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Thermal analysis of doped Bi_2O_3

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Abstract New environmentally inorganic pigments based on Bi_2O_3 doped by metal ions, such as Zr^{4+} and Dy^{3+} have been developed and characterized using the methods thermal analysis, X-ray powder diffraction, and spectral reflectance data. The compounds having formula $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$ ($x = 0.2$, 0.6, 1.0, and 1.2) were prepared by the solid state reaction. Methods of thermal analysis were used for determination of the temperature region of the pigment formation and thermal stability of compounds. The incorporation of doped ions in Bi_2O_3 changes the color from yellow to orange and also contributes to a growth of their thermal stability. This property gives a direction for coloring ceramic glazes.

Keywords ZrO_2–Bi_2O_3 system · Bismuth-rare earth mixed oxides · Thermal analysis · Ecological pigments

Introduction

δ-Bi_2O_3 is the best ionic conductor in intermediate temperature range from 700 to 800 °C. Many attempts have been made to synthesize good ionic conductor which has better stability and ionic conductivity, particularly, in intermediate temperature range from 600 to 800 °C. Therefore, lot of research is focused on the synthesis of new solid electrolyte materials which have better ionic conductivity in the above-mentioned temperature range with good thermal stability for solid oxide fuel cell (SOFC). Similarly, pure Bi_2O_3 and doped bismuth oxide also shows better ionic conductivity than yttria-stabilized zirconia (YSZ) in temperature region but the higher conducting δ-Bi_2O_3 phase is stable in narrow range of temperature from 730 to 825 °C. The stability of the δ-Bi_2O_3 phase at lower temperature can be achieved by substituting Bi^{3+} with different mono- to pentavalent cations. For stabilization, the stabilizing cations must have large ionic radii, lower charge, and higher ionicity. Many attempts have been made to synthesize either ZrO_2-doped Bi_2O_3 or Bi_2O_3-doped ZrO_2 rich phase to achieve higher conductivity [1].

The structure of δ-modification of Bi_2O_3 is characterized by a face centered cubic (fcc) cation sublattice and can be described as a defective fluorite structure where ¼ of the anion sites are vacant. The fcc phase of Bi_2O_3 can be also stabilized by cations of lanthanides. The incorporation of doped ions contributes to a growth of the thermal stability and also affords interesting colors. From this point of view, compounds based on Bi_2O_3 have found increasing popularity because they provide interesting color hue from yellow to orange. Intense colors of these powder materials are results from the incorporation of Ln ions (Ln = rare earth elements) into the stable host lattice of Bi_2O_3 [2–6].

In this study, the new pigments having the formula $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$ ($x = 0.2$, 0.6, 1.0, and 1.2) with various dysprosium and zirconium concentration levels were prepared by the solid state reaction. Their color properties, as possible potential ecological inorganic pigments have been investigated. This type of compounds is synthesized by middle temperature calcination of the starting oxides (Bi_2O_3, ZrO_2, and Dy_2O_3). These powder materials are expected to be new ecological pigments for coloring 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

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information about the temperature region of the pigment formation.

Experimental

The starting materials used for the preparation of $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$ pigments were Bi_2O_3 of 99% purity (Merck, Germany), ZrO_2 of 99% purity (Merck, Germany), and Dy_2O_3 of 99.9% purity (Indian Rare Earths Ltd., India). Mixed oxides of $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$ with nominal compositions $x = 0.2$, 0.6, 1.0, and 1.2 have been prepared. The 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 temperatures of 700, 750, 800, and 850 °C were maintained for 3 h.

The calcinated powder samples were applied to an organic matrix in mass tone. The final paints were evaluated for color change by measuring spectral reflectance in the visible region of light (400–700 nm) using a ColorQuest XE (HunterLab, USA). The measurement conditions were following: an illuminant *D65*, 10° complementary observer and measuring geometry *d*/8° [7]. The CIE 1976 $L^*a^*b^*$ colorimetric system was used as recommended the Commission Internationale de l′Eclairage (CIE), L^* is the lightness axis [black (0) to white (100)], a^* is the green to red, and b^* is the blue to yellow axis. The parameter C (chroma) represents saturation of the color and $H°$ represents the hue angle. The chroma is defined as $C = [(a^*)^2 + (b^*)^2]^{1/2}$. The hue angle $H°$ is expressed in degrees and ranges from 0° to 360° and is calculated using formula $H° = \tan^{-1}(b^*/a^*)$.

The band gap energy E_g was determined from reflectance spectra using the Kubelka–Munk function. The Kubelka–Munk function was obtained by measurement of absorption by powder material. The function *K–M* is given by:

$$K{-}M = (1-R)^2/2R = k/s,$$

where R is the reflectance of the sample, k is absorption coefficient, and s is reflectance coefficient. The absorption edge is determined from the plot *K–M* versus $h\nu$. The wavelength is substituted by value energy $h\nu$ in the formula:

$$h\nu = \frac{1236}{\text{wavelength (nm)}}.$$

The value of band gap was extrapolated from the linear part of the curve from the graph.

The particle size distribution of the samples was investigated in water medium using the laser scattering particle size distribution analyzer (Malvern Instruments, Ltd. GB). The samples were ultrasonically homogenized for 180 s before measurement and the signal was evaluated on the basis of Fraunhofer bending.

The phase purity of the synthesized samples were characterized by powder X-ray diffraction using conventional powder techniques in diffractometer (D8 Bruker, GB) with Cu K_λ radiation.

Thermal gravimetric analysis/differential thermal analysis was performed using STA 449C Jupiter (NETZSCH, Germany) equipment at heating rate 10 °C min^{-1} from 30 to 1,050 °C under air atmosphere. α-Al_2O_3 was used as reference material [8].

Results and discussion

The influence of various dysprosium and zirconium concentration on the color properties of the $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$ pigments, where $x = 0.2$, 0.6, 1.0, and 1.2, was investigated. The color properties of the samples prepared at temperatures 700, 750, 800, and 850 °C and applied into organic matrix in mass tone are given in Table 1.

Based on values L^*, C, and $H°$ of pigments, it can be seen that increasing dysprosium and zirconium content and calcination temperature have not a great influence on the color hue of powder materials. The hue $H°$ values of all prepared samples are in the range approximately from 65° to 80°. Prepared pigments also have similar values of chroma C (52–64). The value of lightness lies in region approximately from 66 to 80. All these pigments are characterized by orange color but for the lowest temperature is lighter. The best results were obtained for the pigment $x = 1.0$ which indicate the lowest hue value $H°$ for calcination temperature 850 °C and at the same time is characterized by the highest value of chroma C.

The color hue value is in agreement with the observed change in band gap energy ($E_g = 2.46$–2.78 eV). The value $E_g = 2.46$ eV means that all colors having energies lower then E_g are transmitted, while the other colors are absorbed. In this case, violet, blue, and part of green color is absorbed and the final color of the powder samples is orange. The value E_g decreases with calcination temperature to value $E_g = 2.54$ eV (Table 2). This absorption edge corresponds with a value of wavelength ~502 nm. The materials with a band gap of about 2.5 eV are absorbing blue and violet part of visible spectra.

The formation of these pigments was also 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

Table 1 The effect of calcination temperature on color properties of the Bi_{2-x} $Dy_{x/2}Zr3_{x/8}O_3$ pigments

x	Temperature/°C											
	700			750			800			850		
	*L**	*C*	*H*°	*L**	*C*	*H*°	*L**	*C*	*H*°	*L**	*C*	*H*°
0.2	80.06	56.83	79.83	66.65	60.38	70.66	66.54	63.19	70.13	67.97	63.03	70.60
0.6	73.57	59.52	71.39	74.15	60.42	71.17	74.91	64.11	71.60	75.40	61.59	71.98
1.0	71.43	56.10	68.43	71.13	56.86	66.13	69.49	56.68	66.89	71.61	58.83	65.76
1.2	71.65	56.21	67.88	70.73	55.20	66.44	69.69	55.31	65.39	67.19	52.57	64.71

Table 2 Band gap (E_g) of the $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$ pigments calcinated at different temperatures

x	Temperature/°C			
	700 E_g/eV	750 E_g/eV	800 E_g/eV	850 E_g/eV
0.2	2.78	2.70	2.67	2.67
0.6	2.47	2.66	2.59	2.58
1.0	2.47	2.63	2.58	2.55
1.2	2.46	2.61	2.54	2.54

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., Dy_2O_3, are not interesting, because no effects were evident on the DTA curve and gradual mass loss at measured temperature range was 0.21%. This process is probably represented by the partial oxygen loss from crystal lattice of this oxide [6]. The last oxide, ZrO_2, in measured temperature interval does not give effects at TG and DTA curves.

Starting mixture for the pigment preparation with composition $x = 0.2$ was homogenized in an agate mortar and studied simultaneously using TG–DTA. TG curve of the mixture indicates the mass loss at the measured temperature range (Table 3). Slight breaks at the DTA curve at temperatures of about 286 and 382 °C correspond with continual oxygen loss from Bi_2O_3 [5]. Growing temperature causes the endothermic effect at the DTA curve with minimum at ~735 °C which is connected with dissolution of Dy_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 both oxides (Fig. 1). The thermoanalytical results are in accordance with color properties that are better for 800 and 850 °C, when intensive orange color was obtained. From DTA curve, it follows that effect corresponding to melting temperature of this compound is evident at 933 °C. The doping of the ions into Bi_2O_3 has positive effect on thermal stability of prepared pigments.

Starting mixtures, where $x = 0.6$, 1.0, and 1.4, were also followed by TG–DTA measurement up to 1,050 °C. The shapes of TG and DTA curves are analogical to record demonstrated in Fig. 1. DTA curves are only characterized by two endothermic effects, slight breaks at the DTA curve at temperature range approximately from 270 to 400 °C, that correspond with continual oxygen loss from Bi_2O_3, are missing. The results of mass loss and peak temperature of these measurements are given in Table 3. The higher content of Dy and Zr causes the shift of temperature corresponding to the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3 to lower temperature. From Table 3, it follows that for $x = 0.6$ it is about 723 °C and 724 °C for $x = 1.0$. In comparison with the starting mixture, where $x = 0.2$, the process moves lower by 10 °C. In the case of sample with $x = 1.2$, this effect appears at temperature 719 °C. The second endothermic effect demonstrates the tendency of the pigment to melt.

Table 3 Thermal demeanor of the mixtures for synthesis $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$

Temperature range/°C	$x = 0.2$		$x = 0.6$		$x = 1.0$		$x = 1.2$	
	Peak temperature/°C	Mass loss/%	Peak temperature/°C	Mass loss/%	Peak temperature/°C	Mass loss/%	Peak temperature/°C	Mass loss/%
100–300	286	0.05	–	0.06	–	0.07	–	0.09
300–430	382	0.19	–	0.19	–	0.16	–	0.14
430–650	–	0.08	–	0.09	–	0.09	–	0.08
650–1,050	735	0.38	723	0.30	724	0.28	719	0.22
	933		1,015		989		998	

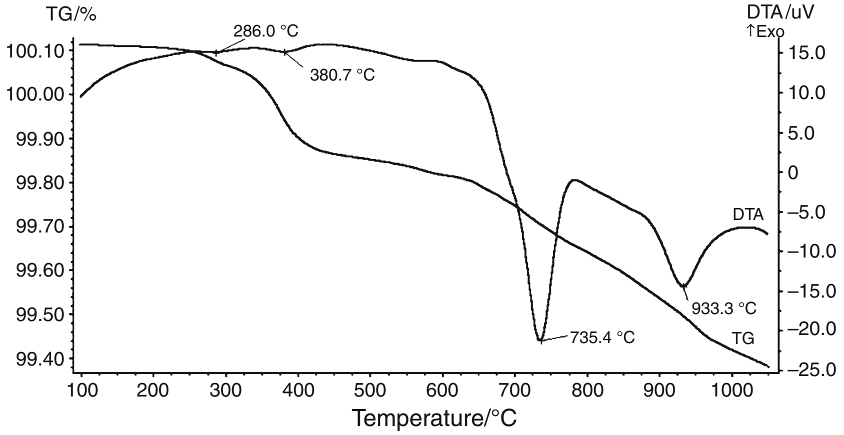

Fig. 1 TG and DTA curves of mixture for synthesis $Bi_{1.8}Dy_{0.1}Zr_{0.075}O_3$ (mass of sample: 654.90 mg, atmosphere: air, heating rate: 10 °C min^{-1})

Table 4 The mean particle size d_{50} of the $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$ pigments calcinated at different temperatures

x	Temperature/°C			
	700 d_{50}/µm	750 d_{50}/µm	800 d_{50}/µm	850 d_{50}/µm
0.2	8.50	6.85	7.60	7.21
0.6	5.21	5.50	7.55	6.92
1.0	3.50	3.84	3.54	3.90
1.2	3.16	2.63	3.34	3.14

From Table 3, it follows that for $x = 0.6$ it is about 1,015 °C, higher content of Dy and Zr causes the decrease of melting temperature of pigment to 989 °C for $x = 1.0$ and 998 °C for $x = 1.2$. This temperature also represents the stability of these pigments [10, 11].

The particle sizes and particle size distribution can markedly affect the color properties of inorganic pigments. The main objective was also to monitor the influence of particle sizes on the color properties of the pigment. For this study, the pigments $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$, where $x = 0.2$, 0.6, 1.0, and 1.2, calcinated at all temperatures were used. The values of pigment particles of unmilled powder samples are in the range from 2.63 µm (d_{50}) to 8.50 µm (d_{50}). The increase in value x, the decline in values d_{50}; the growing calcination temperature has not significant effect on mean particle size. The values of d_{50} are shown in Table 4 and are acceptable for various applications of these pigments.

The compounds, where $x = 1.0$, prepared by calcination at 750, 800, and 850 °C were studied by X-ray diffraction analysis. Sample obtained at 750 °C was three-phased, α-Bi_2O_3, ZrO_2, and $0.7Bi_2O_3 \cdot 0.3Dy_2O_3$ were indicated. Both compounds prepared at temperatures from 800 and 850 °C were double-phased because free ZrO_2 were identified beside cubic modification δ-Bi_2O_3. All peaks of high intensity correspond to Bi_2O_3 that can be indexed in a fcc fluorite-type cell. The presence of Bi_2O_3 as a major phase might be explained by the fact that Dy_2O_3 and ZrO_2 are dissolved in Bi_2O_3. Growing calcination temperature degreases intensity of peaks belonging to free ZrO_2 from 11.52% for 750 °C, 8.02% for 800 °C to 6.7% at 850 °C.

Conclusions

The compounds $Bi_{2-x}Dy_{x/2}Zr_{3x/8}O_3$, where $x = 0.2$, 0.6, 1.0, and 1.4, were studied. Intense orange colors of these compounds are based on the incorporation of doped Dy^{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 and 850 °C. This result is also in accordance with color properties that are better for 850 °C, when intensive orange color was obtained, lower temperature produces lighter hues. The sample with $x = 1.0$ calcinated at 850 °C is characterized by the most intensive orange hue.

The methods of thermal analysis also provided the information about the temperature stability of the pigments that is about 900 °C for $x = 0.2$ and ~950 °C for $x = 1.0$ and 1.2. Prepared pigments indicate the increase of their melting temperatures and this fact can give a direction for coloring of ceramic glazes.

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