bi and Ce atoms associated with the 4a Wyckoff site with an occupancy of ½. The model would demand the oxygen atom to be associated with 8c site. The calcination of the reaction mixtures at all temperature did not result in a single product. XRD diffractograms at the calcination temperature 800, 850, 900 and 950 °C contain next to the lines of cubic CeO₂ (lattice parameters: $a = 0.5411 \text{ nm}$, $b = 0.5411 \text{ nm}$ and $c = 0.5411 \text{ nm}$) with Fm-3m space group and cubic Bi₁₂ZnO₂₀ (lattice parameters: $a = 1.0205 \text{ nm}$, $b = 1.0205 \text{ nm}$ and $c = 1.0205 \text{ nm}$) with I23 space group also the lines of unreacted zinc oxide ZnO (lattice parameters: $a = 0.3250 \text{ nm}$, $b = 0.3250 \text{ nm}$ and $c = 0.5207 \text{ nm}$) with hexagonal space group P63mc. The lines of monoclinic Bi₂O₃ (lattice parameters: $a = 0.5844 \text{ nm}$, $b = 0.8157 \text{ nm}$ and $c = 0.7503 \text{ nm}$) with P21/c space group next to the lines of CeO₂ and ZnO were identified at the diffraction patterns of powder heated at the highest temperature 1000 °C. The detected phases are summarized in Table I. The results of X-ray diffraction analysis confirmed that studied mixed oxide pigment with theoretical composition Bi_{1.5}Zn_{0.5}Ce₂O₇ provides a defect fluorite structure. This fact is confirmed by an ionic radius of studied mixed oxide. In this case the ionic radius is equal to 1.03, which corresponds to the formation of defect fluorite structure.

Table I

The phase composition of mixed oxide inorganic pigment from Bi₂O₃-ZnO-CeO₂ system

Temperature [°C]	Detected phases	Crystal structure	JPDF number
800	CeO ₂	cubic	04-016-6345
	Bi ₁₂ ZnO ₂₀	cubic	01-078-1325
	ZnO	hexagonal	01-075-9742
850	CeO ₂	cubic	04-016-6345
	Bi ₁₂ ZnO ₂₀	cubic	01-078-1325
	ZnO	hexagonal	01-075-9742
900	CeO ₂	cubic	04-016-6345
	Bi ₁₂ ZnO ₂₀	cubic	01-078-1325
	ZnO	hexagonal	01-075-9742
950	CeO ₂	cubic	04-016-6345
	Bi ₁₂ ZnO ₂₀	cubic	01-078-1325
	ZnO	hexagonal	01-075-9742
1000	CeO ₂	cubic	04-016-6345
	Bi ₂ O ₃	monoclinic	04-011-1986
	ZnO	hexagonal	01-075-9742

The optical parameters of synthesized mixed oxide inorganic pigments after their application to the organic matrix are summarized in Table II. The lightness L^* of the samples decreases with an increasing calcination temperature (in the interval from 800 to 900 °C) and it means darkening of the samples. Thereafter, this value has an increasing character up to the 1000 °C. The colour coordinate b^* , expressing an amount of yellow hue,

lies in the whole calcination temperature in the range from approx. 50 to 69. On the other hand, the values of the colour coordinate a^* , which corresponds to the red contribution, are distinctly lower and lies in the interval approx. from 1 to 17. The chroma C of the samples lies in the very narrow interval approx. from 50 to 54. Only at the temperature 900 °C, the chroma disposes of the highest value, which is equal to 70.96. The similar trend occurred at the values of hue angle H° , where values lie in the range from approx. 81 to 89 at the calcination temperature 800, 850, 950 and 1000 °C. The sample, which was calcined at 900 °C produces yellow-orange hue because its hue angle H° has the lowest value (76.54). Based on the investigation and evaluation of colour properties of the samples, the temperature 900 °C is the best for the preparation of dark yellow-orange colour, because the coordinate L^* has the lowest value (76.74) and the value of the hue angle H° approximates the area that is represented by an orange shade.

The values of mean size value (d_{50}) of the mixed oxide pigments vary between 6.5 and 11.3 μm (Table II). For further application of these powders, it would be a necessary need to use of additional intensive milling. For this reason, the sample (calcined at 900 °C) with lower lightness L^* is better to use, because during milling particle size is decreased and lightness increases. Parameter $span$ informs about monodispersivity of the samples. The lowest value was achieved at calcination temperature 950 °C.

Table II

The effect of calcination temperature on colour properties in an organic matrix in mass tone and particle size distribution of mixed oxide inorganic pigment from $\text{Bi}_2\text{O}_3\text{-ZnO-CeO}_2$ system

Temperature [°C]	L^*	a^*	b^*	C	H°	$d_{50}[\mu\text{m}]$	$span$
800	83.87	1.18	53.55	53.56	88.74	10.3	4.3
850	79.63	4.41	50.11	50.30	84.97	9.9	4.4
900	76.74	16.52	69.01	70.96	76.54	11.3	4.5
950	79.23	7.46	49.62	50.18	81.45	8.2	3.7
1000	81.46	4.83	51.69	51.92	84.66	6.5	5.2

The colour shade of mixed oxide pigments applied into ceramic glaze is in all cases light yellow-green. The negative values (from -4.41 to -3.17) of the colour coordinate a^* of samples indicate a certain amount of green hue in the resultant colouration (Table III). This fact is confirmed by the high values of hue angle H° that are located in interval approx. 95-97. In this case, the colour coordinate b^* has an increasing character in the whole temperature range. The prepared samples can be characterized by high grant of lightness L^* , which lies in a narrow interval from 87.44 to 88.42. Visual comparison of this application with the application to the organic binder showed that application into ceramic glaze does not make such attractive colour shades.

Table III

The effect of calcination temperature on colour properties in ceramic glaze of mixed oxide inorganic pigment from $\text{Bi}_2\text{O}_3\text{-ZnO-CeO}_2$ system

Temperature [°C]	L^*	a^*	b^*	C	H°
800	88.42	-3.98	34.13	34.36	96.56
850	87.44	-4.41	35.63	35.90	97.06
900	87.45	-3.17	37.93	38.06	94.78
950	87.60	-3.36	39.65	39.79	94.84
1000	88.35	-3.67	40.60	40.77	95.17

Conclusion

The main aim of the present work was to synthesize mixed oxide pigment from $\text{Bi}_2\text{O}_3\text{-ZnO-CeO}_2$ system with theoretical composition $\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Ce}_2\text{O}_7$ and to find out whether the calcination temperature can affect its phase composition, colour properties and particle size distribution.

The phase analysis showed that the applied calcination interval from 800 to 1000 °C is not sufficient to obtain single phase samples. The samples are characterized by defect structure of CeO_2 with the presence of cubic phase of $\text{Bi}_{12}\text{ZnO}_{20}$ and unreacted hexagonal phase of ZnO. At the highest calcination temperature was detected a monoclinic phase of Bi_2O_3 . The colour properties of these mixed oxide inorganic pigments depended on the calcination condition and particle size distribution, and the most intensive yellow-orange hue after the application to the organic binder was obtained for the sample calcinated at 900 °C. The colour properties of this sample are characterized by $L^*a^*b^*$ colour parameters of $L^* = 76.74$, $b^* = 69.01$, $C = 70.96$ and $H^\circ = 76.54$. In comparison with an application into organic matrix in terms of an acquired colour properties showed that

pigments applied to ceramic glaze provided a lighter yellow colour with green contribution due to negative values of colour coordinate a^* . The main size value d_{50} of the compounds is moved in the range 6.5-11.3 μm in the whole range of calcination temperatures (800 °C-1000 °C).

Obtained mixed oxide inorganic pigments from $\text{Bi}_2\text{O}_3\text{-ZnO-CeO}_2$ system are yellow, yellow-orange and yellow-green compounds, which can be recommended for colouring binders and ceramic glazes (after necessary milling), especially, for the colouring of the decorative lead containing glazes, which have a processing temperature below 1000 °C.

Acknowledgement

This work has been supported by University of Pardubice under the project SGS_2017_007 and by Grant Project of the Czech Science Foundation (No. 16-06697S).

References

1. Rosi F., Manuali V., Miliani C., Brunetti B. G. Sgamellotti A., Grygar T., Hradil D.: *J. Raman Spectrosc.*, **40**, 107-11 (2009).
2. Minervini L., Grimes R. W.: *J. Am. Ceram. Soc.*, **83**, 1873-78 (2000).
3. Sohn J. M., Kim M. R., Woo S. I.: *Catalysis Today*, **83**, 289-97 (2003).
4. Uberuaga B. P., Perriot R.: *Phys. Chem. Chem. Phys.*, **73**, 24215-23 (2015).
5. Norby T.: *J. Mater. Chem.*, **11**, 11-18 (2001).
6. Tyagi A. K., Banerjee S.: *Materials Under Extreme Conditions. Recent Trends and Future Prospects*. Elsevier, United Kingdom 2017.
7. Těšitelová K., Šulcová P.: *J. Therm. Anal. Calorim.*, **125**, 1047-52 (2016).