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THERMAL ANALYSIS OF THE Bi_2O_3–Y_2O_3–ZrO_2 PIGMENTS

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The synthesis of new compounds based on Bi_2O_3 is investigated because they can be used as new colour inorganic pigments. Chemical compounds of the $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$ type were synthetised. The host lattice of these pigments is Bi_2O_3 that is doped by Y^{3+} and Zr^{4+} ions. The incorporation of doped ions provides interesting colours and contributes to a growth of the thermal stability of these compounds. The simultaneous TG-DTA measurements were used for determination of the temperature region of the pigment formation and thermal stability of pigments. This paper also contains the results of the pigment characterization by X-ray powder diffraction and their colour properties.

Keywords: *bismuth–rare earth mixed oxides, colour properties, ecological pigments, inorganic pigments, thermal analysis*

Introduction

The inorganic pigments are widely used in various applications such as paints, plastics, ceramics, enamels and glazes. The pigments for colouring of ceramics are based on mixed metal oxides and must possess thermal and chemical stabilities at high temperatures. Some of inorganic pigments contain toxic metal such as Cd, Pb and Cr [1]. Thus, serious need arises to search for materials of environmentally friendly and economically possible materials for toxic components of pigments. The need to replace cadmium and lead pigments in surface coating applications, especially for colours like yellow and orange, has received wide focus in recent years.

From this point of view just pigments 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, 3]. Intense colours of these pigments are based on the incorporation of doped Ln ions into the host lattice of Bi_2O_3. The Bi_2O_3 itself is a light yellow powder.

The high temperature phase of δ-Bi_2O_3, which is stable in the 730–825°C temperature range, has been intensively studied due to its high oxygen-ion 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 a high oxygen-ion mobility. The δ-phase may be stabilized below room temperature by partial cationic substitution for 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 [4–8].

In the present study, the new pigments having the formula $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$ with various yttrium and zirconium concentration levels have been prepared and their colour properties, as possible ecological inorganic pigments have been investigated. The optimum calcination temperature for pigment synthesis was determined on the base of the simultaneous TG-DTA measurements that can provide the information about the temperature region of the pigment formation.

Experimental

As starting materials we used bismuth oxide(III) of 99% purity (Merck, Germany), ZrO_2 with 95% and Y_2O_3 with 99% purity (Indian Rare Earths Ltd., India). Mixed oxides $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$, where x=0.2, 0.8 and 1.4, have been prepared. The synthesis of the samples was carried out in corundum crucibles from stoichiometric amounts of Bi_2O_3, Y_2O_3 and ZrO_2 which were mixed at an agate mortar. The starting mixtures were then calcinated in air at electric furnace at required temperature (the increase of the temperature was 10°C min^{-1}). The samples were calcinated from 700 to 850°C for 3 h.

All prepared pigments were applied into organic matrix (Balakom, a.s., Czech Republic) in mass tone. The final applications were evaluated with regard to their colour hues by measurements of spectral reflectance in the visible region of light (400–700 nm) using a MiniScan (HunterLab, USA). The measurement conditions [9] were following: an illuminant D65, 10° complementary observer and measuring geometry *d*/8°.

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The colour properties are described in terms of CIE $L^*a^*b^*$ system. 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 as related to a neutral gray 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 hue angle H^o is defined by an angular position in the cylindrical colour space (for the red is $H°$=0–35°, for the orange $H°$=35–70°, for the yellow $H°$=70–105°).

The methods of thermal analysis can provide the first information about the temperature region of the formation of inorganic pigments. The formation of these pigments was followed by thermal analysis using STA 449C Jupiter (Netzsch, Germany) which allows the simultaneous registration of the thermoanalytical curves TG and DTA. The starting raw material and the prepared starting mixtures were studied by thermal analysis in corundum crucible in air in temperature region from 100 to 1050°C. The increase of temperature was 10°C min^{-1}. α-Al_2O_3 was used as reference material [10].

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

Results and discussion

The influence of the increasing content of yttrium and zirconium on the colouring effect of the $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$ pigments was studied. The colour properties of the $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$ samples prepared at temperature 700, 750, 800 and 850°C and applied into organic matrix in mass tone are given in Table 1.

From Table 1 it follows that the increasing content of Y and Zr decreases value L^* (lightness) at all temperatures and the pigments become the darkest. The increase of calcination temperature produces the decrease of value L^* and the colour becomes darker. The value a^* (red hue) and b^* (yellow hue) increases with the growing value x and this increase is also represented by the grow of values C (chroma) depending on x. The growing temperature of calcination makes also the increase of chroma. The values of hue angle $H°$ do not differ for value x at 700, 800 and 850°C, at 750°C the values $H°$ a little decrease according to value x. Considering that the value $H°$ of these pigments lies from 73 and 80, the pigments are also characterized by yellow-orange colour. The intensive hues are produced at higher temperatures (800 and 850°C) but at 850°C pigments begin a little to sinter.

The formation of these pigments was followed by the methods of thermal analysis (TG-DTA). Thermal analysis of starting oxide Bi_2O_3 provided the two endothermic effects on the DTA curve [9]. The first peak with temperature minimum at 736°C corresponded with the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3. This effect is then followed by the second peak with minimum at 820°C that is connected with melting of δ-Bi_2O_3.

Starting mixtures for the pigment preparation with composition $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$ (where x=0.2, 0.8 and 1.4) were homogenized in an agate mortar and studied with using of DTA. TG curves of all mixtures indicated the mass loss at the temperature range from 100 to 600°C (Table 2) that is represented by two slight breaks at the DTA curve at temperature about

Table 1 Colour properties of the $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$ pigments applied into organic matrix

x	700°C			750°C			800°C			850°C		
	L^*	C	$H°$	L^*	C	$H°$	L^*	C	$H°$	L^*	C	$H°$
0.2	88.92	28.51	80.04	70.24	43.66	77.67	64.18	53.37	73.78	64.45	54.35	73.77
0.8	80.83	34.14	79.91	65.06	47.36	76.12	60.31	55.49	73.26	60.52	56.47	73.32
1.4	76.29	40.18	80.16	60.67	50.40	74.73	58.45	58.20	73.03	58.94	59.14	73.17

Table 2 Thermal decomposition of the mixture for synthesis $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$

Temp. range/°C	x=0.2		x=0.8		x=1.4	
	Peak temp./°C	Mass loss/%	Peak temp./°C	Mass loss/%	Peak temp./°C	Mass loss/%
100–325	313	0.06	312	0.05	312	0.04
325–425	396	0.39	396	0.36	396	0.33
425–600	–	0.27	–	0.26	–	0.24
600–1050	744 961	0.01	743 925	0.03	741 906	0.01

312 and 396°C and corresponded with continual oxygen loss from Bi_2O_3 [4]. Growing temperature indicated the endothermic effect at the DTA curve with minimum at approx. 743°C which was connected with dissolution of Y_2O_3 and ZrO_2 in Bi_2O_3 during the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3 forming a solid solution of all oxides (Fig. 1). These results were also confirmed by X-ray powder diffraction. The last endothermic peak on the DTA curve demonstrates the tendency of the pigment to melt. From Table 2 it follows that the increasing content of Y and Zr supports the shift of minimum of the peak to lower temperatures, i.e. from 961°C for x=0.2 to 906°C for x=1.4. In comparison with the starting oxide Bi_2O_3 (820°C), the process moves higher by 140°C. This temperature also represents the stability of these pigments.

Figures 2 and 3 demonstrate the simultaneous measurement TG-DTA of starting mixtures for the pigments with x=0.8 and 1.4. These results show the analogical shape of the DTA curve. The higher content of Y and Zr causes the decreasing of melting temperature of this pigment to 906°C. The pigment with x=0.2 has the highest melting temperature (961°C).

Studies of X-ray diffraction showed that the powders of the $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$ compounds with different composition prepared at temperature 700°C were heterogeneous because free ZrO_2 and Y_2O_3 were also identified. The higher temperature (750°C) produced

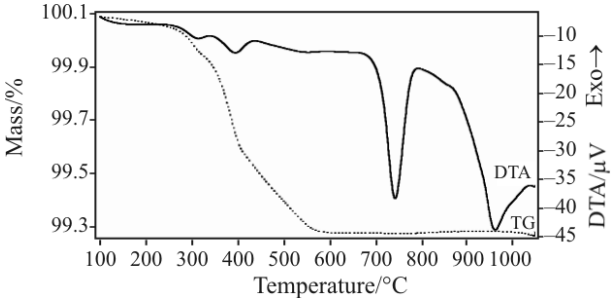

Fig. 1 TG and DTA curves of mixture for synthesis $Bi_{1.8}Y_{0.1}Zr_{0.075}O_3$ (mass of sample: 785.50 mg, atmosphere: air, heating rate: 10°C min^{-1})

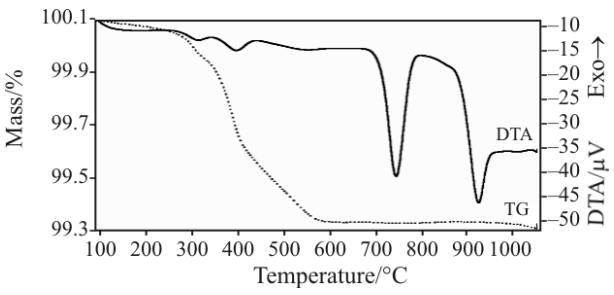

Fig. 2 TG and DTA curves of mixture for synthesis $Bi_{1.2}Y_{0.4}Zr_{0.3}O_3$ (mass of sample: 781.00 mg, atmosphere: air, heating rate: 10°C min^{-1})

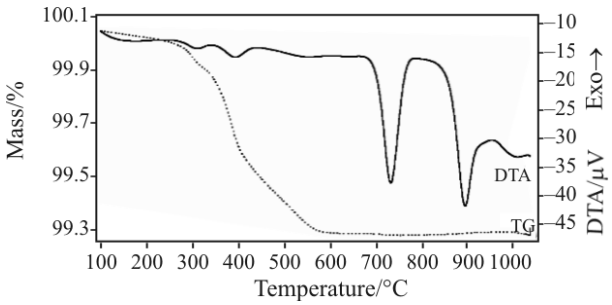

Fig. 3 TG and DTA curves of mixture for synthesis $Bi_{0.6}Y_{0.7}Zr_{0.525}O_3$ (mass of sample: 781.70 mg, atmosphere: air, heating rate: 10°C min^{-1})

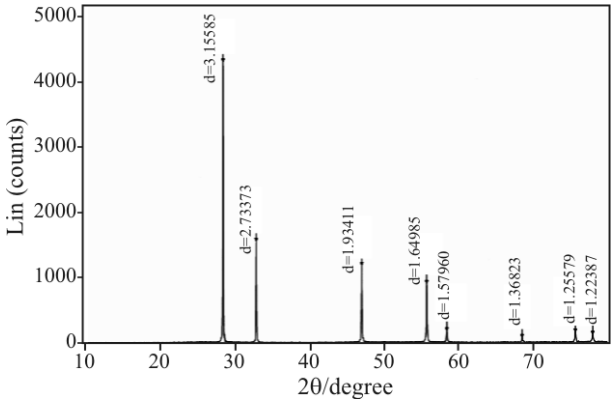

Fig. 4 The X-ray pattern of the sample $Bi_{0.6}Y_{0.7}Zr_{0.525}O_3$ obtaining by calcination at 800°C

double-phased sample, the presence of second phase, i.e. free ZrO_2, was proved beside cubic modification δ-Bi_2O_3. The samples calcinated at 800°C were single-phased for all values x (0.2, 0.8 and 1.4). X-ray diffraction patterns of these compounds can be indexed in an f.c.c. fluorite-type cell.

Conclusions

The compounds $Bi_{2-x}Y_{x/2}Zr_{3x/8}O_3$, where x=0.2 0.8 and 1.4, were studied. Intense yellow-orange colours of these compounds are based on the incorporation of doped Y^{3+} and Zr^{4+} ions into the host lattice of Bi_2O_3. The optimum calcination temperature for pigment synthesis was determined on the base of the simultaneous TG-DTA measurements. These methods provided the information about the calcination temperature of these pigments that is 800°C. This result is also in accordance with colour properties that are better for 800°C, when intensive yellow-orange colour was obtained, lower temperature produces lighter hues.

The methods of thermal analysis also provided the information about the temperature stability of the pigments that is about 960°C (x=0.2). Prepared pigments indicate the increase of their melting temperatures

above 900°C, this result is better than for the $Bi_{2-x}Zr_{3x/4}O_3$ compounds, whose melting temperatures [9] are in the case of x=0.2 about 850°C.

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