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COLOUR PROPERTIES OF $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ PIGMENTS

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$(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ solid solutions were synthesized as new inorganic yellow and orange pigments and their colour properties were investigated as possible ecological materials. The host lattice of these pigments is Bi_2O_3 that is doped with Lu^{3+} ions. The pigments were prepared by the solid state reaction of mixed oxides $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ 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 colours from yellow to orange.*

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 toxic metals such as cadmium, lead and hexavalent chromium. Thus, serious need arises

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to look for materials that are environmentally friendly and economically viable, materials for the replacement of toxic inorganic pigments [1]. From this point of view, just the compounds based on Bi_2O_3 belong to pigments of oxide types and seem to be interesting, because they provide attractive colour hues from yellow to orange [2]. Intense colours of these pigments are based on the incorporation of Ln ions into the host lattice of Bi_2O_3. Bi_2O_3 itself is a light yellow powder.

Bismuth sesquioxide 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 among 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 of 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, was 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 ¼ 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) appeared effective, though a variety of crystal phases were observed depending on the kind and amount of the rare earth cation used and the synthesis conditions employed [6-8].

The aim of the present study is to prepare new pigments having the formula $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ with various concentrations of the rare earth element and examine their properties. These powder materials are expected to be new environmentally friendly pigments for colouring paints or plastics.

Experimental

The starting materials used for the preparation of $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ pigments were Bi_2O_3 of 99 % purity (Lachema Brno, Czech Republic) and Lu_2O_3 (Bochemie Bohumin, the Czech Republic).

Mixed oxides $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ with nominal compositions x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 were prepared. The above-mentioned oxides were weighed in the required stoichiometric amounts and then 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 °C min^{-1} and the calcination temperature of 850 °C was maintained for three hours.

The pigment with the best orange colour was prepared with the agent of mineralization. Agents of mineralization used in this study were NaF, CaF_2, MgF_2, Na_3AlF_6, Na_2SiF_6, AlF_3, KCl. The agent of mineralization was used in the quantity of 5 %. The prepared mixtures were calcinated at 700, 750, 800 and 850 °C for two hours.

The calcinated powder samples were applied to an organic matrix in both mass and reduced tone in the weight ratios of pigment to TiO_2 equal to 1:1 (RG – 15, Precheza a.s., Přerov, the Czech Republic). 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°.

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: $C = (a^{*2} + b^{*2})^{1/2}$. It is also possible to express the colour of pigment as a hue angle ($H° = \text{arc tg}\,(b^*/a^*)$) [9]. The powder pigments were also studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using a Diffractometer D8 (Bruker, GB), CuK_λ radiation with scintillation detector.

Physico-chemical analysis (particle size distribution, specific weight, oil number, and CPVC) was also performed. Specific weight is one of the basic physico-chemical parameters which characterize the powder substance. Its value of the prepared pigments was determined by pycnometric method. The oil number was determined by standard method "mortar-pestle". Linseed oil was used as a binder. The values of *CPVC* (Critical Pigment Volume Concentration) were calculated from the specific weight and the oil number. *CPVC* characterizes a state when a space among the particles of a pigment is only filled with the binder.

Results and Discussion

The effect of increasing content of lutetium on the colour of the Bi_2O_3 based pigments was investigated. First, the influence of the Lu content in the starting mixtures on the colour hue of the pigment was studied. The prepared powder materials were applied to an organic matrix. The colour parameters of

$(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ are given in Table I. Based on values a^* and b^* of pigments, 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^*. The value b^* of all prepared samples is from 55 to 60. Only the pigment with nominal composition $x = 0.9$ has a lower value b^*. The pigments applied to organic matrix in reduced tone have a similar trend for the colour coordinates. The pigments with value x from 0.1 to 0.6 have orange colour ($H° = 68.5$-74.2). The samples with nominal composition $x = 0.7$ and $x = 0.8$ produce a yellow-orange colour ($H° = 79.9$ and 80.8). The highest lutetium content ($x = 0.9$) gives light yellow colour ($H° = 88.3$). The best result was obtained for the pigment $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ which is indicated by its highest colour value a^* (red hue) and lowest hue value ($H° = 68.5$). This sample is characterized by intensive orange colour after application to organic matrix. The reflectance spectra of these pigments are shown in Fig. 1. The high reflectance lies in the region of 610-700 nm. It matches yellow-orange and orange colour. These colour samples have the maximum reflectance at 700 nm. Pigment with nominal composition $x = 0.9$ has the high reflectance in the region of 540-700 nm.

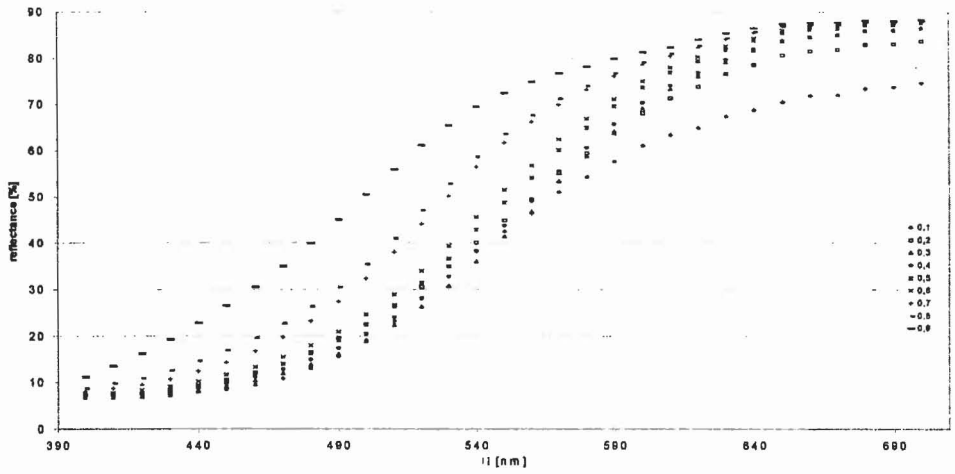

Fig. 1 Reflectance spectra for $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ calcinated at 850 °C (application into organic matrix in mass tone)

The structure of the $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ pigment was investigated by X-ray diffraction analysis. The X-ray pattern of this powdered material is given in Fig.2. All peaks of high intensity can be assigned to 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 in the solid solution $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$. Thus, the structure of Bi_2O_3 is retained. Lu^{3+} entered the Bi_2O_3 as substitutional defects because the

Table I The effect of Lu content on the colour properties of $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ calcinated at 850 °C (an application into organic matrix in both mass and reduced tone)

x	Mass tone					Reduced tone				
	L	a^*	b^*	C	$H°$	L	a^*	b^*	C	$H°$
0.1	70.51	16.13	57.03	59.27	74.21	89.05	1.50	16.30	16.37	84.74
0.2	73.23	18.01	56.40	59.21	72.29	88.95	2.48	17.94	18.11	82.13
0.3	71.95	22.98	58.46	62.81	68.54	88.94	4.08	18.02	18.48	77.24
0.4	73.09	21.37	58.07	61.88	69.80	89.18	3.80	19.17	19.54	78.79
0.5	75.35	19.23	59.50	62.53	72.09	89.01	3.96	20.06	20.45	78.83
0.6	76.62	17.44	58.54	61.08	73.41	89.87	3.05	18.43	18.68	80.60
0.7	80.84	10.41	58.29	59.21	79.87	90.56	1.99	18.50	18.61	83.86
0.8	81.80	8.84	54.68	55.39	80.82	91.11	0.78	17.50	17.52	87.45
0.9	86.14	1.30	44.91	44.93	88.34	92.47	–0.72	12.72	12.74	93.24

lutetium ion [$r(Lu^{3+}) = 0.085$ nm] has a smaller radius than the Bi ion [$r(Bi^{3+}) = 0.120$ nm]. Another heterogeneous phase of free Lu_2O_3 was also detected from XRD pattern.

The pigment $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ calcinated at 850 °C was used for other studies because it should possess the most intense orange colour. The specific

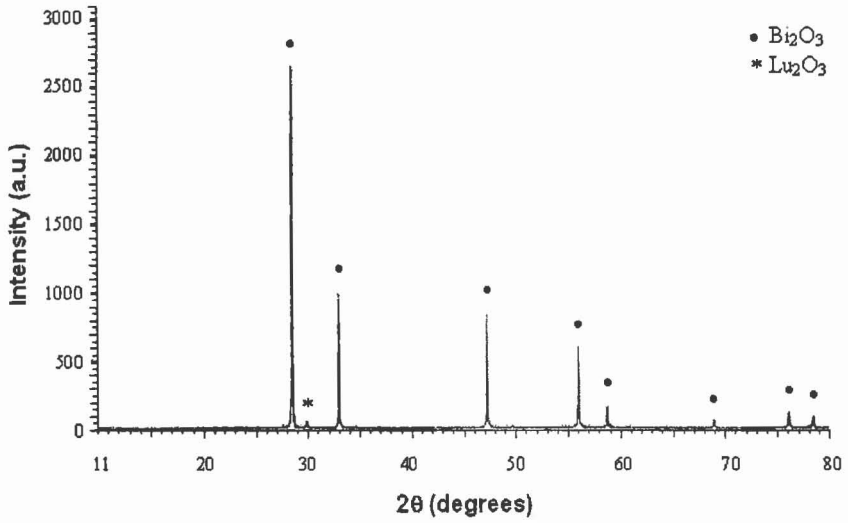

Fig. 2 Powder X-ray diffractions of $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ pigment calcinated at 850 °C

weight of the pigments was measured pycnometrically. The specific weight of $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ is 8.28 g cm^{-3}. Invariability of the pigment production is given by oil consumption. This parameter is 15.77 g/100g for this sample. The calculation of *CPVC* value is based on the known specific weight and oil consumption of a pigment. The value of *CPVC* of the prepared pigment is 41.58 %.

The agent of mineralization can also markedly affect the colour properties of pigments. That is why the prepared samples were also tested from this aspect. The influence of the agent of mineralization on the colour coordinates a^* and b^* for all synthesized samples is shown in Table II. The agent of mineralization can be classified into three groups considering the pigment without content of mineralizers ("clean"). The first group (KCl, NaF and CaF_2) does not markedly affect the colour properties of the pigments. The presence of AlF_3 and Na_3AlF_6 as representatives of the second group influences the colour properties in terms of decreasing colour value a^*. The final hues of these powder samples are yellow-orange. The last group includes pigments containing MgF_2 or Na_2SiF_6. From among all synthesized samples, the pigment with Na_2SiF_6 has the lowest colour values a^* and b^* for temperatures 700 and 750 °C. The colour of these powder materials is light yellow. Increasing calcination temperature shifts their colour into yellow (for 800 and 850 °C). The pigments containing MgF_2 are yellow for all temperatures.

Table II The influence of temperature and agent of mineralization on colour coordinates a^* and b^* of $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ (application into organic matrix in mass tone)

Agent of mineralization	Temperature, °C							
	700		750		800		850	
	a^*	b^*	a^*	b^*	a^*	b^*	a^*	b^*
Clean	18.55	60.38	20.99	56.99	20.36	58.94	21.80	59.32
KCl	17.86	60.66	18.78	56.26	15.84	60.97	20.20	55.92
NaF	17.21	59.84	21.19	54.68	18.80	59.62	17.33	56.83
CaF_2	18.00	56.96	17.31	59.17	18.27	58.99	20.57	56.90
AlF_3	0.36	50.54	8.32	54.63	10.53	59.49	7.96	61.53
Na_3AlF_6	–0.64	45.89	8.35	57.31	9.48	59.77	9.72	60.65
MgF_2	4.32	57.72	5.19	58.64	3.70	59.73	4.11	59.63
Na_2SiF_6	–1.06	24.66	1.30	24.65	5.50	59.77	7.44	65.92

Conclusion

The prepared pigments provide orange colour ($x = 0.1$ up to 0.6) hues shifted to light yellow ($x = 0.9$). The synthesized samples with $x = 0.7$ and 0.8 have yellow-orange colour hues. The sample $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ calcinated at 850 °C possesses the most intensive orange colour. By using an appropriate agent of mineralization, the colour hue of $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ may be changed from orange to yellow over yellow-orange. These new coloured compounds could contribute to the basic assortment of orange and yellow inorganic pigments. These powder materials are resistant to heat and represent potential alternative of inorganic pigments containing chromium and lead (chromate yellows). Thus, pigments of the $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ system are potentially more environmentally friendly than those pigments currently used.

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