SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
10 (2004)

STUDY OF NEW COLOUR PIGMENTS BASED ON Bi_2O_3

Petra ŠULCOVÁ[1] and Dagmar JURČÍKOVÁ
Department of Inorganic Technology, The University of Pardubice,
CZ–532 10 Pardubice

Received September 29, 2004

In this work we have studied the colour properties of the Bi_2O_3 -Ln_2O_3 system. By solid state reaction we have prepared the mixed oxides $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$, where Ln = Er and Ho, with nominal compositions x = 0.1, 0.3 and 0.5, and at calcination temperature 800 °C. The structure of prepared compounds was studied by X-ray diffraction analysis. The obtained orange oxide pigments present f.c.c. fluorite-type structure. The colour properties measured in the visible region of light (400 – 700 nm) indicate that the pigments can be expected as new ecological inorganic pigments.

Introduction

The high-temperature phase (δ-phase) of bismuth oxide (III) is known to show the defect fluorite-type (f.c.c.) crystal structure. This phase is, however, unstable below 730 °C and transforms to the monoclinic phase (α-phase). The δ-phase

---

[1] To whom correspondence should be addressed.

may be stabilized below room temperature by partial cationic substitution for Bi^{3+}. Thus, the use of Ln^{3+} cations (yttrium, erbium or holmium) has 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 [1,2]. The series of lanthanide elements, *Ln*, has chemical properties similar to each other, but their cationic radii decrease from 1.18 Å for La^{3+} to 0.97 Å for Lu^{3+} with increasing atomic number [3]. The crystal phases present in the system $Bi_2O_3 - Ln_2O_3$ are expected to change with the cationic radii.

In this work we have been interested in colour properties of the $Bi_2O_3 - Ln_2O_3$ systems. These pigments are expected to be new ecological pigments for colouring paints or plastics.

Experimental

The starting materials used were bismuth(III) oxide of 99 % purity (Merck, Germany) and oxides of rare earth elements with 99 % purity (Indian Rare Earths Ltd., India). Mixed oxides $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$, where Ln = Er and Ho, with nominal compositions $x = 0.1$, 0.3 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 Ln_2O_3 which were mixed in an agate mortar. The starting mixtures were then and calcinated in air in electric furnace at required temperature (the increase of the temperature was 10 °C min^{-1}). The samples were calcinated at 800 °C for three hours.

All the pigments prepared were applied into organic matrix 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 condition were following: illuminant *D65* (6 500 K), 10° complementary observer with geometry of measurement $d/8°$.

The colour properties are described in terms of *CIE* $L^*a^*b^*$ system (1976). 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 assumes the value from zero (black) to hundred (white). The value *C* (chroma) represents saturation of the colour and is calculated from the formula: $C = (a^{*2} + b^{*2})^{1/2}$.

The powder pigments were studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using a Difractometer D8 (Bruker, GB), CuKα radiation with scintillation detector.

The particle size distribution was measured by means of a Mastersizer 2000 MU (Malvern Instruments, UK). It is a highly integrated laser measuring system (He-Ne laser, $\lambda = 633$ nm) for analysis of particle size distribution. The equipment uses the scattering of incident light on particles. The signal is evaluated on the basis of Mie theory or Frauenhofer bending.

Results and Discussion

The synthesis of pigments based on the fluorite structure of δ-Bi_2O_3 with admixture of selected lanthanides was proposed. The influence of the increasing content of Ln_2O_3 (Ln = Ho and Er) on the colouring effect of the $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$ pigments was studied.

The colour properties of the $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$ samples prepared at temperature 800 °C and applied into organic matrix in mass tone are given in Table I. From Table I it follows that the increasing content of Ho decreases the value L^* (lightness), and the pigments become the darkest. The pigment with $x = 0.3$ has the highest value a^* (red hue) and value C (chroma). This pigment is characterized by intensive yellow-orange colour. The colour of pigment with $x = 0.5$ does not differ from pigment with $x = 0.3$.

Table I The effect of increasing Ho content on the colour properties of the $(Bi_2O_3)_{1-x}(Ho_2O_3)_x$ pigments applied into organic matrix

x	L^*	a^*	b^*	C
0.1	78.21	16.16	58.03	60.24
0.3	70.34	21.77	56.84	60.87
0.5	66.38	18.77	56.68	59.71

The effect of the increasing content of Er on the colour hue of the $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$ pigments applied into organic matrix was also followed (Table II). The increasing Er content decreases the value L^* (lightness) and coordinate a^* (red hue) and, at the same time, increases the value b^* (yellow hue). The chroma value C is the highest for the pigment with $x = 0.3$. This pigment has the best orange colour, too.

Table II 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
0.1	69.63	28.18	48.27	55.89
0.3	64.21	26.79	52.81	59.22
0.5	63.31	25.25	53.16	58.85

From results of colour properties obtained it follows that the prepared samples have orange hues (quite low a^* and high b^* values and high values of

L^* and C); however, the individual hues of the samples differ. The obtained values of colour coordinates a^* and b^* and the values of coordinates of lightness L^* indicate that the samples can be used as inorganic pigments.

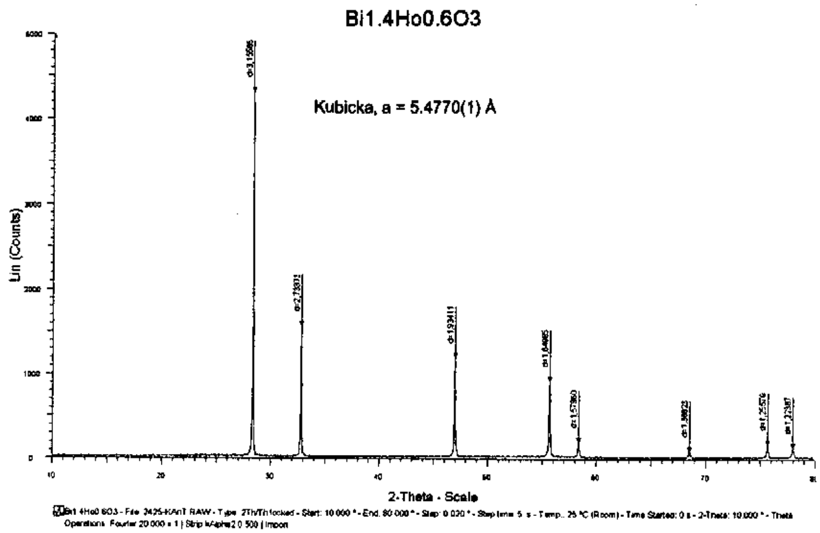

Fig. 1 The X-ray pattern of the sample $Bi_{1.4}Ho_{0.6}O_3$ obtained by calcination at 800 °C

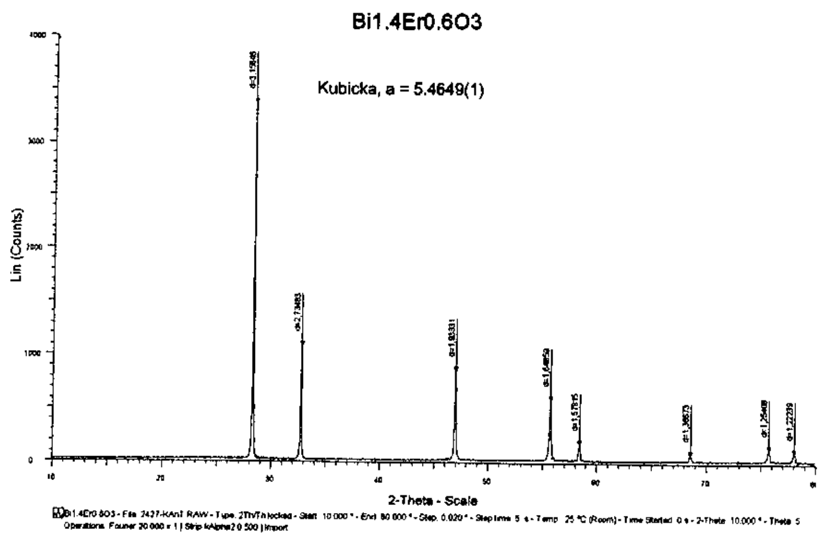

Fig. 2 The X-ray pattern of the sample $Bi_{1.4}Er_{0.6}O_3$B obtained by calcination at 800 °C

The structure of the $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$ pigments (Ln = Ho, Er; x = 0.3) was also investigated by X-ray diffraction analysis (Figs 1 and 2). These samples are homogeneous. The X-ray diffraction patterns of these compounds can be indexed in an f.c.c. fluorite-type cell. The pigments have a cubic symetry with lattice parameter a = 0.54770 nm for Ho and a = 0.54649 nm for Er. These results of calculated lattice parameters are in good agreement with those previously reported [2].

The measurements of particle size distribution were performed with unmilled pigments. The value d_{50} of the pigment $Bi_{1.4}Er_{0.6}O_3$ is 11.48 μm, being 9.86 μm for the pigment $Bi_{1.4}Ho_{0.6}O_3$.

Conclusion

The compounds of the $(Bi_2O_3)_{1-x}(Ln_2O_3)_x$ system, where Ln = Er and Ho are characterized by intensive yellow-orange and orange colours and can be used as new inorganic pigments. They are environmentally friendly and therefore very progressive too. These pigments could complete the basic assortment of colour inorganic pigments and substitute some problematic pigments from the ecological point of view, especially chrome yellows (lead chrome) which belong to the most problematic pigments at present [5].

Acknowledgements

The work was supported by Grant Agency of Czech Republic, grant project No. 104/04/1078. Authors thank doc. Ing. Ludvík Beneš, CSc. for X-ray diffraction analysis.

References

[1] Takahashi T., Iwahara H.: Mater. Res. Bull. **13**, 1447 (1978).
[2] Iwahara H., Esaka T., Sato T., Takahashi T.: J. Solid State Chem. **39**, 173 (1981).
[3] Shannon R.D., Prewitt C.T.: Acta Crystallogr. Sect. B 25, 925 (1969).
[4] Šulcová P.: *Properties of Inorganic Pigments and Methods of their Evaluation* (in Czech), p. 14–37, University of Pardubice, Pardubice, 2000.
[5] Trojan M., Šolc Z, Novotný M.: *Pigments*, Kirk-Othmer Encyclopedia of Chem. Technol., p. 45, Vol. 19, J. Wiley and Sons Inc., New York, 1996.