

Study of ceramic pigments with perovskite structure

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Abstract

Our attention was focused on preparation of inorganic pigments based on the perovskite structure of SrSnO_3 , in which part of tin ions was substituted by ions of terbium and titanium or terbium and cerium. The particle size (d_{50}) of all pigments is between 2-3 μm . Powders with the general formula $\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$, where $x = 0.1-0.6$, provide an intensive yellow colour hue in application into an organic binder, and white glossy surfaces in application into a ceramic glaze. A $\text{SrSn}_{0.4}\text{Ti}_{0.2}\text{Tb}_{0.4}\text{O}_3$ sample offers the best colour parameters in application into the organic binder: the highest amount of yellow hue ($b^* = 58.95$) and the highest saturation ($C = 59.05$). Powders with the general formula $\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$, where $x = 0.1-0.6$, also provide an intensive yellow colour hue in application into the organic binder and dark yellow-orange glossy surfaces in application into the ceramic glaze. The most interesting yellow colour hue has powder $\text{SrSn}_{0.4}\text{Ce}_{0.2}\text{Tb}_{0.4}\text{O}_3$ applied into the organic binder. In application into the ceramic glaze, an increase of cerium ions content in pigment shifts the hue from yellow to dark orange.

Keywords: Inorganic pigments, Stannates, Perovskites, Solid state reaction, Colour properties

BADANIE PIGMENTÓW CERAMICZNYCH O STRUKTURZE PEROWSKITU

Uwagę skupiono na przygotowaniu nieorganicznych pigmentów opartych na perowskitowej strukturze SrSnO_3 , w której część jonów cyny podstawiono jonami terbu i tytanu lub terbu i ceru. Rozmiar cząstek (d_{50}) wszystkich pigmentów mieścił się pomiędzy 2-3 μm . Proszki o wzorze ogólnym $\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$, gdzie $x = 0,1-0,6$, dostarczają intensywny odcień koloru żółtego w zastosowaniu do spoiwa organicznego i białe połyskujące powierzchnie w zastosowaniu do szkliwa ceramicznego. Próbką $\text{SrSn}_{0.4}\text{Ti}_{0.2}\text{Tb}_{0.4}\text{O}_3$ oferuje najlepsze parametry barwne w zastosowaniu do spoiwa organicznego: największy udział odcienia żółtego ($b^* = 58,95$) i największe nasycenie ($C = 59,05$). Proszki o wzorze ogólnym $\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$, gdzie $x = 0,1-0,6$, również dostarczają intensywny odcień koloru żółtego w zastosowaniu do spoiwa organicznego i ciemne żółto-pomarańczowe powierzchnie w zastosowaniu do szkliwa ceramicznego. Najbardziej interesujący odcień koloru żółtego ma proszek $\text{SrSn}_{0.4}\text{Ce}_{0.2}\text{Tb}_{0.4}\text{O}_3$ zastosowany do spoiwa organicznego. W zastosowaniu do szkliwa ceramicznego wzrost stężenia jonów ceru w pigmentcie przesunął odcień żółty do ciemnopomarańczowego.

Słowa kluczowe: pigmenty nieorganiczne, cyniany, perowskity, reakcja w stanie stałym, właściwości barwne

1. Introduction

Research of the authors' group is focused on the synthesis and characterization of inorganic powder materials with high thermal and chemical stability which could find the industrial application for colouring of ceramics, organic matrices, plastics or building materials. Basically, inorganic pigments consist of a stable crystal host lattice doped with transition metal cations which act as chromophore, *i.e.*, are the source of colour properties of the materials. The chromophores interdiffuse into the host lattice structure at high temperatures, and form either a solid solution or a new compound [1]. Pigments are the most often characterized by their chemical composition, structure, and optical or technological properties, *i.e.*, colour parameters, chemical and thermal stability, and particle size.

Most inorganic pigments have been known for a very long time [2, 3]. Nevertheless, due to the high toxicity of some elements and strict environmental laws, research of ceramic and anticorrosion pigments has been lately dedicated to im-

provement of composition of pigments from an environmental point of view while maintaining their colour properties and technological characteristics [1].

The most common method of synthesis of inorganic pigments is the ceramic method, which encompasses the solid state reaction of relevant metal oxides during high temperatures [4, 5]. The classical ceramic route is very often upgraded by mechanochemical activation to decrease the heating temperature [6, 8].

Perovskite materials SrSnO_3 , SrTiO_3 and SrCeO_3 doped by lanthanide ions are widely studied and described in the literature. Strontium stannate compounds doped by rare earth elements, as well as Ln-doped SrTiO_3 , have been widely investigated and reported as photoluminescence materials [9-11]. Tb-Mg doped SrSnO_3 showed sharp emission lines corresponding to Tb ions as a green phosphor [12]. Perovskite oxide SrTiO_3 is also promising photocatalytic material [13]. The main usage of powders $\text{SrCe}_{1-x}\text{Tb}_x\text{O}_3$ is in the field of proton conducting membranes [14, 15]. From the pigmentary point of view, mainly stannates and titanates

were studied [16-19]. In the previous research we studied the pigmentary application properties of strontium stannate doped by terbium ions as a chromophore. Whereas, pigments with the general formula $\text{SrSn}_{1-x}\text{Tb}_x\text{O}_3$ have intensive yellow colour in application into an organic binder, the application into a ceramic glaze brought very light yellow hues and low values of saturation (C) [17].

In the present work we prepared two groups of perovskite materials derived from the previously studied pigment $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$. Pigments with the general formulas $\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$ and $\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$ (where $x = 0.1-0.6$) were synthesized by solid state reaction. Main aim of the research was to study the effect of Ti^{IV} and Ce^{IV} ions on the colour parameters, particle size distribution, thermal stability, and the resistivity to molten glaze of the prepared pigments.

2. Experimental part

Powders $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$, $\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$ and $\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$ (where $x = 0.1-0.6$) were prepared by ceramic route with mechanical activation of initial reagents: SrCO_3 (95% ML Chemica, CR), Tb_4O_7 (99.5% Indian Rare Earth Ltd., India) and SnO_2 (99% Sigma Aldrich) or TiO_2 (Precheza a.s., CR) or CeO_2 (99.5% Indian Rare Earth Ltd., India).

The mechanical activation of initial reaction mixtures was carried out in a planetary mill Pulverisette 5 (Fritsch GmbH, Germany). The high energy milling process at a speed of 200 rps lasted 6 hrs. The reaction mixtures were ground with agate balls (\varnothing 10 mm) at a ball-to-powder weight ratio of 20:1. Then all mixtures and semi-products were heated in the air atmosphere in two stages. The first heating stage was carried out at a temperature of 1000 °C for 3 h; the obtained intermediates were manually ground in an agate mortar with a pestle. Final products were obtained after the next heating at a temperature of 1400 °C for 3 h. After each heating stage, the samples were gradually cooled to room temperature and reground.

The phase composition of the pigments was studied by X-ray diffraction analysis. Diffractograms of the samples were obtained using a diffractometer D8 (Bruker, GB) with a goniometer of 17 cm in the 2θ range of 10-80°. The $\text{Cu K}_{\alpha 1}$ ($\lambda = 0.15418$ nm) radiation was used for the angular range of $2\theta < 35^\circ$ and $\text{Cu K}_{\alpha 2}$ ($\lambda = 0.15405$ nm) for the range of $2\theta > 35^\circ$.

The thermal stability of final pigments was tested by using a heating microscope EM201-15 (Hesse Instruments, Germany). The samples in the tablet form were gradually heated from 30 °C to 1500 °C where a change of sample's area was observed.

For testing of pigment-application, qualities of powders suspensions containing 1 g of the pigment and 1.5 cm³ of a binder (dispersive acrylic paint Parketol, Balakom, a. s. Opava, CZ) were homogenized. Coloured paints were prepared by deposition of the slurries on the white not absorbing paper. Thickness of the wet film was 100 μm . For testing in ceramic glazes, aqueous suspensions containing 10 wt.% of the pigment and 90 wt.% of the frit lustrous colourless glaze (Glazura, a.s., CR) were prepared by handmilling. These slurries were deposited using a brush on wall tile bodies and further fired at 980 °C for 15 min.

The colour properties of pigment applications were objectively evaluated by measuring of spectral reflectance using a spectrophotometer ColourQuerster XE (HunterLab, USA). The measurement conditions were as follows: an illuminant D65, 101 complementary observer and measuring geometry d/8°. For description of colour, the CIE $L^*a^*b^*$ colour space was used. In this colour space, L^* indicates the lightness and a^* and b^* are the chromaticity coordinates. The coordinates a^* , $-a^*$, b^* and $-b^*$ expresses amounts of red, green, yellow, and blue colour hue, respectively. The value L^* is related to the natural grey scale. It is described by numbers from zero (black) to one hundred (white). Saturation of the colour (C) is calculated according to the formula:

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

The colour hue of pigments is also possible to express as a hue angle:

$$H^\circ = \arctan(b^*/a^*) \quad (2)$$

The hue angle H° is expressed in degrees; 0°, 90°, 180°, and 270° corresponds to the red, yellow, green, and blue hue, respectively [21].

The particle size distribution of the samples was measured using a Mastersizer 2000/MU (Malvern Instruments, Ltd. UK).

3. Results and discussion

The phase composition of samples $\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$ ($x = 0.1-0.6$) was studied by the XRD method. The samples $\text{SrSn}_{0.5}\text{Ti}_{0.1}\text{Tb}_{0.4}\text{O}_3$ and $\text{SrSn}_{0.4}\text{Ti}_{0.2}\text{Tb}_{0.4}\text{O}_3$ are single phased. Only peaks of the cubic phase with a lattice parameter $a = 0.4098$ nm were identified at the XRD pattern. The powders $\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$, that contain the higher amount of Ti^{IV} ions ($x \geq 0.4$), are two-phase, and next to the perovskite cubic phase also the peaks of cubic SrTiO_3 , respective tetragonal $\text{Sr}_3\text{Ti}_2\text{O}_7$, were detected (Table 1).

Table 1. The impact of titanium content on the phase composition and lattice parameters of $\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$ powders.

Sample	x	Detected phases	Structure	a [nm]	c [nm]
$\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$	0.1	$\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$	cubic	0.4098	
	0.2	$\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$	cubic	0.4098	
	0.4	$\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$ SrTiO_3	cubic cubic	0.3942	
	0.6	$\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$ $\text{Sr}_3\text{Ti}_2\text{O}_7$	cubic tetragonal	0.4111 0.391186	2.036142

Particle size distribution of samples after calcination at 1400 °C is wide (Table. 2) because after calcination the size of samples were not improved. The values of d_{50} of powders containing titanium ions are slightly higher than the particle size d_{50} of $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$. The particle size distribution (PSD) of samples $\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$ is comparable with PSD of $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$. In next step, the powders were milled in ethanol and zircon crushing bodies for 20 minutes and the particle size distribution and colour parameters were measured. After 20 minutes of milling the particle size distribution of all samples was significantly contracted. Samples containing Ce^{IV} and Ti^{IV} ions have all particles smaller than 10 μm and the values of d_{50} less than 3 μm . These values of particle size are suitable for application of pigment to an organic binder or into a ceramic glaze.

The obtained values of the colour parameters of the applications of pigments into the organic binder are presented in Table 3. An increasing amount of titanium ions, which was incorporated into the crystal lattice of strontium stannate, caused a decrease of the lightness (L^*) and the darkening of colour. The ions of Ce^{IV} added to the structure of yellow

$\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$ have the same effect. The substitution of Sn^{IV} ions by ions of Ti^{IV} or Ce^{IV} causes the darkening of pigment. The values of colour parameter a^* of samples containing the lowest amount of Ti^{IV} ions are placed in the green area of the Hunter colour chart ($-a^*$) the same as the original pigment. With increasing the amount of titanium ions, the values of parameter a^* are shifted to the red field of the Hunter chart and have an increasing trend in the substitution range of $x = 0.1-0.5$. In the case of pigments containing Ce^{IV} ions, the amount of red colour hue ($+a^*$) raises in the whole range of substitution ($x = 0.1-0.6$).

The colour parameter, corresponding to the amount of yellow hue ($+b^*$) of sample $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$, is 52.40. The substitution of tin ions by titanium ones in the range of $x = 0.1-0.3$ increases its value, and therefore the values of saturation C also are increased. After the substitution of Sn^{IV} ions by Ti^{IV} ones, the resultant colour of powder is shifted from bright yellow to very dark sandy yellow. An interesting bright yellow hue was obtained after the substitution of Sn^{IV} ions by Ce^{IV} ones (Table 3). In this case the coordinates b^* are markedly higher in the whole range of substitution and

Table 2. Particle size distribution of samples before and after wet milling.

Sample	x	Before milling		After milling	
		d_{50} [μm]	$d_{10} - d_{90}$ [μm]	d_{50} [μm]	$d_{10} - d_{90}$ [μm]
$\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$		6.30	1.31 - 38.25	2.10	0.48 - 10.77
$\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$	0.1	7.05	1.34 - 18.29	2.57	0.69 - 6.92
	0.2	6.81	1.26 - 19.27	2.37	0.67 - 6.45
	0.3	7.33	1.49 - 22.54	2.28	0.66 - 5.93
	0.4	11.01	2.83 - 44.01	3.04	0.77 - 7.85
	0.5	8.35	2.09 - 28.92	2.70	0.72 - 6.86
	0.6	8.28	2.25 - 32.78	2.56	0.71 - 6.41
$\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$	0.1	6.17	1.42 - 27.45	1.99	0.61 - 5.58
	0.2	5.48	1.21 - 30.64	1.98	0.61 - 6.52
	0.3	5.81	1.19 - 32.69	2.09	0.63 - 6.26
	0.4	6.03	0.97 - 32.20	2.74	0.67 - 8.56
	0.5	10.61	1.62 - 53.56	2.58	0.64 - 7.51
	0.6	5.97	1.13 - 24.39	2.20	0.59 - 6.25

Table 3. Colour parameters of the pigments applied into the organic binder.

Sample	x	L^*	a^*	b^*	C	H°
$\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$		75.74	-2.05	52.40	52.44	92.24
$\text{SrSn}_{0.6-x}\text{Ti}_x\text{Tb}_{0.4}\text{O}_3$	0.1	71.51	0.05	53.85	53.85	89.95
	0.2	73.94	3.53	58.95	59.06	86.57
	0.3	72.34	5.99	56.78	57.10	83.98
	0.4	66.18	6.77	51.88	52.32	82.57
	0.5	65.03	8.02	47.89	48.56	80.49
	0.6	61.25	7.29	40.80	41.45	79.87
$\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$	0.1	79.87	-0.05	64.91	64.91	90.04
	0.2	79.69	3.71	69.45	69.55	86.94
	0.3	75.35	8.55	66.91	67.45	82.72
	0.4	72.98	14.40	68.56	70.06	78.14
	0.5	72.68	16.15	67.44	69.35	76.53
	0.6	71.86	16.17	65.12	67.10	76.05

Table 4. Colour parameters of the pigments applied into the ceramic glaze.

Sample	x	L^*	a^*	b^*	C	H°
$\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$		87.53	0.31	20.02	20.02	89.11
$\text{SrTi}_{0.6}\text{Tb}_{0.4}\text{O}_3$		84.99	0.35	17.91	17.91	88.88
$\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$	0.1	82.45	4.02	37.89	38.10	83.94
	0.2	76.57	12.48	39.94	41.84	72.65
	0.3	76.49	13.31	41.96	44.02	72.40
	0.4	71.42	19.95	40.27	44.94	63.65
	0.5	68.94	22.96	38.90	45.17	59.45
	0.6	67.22	23.28	33.88	41.11	55.51

vary between 65 and 70. The values of colour saturation also show a varying trend. The substitution of tin ions by cerium ones was effective and brought the formation of more intense yellow pigments. The growing amount of Ce^{IV} ions added into the perovskite structure of $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$ shifts the values of hue angle H° , indicating the change of colour from the clear yellow hue to yellow-orange one.

Before the application of pigments into the ceramic glaze, the thermal stability of chosen powders ($\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$, $\text{SrSn}_{0.3}\text{Ce}_{0.3}\text{Tb}_{0.4}\text{O}_3$ and $\text{SrSn}_{0.3}\text{Ti}_{0.3}\text{Tb}_{0.4}\text{O}_3$) was followed by a heating microscope in the temperature range of 30–1500 °C, and compared to each other. The original perovskite $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$ is thermally stable in the whole temperature range. The substitution of tin ions by cerium or titanium ones lowered thermal stability. The powder $\text{SrSn}_{0.3}\text{Ti}_{0.3}\text{Tb}_{0.4}\text{O}_3$ is stable to the temperature of 1350 °C, and the powder $\text{SrSn}_{0.3}\text{Ce}_{0.3}\text{Tb}_{0.4}\text{O}_3$ starts to sinter around the temperature of 1250 °C. Since all samples did not change the area during the thermal treatment at 1200 °C, they could be tested in application into the ceramic glaze. The lead containing transparent colourless glossy glaze ($\text{TEC}_{20-500^\circ\text{C}} = 79 \cdot 10^{-7} \text{ K}^{-1}$) with a processing temperature of 980 °C was chosen for the testing. Although the pigment $\text{SrSn}_{0.6}\text{Tb}_{0.4}\text{O}_3$ is thermally stable, its intensive yellow colour has been lost after the application into the ceramic glaze. The pigments containing Ti^{IV} ions were also not resistant against the melting glaze. The glazed surface was glossy without any defects, but its colour become white (Table 4). The pigments with the general formula $\text{SrSn}_{0.6-x}\text{Ce}_x\text{Tb}_{0.4}\text{O}_3$ provide the dark yellow-orange glossy surface after the application into the ceramic glaze. A link between the change of colour parameters and the increase of Ce^{IV} content is the same as in case of the application into the organic binder. The increasing amount of Ce^{IV} ions caused a drop of lightness (L^*), an increase in the amount of red tint (a^*) and an increase in the amount of yellow tint (b^*) in the substitution range of $x = 0.1$ –0.3. The increased amount of cerium ions caused the repeated decrease of b^* parameter. The hue angle H° of samples is shifted from 83.94 to 41.11, which means that the increase of Ce^{IV} content shifts hues of the glaze applications from yellow to yellow-orange.

4. Conclusions

The main aim of the present work was to synthesize inorganic pigments based on the perovskite structure of strontium stannate doped by terbium cations, and to find out

whether additional substitution of tin ions by ions of cerium or titanium can affect its colour properties and extend their applicability in ceramic industry for colouring of glazes. The pigments were synthesized by the common ceramic method, i.e., solid state reaction, upgraded by an activation of the precursors by mechano-chemical treatment. The particle size d_{50} of all pigments was between 2–3 μm .

Strontium stannate pigments doped by terbium are characterised by intensive yellow colour hue; they are thermally very stable, but in application into a ceramic glaze their colour becomes not interesting. Substitution of Sn^{IV} ions by Ce^{IV} ions has a positive effect on the colour properties. The increasing content of cerium causes the formation of pigments with the increased amount of yellow colour hue; the pigments are thermally stable to the temperature of 1200 °C, and they are applicable into a ceramic glaze. In the ceramic glaze, they form yellow-orange glossy surfaces without any defects. The pigment $\text{SrSn}_{0.4}\text{Ce}_{0.2}\text{Tb}_{0.4}\text{O}_3$ can be recommended for colouring of organic binders and ceramic glazes, especially, for colouring of the decorative, lead containing high temperature glazes.

Substitution of Sn^{IV} ions by ions of Ti^{IV} is effective only in application into an organic binder. In this application the samples provide brighter yellow hues, but in application into the ceramic glaze, the yellow colour hue is lost and the applications become white. The sample $\text{SrSn}_{0.4}\text{Ti}_{0.2}\text{Tb}_{0.4}\text{O}_3$ was evaluated as a pigment with the most interesting colour properties.

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References

- [1] Buxbaum, G.: *Industrial inorganic pigments*, Wiley-VCH, Weinheim 2005.
- [2] Hochleitner, B., Desnica, V., Mantler, M., Schreiner, M.: Historical pigments: a collection analyzed with X-ray diffraction analysis and X-ray fluorescence analysis in order to create a database, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 58, 4, (2003), 641–649.
- [3] Vahur, S., Teearu, A., Leito, I.: ATR-FT-IR spectroscopy in the region of 550–230 cm^{-1} for identification of inorganic pigments, *Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy*, 75, 3, (2010), 1061–1072.
- [4] Gargori, G., Cerro, S., Galindo, R., García, A., Llusar, M., Badenes, J., Monrós, G.: New vanadium doped calcium titanate ceramic pigment, *Ceram. Int.*, 37, (2011), 3665–3670.

- [5] Dohnalová, Ž., Vontorčíková, M., Šulcová, P.: Characterization of metal oxide-doped lutetium orthoferrite powders from the pigmentary point of view, *J. Therm. Anal. Calorim.*, 113, (2013), 1223-1229.
- [6] Boldyrev, V. V.: Mechanochemistry and mechanical activation of solids, *Russ. Chem. Rev.*, 75(3), (2006) 177-179.
- [7] Olegário, R. C., Ferreira de Souza, E. C., Marcelino Borges, J. F., Marimon da Cunha, J. B., Chaves de Andrade, A. V., Masetto Antunes, S. R., Antunes, A. C.: Synthesis and characterization of Fe³⁺ doped cerium-praseodymium oxide pigments, *Dyes and Pigments*, 97, 1, (2013), 113-117.
- [8] Yamanaka, S., Kurosaki, K., Matsuda, T., Kobayashi, S.: Thermal properties of SrCeO₃, *J. Alloys Compd.*, 352, (2003), 52-56.
- [9] Wang S., Lu M., Zhou G., Zhang H., Yang Z.: Systematic investigations into SrSnO₃ nanocrystals (II) photoluminescent properties of the assythesized nanocrystals, 452, *J. Alloys Compd.*, 452, (2008), 432-434.
- [10] Lei B., Li B., Zhang H., Li W.: Preparation and luminescence properties of CaSnO₃:Sm³⁺ phosphor emitting in the reddish orange region, *Opt. Mater.*, 29, (2007), 1491-1494.
- [11] Hen D., Xu W, Zhou Y., Chen Y.: Lanthanide doped BaTiO₃-SrTiO₃ solid-solution phosphors: Structure, optical spectroscopy and upconverted temperature sensing behavior, *J. Alloys Compd.*, 376, (2016), 215-223.
- [12] Kazushige, U., Takahiro, Y., Kensuke, N.: Green, orange, and magenta luminescence in strontium stannates with perovskite-related structures, *Japan. J. Appl. Phys. Part 1 - Regular Papers Brief Communications & Review Papers*, 45, 9A, (2006), 6981-6983.
- [13] Grabovska, E.: Selected perovskite oxides: Characterization, preparation and photocatalytic properties – A review, *Appl. Catal. B: Environ.*, 186, (2016), 97-126.
- [14] Qi X., Lin Y.S.: Electrical conducting properties of proton-conducting terbium-doped strontium cerate membrane, *Solid State Ionics*, 120, (1999), 85-93.
- [15] Wei X., Lin Y.S.: Protonic and electronic conductivities of terbium doped strontium cerates, *Solid State Ionics*, 178, (2008), 1804-1810.
- [16] Mesíková, Ž., Šulcová, P., Trojan, M.: Synthesis and description of SrSn_{0.6}Ln_{0.4}O₃ perovskite pigments, *J. Therm. Anal. Calorim.*, 91, 1, (2008), 163-166.
- [17] Dohnalová, Ž., Gorodylová, N., Šulcová, P., Vlček, M.: Synthesis and characterization of terbium-doped SrSnO₃ pigments, *Ceramics Int.*, 40, (2014), 13637-13645.
- [18] Luňáková, P., Trojan, M., Luxová, J., Trojan, J.: BaSn_{1-x}Tb_xO₃: A new yellow pigment based on a perovskite structure, *Dyes and Pigments*, 96, 1, (2013), 264-268.
- [19] Luxová, J., Šulcová, P., Trojan, M.: Study of perovskite compounds, *J. Therm. Anal. Calorim.*, 93, 3, (2008), 823-827.
- [20] García, A., Galindo, R., Gargori, C., Cerro, S., Llusar, M., Monrós, G.: Ceramic pigments based on chromium doped alkaline earth titanates, *Ceram. Int.*, 39, 4, (2013), 4125-4132.
- [21] Commission Internationale de l'Eclairage, *Recommendations on uniform colour spaces, colour difference equations, psychometric colour terms*, Supplement no. 2 of CIE publication no. 15 (E1-1,31) 1971, Paris Bureau Central de la CIE, 1978.



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