Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 3, 557–559

THERMAL SYNTHESIS AND PROPERTIES OF THE $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ PIGMENTS

Petra Šulcová and M. Trojan*

Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Legions Sq. 565, 532 10 Pardubice Czech Republic

The synthesis of new compounds based on the Bi_2O_3–Ho_2O_3 system, which can be used as new ecological inorganic pigments, is investigated in our laboratory. The optimum conditions for the syntheses of these compounds have been followed by the methods of thermal analysis that can provide first information about the temperature region of the pigment formation. The synthesis of these compounds was followed by thermal analysis using STA 449/C Jupiter (Netzsch, Germany).

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

Introduction

Chromate yellows and oranges were in general found as the most universal inorganic pigments thanks to their extra high covering and colouring power. These pigments found wide use in production of paints, printing inks and plastics, i.e. in areas where their low thermal stability (<200°C) was not an obstructive element. However, there is a major disadvantage of contents of lead and hexavalent chromium [1]. Nowadays these pigments are considered as completely ecologically harmful. The present research is focused on looking for new hygienically and environmentally friendly inorganic pigments which could replace the mentioned yellow and orange pigments by their colour and others pigment properties.

For this reason the compounds based on Bi_2O_3 are synthesized in our laboratory. They seem to be interesting for their yellow and orange colour hues. Intense colours of these pigments are based on incorporation of ions of lanthanides into the host lattice of Bi_2O_3 [2–4]. These pigments are described by the formula $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$. This type of pigments is prepared by middle temperature calcination of the basic starting oxides (Bi_2O_3 and Ho_2O_3). These pigments are expected to be new ecological pigments for colouring of paints or plastics.

Experimental

As starting materials we used bismuth oxide(III) of 99% purity (Merck, Germany) and Ho_2O_3 with 99% purity (Indian Rare Earths Ltd., India). Mixed oxides $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$, where x=0.1, 0.2, 0.3, 0.4 and 0.5, have been prepared. The synthesis of the samples was carried out in corundum crucibles from stoichiometric amounts of Bi_2O_3 and Ho_2O_3 which were mixed at an agate mortar. The starting mixtures were then and calcinated in air at electric furnace at required temperature (the increase of the temperature was 10°C min^{-1}). The samples were calcinated at 800°C for 3 h.

All prepared pigments were applied into organic matrix 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 were following: an illuminant D65, 10° complementary observer and measuring geometry d/8° [5].

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 $H°$ is defined by an angular positron 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 al-

* Author for correspondence: Petra.Sulcova@upce.cz

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

lows 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 1000°C. The increase of temperature was 10°C min^{-1}. α-Al_2O_3 was used as reference material [6].

The products were also analysed by high-temperature microscopy (MHO-2, Zeiss Jena, Germany) to estimate their temperatures of melting.

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 synthesis of pigments based on the fluorite structure of δ-Bi_2O_3 with admixture of selected lanthanides was proposed. The influence of the increasing content of Ho_2O_3 on the colouring effect of the $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ pigments was studied.

The colour properties of the $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ samples prepared at temperature 800°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 decreases value L^* (lightness) and the pigments become the darkest. The value a^* (red hue) increases with the increasing Ho content and at the same time the value b^* decreases from x=0.1 to 0.3 then value b^* a little increases. The pigment with x=0.5 has the highest value C (chroma). This pigment is characterized by intensive yellow–orange colour ($H°$=69.04).

The structure of the $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ pigments was also investigated by X-ray diffraction analysis (Fig. 1). These samples are homogeneous in whole range of x from 0.1 to 0.5. X-ray diffraction patterns of these compounds can be indexed in an f.c.c. fluorite-type cell [3]. The pigments have a cubic symmetry with lattice parameter a=0.54770 nm for x=0.3.

The formation of these pigments was followed by the methods of thermal analysis (TG-DTA). Thermoanalytical curves of starting oxide Bi_2O_3 are

Table 1 The effect of increasing Ho content on the colour properties of the $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ pigments applied into organic matrix

x	L^*	a^*	b^*	C	$H°$
0.1	78.21	16.16	58.03	60.24	74.44
0.2	75.62	16.82	57.25	59.67	73.63
0.3	70.34	18.77	56.68	59.71	71.68
0.4	68.13	20.02	56.72	60.15	70.56
0.5	66.38	21.77	56.84	60.87	69.04

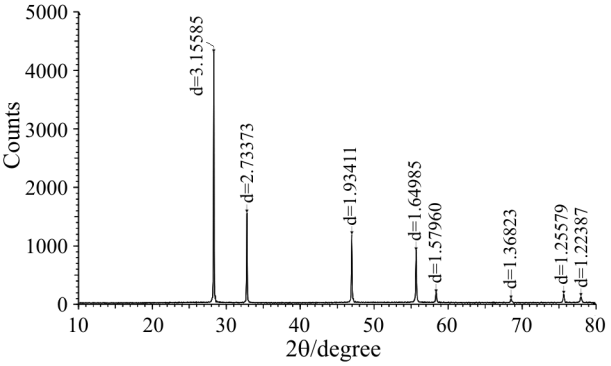

Fig. 1 The X-ray pattern of the sample $Bi_{1.4}Ho_{0.6}O_3$ obtaining by calcination at 800°C

given in Fig. 2. The DTA curve shows the two endothermic effects. The first peak with temperature minimum at 736°C corresponds with the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3. The peak with minimum at 820°C is connected with melting of δ-Bi_2O_3. TG curve of starting oxide Bi_2O_3 indicates the mass loss (0.78%) at the temperature range from 100 to 600°C (Fig. 2). This process is represented by the partial oxygen loss (Table 2) because Bi_2O_3 is known as oxide with the excess of oxygen in its crystal lattice. This effect is connected at the DTA curve only with two slight breaks at the temperature about 308 and 380°C.

Starting mixture for the pigment preparation with composition $Bi_{1.4}Ho_{0.6}O_3$ was homogenized in an agate mortar and studied with using of DTA (Fig. 3). TG curve indicates the mass loss (0.68%) at the temperature range from 100 to 600°C (Table 3).

Table 2 Thermal decomposition of Bi_2O_3 (Fig. 2)

T_{range}/°C	Peak temperature/°C	Mass loss/%
100–270	–	0.08
270–340	308	0.10
340–400	380	0.30
400–600	–	0.30
600–1000	736 820	0.02

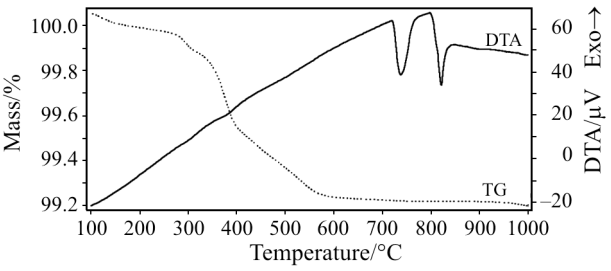

Fig. 2 TG and DTA curves of Bi_2O_3 (mass of sample: 256.90 mg, atmosphere: air, heating rate: 10°C min^{-1})

Table 3 Thermal decomposition of the mixture for synthesis $Bi_{1.4}Ho_{0.6}O_3$ (Fig. 3)

T_{range}/°C	Peak temperature/°C	Mass loss/%
100–325	315	0.14
325–425	404	0.30
425–600	–	0.24
600–1000	724	0.02

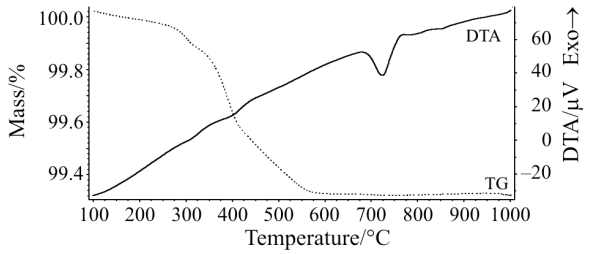

Fig. 3 TG and DTA curves of mixture for synthesis $Bi_{1.4}Ho_{0.6}O_3$ (mass of sample: 903.05 mg, atmosphere: air, heating rate: 10°C min^{-1})

This process is represented by two slight breaks at the DTA curve at temperature about 315 and 404°C and corresponds with continual oxygen loss from Bi_2O_3. In comparison with the starting oxide (308 and 380°C), the processes move 6 and 24°C higher. Growing temperature indicates the endothermic effect at the DTA curve with minimum at 724°C which is connected with dissolution of Ho_2O_3 in Bi_2O_3 during the heat treatment of the starting mixture forming a solid solution of both oxides.

The prepared pigments were also analysed by the high-temperature microscope to estimate their temperatures of melting (Table 4). The growing content of Ho increases melting temperature of pigments from 1060 (x=0.1) to 1220°C (x=0.5), although melting temperature of individual 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.

Table 4 Melting temperatures of the $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ pigments

x	0.1	0.2	0.3	0.4	0.5
T_{melt}/°C	1060	1100	1150	1180	1220

Conclusions

The compounds $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$, where x=0.1, 0.2, 0.3, 0.4 and 0.5, were studied. It was determined that the area of solubility Ho_2O_3 in Bi_2O_3 at temperature 800°C forming solid solution of both oxides is for whole range x. The presence of Ho^{3+} in Bi_2O_3 makes intense orange colour.

It is available to prepare pigments of $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ type having colour hues as chromate pigments by doping of lanthanide ions (Ho^{3+}) into Bi_2O_3 but their high stability is significantly higher. Prepared pigments indicate the increase of their melting temperatures even above 1000°C, although melting temperature of individual Bi_2O_3 was only 820°C. This fact can give a direction for colouring of ceramic glazes. First experiments perform hopeful results after their application into ceramic glazes, too.

Acknowledgements

The work was supported by Grant Agency of Czech Republic by grant No. 104/04/1078.

References

1 M. Trojan, Z. Šolc and M. Novotný, Pigments, Kirk-Othmer Encyclopedia of Chem. Technol., J. Wiley and Sons Inc., New York 1996, Vol. 19, p. 45.
2 T. Takahashi and H. Iwahara, Mater. Res. Bull., 13 (1978) 1447.
3 H. Iwahara, T. Esaka, T. Sato and T. Takahashi, J. Solid State Chem., 39 (1981) 173.
4 P. Prabhakar Rao and M. L. P. Reddy, Dyes Pigments, 63 (2004) 69.
5 P. Šulcová and M. Trojan, J. Therm. Anal. Cal., 77 (2004) 99.
6 V. Petkova, Y. Pelovski, P. Kostadinova and I. Dombalov, J. Therm. Anal. Cal., 80 (2005) 709.

DOI: 10.1007/s10973-005-7392-2