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Influence of Preparation Methods on Colourfulness of $Ce_{1-(x+y)}Tb_xTi_yO_2$

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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 prepared by using the solid state reaction and suspension mixing of raw materials. The goal was to develop conditions for the synthesis of this type of pigments and to determine the influence of preparation methods on the colouring effects of these compounds. The colour properties were investigated depending on the method of preparation, calcination temperature and concentration of Ti^{4+} ions. All prepared pigments were applied into organic matrix and 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 light orange colour hues that are stable in ceramic glazes and dark brown colour shades in the organic matrix.

Keywords: Pigment, Solid state reaction, Colour properties, Ceramic glaze, Particle size

WPŁYW METOD WYTWARZANIA NA ZABARWIENIE $Ce_{1-(x+y)}Tb_xTi_yO_2$

Związki oparte na CeO_2 zsyntezowano jako wysokotemperaturowe, przyjazne dla środowiska, nieorganiczne pigmenty o interesujących barwach. Pigmenty wytworzono wykorzystując reakcję w fazie stałej oraz mieszanie surowców w zawiesinie. Celem było opracowanie warunków syntezy tego typu pigmentów i określenie wpływu metody preparatyki na efekty barwne otrzymanych związków. Właściwości barwne zbadano w zależności od zastosowanej metody wytwarzania, temperatury kalcynacji i stężenia jonów Ti^{4+}. Pigmenty oceniano po względem ich struktury, barwy i rozmiaru cząstek. Uzyskane wyniki wskazały, że otrzymane związki mogą dostarczać odcieni jasnopomarańczowych, które są trwałe w szkliwach ceramicznych, oraz odcieni ciemnego brązu w osnowie organicznej.

Słowa kluczowe: pigment, reakcja w stanie stałym, właściwości barwne, szkliwo ceramiczne, rozmiar cząstki

1. Introduction

The history of inorganic pigments is very rich and dates back to the primeval ages. In former times, there were used various clays, ruddles, ochres and etc. as the pigments for the colouring of cave paintings. In antique period, the pigments were already commonly used to the decoration of ceramics. Old extant paintings indicate long-lasting stability of these pigments.

Nowadays the research is mainly targeted to the enlargement of the colour palette of the inorganic pigments, which do not contain the toxic elements and are not deleterious. The big accent is set on the high chemical resistant and thermal stability [1, 2].

The compounds based on CeO_2 are the colour interesting high temperature pigments, whose principal is the host lattice of cerium oxide, which is of fluorite type [3, 4]. The materials based on this oxide have wide possibility of utilization due to their high chemical activity and conductivity. In many cases, these properties could be enhanced by fitting various elements, e.g., Zr, Ca, Ti, Tb, into the host lattice of cerium oxide [5].

In this work, we tried to prepare an ecological inorganic pigment composed of mixed oxides based on the Ce-Tb-Ti. The raw materials for the preparation of the $Ce_{1-(x+y)}Tb_xTi_yO_2$ pigments, except CeO_2, comprised also dual terbium oxide (Tb_4O_7) and various compounds of titanium, e.g., TiO_2, $Na_2Ti_4O_9$ and $TiOSO_4$. Terbium ions are available in two oxidation states in the Tb_4O_7 mixed oxide, i.e., $2TbO_2 \cdot Tb_2O_3$.

During the high-temperature calcination (1100–1400°C), terbium and titanium ions enter the host lattice of CeO_2 and form the $Ce_{1-(x+y)}Tb_xTi_yO_2$ solid solution. The pigments were synthesized by classical ceramic method, i.e., solid state reaction, and also by a method of suspension mixing of materials. A final colour hue of pigment depends on the content of components, the temperature of calcination, and on the way of application, too.

2. Experimental section

The pigments of $Ce_{1-(x+y)}Tb_xTi_yO_2$ (x = 0.05, y = 0.05, 0.15, 0.25, 0.35 and 0.45) were synthesized by two different methods, i.e., solid state reaction and suspension mixing of material (SMM). The initial compounds for preparation of

Table 1. Influence of the way of application on colour properties of the $Ce_{1-(x+y)}Tb_xTi_yO_2$ pigments prepared by suspension mixing of materials, and calcinated at the temperature of 1100°C; rutile paste was the Ti source.

y	Organic matrix					Ceramic glaze				
	L*	a*	b*	C	H°	L*	a*	b*	C	H°
0.05	63.98	8.26	12.97	15.38	57.51	85.77	4.40	21.49	21.94	78.43
0.15	65.80	7.85	12.90	15.10	58.68	86.18	3.72	21.57	21.89	80.21
0.25	67.70	7.47	12.84	14.85	59.81	86.23	2.84	21.21	21.40	82.37
0.35	70.85	6.77	12.81	14.49	62.14	86.14	2.90	22.43	22.62	82.63
0.45	72.62	6.28	11.90	13.46	62.18	85.52	3.01	23.59	23.78	82.73

the samples were the same for both of methods, i.e., CeO_2 (Trading Bochemie s.r.o., CZ), Tb_4O_7 (Trading Bochemie s.r.o., CZ), and anatase and rutile paste, $Na_2Ti_4O_9$, TiO_2 AV-01 (Precheza a.s., CZ) and $TiOSO_4 \times 2H_2O$ VKR 611 (Heubach GmbH & CO.KG, Germany) were used as a source of titanium. These compounds rank technically pure. The precursors employed for the traditional ceramic way of preparation were homogenized with pestle in a porcelain mortar. The reaction mixtures were divided into corundum crucible and submitted to calcination for 1 hour at four temperatures: 1100, 1200, 1300 and 1400°C in an electric furnace, using a heating rate of 7°C/min.

The second way of preparation of the pigments, suspension mixing of materials, presented a two-step process. In the first step, the initial compounds are homogenized by wet in the porcelain mortar: the final mixture is subsequently assigned to a preheated steel plate (approx. 400°C) and thermally elaborated for a few minutes. The second step constitutes the calcination of gained powder semi-product at the demanded temperatures in the electric furnace for the same conditions like by ceramic method.

In both preparation methods, the final product was applied into organic matrix (Parketol, Balakom a.s. CZ) in mass tone and into ceramic glaze G 05091 (Glazura s.r.o., Roudnice nad Labem, CZ) in amount of 5 % w/w, and the temperature of glazing was 1050°C during the time of 20 minutes.

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**. 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 colour of the pigments is also expressed by the chroma (*C*) and hue angle (*H*°). The value *C* (chroma) represents saturation of the colour and is calculated according to the formula:

$$C = (a^{*2} + b^{*2})^{1/2} \quad (1)$$

The hue angle, H^o, is defined by an angular position in the cylindrical colour space (for the red is $H^o = 0^o–35^o$, for the orange $H^o = 35^o–70^o$, for the yellow $H^o = 70^o–105^o$) and the equation for the calculation is:

$$H^\circ = \text{arctg}\,(b^*/a^*) \quad (2)$$

The distribution of particle sizes of the calcinated powders was obtained by laser scattering using a Mastersizer 2000/MU (Malvern Instruments, Ltd. GB). It is a highly integrated laser measuring system (He-Ne laser, λ = 633 nm) for the analysis of particle size distribution in the range from 0.2 to 2000 μm. The equipment uses scattering of the incident light on particles. The signal is evaluated on the basis of Mie dissipation or Fraunhofer bending [6].

The structure of the prepared pigments was also investigated. The pigments were studied by X-ray diffraction analysis. The X-ray diffractograms were obtained by using a Diffractometer D8 Advance equipment (Bruker, GB) with a goniometer of 17 cm in the 2θ range of 10–80°, and the CuK_α (λ = 0.15418 nm) radiation was used for an angular range of $2\theta < 35°$ and $CuK_{\lambda 2}$ (λ = 0.15405 nm) for the range of $2\theta > 35°$ with scintillation detector.

3. Results and discussion

The aim of this study was to follow the influence of preparation methods on the colour properties of $Ce_{1-(x+y)}Tb_xTi_yO_2$ pigments and on the phase structure, too.

The colour properties of prepared pigments are the most changeable with the temperature of calcination. By applying the pigments into the organic matrix, the final colour shade shifts from light brown through orange brown to the dark brown hue following the temperature increase. The colour shift is less violent after application of the pigments into the ceramic glaze. The colour of pigments moves from cream to lightly orange owing to the rising temperature of calcination. Inexpressive cream colour of the samples is characterized by very low values of colour coordinate *a** (Table 1), which were proceeding around the value of *a** = 3 for the temperature of 1100 and 1200°C, and high values of brightness factor *L** (approx. 86). By the pigments applied into the organic matrix, the values of colour coordinate *a** are higher, i.e., *a** = 6–9 at lower temperature of calcination like this, and on the contrary the values of brightness *L** are lower (approx. 68), which confirmed the darker coloration of the pigments.

From the Table 1, the influence of titanium content on colouring the samples is also evident. The values of colour coordinates *a** are subsequently decreasing with the ascending content of titanium component by both preparation methods. By the pigments applied into the organic matrix, it simultaneously attends to the decline of colour coordinates *b** and chroma C values. Opposite to them, the values of hue angle *H*° and brightness *L** are escalating, which means, that the rising content of titanium component in a pigment causes

Table 2. Influence of initial compounds on colour properties of the $Ce_{0.9}Tb_{0.05}Ti_{0.05}O_2$ pigment prepared by suspension mixing of materials, and calcinated at 1400°C after application into organic matrix.

Initial compound of Ti	L^*	a^*	b^*	C	$H°$
TiO_2 (AV-01)	54.29	10.72	13.94	17.59	52.44
Rutile paste	48.25	13.25	15.25	20.20	49.01
Anatase paste	46.89	12.84	14.00	19.00	47.47
$Na_2Ti_4O_9$	43.45	14.95	17.08	22.70	48.80
$TiOSO_4$ (VKR 611)	46.99	12.32	13.27	18.11	47.13

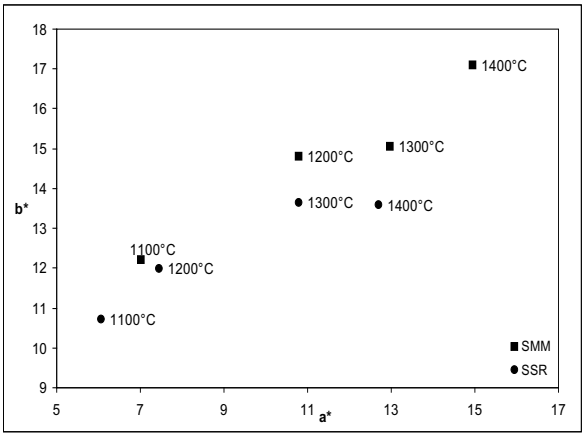
brightening the final colour shade of the sample. This trend is evident for all temperatures applied, when the pigments with the lowest concentration of titanium element, i.e., y = 0.05 achieve the best colour results.

Various titanic compounds (see experimental part) were used as the sources of titanium in the pigments. The pigment prepared from the TiO_2 (AV-01) provides the best results of colouring at the lowest temperature of calcination (1100°C) and for both preparation methods. A compound of formula $Na_2Ti_4O_9$ is approved as the most suitable source of titanium, which delivers the highest values of both a^* and b^* colour coordinates (Table 2) at higher temperatures of calcination.

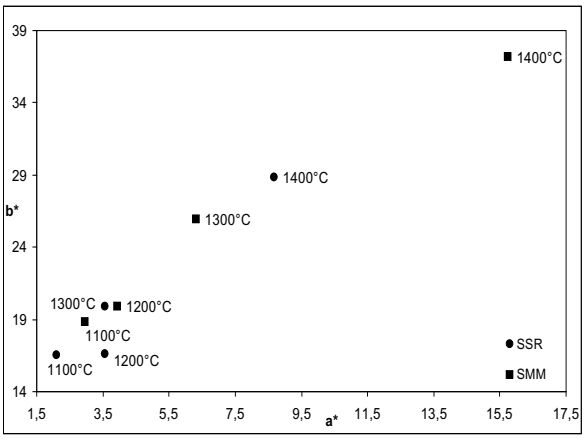
The highest value of chroma C (22.70) and currently the lowest value of brightness L^* (43.45) were also attained by using $Na_2Ti_4O_9$ for the sample preparation. The pigment synthesized from the TiO_2 (AV-01) material at the temperature of 1400°C provides the worst colour properties. From the Table 2 it is evident, that this sample has the lowest values of colour coordinates a^*, chroma C, and on the other hand the values of lightness L^* and hue angle $H°$ are the highest ones unlike other samples.

As it ensues from the previous results, the final colour of synthesized pigments markedly depends on the temperature of calcination. The least interesting colour tinges were obtained by calcination at lower temperatures, i.e., 1100 and 1200°C (Fig. 1). In the case of application into organic matrix the colouring of the samples is bright brown. By the pigments applied into ceramic glaze, the cream shades were obtained at these lower temperatures. The highest values of colour coordinates a^* and b^* are shown by the pigments calcinated at the highest temperature, i.e., 1400°C. These samples present also the most interesting colour properties.

The influence of pigment preparation ways on the colour properties is also shown in Fig. 1. The sample prepared by the suspension mixing of materials (SMM), and calcinated at 1400°C unambiguously achieves the highest values of a^* and b^* colour coordinates, and also has higher value of chroma C (22.70) than the sample prepared by the solid state reaction (SSR). It is evident from Fig. 1a that the values of colour coordinates a^* and b^* are lower in each temperature used by the classical ceramic method (SSR) in comparison to the SMM process. The same trend is shown also by the pigments applied for the ceramic glaze (Fig. 1b), where however there is much bigger difference among the values of colour coordinates at the thermal change from 1300 to 1400°C, reflecting in the colour shift from the cream to bright orange shade. This change is followed by large increase of the value of chroma C ($C_{1300°C}$ = 26.66/$C_{1400°C}$ = 40.34) and also by the reduction of the hue angle value $H°$ ($H°_{1300°C}$ = 76.27/$H°_{1400°C}$ = 67.03). The final value of hue angle (67.03) already lies in the interval of orange shade, i.e., 35–70.



a)



(b)

Fig. 1. Influence of the calcination temperature and preparation method on colour properties of the $Ce_{0.9}Tb_{0.05}Ti_{0.05}O_2$ pigment applied into: a) organic matrix and b) ceramic glaze.

All synthesized samples were submitted to the particle size distribution measurements, which were performed for the unmilled pigments depending on the preparation method of $Ce_{1-(x+y)}Tb_xTi_yO_2$ compounds, calcination temperature and titanium content. It is obvious from the values presented in Table 3 that the mean values of particle size d_{50} increase with the temperature of calcination. These values are not so different from each other and lay in the narrow interval of 2.84–3.82 μm (SSR). The same results were obtained for the samples prepared by the suspension mixing of materials (SSM).

Table 3. Influence of the calcination temperature on the particle size distribution of the $Ce_{0.9}Tb_{0.05}Ti_{0.05}O_2$ pigment.

T [°C]	Solid state reaction (SSR)			Suspension mixing of materials (SMM)		
	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]
1100	0.46	2.84	9.68	0.42	2.37	7.85
1200	0.50	2.93	9.26	0.46	2.99	10.84
1300	0.56	3.23	10.12	0.49	2.92	9.34
1400	0.71	3.82	10.77	0.68	3.96	12.07

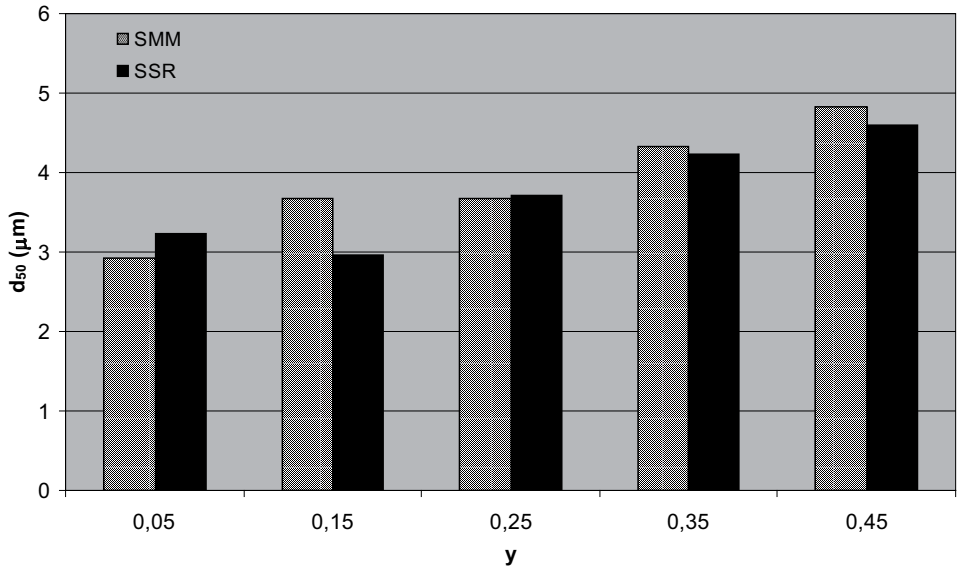


Fig. 2. Influence of the Ti content (y) and the method of preparation on the mean value of particle size (d_{50}) of the $Ce_{0.9}Tb_{0.05}Ti_{0.05}O_2$ pigment calcinated at 1300°C.

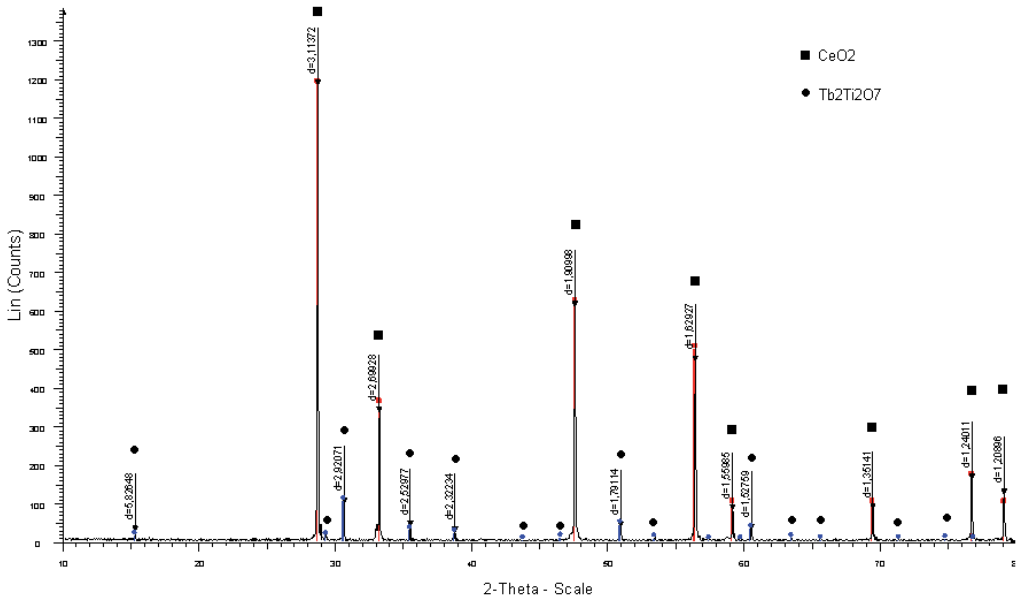


Fig. 3. X-ray diffraction pattern of the $Ce_{0.9}Tb_{0.05}Ti_{0.05}O_2$ pigment calcinated at 1300°C (SMM; $Na_2Ti_4O_9$ was the source of Ti).

It was also found out that the pigment preparation methods have no influence on the mean particle size d_{50} (Table 3). From Fig. 2, it is possible to discover how the Ti content in the sample affects the particle size distribution. The values of d_{50} increase with the content of titanium in the pigment within the range of 2.9-4.8 µm for both methods of pigment preparation. The d_{50} values of the samples synthesized by the SMM process (suspension mixing of materials) are slightly higher than those of SSR (solid state reaction).

The $Ce_{0.9}Tb_{0.05}Ti_{0.05}O_2$ pigments prepared by the methods mentioned above were also studied by X-ray powder diffraction analysis. It has been verified that the compounds prepared at lower temperatures (1100 and 1200°C) were three-phased. Except of the cubic phase of CeO_2, they contained the cubic phase of $Tb_2Ti_2O_7$ and the tetragonal phase of TiO_2. The samples were just double-phased after calcination at the temperature of 1300 and 1400°C (Fig. 3). The majority of phases was formed by CeO_2 with cubic lattice, crystallizing in a space group of symmetry Fm-3m (225), and small amount of the cubic phase of $Tb_2Ti_2O_7$ (227) appeared. The results of X-ray analysis are practically the same for both methods of pigments preparation. The differences within the range of several tens were only in the intensity of the peaks.

4. Conclusion

The goal of this work was to study different methods of $Ce_{1-(x+y)}Tb_xTi_yO_2$ pigment preparation and to compare their influence on the colour properties of the pigments obtained. For synthesis of the samples, a traditional ceramic method based on a solid state reaction (SSR) and a method of suspension mixing of materials (SMM) were used. As the sources of

titanium, various titanic raw materials were used, and the starting mixtures were calcinated at different temperatures.

It was found out for both preparation methods that, at low calcination temperatures of 1100 and 1200°C, the prepared pigments reached very low values of colour coordinates *a** and *b**, and on the other hand very high values of lightness *L**, which reflect on the inexpressive and light colour shades. The pigment with a formula of $Ce_{0.9}Tb_{0.05}Ti_{0.05}O_2$ prepared by suspension mixing of materials and calcinated at 1400°C, where $Na_2Ti_4O_9$ delivered Ti^{4+} ions, achieved the best colour properties. For this sample, dark brown colour is characteristic after application into an organic matrix. In the case of application into ceramic glaze, light orange is the final colour.

For both preparation methods (SMM and SSR), the mean value of particle sizes increases with the temperature of calcination, but only slightly. The pigment with the titanium content of y = 0.05 has maximal value of d_{50} = 4.82 μm at the highest calcination temperature of 1400°C. This result is very good from the point of view of the application into ceramic glaze.

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