Synthesis and study of mixed oxide inorganic pigment from Bi_2O_3-ZnO-CeO_2 system

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Acknowledgements

The work was supported by Grant Project of the Czech Science Foundation No. 16-06697S.

Abstract

Novel environment-friendly yellow mixed oxideinorganic pigment from Bi_2O_3-ZnO-CeO_2 system with the composition 23mol% Bi_2O_3, 15 mol% ZnO and 62mol% $CeO_2$was successfully synthesized by a conventional solid state reaction method. Comprehensive analyses were carried out to characterize the develop pigment powder including simultaneous TG-DTA thermal analysis, colour properties and particle size distribution. The results demonstrated that the optimum calcination for pigment synthesis was located at a range 800-950 °C.The colour of the studied mixed oxide pigment is connected with the calcination condition. The substitution of Zn^{2+}changes the colour from orange to yellow.The colour of the obtained samples was dependent on the calcination condition and the particle size distribution. The most saturatedyellowhue was obtained at the calcination temperature of 950 ºC for 2 h in a furnace of pure air and after its application into organic binder in mass tone. The value *C* of this sample was approx. 65. The mixed oxide pigments were also evaluated from the standpoint of their particle size distribution. $Bi_2Ce_2O_7$ is considered to be a non-toxic compound and the other component (Zn^{2+} ions) is also the safe element. Therefore, the present mixed oxide could be an attractive candidate as a novel environment-friendly inorganic yellow pigment.

Keywords

Mixed oxide pigments,inorganic pigments, thermal analysis, colour properties, yellow colour

Introduction

Inorganic pigments are substances that develop colour in organic solids and are usually a complex mixture of oxides colours [1]. Pigments are generally used to impart colour to other materials such as paints, polymers, rubber, ceramics, glazes, enamels and glass. In general, pigments consist of metal oxides that are thermally and chemically resistant, including resistance to the attack of acids and alkalis. According on the CPMA(Color Pigment Manufacturers Association) and based on the main application of pigments, they can be divided into three categories: pigments suspended in glass matrices, which require extremely high levels of heat stability and chemical resistance to withstand the attack of molten glass; pigments suspended in polymers, which require moderate heat stability; and pigments suspended in liquid vehicles, which require little or no heat stability [2].

Research of inorganic pigments has increasingly focused on the creation of alternative pigment systems with attractive colours[3].The yellow pigments are especially in demand due to their high visibility, cadmium yellow (CdS·ZnS) and lead chromate yellow ($PbCrO_4$) have been popularly used in the past due to their excellent thermal stability and good colouring strength [4]. Nowadays, the global trends for the shade of decorating coatings are changing from pastel to more intensive shades. Heavy metal-based inorganic pigments had to be substituted due to strict regulations, occupational health concerns and costly waste disposal and recycling, which require the complete phase-out of heavy-metal pigments [5].The use of such pigments is strictly limited by the Restriction of Hazardous Substances (RoHS) directive etc. The development of alternative environmentally friendly inorganic pigments is strongly requested although there are lots of commercial inorganic pigments classified by CPMA such as Zirconium Vanadium Yellow Baddeleyite, Lead Antimonate Yellow Pyrochlore, Nickel Antimony Titanium Yellow Rutile and Zirconium Praseodymium Yellow Zircon, etc.

Here, we focused on the mixed based oxide Bi-Zn-Ce as a new inorganic material, since this compound consists of harmless and abundant elements. Most research on bismuth oxide focused on Bi_2O_3 oxide, which presents four polymorphic phases. Bismuth oxide polymorphs are fascinating optical materials with a wide bandgap, high refractive index, large dielectric permittivity, remarkable photoconductivity, and ionic conductivity [6]. The four polymorphs are as follows: α, β, γ and δ-Bi_2O_3. Of the four main Bi_2O_3 polymorphs by far the most interesting are the high-temperature metastable β and δ modifications, because of their extremely high oxygen ion conductivity and their strong visible-light-driven photocatalytic activity. While thermal oxidation of bismuth is inexpensive and easily controlled, synthesis of the desirable β-Bi_2O_3 and its stabilization

at room temperature is not straightforward [7, 8]. In ambient conditions, α-Bi_2O_3 is a stabile low-temperature phase with monoclinic structure in the bismites. The most stable form of the room temperature variety in Bi_2O_3 is the α monoclinic polymorph [9]. At 729 °C, α-Bi_2O_3 converts to δ-Bi_2O_3. A cubic form δ-Bi_2O_3 is best known as an oxide ion conductor and is an appealing material for practical purposes such as use as a solid electrolyte in galvanic cells or in an oxygen sensor. The polymorph of δ-Bi_2O_3 only stabilizes between 730 °C and the melting point 824 °C [10]. The structure of δ-Bi_2O_3 is related to the fluorite structure in which oxygen vacancies are distributed randomly and this phase displays high ionic conductivity due to the high mobility of O^{2-} ions [11]. After natural cooling of δ-Bi_2O_3, one of the metastable forms of bismuth oxide, tetragonal β-Bi_2O_3, can be obtained at 650 °C, or body-centered cubic γ-Bi_2O_3 at 639 °C, which may be transformed into α-Bi_2O_3 between 650 and 500 °C [12].ZnO presents only a hexagonal wurtzite-type crystalline structure up to its fusion at 1977 °C[13].

Pure or substituted cerium dioxide is currently involved in many industrial applications: solid electrolytes in solid oxide fuel cells, ceramics, pigments, gas sensors and catalysts [14-17]. CeO_2 crystallizes in a fluorite (face centered cubic) structure with space group *Fm*3*m*, in which each cerium site is surrounded by eight oxygen sites and each oxygen site as linked to four cerium sites in the tetrahedral configuration [18].

In this work, we focus on the synthesis of mixed oxide pigment from Bi_2O_3-ZnO-CeO_2 system with the composition 23mol% Bi_2O_3, 15 mol% ZnO and 62mol% CeO_2as the novel inorganic yellow pigment which composed of all non-toxic elements and its colour property was investigated. The main aim of the research was to study the thermal stability, particle size distribution and colour propertiesof mixed oxide inorganic pigment from Bi_2O_3-ZnO-CeO_2system.

Experimental

Materials and samples preparation

The mixed oxide pigment from Bi_2O_3-ZnO-CeO_2system was prepared by classical ceramic route, i.e. solid state reaction. The starting materials used for the preparation of mixed oxide pigmentcontaining 23 mol% Bi_2O_3, 15 mol% ZnO and 62 mol% $CeO_2$was Bi_2O_3 (99.8 % purity, LachemaPliva, a.s., CZ), ZnO (98 % purity, SlovZink, a.s., SK) and CeO_2 (99.9 % purity, ML-Chemica, CZ). The reagents were weighted in suitable molar proportions and subsequently ground manually in a porcelain mortar to get a homogenous reaction mixture. These mixtures were then calcined in corundum crucibles in an electric resistance furnace at temperatures 800, 850, 900, 950 and 1000 ºC with the rate of temperature increase 10 ºC/min and the total duration of 2 hours.

The calcined powder samples were applied into an organic matrix of dispersive acrylic paint Parketol (Balakoma.s., CZ) in mass tone and into a medium temperature ceramic glaze G 07091 (Glazura, s.r.o., Roudnicenad Labem, CZ). For testing in an organic matrix, suspensions containing 1 g of the sample and 1.5 cm^3 of a binder were homogenized. This system was converted by a pestle to a dense paste able to a flowing. Coloured coating films were prepared by deposition of the paste on the white non-absorbing paper. The coating layer of film was created by dragging the Bird film applicator. The thickness of the wet film was 100 μm. In the case of application into the ceramic glaze, an aqueous suspension containing 10 wt.% of mixed oxide pigment and 90 wt.% of the transparent ceramic glaze with an appropriate amount of distilled water prepared by hand-grinding. The suspension was applied by using a brush on ceramic tile and after drying in the air it was glazed at 1000 ºC for 15 min.

Characterization of samples

Thermal analyses of the starting mixture for synthesisof mixed oxide pigment fromBi_2O_3-ZnO-CeO_2system and initial oxide ZnO were recorded on STA 449C Jupiter (Netzsch, Germany) with system interface device in the atmosphere of air. The used equipment allows evaluation of data and simultaneous registration of the thermoanalytical curves TG and DTA. The temperature operational range of the instrument was from 100 ºC to 1000 ºC for measurement of both samples. Accurately 500 mg of prepared starting mixturecontaining 23 mol% Bi_2O_3, 15 mol% ZnO and 62 mol% $CeO_2$and 250 mg of starting raw material ZnO were subjected to dynamic TG-DTA scans at the heating rate of 10 ºC/min. α-Al_2O_3 was used as reference material.

The colour properties of final applications were objectively evaluated for their colour change by measuring spectral reflectance in the visible region of light (400-700 nm) by using a spectrophotometer ColorQuest XE (HunterLab, USA). The CIE *L*a*b** (1976) colour space was used. The total colour difference ΔE_{CIE}* in the CIE *L*a*b** diagram, which indicates the degree of colour difference between the two samples, is defined by the following equation:

$$\Delta E_{CIE}^* = \left[\left(\Delta L^*\right)^2+\left(\Delta a^*\right)^2+\left(\Delta b^*\right)^2\right]^{0.5} \quad (1)$$

where ΔL^*, Δa^* and Δb^* are differences in L^*, a^* and b^* values between colours of a sample and a standard [19]. In this case, it was used as reference material pigment $Bi_2Ce_2O_7$, which was studied previously [20].

The distribution of particle size of synthesized mixed oxide pigments was measured by using an equipment Mastersizer 2000/MU (Malvern Instruments, Ltd., UK). Used granulometer is highly integrated laser measuring device for analysis of particle size in the range from 0.02 to 2000 μm. The measurement was performed under the same conditions as the previous study [20].

Results and discussion

Simultaneous thermal analysis

Theformationofstudiedmixed oxide pigment fromBi_2O_3-ZnO-CeO_2system was followed by the methods of thermal analysis (TG-DTA). Thermal analysis of starting oxides Bi_2O_3 and CeO_2 have been published previously [21, 22].Thermoanalytical curves of third starting oxide, i.e. ZnO, are given in Fig. 1. TG curve for the sample of ZnO shows one stage of weight loss accompanied by one endothermic and one exothermic peak on DTA curve. The first endothermic event at the DTA curvewith a minimum 274 ºC can be associated with decomposition of $ZnCO_3$ that is present at starting ZnO. On TG curve, the effect is accompanied by a weight loss of 3.53 % (in the interval from 100 to 300 ºC).The slight exothermic peak on the DTA curve with a maximum 639 ºC is due to oxidation rest of the metallic zinc. Total weight loss at the temperature range up to 1000 ºC is 3.83 %.

Starting mixture containing 23mol% Bi_2O_3, 15 mol% ZnO and 62 mol% $CeO_2$was homogenized in an agate mortar and studied with using of TG-DTA (Fig. 2).TG curve indicated the weight loss of 0.44 % at the measured temperature range up to 1000 ºC.This effect corresponds to the partial oxygen loss from the crystal lattice of starting oxides. Growing temperature indicates the endothermic effect at the DTA curve with the minimum at approx. 752 ºC. Thisendothermicpeak on DTA curveofstartingmixturecorrespondswiththechangeofmonoclinicmodificationα-Bi_2O_3 to cubic modification δ-Bi_2O_3. Probably this peak is also connected to the interaction ZnO and CeO_2.

The content of Zn^{2+}ions has a positive effect on thermal stability of prepared mixed oxide inorganic pigment. The optimum calcination temperature range for the compound $Bi_2Ce_2O_7$ was evaluated from 800 to 1000 ºC [20].

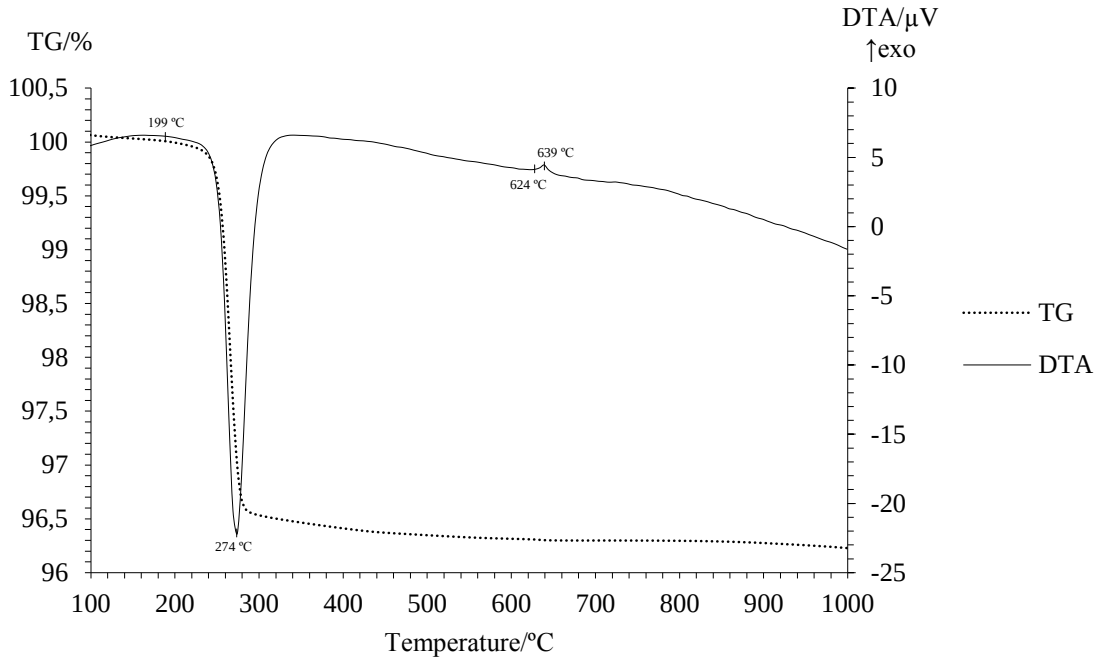

Fig. 1 TG and DTA curves of starting oxide ZnO(mass sample 250 mg, atmosphere: air, heating rate: 10 ºC min^{-1})

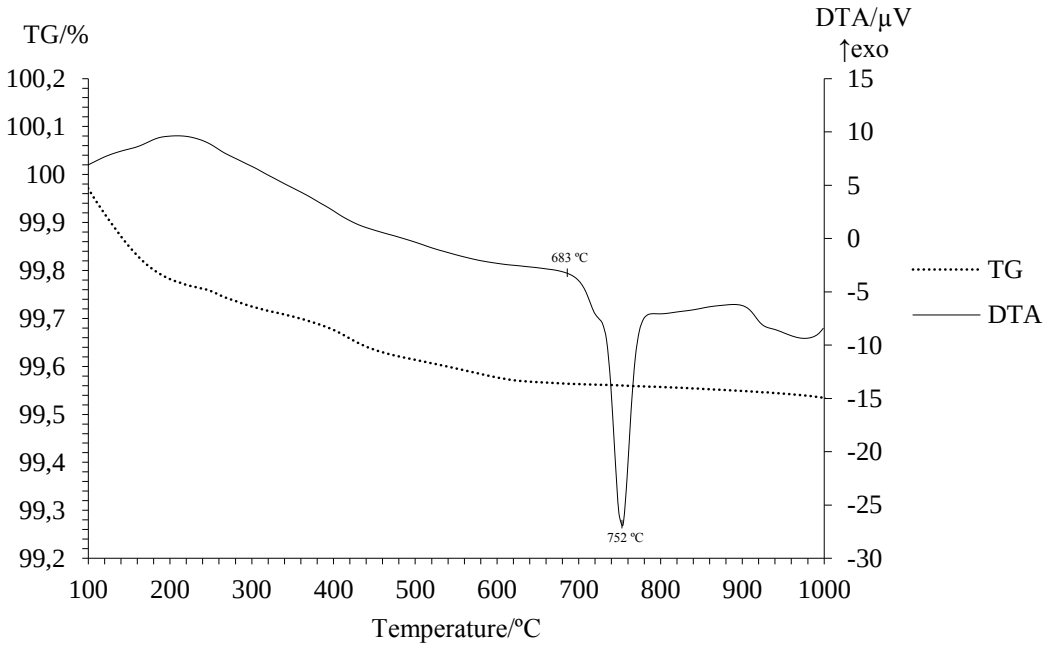

Fig. 2 TG and DTA curves of reaction mixture for the synthesis of mixed oxide inorganic pigment from Bi_2O_3-ZnO-CeO_2 system with the composition 23 mol% Bi_2O_3, 15 mol% ZnO and 62 mol% CeO_2(mass sample 500 mg, atmosphere: air, heating rate: 10 ºC min^{-1})

Colour characteristics

The influence ofthecalcinationtemperature on thecoloureffectofsynthesizedmixed oxide pigmentswasstudied. Thecolourpropertiesofthesamplespreparedattemperature 800, 850, 900, 950 a 1000 °C and applied into organic matrix in mass tone are given in Table 1. From Table 1 it follows the growing calcination temperature of synthesis decreases value *L** (lightness) and the samples become slightly dark. The values of colour coordinate *b** (yellow contribution) and *C* (chroma) are also declining with an ascending temperature of calcination. Only at the temperature of calcination 950 °C, the values of these colour characteristics increase up to values for *b** = 63.62 and for *C* = 64.56. The value of colour coordinate *a** (red contribution) has an alternate character and ranges in the interval from 3.66 to 10.97. Considering that the value *H*º of these samples of studied mixed oxide pigmentliesfrom 80.22 to 86.31, the samples are also characterized by yellow colour. Based on the investigation and evaluation of colour properties of the samples, the temperature 950 °C is the best for the preparation of saturated yellow colour, because the coordinates *C* (64.56) and *b** (63.62) have the highest values. On the other hand, this temperature provides a low value of the lightness *L** (73.99) and for this reason, the resulting hue is dark yellow. The pigment with lower lightness is better to use in painting coats because during milling particle size is decreased and lightness increases. The values of total colour difference ΔE_{CIE}* were very high in the whole calcination range (ΔE_{CIE}* = 8.65-19.15).It means that the colour difference betweenpigment $Bi_2Ce_2O_7$[20], which was used as standard materialtowards prepared pigments, and studied mixed oxide pigmentwas perceptible to the human eye.The highest value of total colour difference ΔE_{CIE}* (19.15) was observed in the case of sample synthesized at 900 °C. This fact is mainly caused by the increase of lightness and the decrease of both colour coordinates at mixed oxide pigment from Bi_2O_3-ZnO-CeO_2system prepared in this study. The obtained yellow hues of samples are also shown in the enclosed colour chart in Table 1.

Table 1 The effect of calcination temperature on colour properties of mixed oxide inorganic pigment from Bi_2O_3-ZnO-CeO_2 system with the composition 23 mol% Bi_2O_3, 15 mol% ZnO and 62 mol% CeO_2applied into organic matrix in mass tone. As a standard material was used pigment $Bi_2Ce_2O_7$[20]

T/°C	*L**	*a**	*b**	*C*	*H*°	ΔE_{CIE}*	Colour
800	86.99	7.56	61.65	62.11	83.01	10.88	
850	80.88	6.44	56.74	57.10	83.52	8.65	
900	85.97	3.66	56.75	56.87	86.31	19.15	
950	73.99	10.97	63.62	64.56	80.22	8.73	

1000	70.68	6.89	48.80	49.28	81.96	8.67	

For the better understanding of the optical properties of the developed pigment powders, the diffuse reflectance spectra of studied mixed oxide pigmenthave been measured and the results are depicted in Figure 3. The results demonstrated that the optical reflectance of samples which were calcinated at temperatures 800, 850 and 900 °C are characterized by the lightest colour, because reflection curves are the top and reflections are from 86 to 100 %. Reflectance reduction was verified with an increase of calcination temperature, concretely at 950 and 1000 °C were observed the darkest yellow hues. These results confirm the study of colour properties using *L*a*b** system. For the comparison, the spectral reflectance curves of the standard pigment $Bi_2Ce_2O_7$ were alsocomplemented to the Figure 3. It is obvious that the dark yellow hue of standard pigment was obtained at thelowest temperature of 800 °C. The reflectance of standard pigment $Bi_2Ce_2O_7$ is moved in the interval from 60 to 85 %.

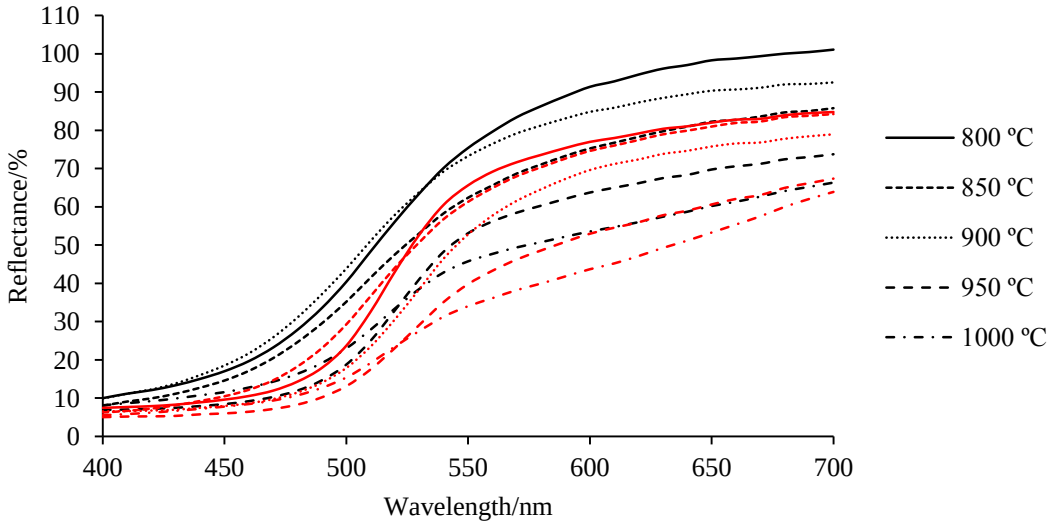

Fig. 3 VIS diffuse reflectance spectra of mixed oxide inorganic pigment from Bi_2O_3-ZnO-CeO_2 system with the composition 23 mol% Bi_2O_3, 15 mol% ZnO and 62 mol% CeO_2(black curves) and standard pigment $Bi_2Ce_2O_7$ (red curves) calcinated in the range 800-1000 °C and applied into organic matrix in mass tone

The prepared mixed oxide pigments were applied into the ceramic glaze as well. The colouration of the samples in this application was different in comparison with the application into the organic binder. The lightness *L** of samples is decreasing with the increasing calcination temperature and is significantly higher than in the case of samples which were applied into the organic binder in mass tone (Tab. 2). The value of *C*is growing with the increasing temperature up to 1000 °C, where it reached its maximum (*C* = 38.30). However, these values are compared to the previous application of studied mixed oxide to the organic binder is significantly lower. In the case of the colour coordinate *a**, which is characterized by negative values in the entire temperature range, samples have a contribution to green tone (from -5.14 to -3.58). This fact is confirmed by the high values of angle *H*°that are located in range(approx. 96°-98°). The mixed oxide pigments applied to ceramic glaze provided lower values of colour coordinate *b** (34.48-38.10). In case of application of the samples into ceramic glaze, this kind of application provides light yellow shades. This fact is also evident from the enclosed colour chart (Tab. 2). In this application, the values of total colour difference were very low at temperatures 950 °C (ΔE_{CIE}* = 1.81) and 1000 °C (ΔE_{CIE}* = 1.33) and the difference between samples was imperceptible to the human eye. The highest value of total colour difference ΔE_{CIE}* (6.72) was observed in the case of sample synthesized at 800 °C. This fact is caused by the noticeable increasing of lightness *L**.

Table 2 The effect of calcination temperature on colour properties of mixed oxide pigment from Bi_2O_3-ZnO-CeO_2 system with the composition 23 mol% Bi_2O_3, 15 mol% ZnO and 62 mol% CeO_2applied to ceramic glaze. As a standard material was used pigment $Bi_2Ce_2O_7$[20]

T/°C	*L**	*a**	*b**	*C*	*H*°	Δ*E**	Colour
800	93.70	-5.14	35.12	35.49	98.33	6.72	
850	93.47	-4.59	34.48	34.78	97.58	6.11	

900	92.57	-4.31	37.32	37.57	96.59	5.98	
950	84.09	-3.58	36.93	37.10	95.54	1.81	
1000	84.03	-3.94	38.10	38.30	95.90	1.33	

The particle size distribution

The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments so that the pigment particle sizes of the prepared compound were also tested. It belongs to one of the most significant measured properties of synthesised powders and it can affect optical properties (final colour of pigments) and opacity.The measurement of particle size distribution was determined for unmilled samples. The values of pigment particles are in a range from approx. 1 (d_{10}) to 34 μm (d_{90}). The results showed that the growing synthesis temperature caused an increase of values d_{50} (Tab. 3). The mean values range from approx. 6 to 8 μm. In comparison with the standard pigment $Bi_2Ce_2O_7$ where the mean values were ranged in the interval from approx. 4 to 10 μm [20], was achieved the narrower interval of values d_{50}.The parameter *span* informs about monodispersivity of the samples and lies in very narrow interval *span* = 3.06-4.18. The appropriate granulometric composition for application of pigments into ceramic glaze is about 5-15 μm. These values were attained for prepared samples fromBi_2O_3-ZnO-CeO_2 system. For potential use of prepared mixed oxide pigments in painting coats, it would be necessary to treat the size mechanically.

Table 3 The effect of calcination temperature on particle size distribution of mixed oxide pigment fromBi_2O_3-ZnO-CeO_2 system with the composition 23 mol% Bi_2O_3, 15 mol% ZnO and 62 mol% CeO_2

T/°C	d_{50}/μm	d_{10}-d_{90}/μm	*span*
800	6.46	0.68-21.21	3.18
850	7.91	0.95-26.94	3.29
900	7.21	0.79-22.85	3.06
950	8.04	0.77-34.38	4.18
1000	8.47	0.97-32.00	3.66

Conclusions

The aim of this research was to synthesize novel environment-friendlyyellow mixed oxide inorganic pigmentfrom Bi_2O_3-ZnO-CeO_2system, and to find out substitution of bismuth ions by ions of zinc can affect its thermal stability, colour properties and particle size distribution, and extend its applicability in paint and ceramic industry for colouring of glazes. The pigment was synthesized by using the classical ceramic method based on the solid state reaction.

The optimum calcination temperature for synthesis of mixed oxide pigment was determined on the base of the simultaneous TG-DTA measurements. The obtained results are in accord with colour properties of studied sample. The studied mixed oxide pigment is thermally stable to the temperature of 1000 °C, although the melting temperature of pure Bi_2O_3 is only 820 °C. This fact can give a direction for the colouring of ceramic glazes. The colour properties of these mixed oxide pigments depended on the calcination condition and particle size distribution, and the most intensive yellow hue was obtained for the sample calcined at 950 °C. The colour properties of this sample in organic binder are characterized by *L*a*b** colour parameters of *L** = 73.99, *b** = 63.62, *C* = 64.56 and *H*° = 80.22. The *b** value, which corresponds to the yellowness, is significantly higher than that of sample without the content of Zn^{2+} ions $Bi_2Ce_2O_7$ (*b** = 48.74). In the ceramic glaze, the mixed oxide pigment forms light yellow glossy surfaces without any defects. The mixed oxide pigment containing23mol% Bi_2O_3, 15 mol% ZnO and 62mol% CeO_2can be recommended for the colouring of organic binders and ceramic glazes, especially, for the colouring of the decorative lead containing glazes, which have a processing temperature below 1000 °C.The mean of particle size d_{50} moved in the range of approx. 6-8 μm in dependence on synthesis temperature and this particle size is appropriate for the potential usage in ceramic glazes.

The studied coloured compound could contribute to the basic assortment of yellow inorganic pigments. The studied mixed oxide pigment fromBi_2O_3-ZnO-CeO_2 systemis resistant to heat and represents potential alternative of yellow inorganic pigments containing toxic elements such as chromium and lead.

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