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Synthesis and colour properties of pigments based on terbium-dopped Mg_2SnO_4

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Abstract The main aim of this work was to synthesize the magnesium orthostannate doped by terbium cations and tested whether these materials can be used for colouring of the different materials, e.g. organic binder and ceramic glazes. Initial composition of pigments was counted according the general formula $2MgO(1 - x)SnO_2$–$xTbO_2$, where values of x varied from 0.1 to 0.5 in 0.1 steps. The simultaneous TG/DTA measurements of mixture containing tin oxide, magnesium carbonate hydroxide and terbium oxide showed that the formation of a new compound started at temperature 1,029 °C, but single-phase system was not prepared. Granulometric compositions of samples that were prepared by calcining at temperatures 1,300–1,400 °C are characterized by values of median (d_{50}) in range 4–8 μm. The calcining temperature 1,500 °C caused the increase of the particle sizes at around 12 μm. The composition of sample $2MgO$–$1.5SnO_2$–$0.5TbO_2$ and heating temperature 1,500 °C are the most suitable conditions for preparation of colourfully interesting pigment that can be recommended also for colouring of ceramic glazes. Especially, for colouring of decorative lead containing glaze G 07091 containing 5 wt% of PbO and 8 wt% of Al_2O_3.

Keywords Inorganic pigments · Yellow pigments · Magnesium orthostannate · Optical properties · Colour measurements

Introduction

Over last decades, the chemistry of rare earth elements has been intensively investigated from several points of view. Our research group is focused on synthesis and characterization of inorganic materials that could find the industrial occupancy for colouring of ceramics, organic matrix, plastics, or building materials. Inorganic pigments are coloured substances produced and marketed as fine powders. Chemically, inorganic pigments are quite simple materials and include elements, their oxides, mixed oxides, sulphides, chromates silicates, phosphates, and carbonates. Mixed metal oxides represent a special class of compounds where several oxides react and form a new compound, or some of the cations of the host lattice of one of the oxide are replaced by the cations of chromofore. The structure of the host lattice is preserved, but it can be disordered. Spinel pigments have a common chemical formula AB_2X_4; structurally they have a cubic symmetry. Based on the ions A, B and X, the spinels can be divided into three categories [1]. Most often, the X ions represent oxygen anions. In classical spinels, the A ions occupy tetrahedral sites and the B ions occupy octahedral sites, $A^{tet}B_2^{oct}O_4$. In inverse spinels, the A ions and half of the B ions swap positions to give $B^{tet}[AB]_{oct}O_4$. Between both of these extremes there are a number of intermediate spinels. The manner in which such sites are occupied depends on the calcination temperature [2, 3]. Magnesium orthostannate is a chemically stable host with nearly perfect cubic inverse spinel crystal structure that belongs to the space group Fd3m [4, 5]. The unit cell has 96 cations sites with 24 being occupied by the cations. The tetravalent Sn ions occupy only the octahedral sites, while one half of the divalent Mg ions are located at octahedral sites, and the other half occupies tetrahedral sites [6]. The Sn ions and Mg ions at the octahedral sits are

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arranged in a systematical disorder. Some of these defects serve as electron or hole traps. For example, the Mg ions at the Sn site can trap a hole; while the Sn ion at the Mg sites forms an electron traps. Oxygen vacancies may also serve as F-center-like electron traps [4].

Magnesium orthostannate is normally synthesized by solid state reaction between MgO and SnO_2 at temperature above ~700 °C, when unstable metastannate disproportionates ion to orthosrtannate and tin oxide [7–9]. In some cases, even the orthostannate cannot be synthesized as a single phase [4, 8, 10]. Novel synthesis of high purity phase Mg_2SnO_4 from metallic precursors via powder metallurgy described Azad [11]. Wet method of preparation from $SnCl_4{\cdot}5H_2O$ and $Mg(NO_3)_2$ was described by Xiao et al. [12].

In this article, the results of research work relating to terbium doped Mg_2SnO_4 are included. The main aim of this research was to propose the optimal conditions of the synthesis of pigments described by general formula $2MgO–(1 - x)SnO_2–xTbO_2$, where values of x vary from 0.1 to 0.5 in 0.1 steps. Their pigment application qualities in order to explore their potential consumption as ceramic pigments were tested.

Experimental

Preparation of samples

Powders of mixed metal oxide which have spinel stoichiometry (Table 1) were prepared in lab-scale; it means it was prepared 30–50 g of products. The powders synthesis was carried out by solid state reaction of metal precursors—tin oxide (95% of purity, Sigma-Aldrich Co.), magnesium carbonate (basic purity, Ronas Chemicals Ind., Ltd.) and terbium oxide (Tb_4O_7 99.5% of purity, Ind. Rare Earths, Ltd.). Initial reagents were mechanochemically activated before heating. The high energy milling process was carried out in a planetary mill Pulverisette 5 (Fritsch GmbH, Germany) for 6 h. The reaction mixture containing the SnO_2, $MgCO_3$ and Tb_4O_7 was ground together with agate balls (∅ 10 mm) in a ball-to-powder mass ratio of 20:1. The activated reaction mixtures were calcined in an electric furnace placing them in alumina crucibles. The first calcination was carried out at temperature 1,000 °C for 2 h, heating the furnace at 10 °C min^{-1}. Resulting powders were obtained after next calcination at different temperatures: 1,300, 1,400 or 1,500 °C for 3 h.

Table 2 Characterization of glazes by their composition and heating temperature

Glaze	SiO_2	B_2O_3	Al_2O_3	CaO	PbO	ZnO	Na_2O	K_2O	T/°C
G 02891	25	14	5	–	5	–	3	1	920
G 05091	35	11	11	6	34	–	1	2	1,000
G 07091	35	3	8	1	53	–	1	1	1,000
P 07491	63	12	11	8	–	1	6	–	1,050

For testing in organic matrix, suspensions containing 1 g of pigment and 1.5 cm^3 of polyurethane binder were homogenized. Colour paints were prepared by deposition of slurries on the white no absorb paper. Wet film thickness was 100 μm. For testing in ceramic glazes, aqueous suspensions containing 3 wt% of pigment and 97 wt% of the frit lustrous coloursless glazes (Glazura, a.s., CR) were prepared by milling. These slurries were deposited on wall tile bodies and further fired at different temperatures (Table 2) for 15 min.

Characterization of samples

Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (NETZSCH, Germany) in the temperature range 30–1,400 °C at heating rate 10 °C min^{-1}. The analysis was carried out in a ceramic crucible under air and α-Al_2O_3 was used as a reference material.

The crystal structures of the product of calcination were studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using the equipment difractometer D8 (Bruker, GB) with a goniometer of 17 cm in the range 2Θ of 10–80°. Cu $K_{\alpha 1}$ ($\lambda = 0.15418$ nm) radiation was used for angular range of $2\Theta < 35°$ and Cu $K_{\alpha 2}$ ($\lambda = 0.15405$ nm) for range of $2\Theta > 35$. A scintillation detector was used.

The optical properties of pigments and their applications were measured by spectrophotometer ColourQuest XE

Table 1 Composition of the powders $2MgO–(1 - x)SnO_2–xTbO_2$

x	Stoichiometry	MgO/mol%	SnO_2/mol%	TbO_2/mol%	Obtained phases/1,500 °C	Obtained phases/1,550 °C
0.1	$2MgO–0.9SnO_2–0.1TbO_2$	66.6	30.0	3.3	Mg_2SnO_4, MgO, TbO_2	Mg_2SnO_4, $Tb_2Sn_2O_7$
0.2	$2MgO–0.8SnO_2–0.2TbO_2$	66.6	26.6	6.6	Mg_2SnO_4, MgO, TbO_2	Mg_2SnO_4, $Tb_2Sn_2O_7$
0.3	$2MgO–0.7SnO_2–0.3TbO_2$	66.6	23.3	10.0	Mg_2SnO_4, MgO, TbO_2	Mg_2SnO_4, $Tb_2Sn_2O_7$
0.4	$2MgO–0.6SnO_2–0.4TbO_2$	66.6	20.0	13.3	Mg_2SnO_4, MgO, TbO_2	$Tb_2Sn_2O_7$, MgO
0.5	$2MgO–0.5SnO_2–0.5TbO_2$	66.6	16.6	16.6	Mg_2SnO_4, MgO, TbO_2	$Tb_2Sn_2O_7$, MgO

(HunterLab, USA) under the following conditions: wavelength 400–700 nm, illuminant D65, standard observer 10°, the geometry of measurement *d*/8° and $BaSO_4$ integrating sphere. The colour was evaluated according to the Commission Internationale de l′Eclairage (CIE) through $L^*a^*b^*$ parameters [13]. In this system, coordinate L^* expresses the colour lightness ($L^* = 100$ for white colour and $L^* = 0$ for black colour). Coordinate ($-a^*$) is green hue, ($+a^*$) is red hue, ($-b^*$) expresses blue hue and (b^*) expresses yellow hue. The values of chroma (C) were calculated according the mathematical formula $C = (a^{*2} + b^{*2})^{1/2}$.

The particle size distribution of the samples was measured using a Mastersizer 2000/MU (Malvern Instruments, UK). The equipment employs the scattering of incident light on particles. The pigments were ultrasonically homogenized in solution of $Na_4P_2O_7$ ($c = 0.15$ mol dm^{-3}) for 90 s and measured. The signal was evaluated on the basis of Fraunhofer bending. Before measurements, the samples were gently ground in an agate mortar.

Results and discussion

Thermal decompositions of raw materials and thermal behaviour of some reaction mixtures were followed by methods of thermal analysis. The TG and DTA curves of magnesium precursor ($2MgCO_3 \times 1.3Mg(OH)_2 \times 3H_2O$) are shown in Fig. 1. The first endothermic effect recorded on the DTA curve is connected with the loss of moisture. The second endothermic effect with minimum at 313 °C complies with the loss of three molecules of crystallic water. This process is recorded on the TG curve and corresponds to mass loss of 18.11%. The next endothermic peak with minimum at temperature 435 °C corresponds to the decomposition of 1.3 molecules of magnesium hydroxide to magnesium oxide. The mass loss detected on the TG curve (9.58%) is in a good agreement with theoretical mass loss (9.57%). The last step of the decomposition of magnesium carbonate hydroxide is the degradation of magnesium carbonate and formation of magnesium oxide. This process is detected on the DTA curve by two endothermic effects with minimum at 502 and 555 °C and on the TG curve by mass loss of 39.46% (Table 3). The gradual decomposition of magnesium carbonate hydroxide is described by the following chemical equations:

$$2MgCO_3 \times 1.3Mg(OH)_2 \times 3H_2O \xrightarrow[313\ ^\circ C]{} 2MgCO_3 \times 1.3Mg(OH)_2 + 3H_2O \tag{1}$$

$$2MgCO_3 \times 1.3Mg(OH)_2 \xrightarrow[435\ ^\circ C]{} 2MgCO_3 \times 1.3MgO + 1.3H_2O \tag{2}$$

$$2MgCO_3 \times 1.3MgO \xrightarrow[502,\,555\ ^\circ C]{} 3.3MgO + 2CO_2 \tag{3}$$

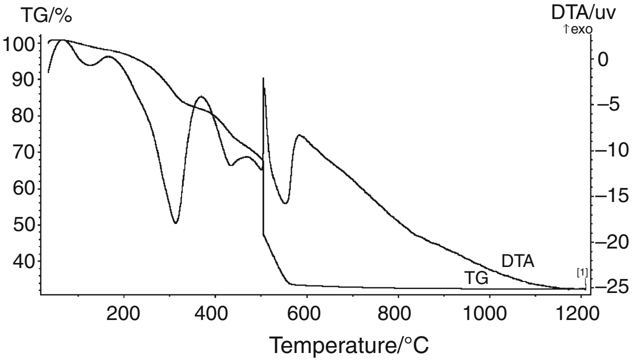

Fig. 1 DTA and TG curves of the decomposition of magnesium precursor (62.300 mg)

Table 3 Thermal decomposition of the magnesium precursor (Fig. 1)

Temperature range/°C	Peak temperature/°C	Mass change/%
30–320	128, 313	−18.11
320–450	435	−9.58
450–580	502, 555	−39.46

The thermal behaviour of terbium precursor ($Tb_2O_3 \times 2TbO_2$) was discussed in previous papers [14, 15]. The TG, DTA curves of the reaction mixture containing magnesium carbonate hydroxide and tin oxide for preparation of Mg_2SnO_4 are shown in Fig. 2. Temperatures, which correspond to the inflex points on the DTA curve and mass loss detected on the TG curve, are summarized in Table 4. The endothermic effects, which were identified on the DTA curve in the temperature interval 30–580 °C, correspond to the thermal decomposition of magnesium precursor. The only one exothermic effect was identified on the DTA curve in the temperature range 580–1,200 °C. The maximum of the peak is at temperature 1,068 °C (Table 4) and it indicates the compound formation. This result of thermal analysis is in a good agree with result published by Al-Shahrani [10] who carried out the TG and DSC of the reaction mixture containing MgO and SnO_2. The DSC curve showed small peak indicating the compound formation at 1,060 °C.

The TG, DTA curves of the reaction mixture containing Mg, Sn and Tb precursors for preparation of $2MgO–0.6SnO_2–0.4TbO_2$ are shown in Fig. 3. The endothermic effects, which were detected on the DTA curve in the temperature interval 30–580 °C, correspond to the thermal decomposition of Mg-precursors and in confrontation with result of thermal treating of Mg precursor itself, the

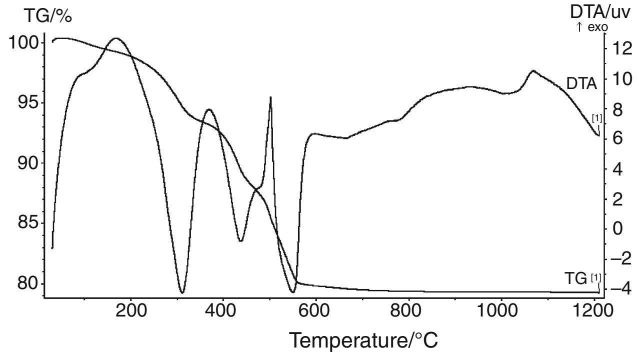

Fig. 2 DTA and TG curves of reaction mixture containing Mg and Sn precursors for preparation of Mg_2SnO_4 (156.600 mg)

Table 4 Thermal decomposition of the reaction mixture containing Mg and Sn precursors for preparation of Mg_2SnO_4 (Fig. 2)

Temperature range/°C	Peak temperature/°C	Mass change/%
30–350	110, 312	−6.57
350–450	438	−5.33
450–560	482, 550	−8.30
580–1200	1,068	–

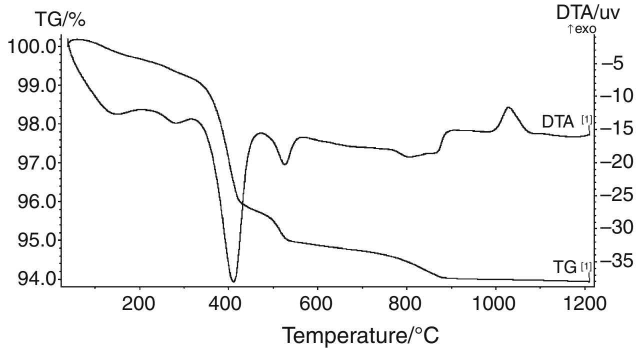

Fig. 3 DTA and TG curves of reaction mixture containing Mg, Sn and Tb precursors for preparation of $2MgO–0.6SnO_2–0.4TbO_2$ (250.100 mg)

minima of peak are slightly shifted to the lower temperatures (Table 5). Two endothermic effects with minima at temperatures 809 and 868 °C are connected with loss of oxygen and formation of lower terbium oxides. These processes are characterized on the TG curve by total mass loss 0.92%. The DTA curve shows one exothermic effect with minimum at 1,029 °C which signalizes the compound formation. Any other effects were not detected by the thermal analysis of the reaction mixture up to 1,200 °C.

Phase composition of samples was analyzed by X-ray diffraction analysis. All samples contain two or three phases. The first phase is formed by cubic spinel compound Mg_2SnO_4 with lattice parameter $a = 0.86376$ nm. The second phase is done by calcining temperature. While samples that were prepared by calcining at 1,500 °C contain next to spinel phase also unreacted magnesium oxide and terbium oxide (IV), samples calcined at 1,550 °C contain next to spinel phase cubic pyrochlore phase formed by $Tb_2Sn_2O_7$. The only in samples containing the biggest amount of terbium ($x = 0.4$ and 0.5), that were prepared by calcining at 1,550 °C, it was not detected the spinel phase. These two samples are formed by $Tb_2Sn_2O_7$ and unreacted magnesium oxide (Table 1).

Table 5 Thermal decomposition of reaction mixture containing Mg, Sn and Tb precursors for preparation of $2MgO–0.6SnO_2–0.4TbO_2$ (Fig. 3)

Temperature range/°C	Peak temperature/°C	Mass change/%
30–200	150	−0.32
200–310	283	−0.42
310–560	412, 526	−4.32
560–900	809, 868	−0.92
900–1,200	1,029	–

Table 6 Particle size distribution of the samples $2MgO–(1-x)SnO_2–xTbO_2$

x	1,300 °C		1,400 °C		1,500 °C	
	d_{50}/µm	d_{10}–d_{90}/µm	d_{50}/µm	d_{10}–d_{90}/µm	d_{50}/µm	d_{10}–d_{90}/µm
0.1	6.01	1.13–20.90	8.82	1.29–26.52	13.40	2.72–42.72
0.2	4.70	0.93–18.75	8.05	1.22–23.57	9.50	1.64–35.87
0.3	6.23	1.12–20.16	6.60	1.07–21.83	7.58	1.31–30.51
0.4	6.53	1.15–20.95	7.24	1.15–23.53	11.05	1.97–57.79
0.5	6.61	1.20–20.35	7.30	1.35–22.12	17.17	3.32–128.92

Measuring of particle size distribution of the pigments shows that coarse grinding of the samples in agate mortar after second heating stage is sufficient for potential application of pigments into organic binder or ceramic glaze. Granulometric composition of samples, that were prepared by calcining at temperatures 1,300–1,400 °C, are characterized by optimum values of median (d_{50}) in range 4–8 µm (Table 6). The increase of calcining temperature to 1,500 and 1,550 °C brings accumulation of bigger particles and in particular wider distribution curves. Any trend was not identified between the increasing range of substitution of tin cations by terbium cations and the increase of particle size distribution. For applications of the samples into some other materials, for example plastics, it is needed to improve their granulometric composition by milling and obtain samples with particles less than two micrometers.

The next aim of the present work is to describe the optical properties of the samples $2MgO–(1-x)SnO_2–xTbO_2$. The increasing temperature from 1,300 to 1,500 °C and the increasing degree of substitution positively affect the sandy yellow hue of the pigments applied into organic

Table 7 Colour properties of the samples $2MgO–(1-x)SnO_2–xTbO_2$ applied into polyurethane binder

x	1,300 °C			1,400 °C			1,500 °C		
	*L**	*a**	*b**	*L**	*a**	*b**	*L**	*a**	*b**
0.1	80.20	4.41	9.84	86.77	2.36	13.46	79.76	5.24	19.76
0.2	66.22	8.22	15.25	72.71	6.76	20.88	73.93	7.59	23.94
0.3	59.07	9.26	16.25	72.11	7.44	24.00	69.42	8.87	24.97
0.4	51.90	8.62	14.36	70.22	8.04	25.20	65.55	9.48	24.94
0.5	48.59	8.67	13.99	64.09	8.71	23.65	59.50	10.20	24.07

Table 8 Colour properties of the samples $2MgO–(1-x)SnO_2–xTbO_2$ applied into ceramic glaze G 07091 (calcining temperature 1,500 °C)

x	*L**	*a**	*b**	*C*
0.1	84.38	2.07	22.16	22.26
0.2	84.70	1.64	23.18	23.24
0.3	83.71	2.55	23.27	23.41
0.4	83.71	1.69	21.96	22.02
0.5	81.68	2.99	27.34	27.50

Table 9 The effect of type of ceramic glaze on the colour properties of the samples $2MgO–0.5SnO_2–0.5TbO_2$ (calcining temperature 1,500 °C)

x	*L**	*a**	*b**	*C*
G 07091	81.68	2.99	27.34	27.50
G 05091	81.90	0.79	20.47	20.49
G 02891	81.90	2.08	23.66	23.75
P 07491	87.07	1.27	13.69	13.75

polyurethane binder in mass tone. The colour parameters, namely *L**, *a** and *b**, of the pigment applications into organic binder are presented in Table 7. The increase of temperature from 1,300 to 1400 °C makes the colours of pigments lighter and the values of lightness (*L**) increase. The other increase of temperature about 100 °C shifts the values of colour coordinate *L** of almost all samples down and it means that these pigment applications are darker. The only application of pigment $2MgO–1.8SnO_2–0.2TbO_2$ forms the exception and in this case the increase of temperature from 1,400 to 1,500 °C caused the formation of lighter pigment application. The change of amount of red hue (*a**) in the resultant colour varies with increasing temperature, but these turns are numerically described by values ±2 and it is not considered as significant shift. The different situation can be observed in the changes of amount of yellow hue (*b**). The increase of temperature from 1,300 to 1,500 °C is connected also with grow of *b** values and pigments application gain through the temperature raise more interesting sandy yellow colour. These results lead to the conclusion that the most suitable calcining temperature for preparation of colourfully interesting perovskite pigments containing Mg, Sn a Tb is 1,500 °C.

Increasing extent of Sn^{IV} substitution by ions of terbium caused the significant change in colour properties of the samples. The colour of pigments applied into organic binder becomes darker with the increasing amount of terbium ions. This change is expressed by drop of values of coordinate *L**. Next change that can be observed on the colour properties of pigments with increasing amount of terbium ions is the raise of red hue (*a**) and simultaneously raise of yellow hue (*b**) in the resultant yellowish colouration. The composition of sample $2MgO–1.5SnO_2–0.5TbO_2$ is the most suitable for preparation of colourfully interesting pigment.

The pigments prepared by calcining at 1,500 °C were tested for their potential use as the materials capable for colouring of ceramic glazes. Composition of 3 wt% of pigment and 97 wt% of ceramic lead containing glaze G 07091 were deposited on wall tile bodies and calcined at temperature 1,000 °C for 15 min. This type of glaze serves only for colouring of decorative items. Colour properties of the pigments applied into ceramic glaze G 07091 are summarized in Table 8. All colour coordinates have fluctuating character in close extent of values and there was not detected any trend in change of the colour properties dependence on the increasing amount of terbium content. Then, the values of colour coordinates (*L**, *a**, *b** and chroma *C*) of the pigments where $x = 0.1–0.4$ can be considered as almost stable and they described light yellow colour of the application. Slightly different values of colour coordinates were obtained by measuring of the colour properties of the sample with composition of $2MgO–1.5SnO_2–0.5TbO_2$. Lower value of lightness *L** signalises that the colour of this application in ceramic glaze is darker. Higher value of coordinate *b** caused formation of deeper yellow hue. The surface of these applications is smooth, glosy and does not contain any cracks nor any other defects.

The next part of the research was focused on the study of the effect of the composition of the ceramic glazes on the quality of this type of pigment application. Pigment with composition $2MgO–0.5SnO_2–0.5TbO_2$ prepared by firing at temperature 1,500 °C was applied into three lead oxide containing glazes and one glaze free of lead oxide. Their composition and reccomanded glazing temperatures are given in Table 2. Results summarised in Table 9 show that the application of pigment into the glaze free of lead oxide (P 070491) provides the worst colour properties. The colour of this application is too pale yellowish. The value of lightness (*L**) is maximum and the values of coordinates expressing hue, particulary coordinates (*b**), are bottom. Nevertheless, the surface of this application is smooth, glosy and does not contain any defects. The lead containing ceramic glazes bring colourfully more interesting surface of the applications. The colour of these applications is sandy yellow. The lightness of these applications is comparable to each other. The bigger difference can be observed in the change of coordinates *a** and *b**. The application into glaze G 07091 contains the maximum amount of yellow hue in the final colouration and the surface is uniformly engrained and does not contain any cracks and defects. This glaze contains the minimium amount of lead oxide (5 wt%). The application of pigment into glaze G 02891 (53 wt% of PbO) also brings colourfully interesting result but the surface of this application is crackled. The colour of pigment application into glaze G 05091 (34 wt% of PbO) is the pale yellowish, but again the surface is without any defects. The connection between the quality of applications and amount of lead oxide was not found out, but seems to be connection between colour of applications and amount of aluminium oxide present in glazes. The bigger amount of yellou hue provides the applications in glazes containing less Al_2O_3 (5 and 8 wt%) than almost milky application in glazes with contents of 11 wt% of Al_2O_3.

Conclusions

The main aim of this work was to synthesize the mixed metal oxide based on magnesium orthostannate doped by terbium cations and find out whether the presence of terbium cations can affect the quality of this kind of ceramic pigment. Initial composition of pigments was counted according the general formula $2MgO–(1 - x)SnO_2–xTbO_2$, where values of x varied from 0.1 to 0.5 in 0.1 steps. The pigments were synthesized by solid state reaction and by calcination at high temperature. By the simultaneous TG/DTA measurements was found out that the formation of a new compound started at temperature 1,029 °C, but single-phase system was not prepared. All prepared samples contain two or three phases; spinel phase, magnesium oxide and pyrochlore phase. The main attention was focused on measuring of pigment-application properties. Granulometric compositions of samples, which were prepared by calcining at temperatures 1,300–1,400 °C, are characterized by optimum values of median (d_{50}) in range 4–8 μm. The increase of calcining temperature to 1,500 °C brings particles with values of median (d_{50}) around 12 μm. The increasing temperature from 1,300 to 1,500 °C and the growing content of terbium cation positively affect the sandy yellow hue of the pigments applied into organic polyurethane binder in mass tone. The composition of sample $2MgO–1.5SnO_2–0.5TbO_2$ and heating temperature 1,500 °C are the most suitable for preparation of colourfully interesting pigment.

This type of yellow pigments can be also recommended for colouring of ceramic glazes. Especially, for colouring of decorative lead containing glaze G 07091 containing 5 wt% of PbO and 5 wt% of Al_2O_3.

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