Synthesis and characterization of the $Bi_2Ce_{2-x}Zr_xO_7$ pigments

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Abstract

This contribution is focused on the synthesis, characterization and optical properties of new inorganic pigments which are environment–friendly and can substitute some toxic metals in interesting colour compounds. The studied pigments were prepared by the solid–state reaction. The colour properties of prepared applications were investigated depending on the content of Zr and temperature of calcination (800–1000 °C after step 50 °C). The optimum conditions for their synthesis were determined. The pigments were evaluated from the standpoint of their particle sizes. Characterization of $Bi_2Ce_{2-x}Zr_xO_7$ pigments (x = 0 to 2 after step 0.25) suggests that they have a potential to be alternative yellow or orange colourants for paints, plastics, ceramics and building materials.

Keywords

Bismuth mixed oxides, inorganic pigments, pyrochlore compounds, colour properties, yellow colour.

Introduction

In the field of powder materials, it is a current need to develop environmental–friendly inorganic pigments to replace the ones containing toxic elements. Commercial yellow pigments used in the industry are based on heavy metals such as Cd, Cr and Pb that are hazardous to health and environment [1]. For this reason, our attention was focused on the preparation of new high–performance ecological pigments with general formula $Bi_2Ce_{2-x}Zr_xO_7$, where x = 0 to 2 after step 0.25 based on pyrochlore solid solutions. The basic representative of pyrochlore pigment is the Naples yellow $Pb_2Sb_2O_7$ that represents sulphur–yellow up to orange–yellow tint depending on the mass ratio of lead and antimony. Lead antimonate yellow is an ancient synthetic pigment that has been producing since antiquity in Middle Eastern ceramic and glass manufacture. Starting from Medieval times, it is used rapidly spread to Western European art for the production of glass and glazed ceramics, of enamels on metals and more recently (since the 16^{th} century) of paintings [2,3].
Materials with the pyrochlore lattice structure have attracted much recent attention due to their wide applications in ceramic thermal barrier coatings, high–permittivity dielectrics, potential solid electrolytes in solid–oxide fuel cells, and immobilization hosts of actinides in nuclear waste. Pyrochlore materials have the general formula

$A_2B_2O_7$, where A and B are metallic cations that can be either trivalent and tetravalent or divalent and pentavalent, respectively. The general formula of pyrochlore can also be written as $A_2B_2O_6O'$. A broad range of chemical substitutions at the A, B and O crystallographic sites could produce hundreds of compositions with a specific set of desired properties for various electrical, magnetic and optical applications. The A element could be a rare earth cation with inert lone pair electrons and B element could be a transition metal with variable oxidation states and/or a post transition metal. The pyrochlore structure (space group Fd–3m) is closely related to the fluorite structure and can be thought of as a cation–ordered anion deficient fluorite lattice, in which the cations form a face–centered cubic array. In X–ray diffraction (XRD) measurements, the weak characteristic superlattice peaks are used to distinguish the pyrochlore from the fluorite structure [4–6].
The compounds on the base of Bi_2O_3 belong to pigments of oxide types and seem to be interesting because they provide colour hues from yellow to orange. Intense colours of these pigments are based on the incorporation of doped Ln ions into the host lattice of Bi_2O_3 [7].
The main attention in our research was focused on the synthesis of yellow and orange pigments which are doped by cerium and zirconium ions. These pigments with general formula $Bi_2Ce_{2-x}Zr_xO_7$ are expected to become new high–performance ecological pigment and a worthy replacement for the currently applied toxic compounds. The goal was to suggest and elaborate the synthesis conditions of these compounds and to determine the influence of doped elements on the colour properties, particle size distribution and application in different binders.

Experimental

The pigments $Bi_2Ce_{2-x}Zr_xO_7$ (x = 0, 0.25, 0.5, 0.75; 1, 1.25, 1.5, 1.75 and 2) were synthetized by solid state reaction. As the initial compounds for preparation of the samples were used Bi_2O_3 (99.8 % purity, Lachema Pliva, a.s., CZ), CeO_2 (99.9 % purity, ML–Chemica, CZ) and ZrO_2 (99 % purity, Riedel–de Haën, DE). The precursors employed for the traditional ceramic way of preparation were homogenized in the porcelain mortar with pestle. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace with the heating rate of 10 °C min^{-1}. The calcination temperatures in interval from 800 to 1000 °C after step 50 °C were maintained for 2 h.
All prepared pigments were applied to an organic matrix (dispersive acrylic paint Parketol, Balakom, a.s., CZ) in mass tone and evaluated for colour change by measuring of spectral reflectance in the visible region of light (400–700 nm) using a ColorQuest XE (HunterLab, USA). The samples (in 12.5% w/w) were applied into a middle–temperature borate–silicate (transparent) glaze G 07091 (Glazura a.s., CZ) and the temperature of glazing was 1000 °C during the time of 15 min. The measurements conditions for colour change were following: an illuminant *D*65, 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 in relation to scale extending from white (*L** = 100) to black (*L** = 0).
The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000 MU (Malvern Instruments, Ltd. GB). It is a highly

integrated laser measuring system, which evaluates the particle size using red light (He–Ne laser, λ = 633 nm) and blue light (solid–state light source, λ = 466 nm).

Results and discussion

The aim of the research was to find the best conditions for the preparation of the pigments and also to determine the influence of growing content of zirconium and calcination temperatures on their colour properties after application into organic matrix and also into a ceramic glaze.

The colour hue of pigments applied into organic matrix is visible dependent on the content of Zr (Table 1 and 2). The colour properties of pigments calcinated at temperature interval 800–900 °C are noticed in Table 1. The increasing content of Zr leads to a considerable shift in tones and primarily to the weakening of the yellow to yellow–orange tone in all analysed pigments. The values of brightness *L** have become lower with the growing amount of Zr. Opposite to them the values of colour coordinates *a** and *b** are escalating at the temperature 800 and 850 °C. From the temperature 900 °C, the value of colour coordinates *a** and *b** have a decreasing character. The samples with zirconium content x = 0–1.25 and temperature 1000 °C can be described as darkest due to the measured values in the interval 67.83–71.84 (Table 2). The highest contribution to the yellow hue record pigments containing Zr 1.5 and 1.75 at the highest calcination temperature. Based on the investigation and evaluation of colour properties of the samples, the temperature 1000 °C is the best for the preparation of dark yellow–orange colour.

The colour of pigments applied into ceramic glaze is in all cases light yellow–green. These applications are characterized by negative values of the colour coordinate *a** in the whole temperature range (Table 3 and 4). In this case, the colour coordinate *b** has a decreasing tendency up to 850 °C with the increasing content of zirconium. After values have an alternate character. The prepared samples can be characterized by high grant of brightness *L**, which lies in narrow interval approx. 87–90. The temperature 1000 °C provides the darkest yellow–green hues. In comparison with an application into organic matrix in terms of an acquired colour properties showed that pigments applied to ceramic glaze provided a lighter yellow colour with a green contribution.

Table 1 Effect of calcination temperature (800–900 °C) on colour properties of pigment $Bi_2Ce_{2-x}Zr_xO_7$ applied into organic matrix in mass tone

	800 °C			850 °C			900 °C		
x	***L****	***a****	***b****	***L****	***a****	***b****	***L****	***a****	***b****
0	85.10	3.94	53.25	77.70	11.78	58.27	76.51	7.29	55.70
0.25	83.34	7.65	62.66	80.42	10.33	54.17	74.18	17.42	56.10
0.5	79.38	12.18	59.75	80.35	9.57	55.98	73.82	17.21	54.92
0.75	80.72	11.06	60.66	80.03	9.75	56.98	76.79	14.45	57.56
1	81.91	10.19	64.58	80.28	10.74	59.93	74.72	14.68	51.98
1.25	79.00	11.63	61.68	78.63	10.51	58.98	76.02	12.91	55.36
1.5	79.89	11.65	65.06	79.32	11.55	61.83	76.17	11.56	52.39
1.75	78.40	13.45	65.25	78.81	10.52	62.00	74.60	10.89	48.91
2	76.63	15.30	66.21	79.26	10.62	61.05	75.54	5.94	44.58

Table 2 Effect of calcination temperature (950 and 1000 °C) on colour properties of pigment $Bi_2Ce_{2-x}Zr_xO_7$ applied into organic matrix in mass tone

	950 °C			1000 °C		
x	***L****	***a****	***b****	***L****	***a****	***b****
0	70.63	1.13	35.11	67.83	10.82	48.73
0.25	76.60	13.46	53.36	70.86	23.31	60.71
0.5	77.18	12.26	54.07	71.83	22.61	62.48
0.75	71.45	21.32	60.62	72.84	21.94	63.88
1	74.05	11.48	50.62	72.70	21.78	63.72
1.25	75.28	8.38	49.38	71.87	21.77	63.94
1.5	77.45	8.67	49.32	76.42	18.00	66.54
1.75	76.26	5.81	43.24	76.09	18.37	66.49
2	75.93	1.59	35.06	74.29	19.32	64.25

Table 3 Effect of calcination temperature (800–900 °C) on colour properties of pigment $Bi_2Ce_{2-x}Zr_xO_7$ applied into ceramic glaze

	800 °C			850 °C			900 °C		
x	***L****	***a****	***b****	***L****	***a****	***b****	***L****	***a****	***b****
0	89.06	-4.25	30.52	87.15	-2.99	38.95	87.47	-3.70	37.49
0.25	89.10	-3.97	30.42	89.24	-3.70	32.06	86.91	-2.71	37.22
0.5	89.36	-3.67	30.30	89.01	-3.45	31.05	87.61	-2.68	35.15
0.75	88.98	-3.44	28.90	88.97	-3.78	30.46	86.99	-2.66	35.13
1	88.34	-1.98	27.37	88.79	-3.18	29.56	86.99	-2.51	33.35
1.25	88.65	-3.02	28.29	88.62	-2.80	29.10	87.52	-2.35	33.43
1.5	88.43	-2.11	27.62	87.79	-1.80	27.63	87.50	-2.99	31.13
1.75	87.48	-1.75	28.35	87.59	-1.51	28.17	87.23	-1.47	28.58
2	87.67	-0.76	21.43	87.47	-0.20	23.47	87.27	-0.35	22.08

Table 4 Effect of calcination temperature (950 and 1000 °C) on colour properties of pigment $Bi_2Ce_{2-x}Zr_xO_7$ applied into ceramic glaze

	950 °C			1000 °C		
x	***L****	***a****	***b****	***L****	***a****	***b****
0	87.01	-3.35	40.24	86.56	-2.86	40.09
0.25	87.31	-2.99	37.82	87.00	-3.42	38.57
0.5	86.70	-2.64	37.69	86.81	-2.49	36.41
0.75	86.48	-2.44	34.31	87.00	-3.60	36.88
1	86.47	-1.52	32.42	86.59	-2.32	34.68
1.25	87.26	-2.62	34.03	87.31	-3.47	32.79
1.5	87.28	-2.07	32.68	86.59	-1.88	30.86
1.75	87.41	-1.80	29.25	87.21	-1.73	29.90
2	87.13	-0.28	21.95	88.07	-0.54	19.60

The particle size distribution of pigments that can significantly affect the colour properties was also measured. Therefore, the synthetized samples were measured from this point of view. The most important value which characterizes particle size and predetermines pigment for various applications is the value d_{50} (median). The parameter *span* informs about the width of the distribution (span = $(d_{90} - d_{10})\cdot d_{50}^{-1}$). The samples of $Bi_2Ce_{2-x}Zr_xO_7$ calcinated at the temperature 800 °C have a main size value d_{50} in the interval from 1.4 to 3.7 μm (Table 5). The lowest value of *span* (3.0) was achieved for the sample with the content of zirconium x = 2. The following temperature of calcination caused an increase of the value d_{50} which is located in the interval from 2.2 to 6.3 μm. The parameter *span* lies in the range 3.4–5.7. The great leap occurred at 900 °C where the value d_{50} increases with the content of Zr (d_{50} = 8.4–17.0 μm). The *span* parameter, in this case, is lowest for the sample with x = 3.6. From the values of samples calcinated at 950 °C it is obviously that the values of d_{50} are varied in the interval from 7.1 to 10.7 μm. Parameter *span* is characterized by values in a narrow range 4.1–4.7. The highest temperature of calcination caused a slight increase in the value d_{50} = 10.0–14.1 μm.

Table 5 Effect of calcination temperature on particle size distribution of pigment $Bi_2Ce_{2-x}Zr_xO_7$

	800 °C		850 °C		900 °C		950 °C		1000 °C	
x	***d*50**	***span***	***d*50**	***span***	***d*50**	***span***	***d*50**	***span***	***d*50**	***span***
0	2.3	8.4	6.3	4.5	8.4	4.4	10.0	4.4	11.2	4.6
0.25	1.6	7.0	2.3	5.7	8.5	4.1	8.3	4.3	11.5	4.2
0.5	1.9	5.7	2.4	5.4	10.1	3.6	9.7	4.4	10.8	4.2
0.75	1.7	5.5	2.2	5.0	12.3	3.8	10.4	4.3	11.9	4.1
1	1.4	4.5	2.3	5.3	14.0	4.0	7.1	4.2	12.9	4.2
1.25	1.9	4.3	2.6	4.7	15.1	4.3	10.3	4.3	14.1	3.9
1.5	2.8	5.2	3.0	4.3	16.9	3.9	8.7	4.4	12.0	4.3
1.75	3.0	3.8	3.3	3.8	11.6	4.1	10.7	4.1	12.5	4.4
2	3.7	3.0	4.5	3.4	17.0	4.2	9.6	4.7	10.0	4.8

Conclusions

The main aim of this study was to suggest the synthesis conditions of studied compounds with general formula $Bi_2Ce_{2-x}Zr_xO_7$ and to determine the influence of doped element (zirconium and cerium) on the colour properties and particle size distribution.

The pigments were prepared by the traditional ceramic method. Samples with the excellent colour properties were obtained at a higher temperature of calcination, i.e. 1000 °C and after application into organic matrix. The colour properties of samples with the content of zirconium from 0 to 2 are characterized dark yellow–orange colour. The darkest yellow-orange shades are obtained for samples containing Zr from 0.25 to 1.25 due to the low values of the brightness L^* (70.86–72.84). In comparison with an application into organic matrix in terms of an acquired colour properties showed that pigments applied to ceramic glaze provided a lighter yellow colour with green contribution due to negative values of colour coordinate a^*. The

main size value d_{50} of the compounds is moved in the range 1.4–17.0 μm in the whole range of calcination temperatures (800 °C–1000 °C).
As a consequence of this result, the studied compounds are suitable for application in paint (after necessary grinding). The very interesting discovery of this study is a fact that the pyrochlore compounds were prepared which are also environmentally friendly and could contribute to the basic assortment of yellow or orange inorganic pigments.

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