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# THERMAL ANALYSIS OF THE $Bi_2O_3$–$Er_2O_3$–$ZrO_2$ PIGMENTS

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The synthesis of new compounds based on $Bi_2O_3$ is investigated because they can be used as new ecological inorganic pigments. Chemical compounds of the $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$ type were synthetized. The host lattice of these pigments is $Bi_2O_3$ that is doped by $Er^{3+}$ 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 have been applied in various applications such as paints, plastics, rubbers, ceramics, enamels and glazes. However, most of the conventional inorganic pigments applicable for the above applications contain the toxic elements such as Cd, Pb, Cr, Hg, Sb and Se that can adversely affect the environment and human health [1]. Therefore, development of safe inorganic pigments has been required in order to replace the toxic inorganic pigments with environment-friendly pigments or less toxic substances. Although the use of high-performance organic pigments is one way to obtain several colours, these pigments have some limitations because of their thermal and UV-ray radiation instabilities. On the other hand, some safe inorganic pigments based on metal oxides and compounds have been proposed by several researchers including our group.

Historically, cadmium pigments and chromate pigments have been very important, as they provided a range of clean, bright hues of yellow, orange and red colours. Their importance, however, has been decreasing continually because of the environmental issues associated with the production and the use of Cd and Cr (6+). As this time, most users around the world are looking for safer replacements of the mentioned pigments and only a few pigment producers are willing to continue their production. Originally, these pigments were produced for artistic paints.

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 $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$ with various erbium 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 $Er_2O_3$ with 99% purity (Indian Rare Earths Ltd., In-

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dia). Mixed oxides $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$, 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 $Bi_2O_3$, $Er_2O_3$ 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 calcined at 700, 750 and 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 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), $CuK_\alpha$ radiation with scintillation detector.

## Results and discussion

The influence of the increasing content of erbium and zirconium on the colouring effect of the $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$ pigments was studied. The colour properties of the $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$ samples prepared at temperature 700, 750 and 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 and Zr increases value $L^*$ (lightness) at all temperatures and the pigments become the lightest. 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) decreases with the growing value $x$ and this reduction is also presented by the decrease of values $C$ (chroma) depending on $x$. The growing temperature of calcination makes the increase of chroma. The values of hue angle $H^0$ a little increase according to value $x$. Considering that the value $H^0$ of these pigments lies from 67 and 75, the pigments are also characterized by yellow-orange colour. The intensive hues are produced at higher temperatures (750 and 800°C).

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-$Bi_2O_3$. The second peak with minimum at 820°C was connected with melting of δ-$Bi_2O_3$.

Starting mixtures for the pigment preparation with composition $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$ (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 312°C and approx. 395°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. 745°C which was connected with dissolution of $Er_2O_3$ 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 endother-

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

| $x$ | 700°C | | | 750°C | | | 800°C | | |
|---|---|---|---|---|---|---|---|---|---|
| | $L^*$ | $C$ | $H^0$ | $L^*$ | $C$ | $H^0$ | $L^*$ | $C$ | $H^0$ |
| 0.2 | 74.08 | 33.34 | 71.55 | 57.48 | 50.05 | 68.73 | 56.78 | 55.56 | 70.70 |
| 0.8 | 80.24 | 26.67 | 72.86 | 61.91 | 41.06 | 68.93 | 58.61 | 46.23 | 71.04 |
| 1.4 | 86.68 | 21.91 | 74.54 | 63.89 | 31.46 | 67.06 | 60.53 | 41.31 | 72.08 |

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

| $T_{range}$/°C | $x$=0.2 | | $x$=0.8 | | $x$=1.4 | |
|---|---|---|---|---|---|---|
| | Peak temperature/°C | Mass loss/% | Peak temperature/°C | Mass loss/% | Peak temperature/°C | Mass loss/% |
| 100–325 | 312 | 0.05 | 312 | 0.03 | 312 | 0.06 |
| 325–425 | 397 | 0.40 | 394 | 0.35 | 395 | 0.33 |
| 425–600 | – | 0.26 | – | 0.23 | – | 0.22 |
| 600–1050 | 748<br>950 | 0.01 | 746<br>945 | 0.03 | 742<br>914 | 0.02 |

mic peak on the DTA curve demonstrates the tendency of the pigment to melt. From Table 2 it follows that the increasing content of Er and Zr supports the shift of minimum of the peak to lower temperatures, i.e. from 950°C for $x$=0.2 to 914°C for $x$=1.4. In comparison with the starting oxide $Bi_2O_3$ (820°C), the process moves higher by 130°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 Er and Zr causes the decreasing of melting temperature of this pigment to 914°C. The pigment with $x$=0.2 having the highest melting temperature (950°C) can be determined as the best, because it has at the same time the best yellow-orange colour with the highest value of chroma.

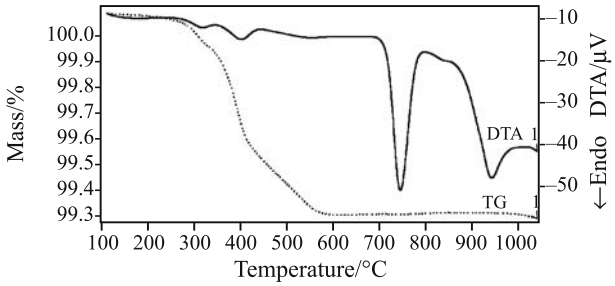


**Fig. 1** TG and DTA curves of mixture for synthesis $Bi_{1.8}Er_{0.1}Zr_{0.075}O_3$ (mass of sample: 805.50 mg, atmosphere: air, heating rate: 10°C $min^{-1}$)

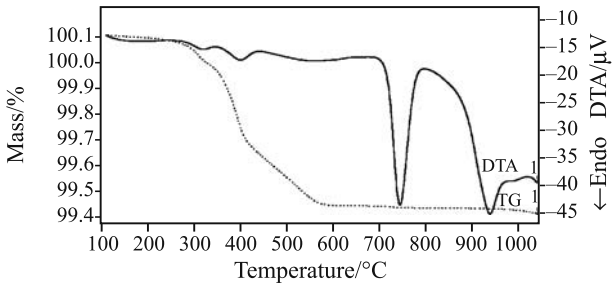


**Fig. 2** TG and DTA curves of mixture for synthesis $Bi_{1.2}Er_{0.4}Zr_{0.3}O_3$ (mass of sample: 805.10 mg, atmosphere: air, heating rate: 10°C $min^{-1}$)

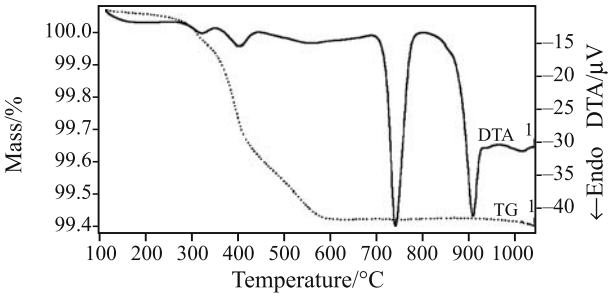


**Fig. 3** TG and DTA curves of mixture for synthesis $Bi_{0.6}Er_{0.7}Zr_{0.525}O_3$ (mass of sample: 808.70 mg, atmosphere: air, heating rate: 10°C $min^{-1}$)

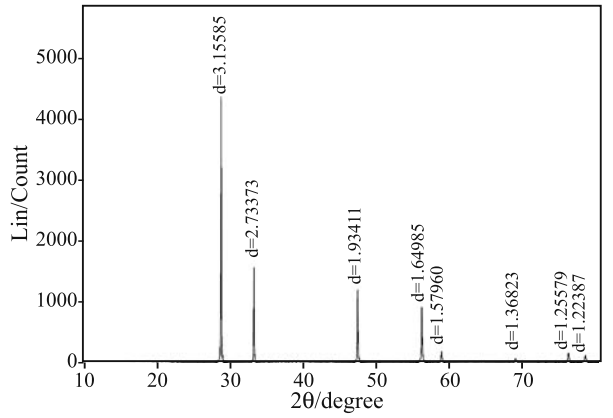


**Fig. 4** X-ray pattern of the sample $Bi_{0.6}Er_{0.7}Zr_{0.525}O_3$ obtaining by calcination at 800°C

The structure of the $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$ pigments was also investigated by X-ray diffraction analysis. The samples prepared at temperature 700°C were heterogeneous because free $ZrO_2$ and $Er_2O_3$ were also identified. The higher temperature (750°C) produced double-phased sample, the presence of second phase, i.e. free $ZrO_2$, was proved beside cubic modification δ-$Bi_2O_3$. The samples calcined 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 $Bi_{2-x}Er_{x/2}Zr_{3x/8}O_3$, 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 $Er^{3+}$ 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 and a little deep hue. The methods of thermal analysis also provided the information about the temperature stability of the pigments that is about 950°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 are in the case of $x$=0.2 about 850°C [9]. 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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