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Thermal analysis of the $Ce_{1-x}Tb_xO_2$ pigments

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Abstract Compounds based on CeO_2 were synthesized as high-temperature environment-friendly inorganic pigments with interesting hues. The pigments have been synthesized by using the solid state reaction in the temperature range from 1,300 to 1,600 °C. The host lattice of these pigments is CeO_2 that is doped by terbium ions. The incorporation of doped ions provides interesting orange colours after application into ceramic glaze. The goal was to develop conditions for the synthesis of these compounds and to determine the influence of calcination temperature on their colouring effects. The simultaneous TG-DTA measurements were used for determination of the temperature region of the pigment formation and thermal stability of pigments. The pigments were also evaluated from the standpoint of their structure and particle sizes.

Keywords Ceramic pigments · Ecological pigments · Rare earth mixed oxides · Thermal analysis · Colour properties

Introduction

The research activities in the field of ceramic pigments are focused on investigation of pigments with thermal stability, ecological purity and interesting colour hues. The most requisite hues are yellow, pink, orange and red. Their presence in the ceramic field is constantly deficient. Nowadays, pigments, which are doped with lanthanides (oxide or sulphide compounds), are intensively studied. These pigments are created by the host crystal structure where ions of lanthanides represent chromophores.

Doped ceria is an important ceramic material, which can be widely studied as three-way catalysts [1], oxygen permeation membranes [2], oxygen gas sensor and fuel cell electrolytes and electrodes [3]. 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 [4, 5]. Their commercial significance is in thermal, chemical and light stability, combined with their low toxicity.

Pigments with supporting structures of the fluorite lattice CeO_2 and ions of terbium which work like a chromophore and look as promising. The raw material for the preparation of the $Ce_{1-x}Tb_xO_2$ pigments was mixed oxide Tb_4O_7. Terbium ions are available in two oxidation states in this mixed oxide Tb_4O_7 ($2TbO_2 \cdot Tb_2O_3$). During the high-temperature calcination (1,300–1,600 °C) terbium ions enter the CeO_2 and forming $Ce_{1-x}Tb_xO_2$ solid solution. The colour of pigment depends on the terbium content and temperature of calcination.

In the present work, the synthesis of terbium-doped ceria is studied. The compound with formula $Ce_{0.9}Tb_{0.1}O_2$ was prepared by the traditional ceramic method. This method involves homogenization of the mixture of the corresponding oxides, their calcination is at very high temperature (about 1,400 °C). These compounds are expected to be new ecological high-temperature pigments for colouring of ceramic glazes. The optimum calcination temperature for pigment synthesis was determined on the base of the simultaneous TG-DTA measurements that can provide the information about the temperature region of the pigment formation.

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Experimental

The $Ce_{0.9}Tb_{0.1}O_2$ compound was prepared by the classical dry process, i.e. solid state reaction. Both oxides of lanthanides as starting compounds (CeO_2 and Tb_4O_7) were with a purity of 99.9% (Merck, Germany). The starting mixtures containing both basic oxides (CeO_2, Tb_4O_7) were homogenised in porcelain mortar. The mixture was submitted to calcination in corundum crucibles in an electric resistance furnace with heating rate 7 °C min^{-1}. The calcination temperatures of 1,300, 1,400, 1,500 and 1,600 °C were maintained for 1 h.

All prepared pigments were applied into the ceramic glaze G 05091 (Glazura, s.r.o. Roudnice nad Labem, CZ). The mixture of pigment in amounts of 10% w/w and glaze was glazed at 1,000 °C and the temperature was held for 15 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 was described in terms of CIE $L^*a^*b^*$ and CIE L^*CH^o system. The values a^* (the axis red–green) and b^* (the axis yellow–blue) indicate the colour hue. The value L^* represents the lightness or darkness of the colour as related to a neutral gray 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. The hue angle H^o is defined by an angular position in the cylindrical colour space (for the red is $H^o = 0$–35^o, for the orange $H^o = 35$–70^o, for the yellow $H^o = 70$–105^o).

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 starting raw material and the prepared starting mixtures were studied by thermal analysis in corundum crucible in air in temperature region from 100 to 1,500 °C. The heating rate was 10 °C min^{-1}, α-Al_2O_3 was used as a reference material [6].

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

The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000/MU (Malvern Instruments, GB). It is a highly integrated laser measuring system (He–Ne laser with 633 nm) for the analysis of particle size distribution.

Results and discussion

The goal was to develop conditions for the synthesis of these compounds and to determine the influence of calcination temperature on their colouring effects after application into ceramic glaze.

The samples prepared by the classical dry process (solid state reaction) and calcinated at the temperature from 1,300 up to 1,600 °C were applied to the ceramic glaze. From the Table 1 it is evident that the values of colour coordinates a^*, b^* and value C (chroma) are subsequently increasing with ascending temperature of calcination. On the other hand the values of coordinates L^* (brightness) and H° (hue angle) decline, this fact is reflected in the shift of colour hue from the light beige to the orange. The best results were obtained at the 1,600 °C because the colour coordinate a^* has the highest value (26.16) from all prepared samples and at the same time the value H° has the lowest value (46.28) that corresponds to the deep orange colour of the sample.

The colour properties of this type of pigments after application into glaze are also influenced by the amount of Tb in the pigment composition. An influence of growing content of terbium on the colouring effect of the $Ce_{1-x}Tb_xO_2$ compounds, where $x = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9, was also tested for calcination temperature 1,600 °C. The samples with lower content of terbium ($x = 0.1$ and 0.2) are characterized by dark orange colour. On the opposite the hue of compounds with content of Tb from $x = 0.3$ to $x = 0.5$ is shifted to yellow–orange and the higher Tb content ($x = 0.6$–0.9) produces light yellow colour [7].

The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments. The pigment grain sizes (particle sizes) of the prepared compounds were also tested. The mean particle sizes (d_{50}) of pigments used for colouring of ceramic glazes or bodies lie in region from 5 to 15 μm. The measurement of particle size distribution was determined for unmilled pigments. The average particle size (d_{50}) of pigment particles is in range approx. from 6 to 11 μm. The growing calcination temperature makes the increase of the particle

Table 1 The effect of calcination temperature on colour properties of the $Ce_{0.9}Tb_{0.1}O_2$ pigment

T (°C)	L^*	a^*	b^*	C	H^o
1,300	84.50	3.05	22.80	23.00	82.38
1,400	81.60	6.20	29.23	29.88	78.02
1,500	64.88	21.61	31.92	38.55	55.90
1,600	50.98	26.16	27.36	37.85	46.28

Table 2 The effect of calcination temperature on particle sizes of the $Ce_{0.9}Tb_{0.1}O_2$ pigment

T (°C)	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
1,300	1.85	6.06	26.70
1,400	2.39	7.21	31.66
1,500	3.15	8.94	38.54
1,600	3.29	10.72	36.56

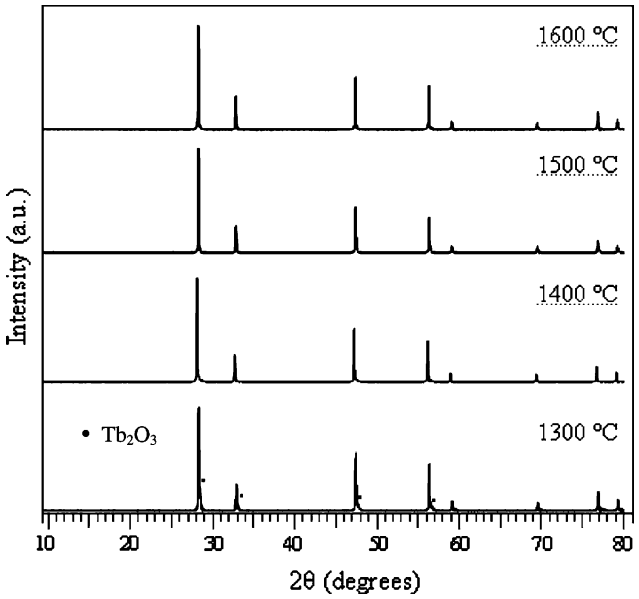

Fig. 1 The X-ray patterns of the sample $Ce_{0.9}Tb_{0.1}O_2$ obtained by calcination at 1,300, 1,400, 1,500 and 1,600 °C

sizes (Table 2). All these values are applicable to colouring ceramic glazes.

All prepared compounds were also studied by X-ray diffraction analysis. The sample calcinated at the 1,300 °C is two-phased (Fig. 1) because free Tb_2O_3 was also identified beside cubic CeO_2. The higher temperature, i.e. 1,400 °C (Fig. 1), produces single-phased compound. The fluorite type CeO_2 structure of the samples with cubic symmetry with lattice parameter $a = 0.5411$ nm for $x = 0.1$ calcinated at 1,400 °C was determined. The same results were obtained for the pigments prepared at temperature 1,500 and 1,600 °C. The samples with Tb content from $x = 0.3$ up to 0.9 prepared by calcination at 1,600 °C were two-phased, because besides the peaks of the fluorite structure the existence of small amount of the secondary phase was detected and its extra peaks can be indexed based on the fluorite structure [8].

The formation of these pigments was followed by the methods of thermal analysis (TG-DTA). The raw materials for the preparation of $Ce_{0.9}Tb_{0.1}O_2$ compound were mixed oxide Tb_4O_7 and CeO_2. The thermal analysis of these two raw oxides have been published previously [9, 10]. Terbium ions are available in two oxidation states in this mixed oxide Tb_4O_7, i.e. $2TbO_2 \cdot Tb_2O_3$. During heat treatment this oxide changes about 950 °C in Tb_2O_3, at the temperature above 1,400 °C the exothermic effect was detected on DTA curve which belongs to the oxidation of trivalent terbium ions to tetravalent ions. The formation of this oxide was also confirmed on the results of X-ray diffraction analysis, but this oxide is better described by formula $TbO_{2-\delta}$, where parameter δ characterises loss of oxygen.

Thermoanalytical curves of starting oxide CeO_2 are given in Fig. 2. 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 [11].

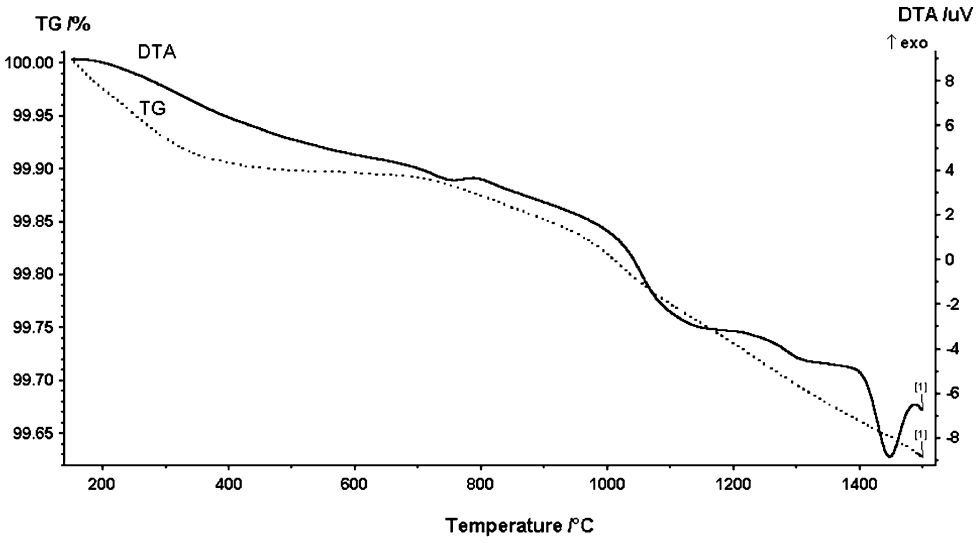

Fig. 2 TG and DTA curves of CeO_2 (mass of sample: 252.20 mg, atmosphere: air, heating rate: 10 °C min^{-1})

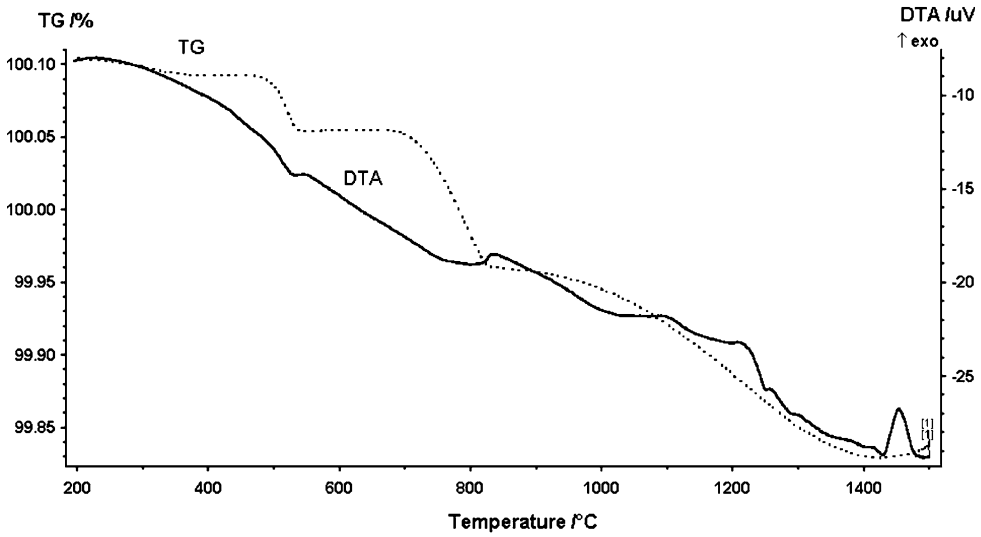

Fig. 3 TG and DTA curves of mixture for synthesis $Ce_{0.9}Tb_{0.1}O_2$ (mass of sample: 507.30 mg, atmosphere: air, heating rate: 10 °C min^{-1})

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

Temperature range (°C)	Peak temp (°C)	Mass change (%)
200–550	532	−0.05
550–850	834	−0.09
850–1,400	1,250	−0.13
1,400–1,500	1,430; 1,455	+0.05

Starting mixture for the pigment preparation with composition $Ce_{0.9}Tb_{0.1}O_2$ was homogenized in an agate mortar and studied with using of DTA (Fig. 3). Several endothermic effects are evident on DTA curve of mixture for synthesis of $Ce_{0.9}Tb_{0.1}O_2$ and correspond with oxidation changes in terbium oxide. These effects are also connected with oxygen loss from both starting oxides, i.e. cerium and terbium oxide. Endothermal effect with minimum at 1,430 °C attributes to formation of the solid solution $Ce_{0.9}Tb_{0.1}O_2$. This fact corresponds with results of X-ray diffraction analysis. The last effect on DTA curve, that is exothermal, with maximum at 1,456 °C belongs to partial reception of oxygen into crystal lattice of prepared compound. This effect is also characterized by an increasing of sample weight (Table 3).

Conclusion

The compounds based on $Ce_{1-x}Tb_xO_2$ were synthetised due to their ability to give interesting orange hues. Intense orange colours of these pigments are based on the incorporation of doped terbium ions into the host lattice of CeO_2. The pigment with $x = 0.1$ prepared by the classical dry process and calcination at 1,600 °C gives the best orange colour after its application into ceramic glaze ($L^* = 50.98$, $C = 37.85$, $H° = 46.28$). The average particle size of this pigment obtained at 50% cumulative mass is about 11 μm and is usable for application into ceramic glazes. The presence of Tb content from $x = 0.3$ to $x = 0.5$ makes yellow–orange hue, the higher content of Tb ($x = 0.6$–0.9) gives light yellow colour.

The optimum calcination temperature for pigment synthesis was determined on the base of the simultaneous TG-DTA measurements. These methods also provided the information about the formation of the solid solution that is about 1,400 °C. This fact was also confirmed by results of X-ray diffraction analysis. The connection of these results with colour properties proves that the best orange sample is pigment prepared at 1,600 °C that is also single-phased and at the same time is characterized by the highest value of chroma C.

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