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THERMAL ANALYSIS OF THE $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ PIGMENTS

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The synthesis of new compounds based on Bi_2O_3 is investigated because they can be used as new ecological inorganic pigments. Chemical compounds of the $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ type were synthesized. The host lattice of these pigments is Bi_2O_3 that is doped by Y^{3+} ions. The incorporation of doped ions provides the 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, inks, plastics, rubbers, ceramics, enamels and glazes. These pigments may impart colour properties and protect the coating from the effects of visible as well as ultraviolet and infrared light. In addition to absorbing light, their ability to scatter or reflect light also contributes to their functionality. In order to by suitable in a wide variety of applications, they need to demonstrate a high degree of light fastness and their high temperature stability. The majority of the inorganic pigments, which are currently employed on an industrial scale, generally, comprise toxic metals (cadmium, lead or hexavalent chromium). The use of the above pigments is becoming increasingly strictly controlled, indeed banned, by government legislation and regulations in many countries due to their reputedly high toxicity. Thus, serious economic and industrial need continues to exist for substituting inorganic pigments devoid of the above drawbacks [1, 2].

Transition metals are used as a chromophore in a vast number of mixed metal oxides pigments. In contrast, rare earths are used quite sparingly in inorganic pigments. The intense coloration of rare earth based materials can arise from mostly charge transfer interactions between a donor and acceptor with the metal ions playing generally the role of an acceptor. Dopants based on rare earth elements in mixed oxides systems offer an opportunity to adjust the colour response through the manipulation of energy gaps and delocalization phenomena in conduction and valence bands. This phenomenon offers wide scope for designing of colorants for specific applications.

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 [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 by described as a defective fluorite structure where 1/4 of the anion sites is 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 $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ with various yttrium 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.

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Experimental

As starting materials we used bismuth oxide(III) of 99% purity (Merck, Germany) and Y_2O_3 with 99% purity (Indian Rare Earths Ltd., India). Mixed oxides $(Bi_2O_3)_{1-x}(Y_2O_3)_x$, 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 Y_2O_3 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 at 800°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 were following: an illuminant D65, 10° complementary observer and measuring geometry d/8° [9].

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^0 is defined by an angular position in the cylindrical colour space (for the red is H^0= 0–35°, for the orange H^0= 35–70°, for the yellow H^0=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 1000°C. The increase of temperature was 10°C min^{-1}. α-Al_2O_3 was used as reference material [10].

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 influence of the increasing content of yttrium on the colouring effect of the $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ pigments was studied. The colour properties of the $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ 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 Y decreases value L^* (lightness) and the pigments become the darkest. The value a^* (red hue) increases with the growing Y content from x=0.1 up to x=0.4, the value a^* for x=0.5 a little decreases. The value b^* (yellow hue) increases from x=0.1 to x=0.2, then the amount of yellow hue decreases. The chroma C demonstrates the same course as value b^*. The highest value C (chroma) has the pigment with x=0.2. This pigment is also characterized by the intensive yellow-orange colour (H^0=71.51). All pigments having x from 0.1 to 0.3 produce yellow-orange hues. The highest Y content (x=0.4 and 0.5) produces intensive orange hue because the value H^0 of these pigments lies from 64 and 66 (Table 1).

The structure of the $(Bi_2O_3)_x(Y_2O_3)_x$ pigments was also investigated by X-ray diffraction analysis. 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. The pigment has a cubic symmetry with lattice parameter a=0.5462 for x=0.5. This value of lattice

Table 1 The effect of increasing Y content on the colour properties of the $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ pigments applied into organic matrix

x	L^*	a^*	b^*	C	H^0
0.1	69.27	14.62	55.31	57.21	75.19
0.2	68.59	20.58	61.56	64.91	71.51
0.3	66.65	22.66	60.04	64.17	69.32
0.4	66.48	23.99	53.70	58.82	65.93
0.5	64.25	21.96	44.45	49.58	63.71

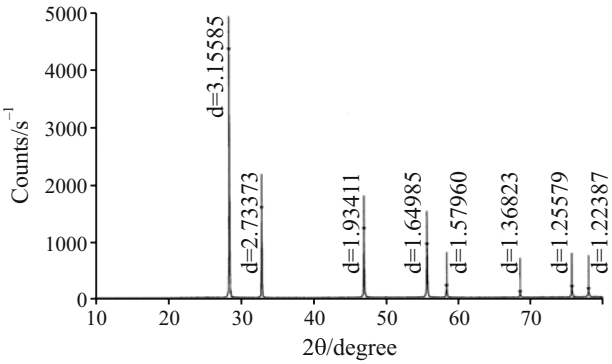

Fig. 1 The X-ray pattern of the sample $BiYO_3$ obtaining by calcination at 800°C

parameter *a* is lower than value of lattice parameter *a*=0.5665 nm of stable modification δ-Bi_2O_3. The decrease observed obviously results from different sizes of bismuth and lanthanides ions ($r(Bi^{3+})$=0.120 nm, $r(Y^{3+})$=0.093 nm).

The formation of these pigments was followed by the methods of thermal analysis (TG-DTA). Thermoanalytical curves of starting oxide Bi_2O_3 are 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 second 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 [3, 4]. 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 $Bi_{1.2}Y_{0.8}O_3$ was homogenized in an agate mortar and studied with using of DTA (Fig. 3). TG curve indicates the mass loss (1.02%) at the temperature range from 100 to 600°C (Table 3). This process is represented by two slight breaks at the DTA curve at temperature about 317 and 399°C and corresponds with continual oxygen loss from Bi_2O_3. In comparison with the starting oxide (308 and 380°C), the processes move 9 and 19°C higher. Growing temperature indicates the endothermic effect at the DTA curve with minimum at 713°C which is connected with dissolution of Y_2O_3 in Bi_2O_3 during the heat treatment of the starting mixture forming a solid solution of both oxides.

Table 2 Thermal decomposition of Bi_2O_3 (Fig. 2)

Temperature 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

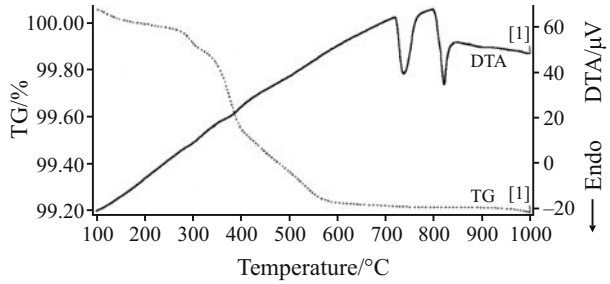

Fig. 2 TG and DTA curves of Bi_2O_3 (mass of sample: 256.90 mg, atmosphere: air, heating rate: 10°C min^{-1})

Table 3 Thermal demeanor of the mixture for synthesis $Bi_{1.2}Y_{0.8}O_3$ (Fig. 3)

Temperature range/°C	Peak temperature/ °C	Mass loss/ %
100–330	317	0.32
330–435	399	0.39
435–600	–	0.31
600–1000	713	0.07

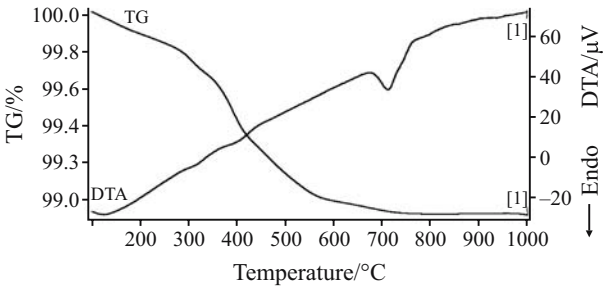

Fig. 3 TG and DTA curves of mixture for synthesis $Bi_{1.2}Y_{0.8}O_3$ (mass of sample: 882.60 mg, atmosphere: air, heating rate: 10°C min^{-1})

Table 4 Melting temperatures of the $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ pigments

x	0.1	0.2	0.3	0.4	0.5
T_{melt}/°C	1070	1120	1140	1160	1180

The prepared pigments were also analysed by the high-temperature microscope to estimate their temperatures of melting (Table 4). The growing content of Y increases melting temperature of pigments from 1070°C (*x*=0.1) to 1180°C (*x*=0.5), although melting temperature of pure Bi_2O_3 is only 820°C (this temperature was determined by high-temperature microscope and is in accord with the result of DTA measurement). The doping of lanthanide ions into Bi_2O_3 has positive effect on thermal stability of prepared pigments.

Conclusions

The compounds $(Bi_2O_3)_{1-x}(Y_2O_3)_x$, where *x*=0.1, 0.2, 0.3, 0.4 and 0.5, were studied. It was determined that the area of solubility Y_2O_3 in Bi_2O_3 at temperature 800°C forming solid solution of both oxides is for whole range *x*. The presence of Y^{3+} in Bi_2O_3 makes intense yellow-orange or orange colour. The pigment

$Bi_{1.6}Y_{0.4}O_3$ gives the best yellow-orange colour, the pigment $BiYO_3$ produces the intensive orange hue.

It is available to prepare pigments of $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ type having colour hues as chromate pigments by doping of lanthanide ions (Y^{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 pure 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.

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