

Synthesis and colour properties of the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ pigments

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Abstract

$(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ solid solutions were synthesized as new inorganic yellow and orange pigments and their colour properties have been investigated as possible ecological materials. The host lattice of these pigments was Bi_2O_3 doped with the Lu^{3+} ions. The pigments were prepared by the solid state reaction of mixed oxides $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ with nominal compositions: $x = 0.1 - 0.9$ (with step 0.1). All the synthesized samples were found to have colour coordinates, low a^* and high b^* and exhibit the colour from yellow to orange.

Keywords: pigments, colour, calcination, Bi_2O_3 , Lu_2O_3

SYNTEZA I WŁAŚCIWOŚCI BARWNE PIGMENTÓW $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$

W pracy syntezowano roztwory stałe typu $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$, jako nowy rodzaj żółtych i pomarańczowych pigmentów o właściwościach korzystnych ze względów ekologicznych. Bazą takich pigmentów był Bi_2O_3 dotowany jonami Lu^{3+} . Pigmenty przygotowano poprzez reakcję w fazie stałej mieszaniny tlenków $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$, gdzie x zmieniało się w zakresie 0,1 – 0,9, co 0,1. Dla wszystkich wytworzonych próbek stwierdzono niską współrzędną barwy a^* i wysoką b^* oraz kolor od żółtego do pomarańczowego.

Słowa kluczowe: pigmenty, barwa, kalcynacja, Bi_2O_3 , Lu_2O_3

Introduction

The inorganic pigments in yellow, orange, red and maroon colours are always insufficiently represented for colouring of plastics, paints and ceramics. The majority of inorganic pigments for these applications currently contains the toxic metals such as cadmium, lead and hexavalent chromium. Thus, serious need arises to research for materials of environmentally friendly and economically viable materials for the replacement of toxic inorganic pigments [1]. From this point of view just 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 [2]. Intense colours of these pigments are based on the incorporation of doped Ln ions into the host lattice of Bi_2O_3 .

Bismuth trioxide has four polymorphs: monoclinic (or pseudo-orthorhombic) α -form, face-centred cubic (*fcc*) δ -form, tetragonal β -form and body-centred cubic (*bcc*) γ -form. From these polymorphs α - Bi_2O_3 is the only stable phase of pure Bi_2O_3 at room temperature. When pure α -phase is heated to about 730°C, transition to the δ - Bi_2O_3 occurs. This phase is stable only between 730°C and its melting point of 825°C. Large thermal hysteresis effects are present upon cooling, and δ phase transforms to one of the two intermediate phases which are β -form (formed at 650 °C) and γ -form (formed at 639°C). The γ -phase can be obtained by controlled cooling of β - Bi_2O_3 . The last two phases are metastable and they usually transform to the α -phase in the temperature range 650–500°C [3-5].

The high temperature phase of bismuth sesquioxides Bi_2O_3 , which is stable in the 730–825°C temperature range, has been intensively studied because of its high oxygen conductivity. The structure of the δ -phase is based on a face-centered cubic cation sublattice and can be described as a defective fluorite structure where 1/4 of the anion sites are vacant. This high oxygen vacancy concentration gives rise to high oxygen-ion mobility. The δ -phase may be stabilized below room temperature by partial cationic substitution of Bi^{3+} . Thus, the use of Ln^{3+} cations (Ln: lanthanide or yttrium) has been appeared effective though a variety of crystal phases have been observed depending on the kind and amount of the rare earth cation used and the synthesis conditions employed [6-8].

In the present study, the new pigments having the formula $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ with various rare earth concentration levels have been prepared. This type solid solution is synthesized by middle temperature calcination of the starting oxides (Bi_2O_3 and Lu_2O_3). These powder materials are expected to be new ecological pigments for colouring of paints or plastics.

Experimental

The starting materials used for the preparation of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ pigments were Bi_2O_3 of 99 % purity (Lachema Brno, Czech Republic) and Lu_2O_3 (Bochemie Bohumin, Czech Republic). Mixed oxides $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ with nominal compositions $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9

have been prepared. Above mentioned oxides were weighed in the required stoichiometric amounts and then were homogenized in an agate mortar. The mixtures were calcinated in porcelain crucibles in an electric resistance furnace. The heating of the furnace was programmed with increasing temperature at a rate of $10\text{ }^\circ\text{Cmin}^{-1}$ and the calcination temperature of 700, 750, 800 and $850\text{ }^\circ\text{C}$ was maintained for three hours.

The calcinated powder samples were applied to an organic matrix in mass tone. The final paints were evaluated for colour change by measuring spectral reflectance in the visible region of light (400-700 nm) using a Color Quest XE (HunterLab, USA). The measurement conditions 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). 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 zero (black) to hundred (white). The value C (Chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. 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: $\Delta E^*_{CIE} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔL^* , Δa^* , Δb^* are differences in L^* , a^* , and b^* values between the sample colour and the standard colour. It is also possible to express the colour of pigment as a hue angle ($H^\circ = \arctg(b^*/a^*)$) [9].

The powder pigments were also studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained by using equipment Diffractometer D8 (Bruker, GB), CuK_α radiation with scintillation detector.

In order to obtain the pigments with optimum particle sizes, the pigments were wet grounded with ethanol and zircon corpuscles (1.8 mm in diameter) in planetary mill Pulverisette 5 (Fritsch, GmbH Germany). The milling times were 15, 30, 45 and 60 minutes. The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000 MU (Malvern Instruments, GB). It is a highly integrated laser measuring system (He-Ne laser, $\lambda = 633\text{ nm}$) for the analysis of particle size

distribution. The equipment uses scattering of the incident light on particles. The signal is evaluated on the basic Mie theory or Fraunhofer bending.

Results and discussion

The effect of the increasing content of lutetium on the colour of the pigments based on Bi_2O_3 was investigated. Initially, the influence of the Lu content in the starting mixtures and calcination temperature on the colour hue of the pigment was studied. The prepared powder materials were applied to an organic matrix. Based on values a^* and b^* of pigments (Table 1), it can be seen that the increasing lutetium content increases the colour value a^* (red hue) up to $x = 0.3$. The next growth of Lu content decreases the colour value a^* . This trend is alike for all four temperatures. The value b^* of all prepared samples is from 50 to 60. Only pigments with nominal composition $x = 0.9$ have lower values b^* . The pigments with value x from 0.1 to 0.6 have orange colour ($H^\circ = 67.75 - 74.21$). The samples with nominal composition $x = 0.7$ and $x = 0.8$ produce a yellow-orange colour. The highest lutetium content ($x = 0.9$) gives light yellow colour. The best result was obtained for the pigment $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$ which indicates the highest colour value a^* (red hue) and the lowest hue value ($H^\circ = 67.75-70.30$) for all calcination temperatures. This sample is characterized by intensive orange colour after application to organic matrix.

The structure of the $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$ pigment was investigated by X-ray diffraction analysis. The X-ray pattern of this powdered material is given in Fig. 1. All peaks of high intensity can be assigned to compound Bi_2O_3 . The presence of Bi_2O_3 as a major phase might be explained by the fact that Lu_2O_3 is completely dissolved in Bi_2O_3 . Bi atoms are substituted by Lu atoms in the crystal lattice, forming electrically neutral defects Lu^x_{Bi} in the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ solid solution. Thus, the structure of Bi_2O_3 is retained. Lu^{3+} entered the Bi_2O_3 as substitutional defects because the lutetium ion [$r(\text{Lu}^{3+}) = 0.085\text{ nm}$] has a smaller radius than the Bi ion [$r(\text{Bi}^{3+}) = 0.120\text{ nm}$]. Another heterogeneous phase of free Lu_2O_3 was also detected from XRD pattern for all four temperatures. Growing calcination temperature increases intensity of peaks of major phases and at the same time decreases intensity of peaks belonging to free Lu_2O_3 .

Tab. 1. The effect of Lu content and temperature on the colour coordinates a^* and b^* and colour hue H° of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ (an application into organic matrix in mass tone)

x	Temperature [$^\circ\text{C}$]											
	700			750			800			850		
	a^*	b^*	H°	a^*	b^*	H°	a^*	b^*	H°	a^*	b^*	H°
0.1	19.44	56.92	71.14	19.32	56.72	71.19	17.93	55.45	72.08	16.13	57.03	74.21
0.2	18.72	55.95	71.50	20.36	56.09	70.05	20.37	55.15	69.73	18.01	56.40	72.29
0.3	20.67	57.73	70.30	22.56	56.64	68.28	22.97	56.15	67.75	22.98	58.46	68.54
0.4	20.34	57.51	70.52	21.83	56.64	68.92	22.21	56.86	68.66	21.37	58.07	69.80
0.5	19.16	56.73	71.34	20.49	57.16	70.28	20.66	55.26	69.50	19.23	59.50	72.09
0.6	17.91	55.13	72.00	18.72	54.90	71.17	18.73	56.18	71.56	17.44	58.54	73.41
0.7	14.98	52.98	74.21	15.81	54.66	73.87	16.09	53.94	73.39	10.41	58.29	79.87
0.8	11.39	49.93	77.15	11.69	51.02	77.09	12.07	51.08	76.71	8.84	54.68	80.82
0.9	4.54	38.73	83.31	4.50	39.88	83.56	4.46	42.00	83.94	1.30	44.91	88.34

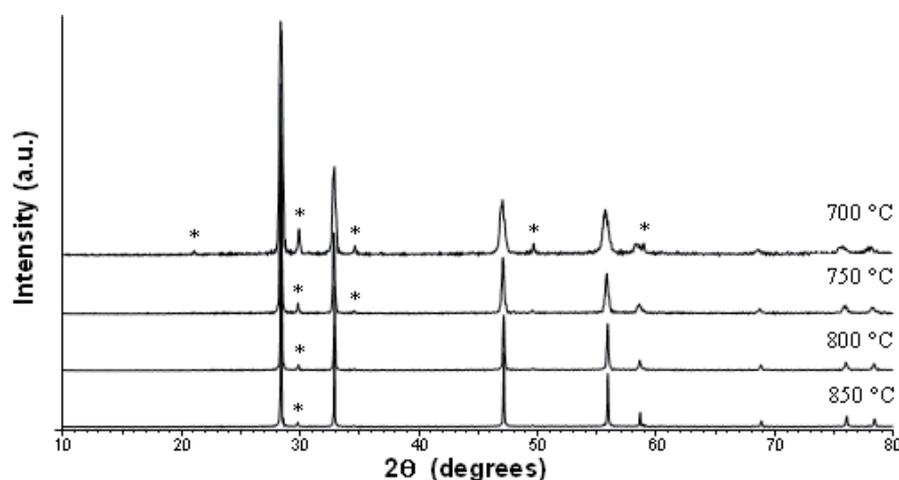


Fig. 1. Powder X-ray diffractions of $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$ pigments (* means Lu_2O_3)

Tab. 2. The effect of milling on colour properties of $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$ pigment calcinated at 850°C (application into organic matrix in mass tone)

Milling time [min]	L^*	a^*	b^*	C	ΔE^*_{CIE}	H°
0	71.64	20.96	55.49	59.32	-	69.31
15	76.26	16.56	53.49	55.99	6.68	72.80
30	76.99	15.61	52.85	55.11	8.02	73.54
45	78.32	11.76	49.79	51.16	12.72	76.71
60	79.71	11.50	49.14	50.47	13.96	76.83

Tab. 3. Particle sizes of the $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$ pigment calcinated at 850°C

Milling time [min]	Particle size [μm]	
	Particle size range (d_{10} - d_{90})	Mean particle size (d_{50})
0	2.26-46.86	6.66
15	0.84-6.85	2.92
30	0.72-6.13	2.51
45	0.58-4.84	1.85
60	0.54-4.89	0.54

For other studies the $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$ pigment calcinated at 850°C was used because it should possess the most intense orange colour. The particle sizes and particle size distributions can markedly affect the colour properties of inorganic pigments. That is why the prepared samples were tested from this point of view. The mean particle sizes of pigments used for colouring of the coatings compositions is approximately $1\ \mu\text{m}$. The main aim was to decrease the particle sizes and monitor the influence of particle sizes on the colour properties of the pigment. Table 2 shows the effect of milling on colour properties of selected sample. The L^* value increases with growing milling time, whilst value of chroma decreases. Grinding has a marked effect on the values ΔE^*_{CIE} . The colour coordinates a^* decrease as well as the colour coordinates b^* . The hue of the sample, with increasing milling time, is shifted from orange to a light yellow-orange colour. The optimal milling time is 15 minutes for colour properties, as there is not a large change of the colour

hue of the pigment ($H^\circ = 69.31$ for not grinding pigment and $H^\circ = 72.80$ for milling pigment). The optimal grinding time is 60 minutes for the particle size of the powdered sample, the particle size decreased from $6.66\ \mu\text{m}$ to $0.54\ \mu\text{m}$. Wet grinding in the planetary mill Pulverisette 5 in ethanol medium leads to decreasing of the particle size of the pigment $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$. The values of particle sizes of the samples are shown in the Table 3.

Conclusions

The prepared pigments provide orange colour ($x = 0.1$ up to 0.6) hues shifted to light yellow ($x = 0.9$). Synthesized samples with $x = 0.7$ and 0.8 have yellow-orange colour hues. The sample $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Lu}_2\text{O}_3)_{0.3}$ calcinated at 850°C possesses the most intensive orange colour. The optimum milling time for colour properties of this powdered material is 15 minutes. For the particle size of pigment, 60 minutes is the optimum grinding time. New coloured compounds could contribute to the basic assortment of orange and yellow inorganic pigments. These pigments are resistant to heat and represent potential alternative of inorganic pigments containing chromium and lead (chromate yellows). Thus, pigments of the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Lu}_2\text{O}_3)_x$ system are potentially more environmentally friendly than those pigments currently used.

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