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THE EFFECT OF LANTHANIDES ON COLOUR PROPERTIES OF THE $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ COMPOUNDS

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Dedicated to Prof. Ing. Jaroslav Šesták, DrSc. at the occasion of his 70^{th} birthday

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Abstract

$(Bi_2O_3)_{0.7}(Ln_2O_3)_{0,3}$ solid solutions were synthesized as new inorganic yellow and orange pigments and their colour properties have been investigated as possible ecological materials. The pigments were prepared by the solid state reaction of mixed oxides $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ of various rare earth cations (Ln = Eu, Gd, Tm, Yb and Lu). All the synthesized pigment samples were found to have colour coordinates, low a and high b* and exhibit the colour from pale light yellow to orange. Reflectance spectra of the samples show high reflectance percentage in the 600 - 700 nm range. Characterization of the $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0,3}$ solid solutions suggests that they have a potential to be alternative yellow colorants for paints, inks, plastics, and ceramics.*

Keywords: Bismuth – rare earth mixed oxides, Ecological pigments, Colour properties

1. Introduction

The pigments for colouring ceramics, usually inorganic products composed of metal oxides or compounds formed from metal oxides, must possess thermal and chemical stability at high temperature and must be inert to the chemical action of the molten glaze. The inorganic pigments are widely used in various applications such as

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paints, inks, plastics, rubbers, ceramics, enamels and glazes. Unfortunately, the majority of inorganic pigments for the above applications currently employed are the toxic metals such as cadmium, lead, chromium or cobalt [1]. Nowadays these pigments are considered as completely ecologically harmful. The present research is focused on looking for new hygienically and environmentally friendly inorganic pigments which could replace the mentioned yellow and orange pigments by their colour and others pigment properties.

From this point of view just compounds 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^{3+} ions into the host lattice of Bi_2O_3. These compounds produce not only interesting colours but also contribute to a growth of the thermal stability.

The high temperature phase of bismuth sesquioxides δ-Bi_2O_3 stable between 730°C and 825°C has the oxygen-deficient fluorite-type structure with face-centered cubic lattice [3]. The δ-phase may be stabilized below room temperature by partial cationic substitution of Bi^{3+}. Thus, the use of rare-earth cations has appeared effective though a variety of crystal phases that 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 $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ with various rare earth cations (Ln = Eu, Gd, Tm, Yb and Lu) have been prepared. Their colour properties, as possible potential ecological inorganic pigments have been investigated.

2. Experimental

Starting materials for the preparation of the $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ pigments were Bi_2O_3 of 99 % purity (Lachema Brno, Czech Republic) and Ln_2O_3 (Ln = Gd, Eu, Lu, Yb and Tm) obtained from Bochemie Bohumin. The starting mixtures containing both oxides were then homogenized in an agate mortar. The mixtures were calcinated in porcelain crucibles in an electric resistance furnace with the heating rate of 10 °C/min. The calcination temperature was maintained for three hours at 850 °C.

The calcinated samples were applied to an organic matrix in both mass and reduced tone in weight ratio pigment to TiO_2 1:1 (RG – 15, Precheza a.s., Přerov, Czech Republic). 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 (6 500 K), 10° complementary observer and measuring geometry *d/8*°.

The colour coordinates were determined using CIE L*a*b* (1976) colour system. The value a* (the red-green axis) and b* (the yellow-blue axis) indicate the colour hue. The value L* represents the lighness 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 colour of pigments is also expressed by chroma $(C = a^{*2} + b^{*2})^{1/2}$

and a hue angle (H° = arc tg(b*/a*)). 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°=0–35°, for the orange H°=35–70°, for the yellow H°=70–105°).

The powder pigments were also studied by the X-ray diffraction analysis. The X-ray diffractograms were obtained by using equipment Diffractometer D8 (Bruker, GB), CuK_{λ} radiation with scintillation detector.

The thermal behaviour of the starting compounds was followed by thermal analysis using STA 449C Jupiter (NETZSCH, Germany) which allows the simultaneous registration of the thermoanalytical curves TG and DTA. The measurements were carried out in corundum crucibles in air in temperature region from 100 to 1000°C. The heating rate was 10°C min^{-1}, α-Al_2O_3 was used as a reference material.

The particle sizes distribution of the calcinated powders was obtained by laser scattering using Mastersizer 2000 MU (Malvern Instruments, GB). It is a highly integrated laser measuring system (He-Ne laser, λ = 633 nm) for the analysis of particle size distribution in the range from 0.02 to 2000 μm. The equipment uses scattering of the incident light on particles. The signal is evaluated on the basis of Mie theory or Fraunhofer bending [6].

3. Results and discussion

All the powder materials were characterized at the room temperature by X-ray diffraction analysis. Figure 1 shows the powder XRD patterns of prepared $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ (Ln = Eu, Gd, Tm, Yb and Lu) compounds. The X-ray analysis of samples with smaller ions radius of Ln^{3+} [$r(Tm^{3+})$=0.087 nm, $r(Yb^{3+})$=0.086 nm, $r(Lu^{3+})$=0.085 nm] that Bi^{3+} ion [$r(Bi^{3+})$=0.12 nm] revealed that they contained single phase. All peaks with high intensity belong to Bi_2O_3. The presence of Bi_2O_3 as a major phase might be explained by the fact that oxides of earth rare with relatively smaller ions are completely dissolved in Bi_2O_3. Bismuth atoms are substituted by these atoms in the crystal lattice, forming electrically neutral defects (Ln = Tm, Yb and Lu) in the solid solution $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$.

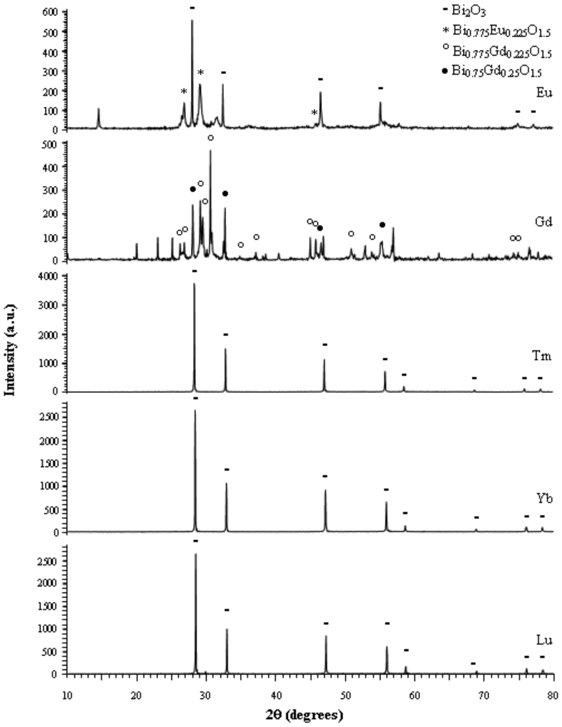

Fig. 1: Powder X-ray diffraction patterns of pigments $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ (Ln = Eu, Gd, Tm, Yb and Lu).

Diffractograms of the system doped with relatively larger Ln^{3+} ions (Eu and Gd) than the Bi^{3+} ions are heterogeneous. The mixed hexagonal and cubic phases are formed in the system doped with Gd_2O_3, the cationic radius of Gd^{3+} (0.094 nm) ion is comparatively large. $Bi_{0.775}Gd_{0.225}O_{1.5}$ has hexagonal cells with the rhombohedral symmetry. The $Bi_{0.75}Gd_{0.25}O_{1.5}$ forms the cubic phase. The XRD pattern detected two heterogeneous phases in the sample containing Eu_2O_3 [$r(Eu^{3+})$=0.095 nm]. The most intensive peaks can be assigned to Bi_2O_3. $Bi_{0.775}Eu_{0.225}O_{1.5}$ was detected as second phase from XRD pattern. Phases $Bi_{0.775}Gd_{0.225}O_{1.5}$ and $Bi_{0.775}Eu_{0.225}O_{1.5}$ were prepared and characterized before [7].

The effect of rare earth metals on the colour of the pigments based on Bi_2O_3 was analyzed from the reflectance spectra and from the colour coordinates data. The dominant reflectance and colour parameters of samples applied to an organic matrix in mass tone are given in Table 1. The dominant reflectance band lies in the 600 – 700 nm. Investigated pigments have the maximum reflectance at wavelength 700 nm. Only $(Bi_2O_3)_{0.7}(Tm_2O_3)_{0.3}$ has the highest reflectance at wavelength 650 nm. The reflection percentage in the high wavelength region is lower than the values of other samples. Pigments containing Yb, Lu and Tm provide intensive orange colour hue (H°=66–69°). These samples are characterized by high coordinates b* and a*.

The $(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$ possesses orange-yellow colour (H° = 76°). This powdered material has very high b* coordinate and low a* coordinate. The pigment with Gd produces intensive yellow colour (H° = 85°).

The $(Bi_2O_3)_{0.7}(Gd_2O_3)_{0.3}$ has the highest value of brightness L*. Figure 2 presents the comparison of colour coordinates a* and b* of samples applied to an organic matrix in mass and reduced tone. In both cases they have similar trends for the colour coordinates.

These results are very interesting because the Bi_2O_3 itself is a light yellow powder. This oxide was also studied by methods of thermal analysis that can provide the information about its thermal behaviour.

Table 1: Colour parameters and reflection percentage (R) of the $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ *pigments (mass tone)*

Nominal composition of compounds	L*	a*	b*	C	H°	Dominant reflectance [nm]	R [%]
$(Bi_2O_3)_{0.7}(Eu_2O_3)_{0.3}$	78.94	11.99	46.81	48.32	75.63	600 - 700	74 - 86
$(Bi_2O_3)_{0.7}(Gd_2O_3)_{0.3}$	80.43	5.43	58.54	58.79	84.7	600 - 700	73 - 84
$(Bi_2O_3)_{0.7}(Lu_2O_3)_{0.3}$	71.95	22.98	58.46	62.81	68.54	620 - 700	76 - 86
$(Bi_2O_3)_{0.7}(Tm_2O_3)_{0.3}$	68.56	24	54.43	59.49	66.21	630 - 670	75 - 79
$(Bi_2O_3)_{0.7}(Yb_2O_3)_{0.3}$	71.54	24.19	59.26	64.01	67.79	620 - 700	76 - 86

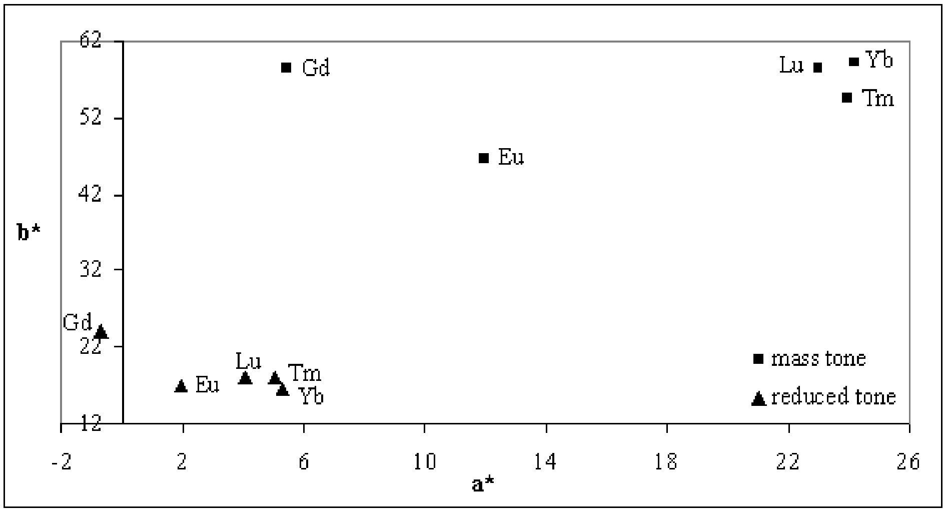

Fig.2 The effect of rare earth doping on the colour coordinates a and b* of* $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ *pigments applied to an organic matrix in both mass and reduced tone*

Thermoanalytical curves of Bi_2O_3 are given in Figure 3. The DTA curve shows two endothermic effects. The first peak with the minimum at 736°C corresponds to the change of monoclinic modification α-Bi_2O_3 to cubic modification δ- Bi_2O_3. The peak with the minimum at 820°C is connected with melting of δ-Bi_2O_3. TG curve of Bi_2O_3 indicates the mass loss (0.78%) in the temperature range from 100 to 600°C (Fig. 3). This process is represented by the partial oxygen loss (Table 2) since Bi_2O_3 is known to possess the excess of oxygen in its crystal lattice [3]. In the DTA curve, this effect is connected only with two slight traces of peak at the temperature about 308°C and 380°C.

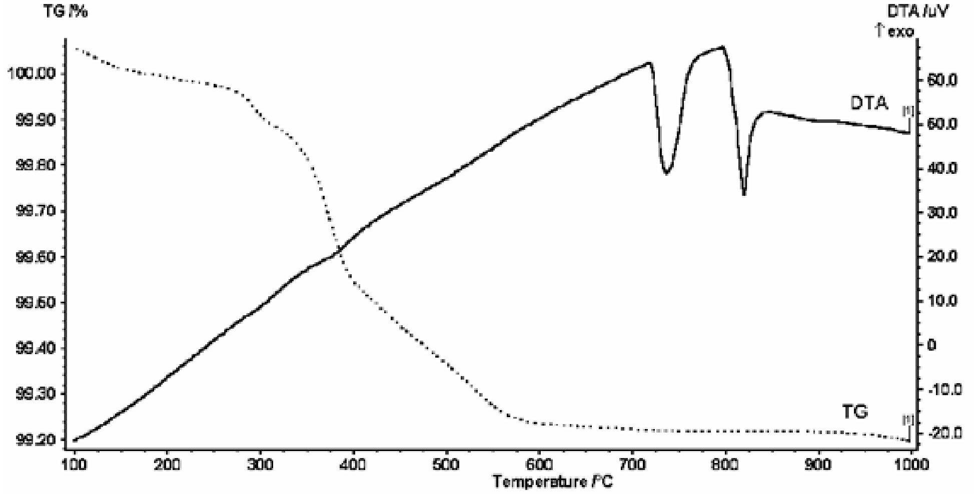

Fig. 3: TG and DTA curves of Bi_2O_3 *(sample mass 256.90 mg, air, heating rate* $10^oC\ min^{-1}$*).*

Table 2: Thermal behaviour of Bi_2O_3 *(Fig. 3)*

Temperature range [^oC]	Peak temperature [^oC]	Mass loss [%]
100-270	-	0.08
270-340	308	0.1
340-400	380	0.3
400-600	-	0.3
600-1000	736	0.02
	820	

Table 3: Particle size of the $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$ *pigments*

$(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$	Particle sizes [μm]	
	Particle size range	Mean particle size
Eu	0.97 - 8.63	3.4
Gd	0.70 - 33.14	3.64
Yb	3.01 - 21.47	7.48
Tm	2.91 - 19.06	6.81
Lu	2.70 - 21.91	7.13

The methods of thermal analysis were used for determination of thermal stability of prepared pigments. It was determined that the incorporation of doped ions of lanthanides provides the interesting colours and also contributes to a growth of the thermal stability of these compounds because all prepared pigments are characterized by the increase of their melting temperatures above 1100°C while the temperature of melting of pure Bi_2O_3 is only 820°C.

The pigment grain sizes were measured because the particle sizes and their distribution can markedly affect the colour properties of inorganic pigments. The mean particle sizes of pigments used for colouring of coating composition is approximately 1 μm. The measurement of particle size distribution was determined for unmilled samples. The values of pigment particles are in range from 1 μm to 33 μm. The mean particle size of the prepared pigments is from 3.4 μm to 7.5 μm. The values of particle sizes are show in Table 3. The samples with larger particles, i.e. containing Lu, Tm or Yb, are characterized by smaller value of brightness L*. These pigments have intensive orange colour. The powdered materials containing Gd and Eu have a smaller value of mean particle size (approx. about 3.5 μm). This fact makes that their colour becomes lighter.

4. Conclusion

The compounds $(Bi_2O_3)_{0.7}(Ln_2O_3)_{0.3}$, where Ln = Eu, Gd, Tm, Yb and Lu, were synthesized. The presence of these rare earth cations makes interesting hue of prepared samples and at the same time contributes to increase of their thermal stability. Compounds containing Yb, Lu and Tm provide intensive orange colour hue. Pigments with Eu and Gd possesses orange-yellow and intensive yellow colour. The X-ray analysis of powdered material containing Yb, Lu and Tm revealed single phase, whereas systems doped Eu and Gd are heterogeneous. The mean particle size of the prepared samples is in the range from 3.4 μm to 7.5 μm. These pigments are resistant to heat and represent potential alternative of inorganic pigments containing chromium and lead (chromate yellows). New coloured compounds could contribute to the basic assortment of orange and yellow inorganic pigments.

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References

1. M. Trojan, Z. Šolc, M. Novotný: Pigments, Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 19, J. Wiley and Sons Inc., New York 1996.
2. P. Prabhakar Rao and M. L. P. Reddy, *Dyes Pigments* 63 (2004) 169.
3. H.A. Harwig, Z. Anorg. *Allg. Chem.* 444 (1978) 151.
4. T. Takahashi, H. Iwahara: *Mater. Res. Bull.* 13 (1978) 1447.
5. B. Gonzalvo, J. Romero, F. Fernandez and M. J. Torralvo, *J. Alloys Compd.* 323-324 (2001) 372.
6. P. Šulcová, E. Proklešková, *Sci. Pap. Univ. Pardubice*, A13 (2007) 105.
7. M. Drache, S. Obbade: *J. Solid State Chem.* 142 (1999) 349.