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SYNTHESIS AND CHARACTERIZATION OF THE $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$ COMPOUNDS

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Abstract

*A series of novel environmentally inorganic pigments based on Bi_2O_3 doped by metal ions such as Zr^{4+} and Ho^{3+} have been developed and characterized using of methods of thermal analysis, X-ray powder diffraction and CIE L*a*b* colour scales. The compounds were prepared by the solid state reaction. The incorporation of doped ions in Bi_2O_3 changes the colour from yellow to yellow-orange and orange, and also contributes to a growth of their thermal stability. This property is necessary precondition for application of studied compounds for colouring ceramic glazes.*

Keywords: Ecological pigments; Bismuth-rare earth mixed oxides; Thermal analysis; Colour properties.

1. Introduction

Yellow is particularly important colour in the pigment industry and the consumption of the yellow exceeds that of any other coloured pigments. There are various important yellow pigment families for high temperature utilization (e.g. tin vanadium yellow cassiterite, zirconium praseodymium yellow zircon, zirconium vanadium yellow baddeleyite, nickel antimony titanium yellow rutile or lead antimonite yellow pyrochlore) and for colouring of paints or plastics (e.g. cadmium yellow, lead chrome yellow, bismuth vanadate). Some of the yellow pigments commonly used such as $Pb_2Sb_2O_7$, $PbCrO_4$ or CdS are now being expelled from the market because of their

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toxicity [1, 2].

The characteristics required for commercial use of pigments are coloured tone and saturation, covering, tint strength, brightening and brilance ability, non-reactivity, insolubility and dispersibility. In addition to absorbing light, their ability to scatter or reflect light also contributes to their functionality. Recently, many rare erath-based inorganic pigments have been proposed by several researchers inluding our group. Among several pigments for the alternative non-toxic yellow pigments, Bi_2O_3 doped by Ln^{3+} ions and related materials have been attracted because of the opacity and low toxicity. Pigments based on Bi_2O_3 belong to pigments of oxide types and seem to be interesting, because they provide interesting colour hues from yellow to orange [3-10].

Thus, the present paper is focused on the development of novel yellow-orange pigments based on doped Bi_2O_3 system from an environmental point of view. The new pigments of the formula $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$ have been synthesized by solid-state reaction of the respective oxides and characterized for their optical properties, thermal stability and structure.

2. Experimental

As starting materials we used bismuth oxide (III) of 99% purity (Merck, Germany), ZrO_2 with 95% and Ho_2O_3 with 99% purity (Indian Rare Earths Ltd., India). Mixed oxides $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$, where x = 0.2, 0.6, 1.0 and 1.2, have been prepared. The synthesis of the samples was carried out in crucibles from stoichiometric amounts of Bi_2O_3, Ho_2O_3 and ZrO_2 which were mixed at 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 700, 750, 800 and 850°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°. 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° = arc tg (b*/a*)).

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_λ radiation with scintillation detector.

The methods of thermal analysis can provide the 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 1050ºC. The increase of temperature was 10ºC min^{-1}. α-Al_2O_3 was used as reference material [11, 12].

The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000 MU (Malvern Instruments, Ltd. GB).

3. Results and Discussion

The influence of the increasing content of holmium and zirconium on the colouring effect of the $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$ pigments was studied. The colour properties of the $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$ 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 Ho and Zr decreases value L* (lightness) at all temperatures and the pigments become the darkest. The increase of calcination temperature does not affect the values L*, only for the higher temperature, i.e. 850°C, the values L* begin a little to increase. The values C (chroma) for temperatures 700, 750 and 800°C are in range from 68 to 79, the increase of temperature up to 850°C makes the grow of this range up to 86. The growing value x has no significant effect on values C (chroma). The values of hue angle H° do not differ for value x at 700, 750 and 800°C, at 850°C the values H° a little increase. Considering that the value Hº of these pigments lies from 68 and 86, the pigments are also characterized by yellow-orange and orange colour.

The intensive hues are produced at higher temperatures (800 and 850°C). The highest value C corresponds to compound with x=1.0 and this pigment gives intensive orange colour.

The formation of these pigments was followed by the methods of thermal analysis (TG-DTA). Thermal analysis of starting oxide Bi_2O_3 has been published previously [13, 14]. Bi_2O_3 is characterized by the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3 at 736ºC and δ-Bi_2O_3 melts at 820ºC.

Starting mixtures for the pigment preparation with composition $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$ (where x=0.2, 0.6, 1.0 and

Table 1: The effect of calcination temperature on colour properties of the $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$ pigments

x	700°C			750°C			800°C			850°C		
	*L**	*C*	*H°*	*L**	*C*	*H°*	*L**	*C*	*H°*	*L**	*C*	*H°*
0.2	80.19	54.32	79.03	77.15	64.58	77.53	77.22	62.89	79.1	80.59	41.25	86.05
0.6	74.25	59.58	72.65	76.74	64.01	74.82	76.34	62.59	74.11	81.43	61.94	81.21
1	73.86	59.71	70.29	71.59	60.94	68.99	73.78	61.38	69.45	76.44	63.15	72.81
1.2	73.37	57.74	70.76	71.36	59.24	68.74	72.74	60.55	68.47	71.69	59.78	68

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 corresponded with continual oxygen loss from Bi_2O_3 [4]. Growing temperature indicated the endothermic effect at the DTA curve with minimum at approx. 720°C for x = 0.2 which was connected with dissolution of Ho_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). The last endothermic peak on the DTA curve demonstrates the tendency of the pigment to melt. From Table 2 it follows that for x = 0.2 it is about 860°C. In comparison with the starting oxide Bi_2O_3 (820°C), the process moves higher by 40°C.

The figures 2 and 3 demonstrate the simultaneous measurement TG-DTA of starting mixtures for the pigments with x = 0.6 and 1.0. These results show the analogical shape of the DTA curve. The higher content of Ho and Zr causes the increasing of melting temperature of pigment to 863°C for x = 0.6 and 982°C for x = 1.0. This temperature also represents the stability of these pigments.

Table 2. Thermal demeanor of the mixtures for synthesis $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$

Temperature range / °C	x = 0.2		x = 0.6		x = 1.0		x = 1.2	
	Peak temperature / °C	Mass loss / %	Peak temperature / °C	Mass loss / %	Peak temperature / °C	Mass loss / %	Peak Temperature / °C	Mass loss / %
100-325	-	0.08	-	0.08	-	0.08	-	0.08
325-600	-	0.35	-	0.23	-	0.19	-	0.12
600-1050	722	0.11	718	0.04	717	0.03	715	0.16
	860		863		982		-	

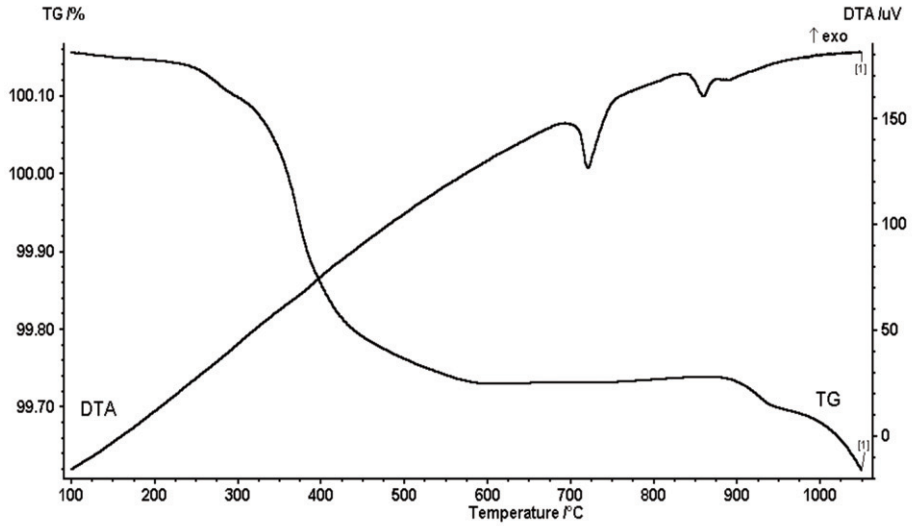

Fig. 1. TG and DTA curves of mixture for synthesis $Bi_{1.8}Ho_{0.1}Zr_{0.075}O_3$ (mass of sample: 461.30 mg, atmosphere: air, heating rate: 10°C min^{-1})

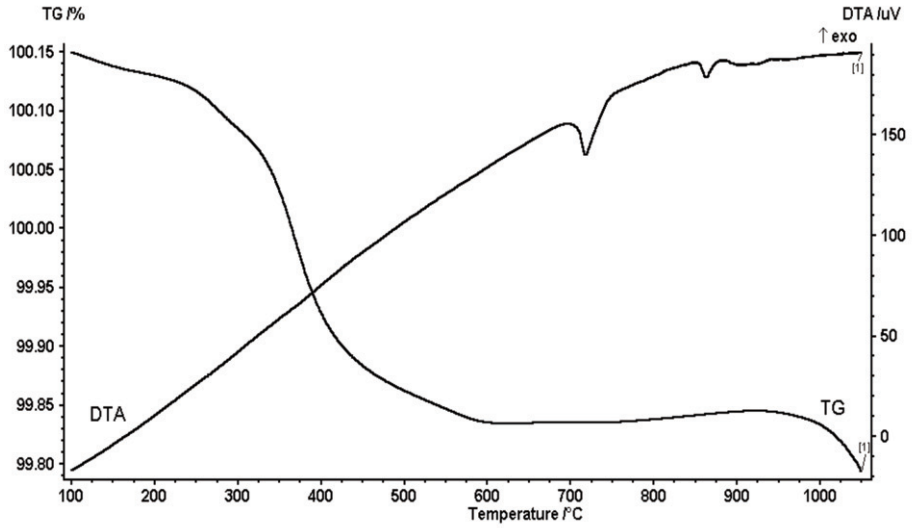

Fig. 2. TG and DTA curves of mixture for synthesis $Bi_{1.4}Ho_{0.3}Zr_{0.225}O_3$ (mass of sample: 464.30 mg, atmosphere: air, heating rate: 10°C min^{-1})

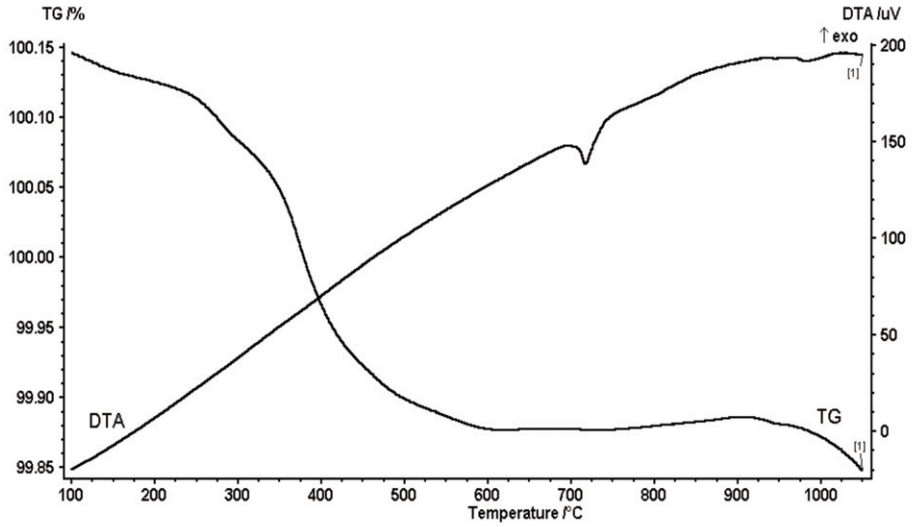

Fig. 3. TG and DTA curves of mixture for synthesis $Bi_{1.0}Ho_{0.5}Zr_{0.375}O_3$ (mass of sample: 462.30 mg, atmosphere: air, heating rate: 10°C min^{-1})

Fig. 4 shows thermoanalytical curves for pigment with x = 1.4. Only one endothermic peak is on DTA curve that is connected with the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3. The effect corresponding to melting temperature of these compounds is no evident on DTA curve in measured temperature range, i.e. 1050°C, although melting temperature of pure Bi_2O_3 is only 820°C. The doping of lanthanide ions into Bi_2O_3 has positive effect on thermal stability of prepared pigments.

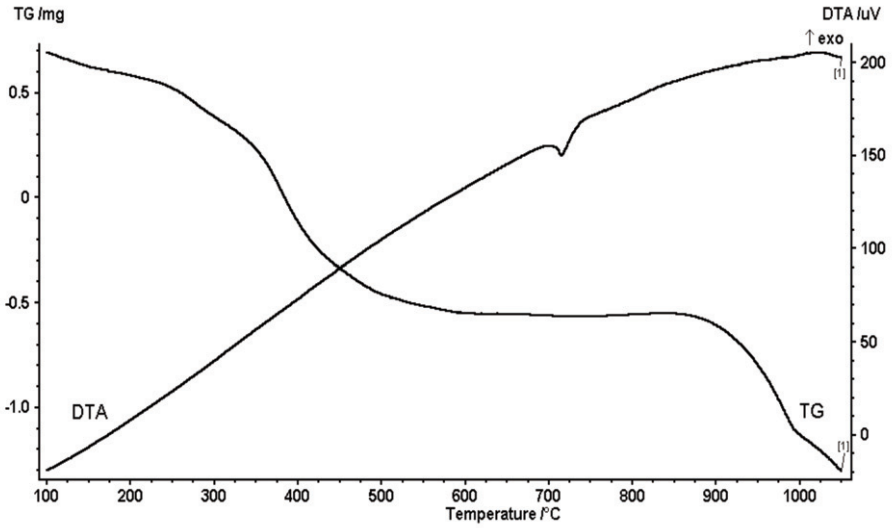

Fig. 4. TG and DTA curves of mixture for synthesis $Bi_{0.8}Ho_{0.6}Zr_{0.45}O_3$ (mass of sample: 461.00 mg, atmosphere: air, heating rate: 10°C min^{-1})

The thermoanalytical results are in accordance with colour properties that are better for 800 and 850°C, when intensive orange colour was obtained.

The compounds, where x = 1.2, prepared by calcination at 700, 750, 800 and 850°C were studied by X-ray diffraction analysis. All compounds prepared at temperatures from 700 to 800°C were double-phased because free Ho_2O_3 and ZrO_2 were identified beside cubic modification δ-Bi_2O_3. All peaks of high intensity correspond to Bi_2O_3 that can be indexed in a face centered cubic fluorite-type cell. The presence of Bi_2O_3 as a major phase might be explained by the fact that Ho_2O_3 and ZrO_2 are dissolved in Bi_2O_3. The sample calcinated at 850°C was single-phased (Fig. 5).

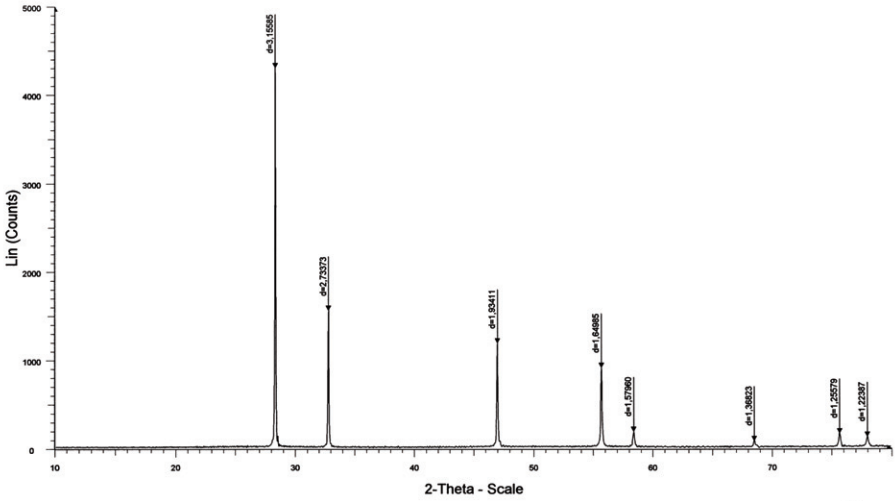

Fig. 5. The X-ray patterns of the sample $Bi_{0.8}Ho_{0.6}Zr_{0.45}O_3$ obtained by calcination at 850°C

The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments so that the pigment grain sizes (particle sizes) of the prepared compounds were also tested. For this study the pigment $Bi_{0.8}Ho_{0.6}Zr_{0.45}O_3$ calcinated at all temperatures was used.

The mean particle sizes (d_{50}) of pigments usually lie in region from 7 to 9 μm. The measurement of particle size distribution was determined for unmilled pigments. The values of pigment particles are in range from 3 μm (d_{10}) to 28 μm (d_{90}). The mean particle sizes (d_{50}) of the prepared pigments is about 8 μm. These pigments are characterized by intense orange colour. The values of particle sizes are shown in Table 3 and are acceptable for various application of these pigments.

Table 3. The effect of calcination temperature on particle sizes of the $Bi_{0.8}Ho_{0.6}Zr_{0.45}O_3$ pigment

T/°C	*d_{10}/μm*	*d_{50}/μm*	*d_{90}/μm*
700	2.88	7.31	21.77
750	3.22	8.14	24.47
800	3.25	8.87	27.14
850	3.41	9.06	28.46

4. Conclusion

The compounds $Bi_{2-x}Ho_{x/2}Zr_{3x/8}O_3$, where x = 0.2 0.6, 1.0 and 1.4, were studied. Intense yellow-orange colours of these compounds are based on the incorporation of doped Ho^{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 and 850°C. This result is also in accordance with colour properties that are better for 850°C, when intensive yellow-orange colour and orange 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 860ºC for x = 0.2 and 0.6, 980°C for x=1.0. Prepared pigments indicate the increase of their melting temperatures above 1050ºC for pigments [13], where x = 1.2, this result is better than for the $Bi_{2-x}Zr_{3x/4}O_3$ compounds, whose melting temperatures [14] are in the case of x = 0.2 about 850ºC. This fact can give a direction for colouring of ceramic glazes.

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