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Thermal study of the $Ce_{0.9}Tb_{0.1}O_2$ pigment prepared by different synthesis

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Abstract The inorganic ceramic compounds based on the CeO_2 belong into the group of high-temperature pigments. The pigments have been prepared by the classical dry process (i.e. solid-state reaction) in the temperature range from 1,300 to 1,600 °C and by the coprecipitation at the three different temperatures: 400, 600 and 1,100 °C. The principal of these pigments makes the host lattice of the CeO_2, which is doped by terbium ions. This incorporation of the doped ions leads to obtaining of the interesting dark orange colour after application into ceramic glaze. The aim of our research was to improve and optimize the synthesis conditions of these pigments. The samples were submitted to thermal analysis (TG–DTA) for determination of the temperature interval of the pigment formation and the thermal stability of pigments. The compounds were also measured from the point of view of their colouring, structure and particle size distribution.

Keywords Ceramic pigments · High-temperature pigments · Colour properties · Thermal analysis

Introduction

Ceramic pigments are inorganic structures containing chromophore ions, which impart colour to ceramic wares by forming a heterogeneous mixture with the body or glaze, in which they are dispersed [1]. Inorganic pigments have been utilized by mankind since ancient times and still are widely used to colour materials exposed to elevated temperatures during processing and applications [2]. The problem with high performance inorganic pigments is the limitation in available chemistry, so that very few really new compounds have been developed in recent years. Today, there have been the high performance inorganic pigments (with high thermal, chemical and UV stability) in the colour range from red to yellow, but these pigments usually contain the toxic elements such as lead, cadmium, mercury etc. Therefore, the endeavour to replace the toxic inorganic pigments with environment-friendly pigments has come to the fore [3–5].

In the past several years, CeO_2-based materials have been intensely investigated as catalysts, structural and electronic promoters of heterogeneous catalytic reactions, and oxide-ion conducting solid electrolytes in electrochemical cells. The compounds based on CeO_2 can be also used as ceramic pigments; in this case, the fluorite lattice CeO_2 is doped by Pr^{4+} ions that perform as chromophore [6, 7]. Their commercial significance is in thermal, chemical and light stability, combined with their low toxicity.

The materials based on the CeO_2 have, thus, huge possibilities of utilization due to their high chemical activity and conductivity. In many cases, the redox properties and chemical activity of pure CeO_2 can be enhanced by introducing different types of metals, i.e. Zr, Ca, Mn and Tb, into the host lattice of cerium oxide [8, 9]. The dopant or second metal can introduce a stress into the host lattice, inducing in this way the formation of defects that have a high chemical activity. On the contrary, the lattice can impose on the dopant element nontypical coordination modes with a deviation in the dopant chemical properties.

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It is interesting to note that in connection of element cerium terbium, the Ce exists in a two oxidation state, namely, 4+ and 3+, which contribute to the very good ionic and electronic conductivity and catalytic properties. On the contrary, the cerium is retaining the valence state 4+ by using other dopant (Y^{3+}, Gd^{3+} and Sm^{3+}) [10].

By the $Ce_{1-x}Tb_xO_2$ compounds were recognized high ability oxygen release and storage and also it is assumed that inherency of oxygen vacancies connected to ions of Tb^{3+} conduce to increase of the oxygen mobility [11]. In bulk $Ce_{1-x}Tb_xO_2$ nanoparticles ($x \leq 0.5$) there is a small contraction ($\leq$0.08 Å) in the cell dimensions with respect to pure CeO_2. The presence of terbium generates strain in the lattice through the creation of crystal imperfections and oxygen vacancies. It was found, that the strain increases with the content of Tb [8].

These research work is focused on synthesis and characterization of new inorganic ceramic pigments based on the CeO_2, which is doped by rare earth elements (Ln), in this case terbium. In the present work the different methods of preparation $Ce_{0.9}Tb_{0.1}O_2$ pigment were studied. This compound was synthesized by two various routes, i.e. classical ceramic method and coprecipitation with assistance of urea. In both methods the appropriate starting reactants were homogenized and calcinated at the different temperature of calcination (in the range from 1,100 to 1,600 °C). The optimum synthesis conditions were determined with the aid of simultaneous TG–DTA analysis which provides the important information about the temperature region of the pigment creation. This pigment look as promising from the ecological point of view and is also very good applicable into ceramic glaze.

Experimental

The compound $Ce_{0.9}Tb_{0.1}O_2$ was prepared by classical dry process (solid-state reaction). The precursors employed for this traditional synthesis route are CeO_2 (99.9%, Strem Chemicals Inc.) and Tb_4O_7 (99.9%, Strem Chemicals Inc.). These oxides were homogenized in a porcelain mortar with a pestle. The reaction mixtures were calcinated at the four temperatures: 1,300, 1,400, 1,500 and 1,600 °C in an electric resistance furnace with heating rate 7 °C min^{-1} for 1 h. Except classical dry process (CE), the pigment was prepared by coprecipitation (CO) with urea. The starting materials for synthesizing of $Ce_{0.9}Tb_{0.1}O_2$ were $Ce(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 5H_2O$ (Strem Chemicals Inc.) and $(NH_2)_2CO$ (urea) (Panreac Química S.A.). Rate of urea and metals (Ce + Tb) was 1.3:1. The solution was precipitated by the aqueous solution of ammonia up to pH around 9. The sample was dried and subsequently calcinated at the temperature of 400, 600 and 1,100 °C for 6 h in the electric resistance furnace with heating rate 7 °C min^{-1}.

All prepared pigments were applied into the organic matrix in a mass tone and into medium temperature ceramic glaze G 05091 (Glazura, s.r.o., Roudnice nad Labem, CZ). The mixture of pigment in amounts of 5% w/w a glaze was glazed at 1,000 °C for 20 min.

The colour of pigments was measured in the visible region of light (400–700 nm) using 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). In this system, L^* is a degree of lightness and darkness of colour in relation to scale extending from white ($L^* = 100$) to black ($L^* = 0$), the values a^* [the green ($-a^*$) to red ($+a^*$) axis] and b^* [the blue ($-b^*$) to yellow ($+b^*$) axis] indicate the colour hue. The value C (chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The colour of pigments is also expressed by the hue angle $H°$. The equation for calculation of the hue angle is $H° = \text{arc tg}\ (b^*/a^*)$.

The formation of the 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 temperature region for this analysis was from 35 to 1,500 °C. The heating rate was 10 °C min^{-1}, α-Al_2O_3 was used like a reference material [12].

The structure of the prepared pigments was also investigated by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using by an equipment Diffractometer D8 (Bruker, GB), Cu K_α radiation with scintillation detector [12].

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 (He–Ne laser, $\lambda = 633$ nm) for the analysis of particle size distribution.

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 application into organic matrix and mainly ceramic glaze.

Colour properties are the most important characteristic of the ceramic pigments. From the Table 1 it follows the change of the colour coordinates in dependence on the temperature of calcination and also on the way of application for the pigments prepared by the ceramic method.

Table 1 The effect of calcination temperature and way of application on colour properties of the $Ce_{0.9}Tb_{0.1}O_2$ pigment prepared by CE

T/°C	Organic matrix					Ceramic glaze				
	*L**	*a**	*b**	*C*	*H*°	*L**	*a**	*b**	*C*	*H*°
1,300	48.21	9.52	10.22	13.97	47.03	84.50	3.05	22.80	23.00	82.38
1,400	41.06	9.78	9.02	13.30	42.69	81.60	6.20	29.23	29.88	78.02
1,500	35.88	12.26	10.03	15.84	39.29	64.88	21.61	31.92	38.55	55.90
1,600	34.77	13.88	9.65	16.90	34.81	50.98	26.16	27.36	37.85	46.28

In both of the ways of application the levels of colour coordinates *a** and *C* (chroma) subsequently increasing with growing temperature of calcination. Opposite them the levels of the colour coordinates *L** and *H*° decreasing. The pigments applied into glaze are much more interesting in term of colouring. These pigments reach much higher values of colour coordinates *a** and *b**, which corresponding with higher benefit of reddish hue. The final colour of these pigments is moving from cream to dark orange with rising temperature of calcination. These statements confirm also values of hue angle *H*° (46.28–82.38).

The sample prepared by coprecipitation and calcinated at the temperature of 1,100 °C is characterized by values of colour coordinates *a** and *b** that lie in a narrow interval (22.61–26.16) (Table 2). The value *L** of this sample is lower and this sample is a slightly darker than sample prepared by ceramic method and calcinated at the 1600 °C, opposite this the value of chroma is higher in compare with a ceramic method ($C_{\text{CO-1100 °C}} = 38.39/C_{\text{CE-1600 °C}} = 37.85$) and also the value of hue angle *H*° is higher ($H°_{\text{CO-1100 °C}} = 53.91/H°_{\text{CE-1600 °C}} = 46.28$) but both values lie in the interval for orange tinge, i.e. 30–70. All samples prepared by coprecipitation are characterized by cream colour hue and their hues are practically unchanging with the temperature of calcination (400 and 600 °C), i.e. the colour properties do not differ for these both temperatures. The change in the colour hue is apparent for the pigment obtained by calcination at the temperature of 1,100 °C, when the colour shifts from the cream to orange.

All of the samples were submitted to the measuring of the particle size distribution using the Mastersizer 2000/MU. For optimal application into ceramic glaze it is important that the values of mean particle size should lie in the interval from 5 to 15 µm. The range of the mean particle size of the pigment calcinated at the highest temperature (1,600 °C for ceramic method, 1,100 °C for coprecipitation) is proceed from 5 to 12 µm and it means that these compounds fulfil the conditions and they are applicable to colouring glazes.

Table 2 The effect of calcination temperature on colour properties of the $Ce_{0.9}Tb_{0.1}O_2$ pigment prepared by coprecipitation and applied into ceramic glaze

T/°C	*L**	*a**	*b**	*C*	*H*°
400	72.48	14.95	30.54	34.00	63.92
600	71.26	15.79	30.56	34.40	62.68
1,100	57.68	22.61	31.02	38.39	53.91

The pigment $Ce_{0.9}Tb_{0.1}O_2$ prepared by two 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. 1,400 °C. It means that ions of terbium are completely entered to the host lattice of CeO_2. The sample prepared by coprecipitation was single-phased at the temperature of 1,100 °C (Fig. 1). The single-phased samples have the fluorite structure with cubic symmetry with lattice parameter: for ceramic method (1,400 °C) $a = 0.5411$ nm and for coprecipitation (1,100 °C) $a = 0.5398$ nm. The sample prepared by coprecipitation route at the lowest temperature of calcination (400 °C) is polyphased because beside the cubic phase of CeO_2 nonreacted Tb_2O_3 with cubic symmetry and triclinic system of $Ce_{11}O_{20}$ were also detected. By the same sample but after calcination at the 600 °C two cubic phases were found. In this sample nonreacted Tb_2O_3 was presented except the cubic phase of CeO_2.

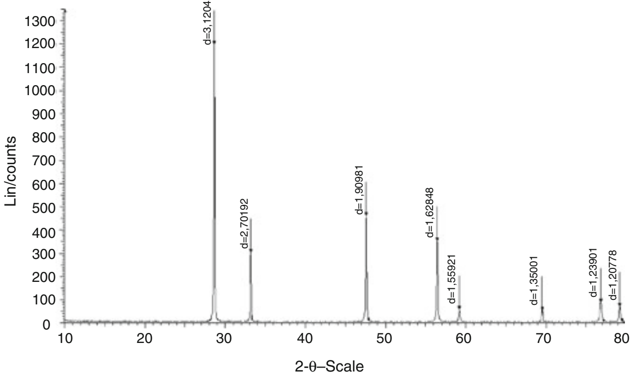

Fig. 1 The X-ray patterns of the sample $Ce_{0.9}Tb_{0.1}O_2$ prepared by CO and obtained by calcination at 1,100 °C

The reaction mixture for pigment with $x = 0.1$ ($Ce_{0.9}Tb_{0.1}O_2$) prepared by ceramic method and coprecipitation were also followed by TG–DTA. The formation of the pigments was detected using method of thermal analysis (TG–DTA) and examined in the temperature range of 35–1,500 °C. The starting reactants for the synthesis $Ce_{0.9}Tb_{0.1}O_2$ compound by ceramic method were mixed oxide Tb_4O_7 and CeO_2. The behaviour of these oxides during the thermal analysis is already known [12, 13]. It was found out, that during the heat treatment the terbium oxide changes from $2TbO_2{\cdot}Tb_2O_3$ 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.

In the case of CeO_2 partial oxygen loss was detected by TG–DTA measuring which corresponds with one endothermic effect at the temperature 1,449 °C [14]. The thermal analysis of the reacting mixture prepared by the ceramic method has been published previously [15]. The results of this analysis confirmed formation of solid solution of the $Ce_{0.9}Tb_{0.1}O_2$ at the temperature above 1,400 °C.

The starting mixture for synthesis of $Ce_{0.9}Tb_{0.1}O_2$ compound by coprecipitation route was also submitted to the measure of simultaneous thermal analysis (TG–DTA). The TG–DTA curves for this mixture are shown in the Fig. 2. During the heat treatment to the 200 °C there were obtained two endothermic effects appropriate to the dehydration of the initial mixture [16, 17]. The next endothermic peak with minimum at 260 °C corresponds to decomposition of the unreacted nitrates ions from precursors. This effect is also connected with decreasing of sample weight (Table 3). The last effect on the DTA curve is exothermal and has maximum at 1,075°C. This effect is associated to the formation of the solid solution of $Ce_{0.9}Tb_{0.1}O_2$ pigment and is accompanied by gradual mass loss 0.42% at the temperature range from 500 to 1,100 °C. This fact corresponds with X-ray analysis.

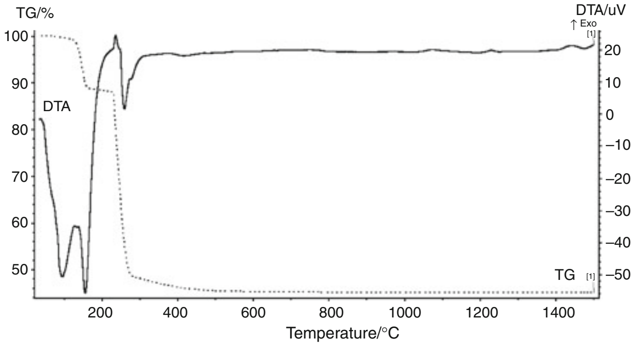

Fig. 2 TG and DTA curves of mixture for synthesis $Ce_{0.9}Tb_{0.1}O_2$ by CO (mass of sample: 401.80 mg, atmosphere: air, heating rate: 10 °C min^{-1})

Table 3 Thermal demeanor of the mixture for synthesis $Ce_{0.9}Tb_{0.1}O_2$ (Fig. 2) by CO

Temperature range/°C	Peak temp./°C	Mass change/%
30–170	156	11.34
170–245	237	17.19
245–500	260; 279; 420	26.09
500–1,500	1,074; 1,230; 1,445	0.42

Conclusions

The main aim of the research was to prepare solid solution of compound $Ce_{0.9}Tb_{0.1}O_2$ and to test their 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 highest temperature of calcination, i.e. 1,600 °C and after application into ceramic glaze. The method of coprecipitation (CO) was also used for the preparation of the $Ce_{0.9}Tb_{0.1}O_2$ compound for the reason of decrease of the final temperature of calcination. Very similar result was achieved with using of this method dealing with colour properties ($C_{\text{CE-1600 °C}} = 37.85/C_{\text{CO-1100 °C}} = 38.39$) and it was extended the decrease of temperature of synthesis to the 1,100 °C.

These results confirm also findings from simultaneous TG–DTA measurement. It was found from the TG/DTA analysis that the formation of final solid solution $Ce_{0.9}Tb_{0.1}O_2$ runs from 1,400 °C for ceramic method (CE) and corresponds with results of the X-ray analysis. In the case of pigments prepared by coprecipitation, the thermal analysis confirmed the formation of solid solution at the temperature about 1,100 °C. This fact was also validated by the results form X-ray analysis, when the samples at the lower temperature (400, 600 °C) are poly-phased while at the temperature 1100 °C the single-phased sample was obtained.

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