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Thermal analysis of the $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ compounds

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Abstract New inorganic compounds having the general formula $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ (x ranges from 0.1 to 0.5) displaying orange colours have been synthesized by traditional solid-state route, as viable alternatives to lead, cadmium and chromium based yellow toxic inorganic pigments. The host lattice of these pigments is Bi_2O_3 that is doped by Lu^{3+} ions. The goal was to develop conditions for the synthesis of these compounds and to determine the influence of calcination temperature and lutetium content on their colouring effects. The simultaneous TG-DTA measurements were used for determination of the temperature region of the pigment formation and thermal stability of pigments. The pigments were also evaluated from the standpoint of their structure and particle sizes.

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

Introduction

In recent years there is a great demand for the development of new yellow coloured inorganic materials to substitute for industrial pigments that are based on heavy metals hazardous to health and environment. Inorganic pigments are widely used in various applications such as paints, plastics, rubbers, ceramics, enamels and glazes. Although $PbCrO_4$, $PbMoO_4$, $Pb_2Sb_2O_7$ and CdS have been widely employed as conventional yellow inorganic pigments, the use of these pigments has been restricted because they contain toxic elements. Praseodymium yellow ($ZrSiO_4$:Pr) has been known as one of the environmentally benign yellow pigments, which has been applied for many surface coating applications. However, this pigment is characterized by bigger particles and therefore it is difficult to apply the praseodymium yellow to paints and inks in which fine dispersions of the pigments are essentials.

Recently, several rare earth-based yellow inorganic pigments have been proposed by many researchers including our group as viable atrernatives to the existing traditional toxic pigments. 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 [1, 2]. Intense colours of these pigments are based on the incorporation of doped Ln ions into the host lattice of Bi_2O_3.

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 ¼ of the anion sites are vacant. This high oxygen vacancy concentration gives rise to a high oxygen-ion mobility [3]. The δ-phase may be stabilized below room temperature by partial cationic substitution for Bi^{3+}. Thus, the use of Ln^{3+} cations 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 [4–7].

In the present study, the new pigments having the formula $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ with various lutetium concentration levels have been prepared and their colour properties,

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as possible ecological inorganic pigments have been investigated. This type of compounds is synthesized by middle temperature calcination of the starting oxides (Bi_2O_3 and Lu_2O_3). These powder materials are expected to be new ecological pigments for colouring of paints or plastics. 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

The starting materials used for the preparation of $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ pigments were Bi_2O_3 of 99% purity (Merck, Germany) and Lu_2O_3 (Indian Rare Earths Ltd., India). Mixed oxides $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ with nominal compositions $x = 0.1$, 0.2, 0.3, 0.4 and 0.5 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 furnace was programmed with increasing temperature at a rate of 10 °C min^{-1} and the calcination temperature of 700, 750, 800 and 850 °C was maintained for three hours.

The calcinated powder samples were applied to an organic matrix 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°. The colour properties are described in terms of CIE $L^*a^*b^*$ system (1976). The value a^* (the red-green axis) and b^* (the yellow-blue axis) indicate the colour hue. The value L^* represents the lightness or darkness of the colour as related to the 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 and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. It is also possible to express the colour of pigment as a hue angle ($H° = \text{arc tg}\ (b^*/a^*)$).

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_λ 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 1050 °C. The increase of temperature was 10 °C min^{-1}. α-Al_2O_3 was used as reference material [8].

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

Results and discussion

The influence of the increasing content of lutetium on the colouring effect of the $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ pigments, where $x = 0.1$, 0.2, 0.3, 0.4 and 0.5, was studied. The colour properties of the samples prepared at temperature 700, 750, 800 and 850 °C and applied into organic matrix in mass tone are given in Table 1.

From Table 1 it follows that the growing content of Lu increases value L^* (lightness) at all temperatures and the pigments become slightly light. The increase of calcination temperature does not affect the values L^*, only for the higher temperature, i.e. 850 °C, the values L^* begin a little to increase. The values C (chroma) for temperatures 700, 750 and 800 °C are in range from 58 to 61, the increase of temperature up to 850 °C makes the grow of this range up to 63. The growing value x has no significant effect on values C (chroma). The values of hue angle $H°$ do not differ for value x at 700, 750 and 800 °C, at 850 °C the values $H°$ a little increase. Considering that the value $H°$ of these pigments lies from 68 and 74, the pigments are also characterized by orange colour. The intensive hues are

Table 1 The effect of calcination temperature on colour properties of the $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ pigments

x	700 °C			750 °C			800 °C			850 °C		
	*L**	*C*	*H*°	*L**	*C*	*H*°	*L**	*C*	*H*°	*L**	*C*	*H*°
0.1	67.99	60.15	71.14	67.44	59.92	71.14	68.18	58.28	72.08	70.51	59.27	74.21
0.2	70.48	59.00	71.50	70.70	59.67	70.05	69.97	58.79	69.73	71.95	59.21	72.29
0.3	72.21	61.32	70.30	70.86	60.97	68.28	70.95	60.67	67.75	73.09	62.81	68.54
0.4	73.23	61.00	70.52	71.44	60.70	68.92	71.67	61.04	68.66	73.31	61.88	69.80
0.5	74.67	59.88	71.34	73.78	60.72	70.28	72.51	59.00	69.50	75.35	62.53	72.09

produced at higher temperatures (800 and 850 °C). The highest value C and at the same time the lowest value $H°$ corresponds to compound with $x = 0.3$ and this pigment gives intensive orange colour (Fig. 1).

The formation of these pigments was followed by the methods of thermal analysis (TG-DTA). Thermal analysis of starting oxide Bi_2O_3 has been published previously [9]. Bi_2O_3 is characterized by the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3 at 736 °C and δ-Bi_2O_3 melts at 820 °C. Thermoanalytical curves of the second starting oxide, i.e. Lu_2O_3, are given in Fig. 2. No effects are evident on the DTA curve and gradual mass loss at measured temperature range is 0.32%. This process is probably represented by the partial oxygen loss from crystal lattice of this oxide.

Starting mixtures for the pigment preparation with composition $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$ (where $x = 0.3$ and 0.5) were homogenized in an agate mortar and studied with using of DTA.

TG curves of both mixtures indicated the mass loss at the measured temperature range (Table 2). Slight breaks at the DTA curve at temperature about 384 °C ($x = 0.3$) and 391 °C ($x = 0.5$) correspond with continual oxygen loss from Bi_2O_3 [4]. Growing temperature indicates the endothermic effect at the DTA curve with minimum at approx. 735 °C which is connected with dissolution of Lu_2O_3 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 both oxides (Figs. 2 and 3). From Table 2 it follows that the increasing content of Lu does not affect the shift of peak temperature.

The Figs. 2 and 3 demonstrate the analogical shape of the DTA curve. The thermoanalytical results are in accordance with colour properties that are better for 800

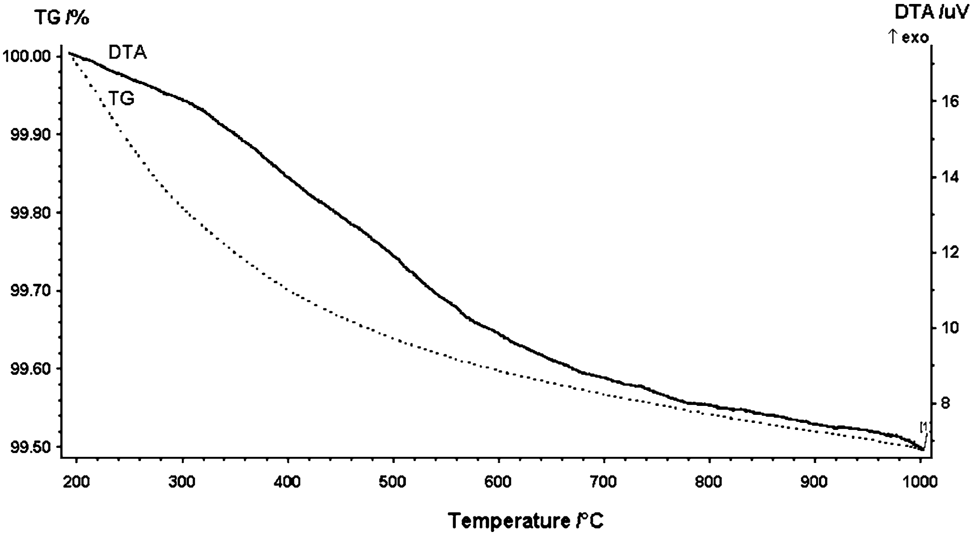

Fig. 1 TG and DTA curves of Lu_2O_3 (mass of sample: 330.10 mg, atmosphere: air, heating rate: 10 °C min^{-1})

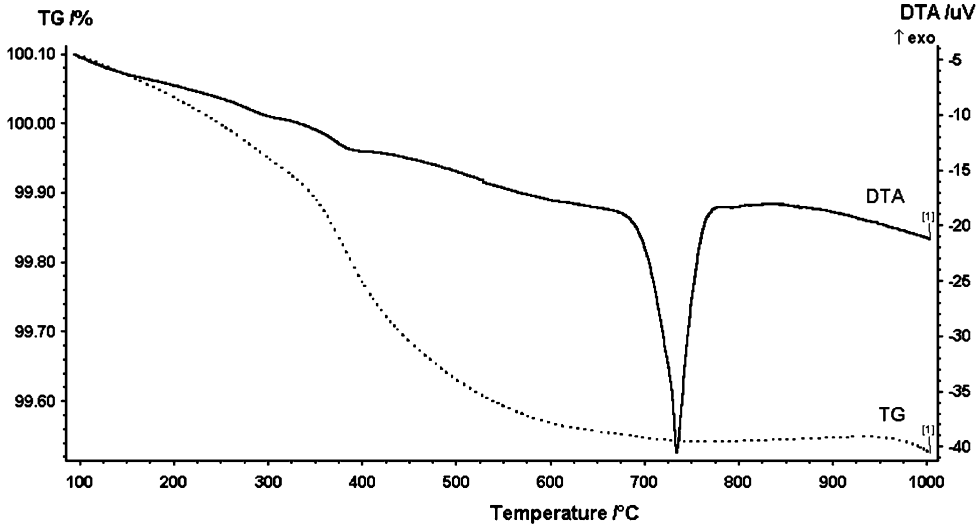

Fig. 2 TG and DTA curves of mixture for synthesis $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ (mass of sample: 628.90 mg, atmosphere: air, heating rate: 10 °C min^{-1})

Table 2 Thermal demeanor of the mixture for synthesis $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$

Temperature range/°C	$x = 0.3$		$x = 0.5$	
	Peak temperature/°C	Mass change/%	Peak temperature/°C	Mass change/%
100–325	–	−0.17	–	−0.22
325–800	384; 735	−0.38	391; 734	−0.38
800–1050	–	−0.02	–	−0.02

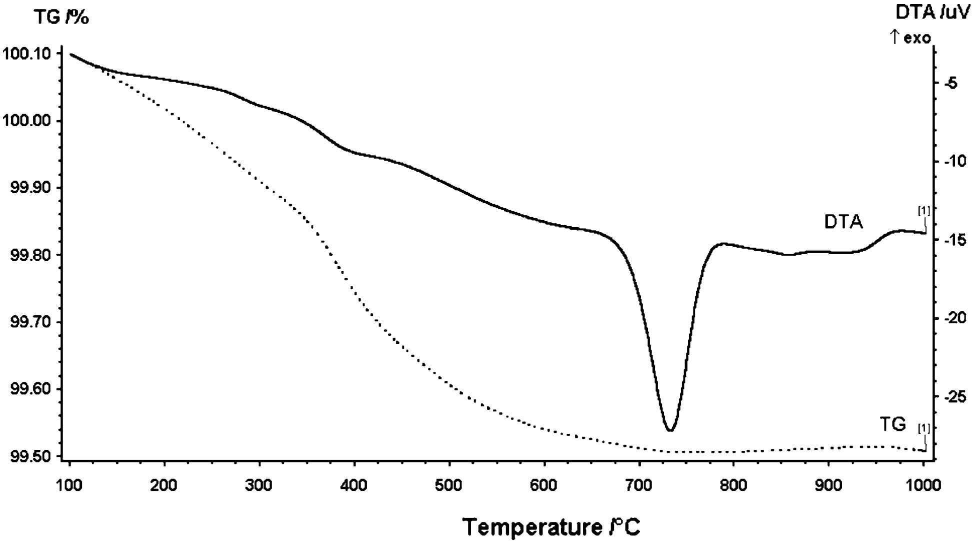

Fig. 3 TG and DTA curves of mixture for synthesis $(Bi_2O_3)_{0.5}(Lu_2O_3)_{0.5}$ (mass of sample: 663.90 mg, atmosphere: air, heating rate: 10 °C min^{-1})

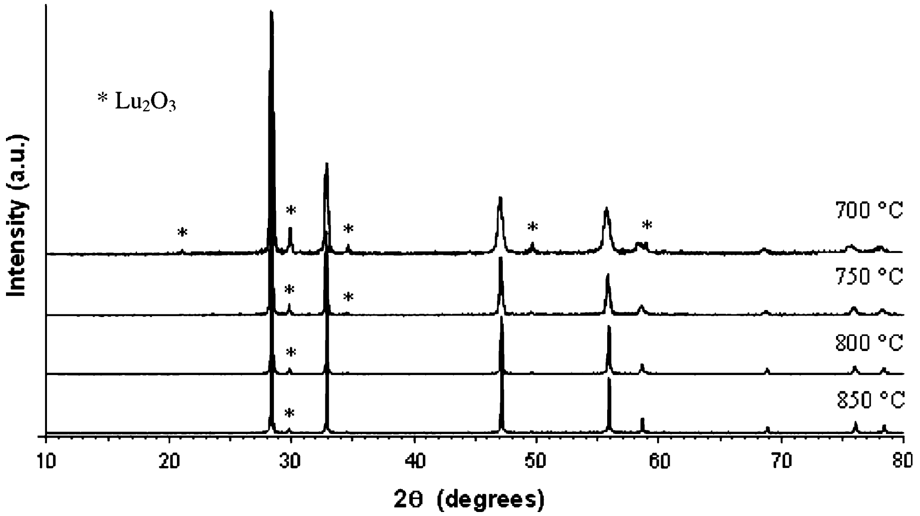

Fig. 4 The X-ray patterns of the sample $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ obtained by calcination at 700, 750, 800 and 850 °C

and 850 °C, when intensive orange colour was obtained. From DTA curves it follows that effect corresponding to melting temperature of these compounds is no evident in measured temperature range, i.e. 1050 °C, 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.

The compounds, where $x = 0.3$, prepared by calcination at 700, 750, 800 and 850 °C were studied by X-ray diffraction analysis. The X-ray pattern of this powdered material is given in Fig. 4. All compounds prepared at different temperatures were double-phased because free Lu_2O_3 was identified beside cubic modification δ-Bi_2O_3. All peaks of high intensity correspond to Bi_2O_3 that can be indexed in an f.c.c. fluorite-type cell. The presence of Bi_2O_3 as a major phase might be explained by the fact that Lu_2O_3 is dissolved in Bi_2O_3. Bi atoms are substituted by Lu atoms in the crystal lattice, forming electrically neutral

Table 3 The effect of calcination temperature on particle sizes of the $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ pigment

T/°C	d_{10}/μm	d_{50}/μm	d_{90}/μm
700	1.89	4.79	10.30
750	1.70	4.91	12.05
800	1.85	5.26	14.31
850	1.81	5.91	23.94

defects Lu_{Bi}^{x} in the solid solution $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$. Thus, the structure of Bi_2O_3 is retained. Lu^{3+} entered the Bi_2O_3 as substitutional defects because the lutetium ion $[r(Lu^{3+}) = 0.085$ nm$]$ has a smaller radius than the Bi ion $[r(Bi^{3+}) = 0.120$ nm$]$. Second phase of free Lu_2O_3 was also detected for all four temperatures but growing temperature increases intensity of peaks of major phase (δ-Bi_2O_3) and at the same time decreases intensity of peaks belonging to free Lu_2O_3.

The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments so that the pigment grain sizes (particle sizes) of the prepared compounds were also tested. For this study the pigment $(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$ calcinated at all temperatures was used.

The mean particle sizes (d_{50}) of pigments usually lie in region from 5 to 15 μm. The measurement of particle size distribution was determined for unmilled pigments. The values of pigment particles are in range from 2 (d_{10}) to 24 μm (d_{90}). The mean particle size (d_{50}) of the prepared pigments is about 5 μm. These pigments with small particles are characterized by intense orange colour. The values of particle sizes are shown in Table 3 and are acceptable for various application of these pigments.

Conclusion

The compounds $(Bi_2O_3)_{1-x}(Lu_2O_3)_x$, where $x = 0.1$ up to 0.5, were studied. Intense orange colours of these compounds are based on the incorporation of doped Lu^{3+} ions into the host lattice of Bi_2O_3. The sample with $x = 0.3$ calcinated at 850 °C possesses the most intensive orange colour.

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 orange colour was obtained, lower temperature produces lighter hues. Prepared compounds indicate the increase of their melting temperatures above 1050 °C, although melting temperature of pure Bi_2O_3 is only 820 °C. This fact can give a direction for colouring of ceramic glazes.

New coloured compounds could contribute to the basic assortment of orange and yellow inorganic pigments. These pigments are resistant to heat and represent potential alternative of inorganic pigments containing chromium and lead (chromate yellows). Thus, pigments of the $(Bi_2O_3)_{1-x}$ $(Lu_2O_3)_x$ system are potentially more environmentally friendly than those pigments currently used.

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