

Thermal stability and colour properties of new pigments based on BiREO₃

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Abstract A series of novel environmentally inorganic pigments based on Bi₂O₃ doped by rare-earth elements RE (Er, Ho, La, Nd, Dy, Lu and Y) have been developed and characterized using methods of thermal analysis, X-ray powder diffraction and by reflectance spectral data. The new pigments have been synthesized from mixtures containing Bi₂O₃ and RE₂O₃ by traditional solid-state route. The incorporation of RE³⁺ into crystal lattice Bi₂O₃ changes the colour from yellow, yellow-orange to orange. The simultaneous TG–DTA measurements were used for determination of the temperature region of the pigment formation and thermal stability of pigments. The results confirm the positive effect of rare-earth ions doped into Bi₂O₃ that contribute to a growth of thermal stability of prepared pigments.

Keywords Ecological pigments · Bismuth-rare earth mixed oxides · Thermal analysis · Colour properties

Introduction

Lot of research is focused on investigation of new inorganic pigments which can substitute the problematic pigments (chromate compounds) with regard to the environmental point of view. The main attention is directed to the synthesis of pigments with yellow, orange and red colour hues. Such pigments are very convenient for colouring of plastics, paints or building materials.

From this point of view just compounds on the base of Bi₂O₃ belong to pigments of oxide types and seem to be interesting, because they provide interesting colour hues from yellow to orange. Intense colours of these pigments are based on the incorporation of doped RE ions into the host lattice of Bi₂O₃. The Bi₂O₃ itself is a light yellow powder [1].

The high temperature phase of δ -Bi₂O₃, 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 centred cubic cation sublattice and can be described as a defective fluorite structure, where ¼ 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 Bi³⁺. Thus, the use of RE³⁺ cations (RE: 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 [2–4]. If the difference between the ionic radius of Bi³⁺ (0.103 nm [2–4]) and the substituted RE³⁺ is large (for example Er³⁺), the substitution will result in a large distortion of the host lattice and only a small amount of substituent is necessary to stabilize the fcc phase of Bi₂O₃. Conversely, a small difference between the ionic radii of Bi³⁺ and RE³⁺ (for example Gd³⁺) requires a large amount of substituent to stabilize the fcc phase. Too large difference between the ionic radii of the RE³⁺ and Bi³⁺ ions makes the fcc phase unstable [4].

The rare-earth oxides are thermally very stable and they are usually the final product when fired in the presence of oxygen. The final stoichiometry is closely dependent upon the temperatures and the oxygen pressure in the ambient atmosphere [5]. The rare-earth sesquioxides become hydrated and

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carbonated if they are exposed to atmospheric carbon dioxide and water vapour at ambient temperature and pressure. Oxides that belong to group I (La, Nd and Sm), corresponding to the lighter rare-earth series, transform to the lighter rare-earth series, transform partially to carbonated hydroxides. For the sesquioxides of group II (Eu), holding the cubic phase, the transformation is only partial. In the case of the heaviest sesquioxides, group III (Dy, Ho, Yb), the transformation of the oxides is also only fractional. The melting points of the sesquioxides correspond to the atomic number and can be divided into two groups. The ceric group increases from La to Gd, the second one is yttric group in which the temperature also rises from Dy to the end of the family of Lu. The typical explanation for the Gd anomaly is ascribed to the result of the Gd^{3+} electronic state with the half-filled 4f subshell ($4f^7$). All the sesquioxides transform to high-temperature form (two phases in some cases) above 2,000 °C. All the sesquioxides melt in the range from 2,300 to 2,500 °C [5].

The main attention was focused on the pigment synthesis based on Bi_2O_3 doped by rare-earth ions ($Bi_{2(1-x)}RE_{2x}O_3$). The object was to suggest and elaborate synthesis conditions of these pigments, investigate their colour possibilities and verify their applicability [6]. Bi_2O_3 is interesting for its environmental popularity. The environmental regulatory restrictions make it necessary to modify current pigments containing the toxic metals and substitute or reduce them. The fcc phase of Bi_2O_3 can be stabilized by cations with smaller radii (for example rare earths), and at the same time gives intensive colours. These powder materials are expected to be new ecological pigments.

Experimental

The starting materials used for the preparation of $Bi_{2(1-x)}RE_{2x}O_3$ pigments were Bi_2O_3 of 99 % purity (Merck, Germany) and RE_2O_3 of 99.9 % purity (Indian Rare Earths Ltd., India). Mixed oxides $(Bi_2O_3)_{1-x}(RE_2O_3)_x$ with nominal composition $x = 0.5$ and RE = Er, Ho, La, Nd, Dy, Lu and Y have been prepared. Above mentioned oxides were weighed in the required stoichiometric amounts and then were homogenized in an agate mortar. The mixtures were calcinated in porcelain crucibles in an electric resistance furnace. The heating of the samples in furnace was programed with increasing temperature at a rate of 10 °C min^{-1} and the calcination temperature at 800 °C was maintained for 3 h. The samples were gradually cooled to room temperature and ground in an agate mortar.

The calcinated powder samples were applied to an organic matrix (Balakom, a.s., Czech Republic) 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 $d/8^\circ$.

The colour was described in terms of CIE $L^*a^*b^*$ and CIE L^*CH° 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 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. The hue angle H° is defined by an angular position in the cylindrical colour space (for the red is $H^\circ = 0^\circ\text{--}35^\circ$, for the orange $H^\circ = 35^\circ\text{--}70^\circ$, for the yellow $H^\circ = 70^\circ\text{--}105^\circ$).

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_α 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 1,050 or 1,300 °C. The increase of temperature was 10 °C min^{-1} . $\alpha\text{-Al}_2O_3$ was used as reference material [7–9]. The samples to be examined by this thermoanalytical method, in portions of 750 mg for mixtures and 500 mg for pigments, were placed in corundum crucibles.

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

Results and discussion

In the present study, the optimum calcination temperature for pigment synthesis was also determined on the base of the simultaneous TG–DTA measurements. Thermal analysis of starting oxide Bi_2O_3 has been published previously [10]. Bi_2O_3 is characterized by the change of monoclinic modification $\alpha\text{-Bi}_2O_3$ to cubic modification $\delta\text{-Bi}_2O_3$ at 736 °C and $\delta\text{-Bi}_2O_3$ melts at 820 °C. These effects are on DTA curve characterized by two endothermic peaks.

Starting mixtures for the pigment preparation with composition $(Bi_2O_3)_{0.5}(RE_2O_3)_{0.5}$ (RE = Er, Ho, La, Nd, Dy, Lu and Y) were homogenized in an agate mortar and studied with using of simultaneous TG–DTA. TG curves of the mixtures indicate the mass loss at the measured temperature range up to 1,050 °C (Table 1) that is in interval from 0.60 to 0.70 % for Dy, Lu, Er and Ho. Samples

containing Y (0.92 %), Nd (0.96 %) and La (0.98 %) show the higher loss of mass. This effect corresponds with continual oxygen loss from Bi₂O₃ [3].

DTA curves for all starting mixtures have analogical shape in measured temperature range to 1,050 °C that are only characterized by one endothermic peak. This effect is connected with the change of monoclinic modification α -Bi₂O₃ to cubic modification δ -Bi₂O₃. Used RE₂O₃ dissolves in Bi₂O₃ during its modification change forming a solid solution of both oxides (Fig. 1). Presence of Dy and La causes the shift of temperature corresponding to the change of monoclinic modification α -Bi₂O₃ to cubic modification δ -Bi₂O₃ to higher temperature. From Table 1 it follows that for Dy it is about 740 and 741 °C for La. In comparison with the pure Bi₂O₃, the process moves higher by 5 °C. In the case of samples with Er, Lu and Nd, this effect appears at temperature range from 731 °C (Er) to 736 °C (Nd). The presence of Ho and Y produces the shift of temperature corresponding to the modification change to lower temperature. In comparison with the pure Bi₂O₃, the process moves lower by 12 °C (Ho) and 23 °C (Y).

Only one endothermic peak is evident on all DTA curves that is connected with the change of monoclinic modification α -Bi₂O₃ to cubic modification δ -Bi₂O₃. The

effect corresponding to melting temperature of these pigments is no evident on DTA curve in measured temperature range, i.e. 1,050 °C, although melting temperature of pure Bi₂O₃ is only 820 °C. The doping of rare-earth ions into Bi₂O₃ has positive effect on thermal stability of prepared pigments. Therefore, the pigments calcinated at 800 °C were also studied once again by the thermoanalytical measurements in range up to 1,300 °C to estimate their temperatures of melting.

The presence of doped RE increases melting temperature of pigments, the highest is for Er (1,250 °C), the lowest is for La and Lu (1,160 °C). The melting temperature of pure Bi₂O₃ is only 820 °C. The doping of rare-earth ions into Bi₂O₃ has very positive effect on thermal stability of prepared pigments. This fact can give a direction for colouring of ceramic glazes.

Prepared pigments of (Bi₂O₃)_{0.5}(RE₂O₃)_{0.5}, where RE = Er, Ho, La, Nd, Dy, Lu and Y [10–13], were tested to determine their colour properties. Colour properties of pigments based on Bi₂O₃ with content of rare earths after their application into organic matrix are given in Table 2. From Table 2 it follows that pigment containing Er has the highest value *a** (red hue) and the lowest value of hue angle from all prepared pigments (*H*^o = 63.10). This pigment is characterized by intense orange colour. Pigments

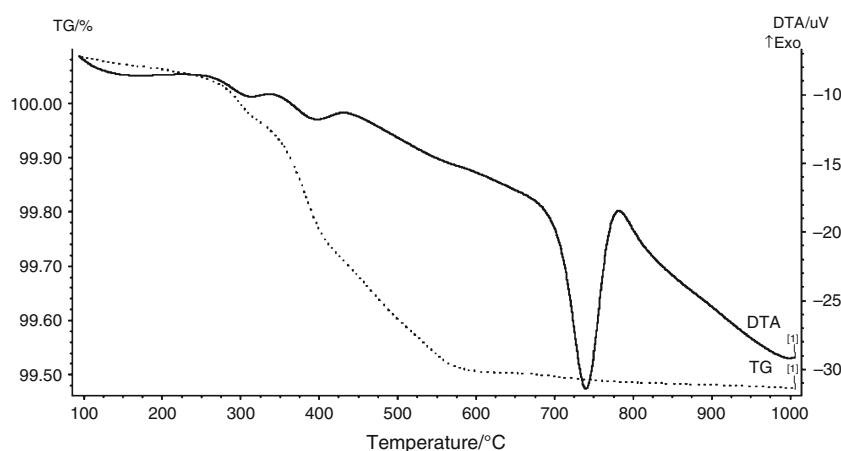
Table 1 The effect of doped rare earth elements on thermal behaviour and thermal stability of BiREO₃ compounds

RE	Mass change (100–1,050 °C)/%	Peak temperature of change α to δ /°C	Peak temperature of melting/°C
Er	0.66	731	1,250
Ho	0.70	724	1,220
Y	0.92	713	1,180
Dy	0.60	740	1,170
Lu	0.64	734	1,160
Nd	0.96	736	1,170
La	0.98	741	1,160

Table 2 The effect of doped rare earth elements on colour properties and mean particle size of BiREO₃ compounds

RE	L*	C	H ^o	<i>d</i> ₅₀ /μm
Er	64.21	59.22	63.10	9.49
Ho	70.34	59.71	71.68	9.87
Y	66.48	58.71	68.04	9.73
Dy	73.78	62.53	72.09	4.08
Lu	66.83	56.86	69.73	6.66
Nd	67.12	33.41	74.35	6.07
La	85.99	42.30	88.24	7.37

Fig. 1 TG and DTA curves of mixture for synthesis BiDyO₃ (mass of sample: 755.00 mg, atmosphere: air, heating rate: 10 °C min⁻¹)



with Y ($H^\circ = 68.04$), Lu ($H^\circ = 69.73$), Dy ($H^\circ = 72.09$) and Ho ($H^\circ = 71.68$) have the yellow–orange hue. Presence of Nd also produces yellow–orange colour but with low richness ($C = 33.41$). Pigment, that contains La, has the lowest value a^* (red colour) and therefore lies near axis b^* (yellow). The value of its hue angle is the highest ($H^\circ = 88.24$) and corresponds to yellow colour. But this yellow colour is very light because the value L^* is the highest from all prepared pigments ($L^* = 85.99$).

The best result was obtained for the pigment containing Er which indicates the lowest hue value H° for calcination temperature 800 °C and at the same time is characterized by the highest value of chroma C .

Particle sizes of prepared pigments were also tested. The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments. The mean particle sizes (d_{50}) of pigments used for colouring of different materials (paints, ceramic glazes or bodies) lie in region from 5 to 15 μm . The measurement of particle size distribution was determined for unmilled pigments. From Table 2 it follows that the presence of Er, Ho and Y in pigments is characterized by higher value d_{50} that is from 9.49 μm (Er) to 9.87 μm (Ho). Pigment containing La has value of mean particle size about 7.4 μm . Pigments doped by Nd (6.07 μm) and Lu (6.66 μm) have smaller pigment particles. Pigment with Dy is characterized by the lowest value d_{50} (4.08 μm). The mean particle sizes (d_{50}) of the all prepared pigments lie in range approximately from 4 to 10 μm (Table 2) and therefore these pigments are acceptable for various application.

The structure of the BiREO_3 pigments was also investigated by X-ray diffraction analysis. The observed results confirm that the samples containing Er, Ho and Y are single-phased [10–12] and are formed by solid solution of both oxides, i.e. BiREO_3 . X-ray diffraction patterns of these compounds can be indexed in f.c.c. fluorite-type cell. The pigments have a cubic symmetry with lattice parameter $a = 0.5465$ nm for Er, $a = 0.5477$ nm for Ho and $a = 0.5462$ nm for Y. These values of lattice parameter a are lower than value of lattice parameter $a = 0.5665$ nm of stable modification δ - Bi_2O_3 [14]. The decrease observed obviously results from different sizes of bismuth and rare-earth ions ($r(\text{Bi}^{3+}) = 0.120$ nm, $r(\text{Er}^{3+}) = 0.096$ nm, $r(\text{Ho}^{3+}) = 0.097$ nm, $r(\text{Y}^{3+}) = 0.093$ nm). In the case of La and Nd, the samples were three-phased because free Bi_2O_3 and starting oxide RE_2O_3 ($\text{RE} = \text{La}, \text{Nd}$) were identified next to compound BiREO_3 .

Conclusions

Pigments of the $\text{Bi}_{2(1-x)}\text{RE}_{2x}\text{O}_3$ type, where $x = 0.5$ and $\text{RE} = \text{Er}, \text{Ho}, \text{La}, \text{Nd}, \text{Lu}, \text{Dy}$ and Y , were studied. The results of research allow the following statements:

- The colour of these compounds is orange (with Er), yellow–orange (Ho, Y, Lu, Dy and Nd) and light yellow (for La). Intense orange colours of these pigments are based on the incorporation of doped rare-earth ions into the host lattice of Bi_2O_3 .
- In the case of Er, Ho, Lu, Dy and Y the samples are single-phased and formed by BiREO_3 . The presence of other lanthanides (La or Nd) produces more-phased samples with content of unreacted starting oxides.
- Prepared pigments indicate the increase of their melting temperatures even above 1000 °C, although melting temperature of pure Bi_2O_3 is only 820 °C. This fact can give a possibility of their utilization for colouring of ceramic glazes. First experiments perform hopeful results, especially pigments containing Er hold the orange hue even after their application into ceramic glazes, too.

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