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Study of doped CeO_2 prepared by different synthesis

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Abstract The compounds based on CeO_2 belong to the group of high-temperature pigments. The principal of these pigments makes the host lattice of the CeO_2, which is doped by terbium and zirconium ions, that lead to obtaining of the interesting dark orange colour. The research is focused on three different methods of synthesis. The pigments have been prepared by the classical dry proces (i.e. solid-state reaction) in the temperature range from 1,200 to 1,600 °C, by the precipitation and as the last method a simulation of 'Mixer Dryer Reactor'(MDR) under laboratory conditions (two-step process) was used. The aim was to improve and optimize the synthesis conditions of studied pigments. The compounds were also evaluated from the point of view of their colour properties and structure.

Keywords CeO_2 · Ecological pigments · Red ceramic pigments

Introduction

Pr-doped ceria is also employed in the ceramic industry since 1960 as red ceramic pigment. In response to growing concerns demanding environmentally benign (and commercially viable) ceramic pigments, Pr-doped and related ceria-based solid solutions have become interesting low-toxicity alternatives to other traditionally used orange-red ceramic pigments [1, 2]. Indeed, the choice of available reddish ceramic pigments is restricted either to pigments involving toxicity problems (associated to Cd, Pb and Cr), such as $CdS_{1-x}Se_x$ (in a zircon matrix), Pb_3O_4 (in tin oxide matrixes) or $Ln_x(Al_{2-x-y}Cr_y)O_3$ perovskites, or to pigments which lack of sufficient colour purity and reproducibility, such as α-Fe_2O_3 included in a zircon matrix [3].

Different aspects of Pr–CeO_2 system have been profusely investigated in the last decade. In these studies the pigmenting solid solutions were prepared by the ceramic method and also through many other non-conventional routes. Noteworthy, previous investigations have demonstrated that ceramic pigments based on Tb–CeO_2 solid solutions may also yield good red hues, which may be comparable to those obtained with Pr–CeO_2. Nevertheless, the studies about synthesis optimization and pigmenting properties of Tb-doped ceria are still rather scarce, since most of research concerning this system is centred on catalytic or redox properties [4–6].

In this study, we verify the synthesis of compounds based on CeO_2, which are doped by terbium and zirconium ions, that lead to obtaining of the interesting dark orange colour. First, the optimal composition ($Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$) giving the best orange colour was selected from ceramic samples fired at 1,200–1,600 °C. Second, the effect of using different classical and non-conventional routes on the synthesis and colouring performance of studied pigment was analyzed. The formation and homogeneity of samples has been followed by XRD, the colour performance has analyzed through reflectance diffuse spectroscopy and colour measurements. Simultaneous TG-DTA measurements were used for following of optimum calcination temperature for pigment synthesis.

Experimental

The pigment $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ was prepared by three methods of preparation. The first method is based on the

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classical ceramic method. The reagents CeO_2 (Indian Rare Earths Ltd., India), Tb_4O_7 (Indian Rare Earths Ltd., India) and ZrO_2 (Merck, Germany) were weighed in suitable molar proportions and subsequently ground manually in a porcelain mortar to obtain a homogenous reaction mixture. The reaction mixtures were heated at temperature range from 1,200 to 1,600 °C (2 h) in electric resistence furnace. The heating rate was 7 °C min^{-1}. Corundum crucibles were used. The samples were gradually cooled to room temperature and ground in an agate mortar.

The second method represents a simulation of 'Mixer Dryer Reactor'(MDR) under laboratory conditions. This is two-step method. The first step is based on mixing of the initial reagents, as suspensions, in a porcelain mortar. The suspension was then deposited on an alloy steel sheet and heated at 400 °C on an alloy steel sheet. The reaction mixture contained equimolar amounts of CeO_2 (Indian Rare Earths Ltd., India), Tb_4O_7 (Indian Rare Earths Ltd., India) and ZrO_2 (Merck, Germany). The second step represents a classical calcination in an electric furnace with increase of temperature of 7 °C min^{-1}. The final temperatures of the second step were the same as for classical ceramic method. Then, the fired samples were decanted in hot water, filtered and dried.

Except classical ceramic method and two-step process, the pigment was also prepared by precipitation with NaOH. The starting materials were $Ce(SO_4)_2.4H_2O$, $Zr(SO_4)_2.4H_2O$ and $Tb(NO_3)_3.5H_2O$. The solution was precipitated by the solution of NaOH up to pH around 9. The sample was dried and subsequently calcinated at the same temperature range mentioned above.

All prepared pigments were applied into the organic matrix and into medium temperature ceramic glaze G05091 (Glazura, s.r.o., CZ). The mixture of pigment in amounts of 10% w/w a glaze was glazed at 1,000 °C for 20 min.

The final applications were evaluated for colour 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°. 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 as related to the neutral grey scale. In the $L^*a^*b^*$ system, it is described by numbers from zero (black) to hundred (white). The value C (Chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. It is also possible to express the colour of pigment as a hue angle ($H° = \text{arc tg } (b^*/a^*)$). The hue angle $H°$ is defined by an angular position [7] in the cylindrical colour space ($H° = 0–35°$ for the red, $H° = 35–70°$ for the orange, $H° = 70–105°$ for the yellow).

The methods of thermal analysis can provide the information about the temperature region of the formation of inorganic pigments. The formation of these pigments was followed by thermal analysis using STA 449C Jupiter (NETZSCH, Germany) which allows the simultaneous registration of the thermoanalytical curves TG and DTA. The starting raw material and the prepared starting mixtures were studied by thermal analysis in corundum crucible with the increase of temperature 10 °C min^{-1}. α-Al_2O_3 was used as reference material [8].

The powder pigments were also studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained by using equipment Diffractometer D8 (Bruker, GB), Cu K_λ radiation with scintillation detector. The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000 MU (Malvern Instruments, Ltd. GB).

Results and discussion

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

Colour properties are the most important characteristic of the ceramic pigments. From Table 1 it follows the

Table 1 The effect of calcination temperature and way of preparation on colour properties of the pigment $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ applied into ceramic glaze

T/°C	Ceramic method			Two-step process			Precipitation		
	*L**	*C*	*H°*	*L**	*C*	*H°*	*L**	*C*	*H°*
1,200	86.33	20.95	82.82	84.74	23.04	82.47	78.17	36.19	70.18
1,300	83.79	26.33	74.47	83.70	27.74	79.09	74.21	41.07	66.22
1,400	70.87	34.46	61.13	75.96	38.64	68.50	73.99	41.85	66.11
1,500	68.06	48.76	60.91	69.71	50.33	63.15	70.46	46.52	63.37
1,600	70.89	48.26	64.09	71.52	49.75	65.27	70.10	47.72	63.88

Table 2 The effect of calcination temperature and way of preparation on mean particle size *d_{50}* of $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ pigment

Calcination temperature/°C	Mean particle size d_{50}/μm		
	Ceramic method	Two-step synthesis	Precipitation
1,200	6.98	7.88	4.88
1,300	7.16	7.96	5.98
1,400	8.54	9.87	7.61
1,500	10.99	10.25	8.75
1,600	12.01	12.25	10.96

Table 3 The phase composition of $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ pigment prepared by different synthesis at chosen temperatures

Calcination temperature/°C	Ceramic method	Two-step synthesis	Precipitation
1,200	CeO_2, ZrO_2, $Tb_{11}O_{20}$	$Ce_{0.68}Tb_{0.32}O_2$, $Ce_2Zr_2O_{7.04}$	$Ce_{0.75}Zr_{0.25}O_2$
1,300	CeO_2, ZrO_2, Tb_2O_3	$Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_2$
1,400	CeO_2, ZrO_2, $Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_2$
1,500	CeO_2, Tb_2O_3, $Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_2$
1,600	$Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_2$

change of the colour coordinates in dependence on the temperature of calcination (T) and also on the way of preparation. The increasing calcination temperature decreases value *L** (lightness) for all ways of preparation and pigments become the darkest. The values *C* (chroma) are in range from approx. 21 to 50, the growing calcination temperature makes the increase of this value, for ceramic method and two-step process the highest value *C* is at temperature 1,500 °C, for precipitation at 1,600 °C. The values of hue angle *H*° with calcination temperature decrease for all ways of preparation. Considering that value *H*° of these pigments lies from 83 to 61, the pigments are characterized by yellow-orange (70°–80°) and orange colour (60°–70°). The intensive hues are produced at temperature 1,500 °C for ceramic and two-step process and at 1,600 °C for precipitation. The lowest value of *H*° corresponds to temperature 1,500 °C and ceramic method, this pigment gives intensive orange colour ($H° = 60.91$).

The preparation method and the calcination temperature affect not only colour related properties, but also particle size distribution (Table 2). Samples of pigments, that were prepared by the ceramic method and by two-step process, are characterized by higher mean values (d_{50}) of particles in the interval from approx. 7 to 12 μm. The growing calcination temperature makes the increase of values d_{50} for all three preparation methods. However, the mean values of the pigment particles, that were prepared by the precipitation, are in number interval from 5 to 11 μm. Better granulometric composition for application of pigments into ceramic glaze is about 10 μm. These values were obtained for pigment prepared by ceramic method and two-step process at temperature 1,500 °C. In the case of precipitation, higher temperature, i.e. 1,600 °C, is necessary. The results of particle size distribution are in accordance with the colour properties of pigments applied into ceramic glaze (the highest value *C*).

The pigment $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ prepared by three methods mentioned above was also studied by powder X-ray diffraction analysis. The sample prepared by ceramic method was homogenous at higher temperature, i.e. 1,600 °C. It means that starting oxides of terbium, cerium and zirconium form new phase. The XRD pattern indicates that this new phase is indexed as $Ce_{0.75}Zr_{0.25}O_2$. This phase is characterized by cubic symmetry with fluorite structure. At lower temperatures the samples contain small amounts of the starting oxides and new phase $Ce_{0.75}Zr_{0.25}O_2$ appears at 1,400 °C beside non-reacted CeO_2 and ZrO_2 (Table 3).

The sample prepared by two-step process is single-phased at the temperature 1,300 °C and sample prepared by

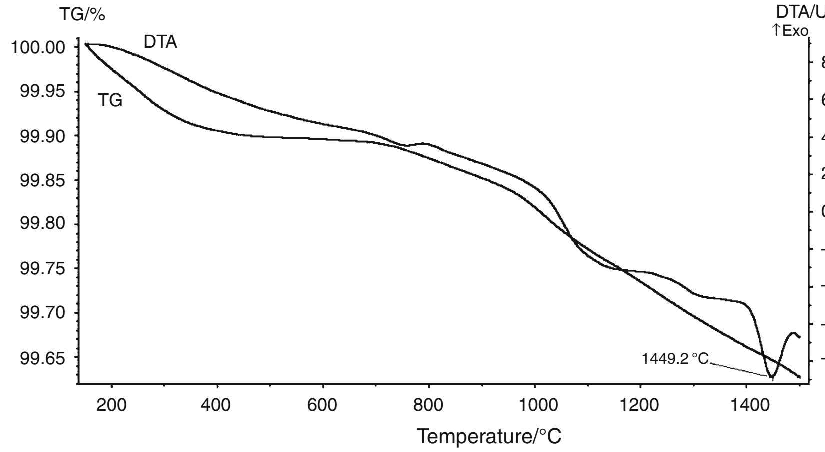

Fig. 1 TG and DTA curves of CeO_2 (mass of sample: 252.20 mg, atmosphere: air, heating rate: 10 °C min^{-1})

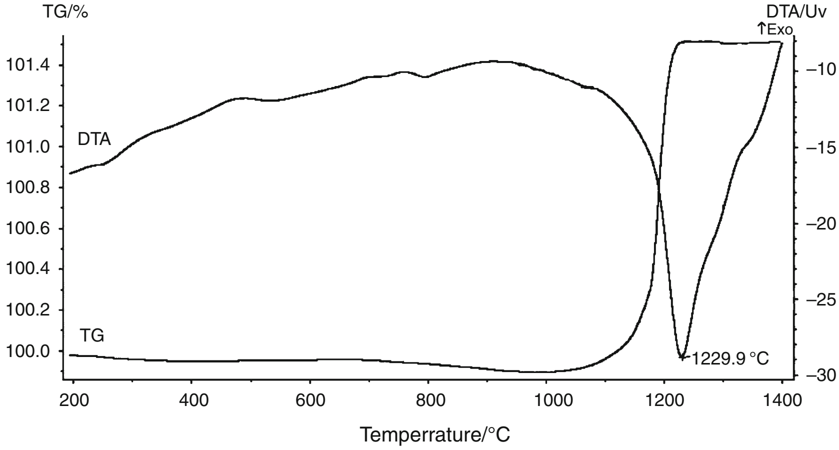

Fig. 2 TG and DTA curves of ZrO^2 (mass of sample: 626.45 mg, atmosphere: air, heating rate: 10 °C min^{-1})

precipitation was single-phased at all temperatures, i.e. from 1,200 °C. The single-phased samples have the fluorite structure with cubic symmetry [9] with lattice parameter: for ceramic method (1,600 °C) $a = 0.5361$ nm, for two-step process (1,300 °C) $a = 0.5405$ nm and for precipitation (1,200 °C) $a = 0.5353$ nm.

The starting reactants for the synthesis of $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ compound by ceramic method and two-step process were mixed oxide Tb_4O_7, ZrO_2 and CeO_2. The behaviour of these oxides during the thermal analysis is already known [10, 11]. It was found out, that during the heat treatment the terbium oxide changes from $2TbO_2.Tb_2O_3$ to Tb_2O_3 at the temperature approx. 950 °C. The next change of the oxidation state was appeared at the temperature above 1,400 °C. This change is presented by the exothermic effect on the DTA curve which belongs to the oxidation of trivalent ions to tetravalent ions of terbium. Thermoanalytical curves of starting oxide CeO_2 are given in Fig. 1. The DTA curve shows the one endothermic effect with temperature minimum at 1,449 °C that is connected with gradual mass loss (0.37%) at temperature range from 100 to 1,500 °C. This process is represented by the partial oxygen loss because CeO_2 is known as oxide with oxygen deficiency in its crystal lattice [12, 13].

ZrO_2 is characterized by the change of monoclinic modification to tetragonal [14]. The phase transition on DTA curve is represented at temperature range from 1,000 to 1,400 °C by endothermic effect with temperature minimum at 1,230 °C and at the same time is attended by mass change (Fig. 2). From TG and DTA curve it follows that monoclinic modification ZrO_2 is stable up to 1,000 °C. The phase transition of monoclinic to tetragonal modification is connected with increase of weight that is +1.62% as TG curve shows.

The thermoanalytical results are in accordance with phase composition of samples prepared by solid state reaction (ceramic method) at temperature range form 1,200 to 1,600 °C. New phase $Ce_{0.75}Zr_{0.25}O_2$ appears at 1,400 °C beside non-reacted CeO_2 and ZrO_2. CeO_2 is stable up to 1,400 °C and ZrO_2 is characterized by higher reactivity as a consequence of phase transition of monoclinic to tetragonal modification at temperature range from 1,000 to 1,400 °C. Calcination temperature below 1,400 °C is not sufficient for synthesis of studied pigments in case of ceramic method [15–17].

Conclusions

The main aim of the research was to prepare a solid solution of the compound $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ and to test its colour properties and possibility utilization as the new inorganic ceramic pigments.

At first the pigment was prepared by the ceramic method (classical dry process). Pigment with the best colour properties, i.e. dark orange colour, was obtained at the temperature of calcination, i.e. 1,500 °C and after application into ceramic glaze. The method of precipitation and two-step process was also used for the preparation of the $Ce_{0.7}Tb_{0.05}Zr_{0.25}O_2$ compound for the reason of decrease of the final temperature of calcination. Very similar result was achieved with using of these methods dealing with colour properties and it was established that for interesting colours the temperature of synthesis 1,500 °C (two-step process) or 1,600 °C (precipitation) is necessary.

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