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# THERMAL SYNTHESIS OF THE $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ PIGMENTS

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The synthesis of new compounds based on $Bi_2O_3$ is investigated because they can be used as new environmentally friendly inorganic pigments. Chemical compounds of the $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ type were synthetized. The host lattice of these pigments is $Bi_2O_3$ that is doped by $Er^{3+}$ ions. The incorporation of doped ions provides interesting colours and contributes to an increase in 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.

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

## 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 the toxic metals such as cadmium, lead and hexavalent chromium. Thus, serious need arises to research for materials of environmentally friendly and economically viable materials for the replacement of toxic inorganic pigments [1].

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]. 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 $\delta$-$Bi_2O_3$, which is stable in the 730–825°C temperature range, has been intensively studied due to its high oxygen-ion conductivity [3]. The structure of the $\delta$-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 $\delta$-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, 5].

In the present study, the new pigments having the formula $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ with various erbium 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) and $Er_2O_3$ with 99% purity (Indian Rare Earths Ltd., India). Mixed oxides $(Bi_2O_3)_{1-x}(Er_2O_3)_x$, 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 $Er_2O_3$ 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° [6].

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 dark-

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ness 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$^{-1}$. $\alpha$-$Al_2O_3$ was used as reference material [7].

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$_\alpha$ radiation with scintillation detector.

## Results and discussion

The influence of the increasing content of erbium on the colouring effect of the $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ pigments was studied. The colour properties of the $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ 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 Er decreases value $L^*$ (lightness) and the pigments become the darkest. The value $a^*$ (red hue) decreases with the increasing Er content and at the same time the value $b^*$ (yellow hue) increases. The chroma $C$ increases from $x$=0.1 to $x$=0.3 then value $C$ a little decreases. The pigment with $x$=0.3 has the highest value $C$ (chroma). This pigment gives the best colour result because is characterized by intensive orange colour ($H^0$=63.10). The pigments having $x$ from 0.1 to 0.3 produce light orange hues. The highest Er content makes intensive yellow–orange hues ($H^0$ is about 64).

**Table 1** The effect of increasing Er content on the colour properties of the $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ pigments applied into organic matrix

| x | $L^*$ | $a^*$ | $b^*$ | $C$ | $H^o$ |
|---|---|---|---|---|---|
| 0.1 | 69.63 | 28.18 | 48.27 | 55.89 | 59.72 |
| 0.2 | 67.53 | 27.71 | 50.52 | 57.62 | 61.26 |
| 0.3 | 64.21 | 26.79 | 52.81 | 59.22 | 63.10 |
| 0.4 | 63.96 | 26.11 | 53.09 | 59.16 | 63.81 |
| 0.5 | 63.31 | 25.25 | 53.16 | 58.85 | 64.59 |

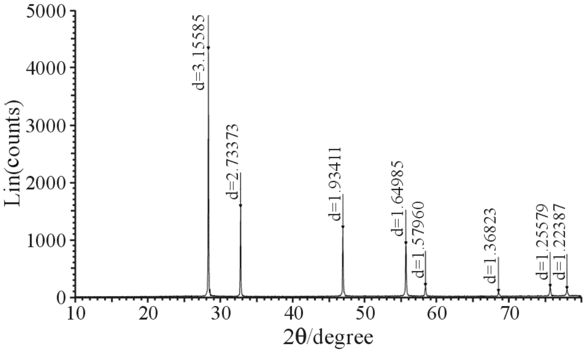

**Fig. 1** The X-ray pattern of the sample $Bi_{1.4}Er_{0.6}O_3$ obtaining by calcination at 800°C

The structure of the $(Bi_2O_3)_x(Er_2O_3)_x$ 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 symetry with lattice parameter $a$=0.5465 for $x$=0.3. This value of lattice parameter $a$ is lower than value of lattice parameter $a$=0.5665 nm of stable modification $\delta$-$Bi_2O_3$. The decrease observed obviously results from different sizes of bismuth and lanthanides ions ($r(Bi^{3+})$=0.120 nm, $r(Er^{3+})$=0.096 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 $\alpha$-$Bi_2O_3$ to cubic modification $\delta$-$Bi_2O_3$. The second peak with minimum at 820°C is connected with melting of $\delta$-$Bi_2O_3$. 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

**Table 2** Thermal demeanor 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<br>820 | 0.02 |

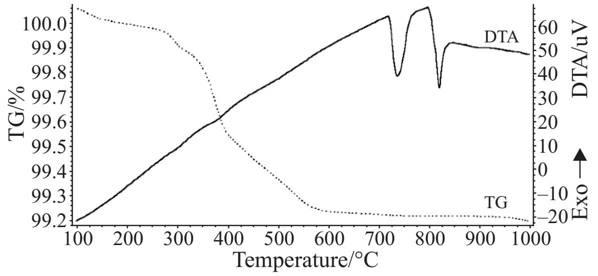

**Fig. 2** TG and DTA curves of $Bi_2O_3$ (mass of sample: 256.90 mg, atmosphere: air, heating rate: 10°C $min^{-1}$)

**Table 3** Thermal demeanor of the mixture for synthesis $Bi_{1.4}Er_{0.6}O_3$ (Fig. 3)

| Temperature range/°C | Peak temperature/°C | Mass loss/% |
|---|---|---|
| 100–320 | 314 | 0.12 |
| 320–435 | 401 | 0.28 |
| 435–600 | – | 0.24 |
| 600–1000 | 731 | 0.02 |

lattice [4, 5]. 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 $Bi_{1.4}Er_{0.6}O_3$ was homogenized in an agate mortar and studied with using of DTA (Fig. 3). TG curve indicates the mass loss (0.64%) 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 314 and 401°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 21°C higher. Growing temperature indicates the endothermic effect at the DTA curve with minimum at 731°C which is connected with dissolution of $Er_2O_3$ in $Bi_2O_3$ during the heat treatment of the starting mixture forming a solid solution of both oxides.

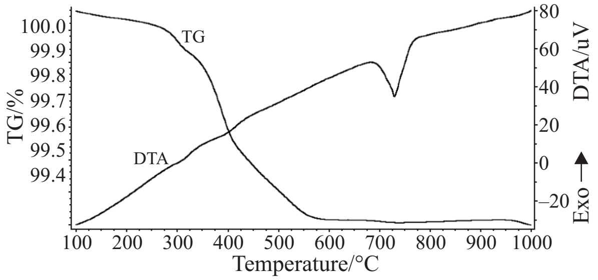

**Fig. 3** TG and DTA curves of mixture for synthesis $Bi_{1.4}Er_{0.6}O_3$ (mass of sample: 898.30 mg, atmosphere: air, heating rate: 10°C $min^{-1}$)

**Table 4** Melting temperatures of the $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ pigments

| x | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|---|---|---|---|---|---|
| $T_{melt}$/°C | 1080 | 1130 | 1180 | 1220 | 1250 |

The prepared pigments were also analysed by the high-temperature microscope to estimate their temperatures of melting (Table 4). The growing content of Er increases melting temperature of pigments from 1080°C ($x$=0.1) to 1250°C ($x$=0.5), 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.

## Conclusions

The compounds $(Bi_2O_3)_{1-x}(Er_2O_3)_x$, where $x$=0.1, 0.2, 0.3, 0.4 and 0.5, were studied. It was determined that the area of solubility $Er_2O_3$ in $Bi_2O_3$ at temperature 800°C forming solid solution of both oxides is for whole range $x$. The presence of $Er^{3+}$ in $Bi_2O_3$ makes intense orange or yellow–orange colour. The best orange colour gives pigment $Bi_{1.4}Er_{0.6}O_3$.

It is available to prepare pigments of $(Bi_2O_3)_{1-x}(Er_2O_3)_x$ type having colour hues as chromate pigments by doping of lanthanide ions ($Er^{3+}$) 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 because most of glazes melt at temperatures about 1000°C. First experiments perform hopeful results after their application into ceramic glazes, too.

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