MATERIAŁY CERAMICZNE /CERAMIC MATERIALS/, 60, 4, (2008), 136-138

Synthesis and characterization of the $Ce_{0.9}Tb_{0.1}O_2$

Petra Šulcová, Lucie Vitásková, Michal Vondrášek, Miroslav Trojan

Department of Inorganic Technology, Faculty of Chemical Technology, The University of Pardubice
e-mail: petra.sulcova@upce.cz

Abstract

Compound $Ce_{0.9}Tb_{0.1}O_2$ has been synthesized by using the solid state reaction and by precipitation. The goal was to develop conditions for the synthesis of this type of pigments and to determine the influence of preparation method on the colouring effects of these compounds. Their colour properties were investigated depending on method of preparation and calcination temperature. All prepared pigments were applied into ceramic glaze. The pigments were evaluated from the standpoint of their structure, colour properties and particle sizes. Our results indicated that these compounds can provide orange hues that are stable in ceramic glazes.

Keywords: Pigments, colour, CeO_2, solid state reaction, coprecipitation

SYNTEZA I CHARAKTERYSTYKA WŁAŚCIWOŚCI $Ce_{0,9}Tb_{0,1}O_2$

Związek chemiczny $Ce_{0,9}Tb_{0,1}O_2$ syntezowano poprzez reakcję w fazie stałej oraz poprzez współstrącanie. Celem pracy było określenie optymalnych warunków syntezy tego typu pigmentów oraz określenie wpływu metody syntezy na barwę tych związków. Właściwości barwne były badane pod względem zarówno rodzaju metody wytwarzania, jak i temperatury kalcynacji. Wszystkie wytworzone pigmenty zastosowano w szkliwach. Były one oceniane z punktu widzenia struktury, właściwości barwnych i wielkości ziaren. Wyniki wskazują, że badany związek może dawać odcienie pomarańczowe, stabilne w szkliwach ceramicznych.

Słowa kluczowe: pigmenty, barwa, CeO_2, reakcje w stanie stałym, współstrącanie

Introduction

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 [1, 2]. 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 pigment is created by the solid solution $Ce_{1-x}Tb_xO_2$ and is produced during high-temperature calcination (>1300°C), i.e. when the terbium oxide is dissolved in CeO_2. The colour hue of pigment depends on the terbium content.

The raw material for the preparation of the $Ce_{1-x}Tb_xO_2$ pigment was mixed oxide Tb_4O_7. Terbium ions are available in two oxidation states in this mixed oxide Tb_4O_7 ($2TbO_2.Tb_2O_3$). During the high-temperature calcination (1300–1600°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, temperature of calcination and on the way of application, too [3].

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 for the first time. This method involves homogenization of the mixture of the corresponding oxides, their calcination is at very high temperature (about 1400°C). The compound with the same formula was also prepared by precipitation and compared with corresponding samples prepared by solid state techniques.

Experimental

The $Ce_{0.9}Tb_{0.1}O_2$ pigment 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 99.5 % (Trading Bochemie, a.s., CZ). 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 1300, 1400, 1500 and 1600 °C were maintained for 1 hour. The starting materials for synthesizing of $Ce_{0.9}Tb_{0.1}O_2$ by precipitation were $Ce(NO_3)_3.6H_2O$ and $Tb(NO_3)_3·5H_2O$ with a purity of 99.5 % (Aldrich). They were mixed according to the designed molar ratio, dissolved in 300 ml distilled water and coprecipitated with ammonium hydroxide at pH = 10. The precipitate was washed three times with distilled water and dried. The resultant precursors were calcinated at temperature range from 850 to 1400°C to yield oxide powders.

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 1000 °C and the temperature was held for 15 min.

Tab. 1. The effect of calcination temperature on colour properties and particle sizes of the $Ce_{0.9}Tb_{0.1}O_2$ pigment prepared by classical method

T [°C]	Colour properties in ceramic glaze					Particle sizes [μm]		
	L^*	a^*	b^*	C	H^o	d_{10}	d_{50}	d_{90}
1300	84.50	3.05	22.80	23.00	82.38	1.85	6.06	26.70
1400	81.60	6.20	29.23	29.88	78.02	2.39	7.21	31.66
1500	64.88	21.61	31.92	38.55	55.90	3.15	8.94	38.54
1600	50.98	26.16	27.36	37.85	46.28	3.29	10.72	36.56

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 $H°$ defined by an angular position in the cylindrical colour space (for the red is $H°$= 0-35°, for the orange $H°$= 35-70°, for the yellow $H°$= 70-105°). The equation for calculation of the hue angle is $H°$= arc tg (b^*/a^*) [5].

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, λ = 633 nm) for the analysis of particle size distribution.

Results and discussion

The goal was to develop conditions for the synthesis of this type of pigments and to determine the influence of preparation method on the colouring effects of these compounds.

The samples prepared by the classical dry process (solid state reaction) and calcinated at the temperature from 1300 up to 1600°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 1600°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 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 μm to 11 μm. The growing calcination temperature makes the increase of the particle sizes (Table 1). All these values are applicable to colouring ceramic glazes.

The compound $Ce_{0.9}Tb_{0.1}O_2$ was also prepared by precipitation method and calcinated at the temperature range from 850 up to 1400°C and was also applied into the ceramic glaze. The colour properties of pigments are changing in dependence on the calcination temperature. This influence is described in Table 2. The values of colour coordinate a^* and value C rise with growing temperature. On the contrary, the values of L^* and $H°$ decrease. The biggest shift in the values of colour coordinates is appearing between temperature of calcination 1300°C (a^* = 16.43) and 1400°C (a^* = 23.31). From the values of $H°$, that lie in the interval from 77 to 49, it follows that colour hue of the samples changes from beige to orange-brown and orange. The sample calcinated at the temperature 1400°C is the best because its value of the colour coordinate a^* (red hue) is the highest and at the same time is characterized by the lowest value L^* (lightness). This pigment gives the intensive orange colour ($H°$ = 49.01).

The values of pigment particles were also measured (Table 2). The average particle size of the $Ce_{0.9}Tb_{0.1}O_2$ pigment prepared by precipitation obtained at 50% cumulative mass is approx. from 2 μm to 15 μm. The increase of calcination temperature makes the growth of particle sizes but all values of the mean particle size are usable for application into ceramic glazes.

The pigment $Ce_{0.9}Tb_{0.1}O_2$ prepared by classical dry process and precipitation was also studied by powder X-ray diffraction analysis. The samples prepared by classical method were homogenous at higher temperature, i.e. 1400, 1500

Tab. 2. The effect of calcination temperature on colour properties and particle sizes of the $Ce_{0.9}Tb_{0.1}O_2$ pigment prepared by precipitation

T [°C]	Colour properties in ceramic glaze					Particle sizes [μm]		
	L^*	a^*	b^*	C	H^o	d_{10}	d_{50}	d_{90}
850	85.21	6.27	27.45	28.16	77.13	0.61	1.97	28.46
900	84.69	6.06	26.03	26.73	76.89	0.49	2.26	31.02
950	84.72	6.87	26.96	27.82	75.70	0.62	3.57	34.20
1000	83.69	7.11	28.34	29.22	75.92	0.48	3.65	35.12
1050	82.09	8.19	29.48	30.60	74.47	0.59	3.92	35.33
1100	80.81	9.15	29.90	31.27	72.98	0.61	6.30	40.02
1200	79.18	11.85	31.30	33.47	69.26	0.80	6.45	40.09
1300	72.34	16.43	32.29	36.23	63.03	0.80	10.98	50.09
1400	51.39	23.31	26.82	35.53	49.01	1.26	14.98	53.01

and 1600°C. Pigment calcinated at 1300°C was heterogeneous because free oxide Tb_2O_3 was also identified beside fluorite compound CeO_2. Samples prepared by precipitation were single-phased at temperature 900°C and higher. Only sample calcinated at the lowest temperature (850°C) was heterogeneous.

Conclusion

The aim of the research was to verify the different ways of the preparation for the pigment $Ce_{0.9}Tb_{0.1}O_2$. The samples were synthesized by classical dry process (solid state reaction) and by precipitation. The starting mixtures were calcinated at the various temperatures, the optimal calcination temperature was searched and the colour properties of prepared samples were compared.

The pigment prepared by the classical dry process gives the best orange colour at the 1600°C (L^* = 50.98, C = 37.85, $H°$ = 46.28), the pigment prepared by precipitation also produces the intensive orange hue (L^* = 51.39, C = 35.53, $H°$ = 49.01) at temperature 1400°C. Both the pigments are colourfully comparable. The pigment prepared by solid state reaction is characterized by the smaller mean particle sizes (d_{50} = 10.72 μm) than pigment prepared by precipitation (d_{50} = 14.98 μm).

The precipitated compound $Ce_{0.9}Tb_{0.1}O_2$ was single-phased at lower temperatures (900°C) compared to the solid state reaction, when the pigment is single-phased from the temperature 1400°C. The connection of these results with colour properties proves that the best orange sample is pigment prepared by solid state reaction at 1600°C that is also single-phased and at the same time is characterized by the highest value of chroma C.

Acknowledgements

The authors would like to thank for the financial support from the Ministry of Education, Youth and Sports of Czech Republic (No. 0021627501) and Grant Agency of Czech Republic (No. 104/08/0289). Authors also thank to doc. Ing. Ludvík Beneš, CSc. for X-ray crystallography.

Literature

[1] Tumanov S.O., Pavlova V.A.: Steklo i keramika, 2, (1974), 28.
[2] Šulcová P., Trojan M., Šolc Z.: Dyes and Pigments, 37, (1998), 65.
[3] Tomaszewicz E.: J. Thermal Anal. and Cal., 90, (2007), 235.
[4] Šulcová P., Vitásková L.: Sci. Pap. University of Pardubice A13 (2007) 121.
[5] Šulcová P., Trojan M.: J. Thermal Anal. and Cal., 91, (2008), 151.