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PREPARATION AND SELECTED PROPERTIES OF PIGMENTS ON BASE OF Ln-DOPED CaSnO$_3$

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Inorganic pigments containing lanthanides based on orthorhombic perovskite structure of $CaSnO_3$ have been prepared by solid state reaction of $CaCO_3$, SnO_2 and lanthanide oxides (Tb_4O_7, Pr_6O_{11}, CeO_2). The TG-DTA analysis indicates the formation of Ca-stannates around of temperature 1200°C, but from the pigmentary – application point of view, it is better to synthesize the product at higher temperature (1400 or 1500°C). The resultant materials were characterised by XRD, particle size distribution and measurement of colour properties. The doping of Ca-stannates by ions of rare earth elements (Tb, Pr, Ce) brings the production of two- and three-phase systems. The most interesting colour properties provided the stannate doped by ions of terbium and cerium and synthesized by heating at temperature 1400°C. The pigment has reddish brown colour hue.

Keywords: *$CaSn_{1-x}Ln_xO_3$, $CaSnO_3$, inorganic pigments, solid-state reaction, stannates*

Introduction

Over last decades, the chemistry of rare earth elements (Ln) has been intensively investigated from several points of view [1–3]. Our research group is focused on synthesis and characterization of inorganic materials that could find the industrial occupancy as inorganic pigments. In present paper, the results of research work relating to Ln-doped $CaSnO_3$ are included.

The compound $CaSnO_3$ belongs to the family of analogous alkaline-earth stannates, $MSnO_3$ (where M=Ca, Sr and Ba). In the case of $SrSnO_3$ and $CaSnO_3$ the cubic perovskite structure is disordered by an octahedral tilting distortion and the crystal structure becomes orthorhombic [4]. $CaSnO_3$ with orthorhombic perovskite structure is the most often prepared by simply method of synthesis which is based on solid state reaction between SnO_2 and $CaCO_3$ or CaO (1000–1350°C) [5–7], but there are several different possibilities of synthesis stannates. One of them, the closest to solid state reaction, is based on mechanical milling of equimolar mixture of calcium(II) oxide and tin(IV) oxide in planetary ball mill for 116 h. The advantage of that method is the preparation of small particle size of $CaSnO_3$ (>50 nm) [8]. A novel preparative method called self-heat sustained (SHS) reaction technique has been reported [6, 9]. The most attractive feature of SHS technique is the ability of highly exothermic reactions to be self-sustained and therefore, energetically efficient. Preparation of calcium stannates is also possible by hydrothermal reaction (500°C) [10, 11] or by polymeric precursor method (700–800°C) [7, 12]. An alternative way for preparation of high purity stannates is the wet peroxide route (1200–1400°C) [13, 14].

Stannates are currently being investigated for their attractive dielectric characteristics which are important in ceramic industry and in electronic industry where they are finding application as thermally stable capacitors [14, 15]. Sharma *et al.* [7] studied and reported $CaSnO_3$ as promising high capacity anode material for Li-ion batteries. Stannates are also important materials due to their application as humidity and gas sensors [6, 11]. Stannate compounds doped by rare earth elements have been widely investigated and reported as photoluminescence materials, especially systems $CaSnO_3$:Sm^{3+} [16], $CaSnO_3$:Tb^{3+} [17, 18] or similar perovskite system based on titanate compound $CaTiO_3$:Pr^{3+} [19]. In these systems Ln^{3+} ions are expected to occupy Ca^{2+} sites into the $CaSnO_3$ host, because of small ionic radii difference between Ca^{2+} (0.11 nm) and Sm^{3+} (0.096 nm) respective Tb^{3+} (0.092 nm) or Pr^{3+} (0.101 nm). Due to the non-equivalent substitution, an excess of positive charge in the lattice must be compensated [16, 17, 20]. But it is also possible for Ln^{3+} ions to substitute Sn^{4+} ions [16, 21]. The formation of defects and vacancies in these host materials due to different valence states of Ca^{2+} and Ln^{3+} and Sn^{4+} can be express as follows [16]:

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$$\mathrm{Ln_2O_3} \xrightarrow{\mathrm{CaSnO_3}} 2\mathrm{Ln}^{\bullet}_{\mathrm{Ca}} + V''_{\mathrm{Ca}} + 3\mathrm{O}^{\mathrm{X}}_{\mathrm{O}} \qquad (1)$$

$$\mathrm{Ln_2O_3} \xrightarrow{\mathrm{CaSnO_3}} 2\mathrm{Ln}'_{\mathrm{Sn}} + V^{\bullet\bullet}_{\mathrm{O}} + 3\mathrm{O}^{\mathrm{X}}_{\mathrm{O}} \qquad (2)$$

Experimental

The solid solution of general formula $CaSn_{1-x}Ln_xO_3$, where *Ln*=Tb, Ce, Pr and x=0.4 respective 0.2, were prepared by solid-state reaction between SnO_2, $CaCO_3$ (95% of purity) and lanthanide oxides (Tb_4O_7 99.5% of purity, Pr_6O_{11} 90% of purity and CeO_2 95% of purity). Initial reagents were weighed in suitable molar proportion (Table 1) and subsequently ground manually in a porcelain mortar to obtain homogenous reaction mixture. The reaction mixtures No. 1, 4 and 7 were heated at temperature 1000°C (2 h)+ 1300°C (3 h) in an electric resistance furnace. The reaction mixtures No. 2, 5 and 8 were heated at temperature 1000°C (2 h)+1400°C (3 h) and the reaction mixtures No. 3, 6, 9 were heated at temperature 1000°C (2 h)+1500°C (3 h). The heating rate was 10°C min^{-1} and corundum crucibles were used. After each heating cycle the samples were gradually cooled down to room temperature and ground in an agate mortar.

The first information about formation of these types of pigments was followed by simultaneous TG/DTA measurements using equipment STA 449 Jupiter (Netzsch, Germany). The reaction mixtures of initial reagents before heating were studied by thermal analysis within the temperature range of 35–1300°C, under the air atmosphere, using corundum crucibles and the heating rate 10°C min^{-1}. α-Al_2O_3 was used as a reference material.

The crystal structures of the pigment samples No. 3, 6, 9, obtained after the second heating cycle (1500°C), were studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using the equipment diffractometer D8 (Bruker, GB) with a goniometer of 17 cm in the range 2Θ of 10–80°. $CuK_{\alpha1}$ (λ=0.15418 nm) radiation was used for angular range of $2\Theta<35°$ and $CuK_{\alpha2}$ (λ=0.15405 nm) for range of $2\Theta>35$. A scintillation detector was used.

The samples of pigments were applied into organic matrix in mass tone and evaluated with respect to their colour properties by measurements of spectral reflectance. The measurement was carried out in the visible region of light by equipment ColourQuest XE (HunterLab, USA). The measuring system uses colour space CIE $L^*a^*b^*$, where coordinate L^* expresses degree of brightness and coordinates a^* and b^* describe the colour hue. Thorough description of colour is done by recalculation of chrome extent C according mathematical formula $C=(a^{*2}+b^{*2})^{1/2}$. The next measurement conditions were following: illuminant D65 (6500 K), 10° complementary observer and geometry of measurements *d*/8°.

The particle size distribution of the samples was measured by equipment of Mastersizer 2000/MU (Malvern Instruments, UK). It is a highly integrated laser measuring system for analysis of particle size distribution. The equipment uses the scattering of incident light on particles. The solids were homogenized for 90 s by ultrasonic devices and measured in solution of $Na_4P_2O_7$ (c=0.15 mol dm^{-3}). The signal was evaluated on the base of Fraunhofer bending.

Results and discussion

The compositions of the initial mixtures used for preparation of samples $CaSn_{1-x}Ln_xO_3$, heating cycles and results of XRD-analysis of the chosen final products are given in Table 1. Information presented in Table 1 show that the synthesized pigments are based on substitution of Sn^{4+} ions by ions of rare earth elements. This substitution was chosen with respect to the fact, that ions of rare earth elements (Ce, Tb, Pr) are relatively stable in oxidation state (IV) respective (III–IV) [22]. The identified phases of the

Table 1 Composition of reaction mixtures, heating cycles and identified phases

No.	Heating cycle	Initial composition	Identified phases
1	1000°C (2 h)+1300°C (3 h)	$CaSn_{0.6}Tb_{0.4}O_3$	
2	1000°C (2 h)+1400°C (3 h)	$CaSn_{0.6}Tb_{0.4}O_3$	
3	1000°C (2 h)+1500°C (3 h)	$CaSn_{0.6}Tb_{0.4}O_3$	$CaSnO_3$, Ca_2SnO_4
4	1000°C (2 h)+1300°C (3 h)	$CaSn_{0.6}Tb_{0.2}Pr_{0.2}O_3$	
5	1000°C (2 h)+1400°C (3 h)	$CaSn_{0.6}Tb_{0.2}Pr_{0.2}O_3$	
6	1000°C (2 h)+1500°C (3 h)	$CaSn_{0.6}Tb_{0.2}Pr_{0.2}O_3$	$CaSnO_3$, Ca_2SnO_4
7	1000°C (2 h)+1300°C (3 h)	$CaSn_{0.6}Tb_{0.2}Ce_{0.2}O_3$	
8	1000°C (2 h)+1400°C (3 h)	$CaSn_{0.6}Tb_{0.2}Ce_{0.2}O_3$	
9	1000°C (2 h)+1500°C (3 h)	$CaSn_{0.6}Tb_{0.2}Ce_{0.2}O_3$	$CaSnO_3$, Ca_2SnO_4, Tb_2O_3

samples Nos 3, 6, 9 show that placing ions of rare earth elements into the lattice of stannates is possible despite of their big ionic radii.

Thermal behavior of reaction mixture containing $CaCO_3$, SnO_2 and Tb_4O_7 in an adequate molar ratio of initial composition $CaSn_{0.6}Tb_{0.4}O_3$ was followed by methods of thermal analysis. TG and DTA curves of the reaction mixture No. 1 (before thermal treatment) are shown in Fig. 1. On the DTA curve (Fig. 1), there are several endothermic effects that are connected with thermal decomposition of initial reagents. The temperatures of peaks minima/maxima are given in Table 2. The oxidation changes in terbium oxide ($Tb_2O_3 \cdot 2TbO_{2-\delta}$) are connected with temperatures of peaks minima 516 and 940°C. The temperature of peak minima 940°C and mass change –15.74% also corresponds to decomposition of calcium carbonate. The temperature of formation of solid solution of hypothetical stannate composition $CaSn_{1-x}Tb_xO_3$ and the by-product of the reaction Ca_2SnO_4 is the most probably covered in temperature range 1150–1250°C. The result of thermal analysis was used for the selecting of lowest suitable heating temperature of the second heating cycle (1300°C) for the first group of reacting mixtures (No. 1, 4, 7). Although the compositions of mixtures No. 4 and 7 are different from analyzed mixture No. 1, we supposed their very similar or same thermal behavior.

The results of XRD analysis of samples $CaSn_{1-x}Ln_xO_3$ (No. 3, 6, 9) indicate that the solid-state reaction between initial reagents (Table 1) heated at 1500°C does not lead to the formation of monophase system (Fig. 2). The peaks of by-product Ca_2SnO_4 (JCPDS card 46-0112) were identified next to peaks of orthorhombic main product $CaSnO_3$ (JCPDS card 31-0312) on the XRD patterns of samples No. 3 and 6. The X-ray diffraction pattern of the third sample No. 9 corresponds to three-phase system. It also contains the diffraction lines of $CaSnO_3$ and Ca_2SnO_4 and the third phase is ascribed to the unreacted terbium oxide (Fig. 2). Although, the samples prepared are not monophase, the shift of diffraction lines of $CaSnO_3$ shows that the rare earth elements were placed into the crystal lattice of $CaSnO_3$ (Table 3). The molar composition of initial reaction mixtures were counted for preparation of solid solutions $CaSn_{1-x}Ln_xO_3$, but it is possible that the Ln ions replaced the Ca^{2+} ions in the lattice.

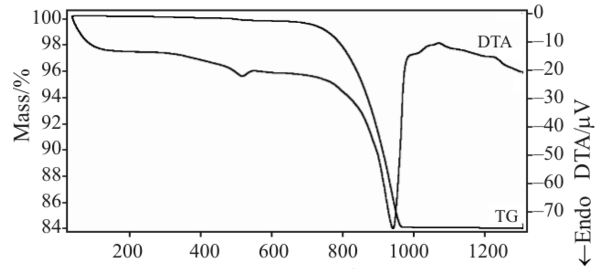

Fig. 1 DTA and TG curves of the reaction mixture No. 1 containing $CaCO_3$, SnO_2, Tb_4O_7 (474.500 mg)

Table 2 Thermal behavior of reaction mixture No. 1 containing $CaCO_3$, SnO_2, Tb_4O_7 (Fig. 1)

Temp. range/°C	Peak temp./°C	Mass change/%
35–540	516	–0.28
540–1000	940	–15.74
1000–1300	1037, 1069, 1226	–0.08

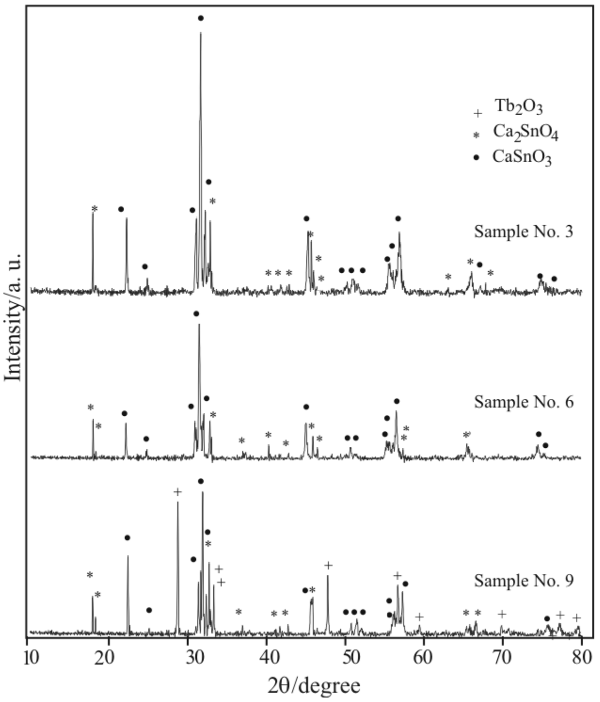

Fig. 2 X-ray diffraction patterns of the samples Nos 3, 6, 9

The crystallinity of samples decreases in the line from Ca–Sn–Tb system onwards to Ca–Sn–Tb–Pr system and to Ca–Sn–Tb–Ce system. It is probably caused by increasing of ionic radii of rare earth elements.

Generally, the results of XRD analysis of samples that are not single phase, usually lead to exchange of method of synthesis or the parameters of synthesis. In the case of solid-state reaction it is usually longer time period of heating or higher temperature. In the pigmentary field it is not always necessary to obtain single phase system but the conditions of synthesis have to be appropriate for the industrial occupancy. That was the reason why the method of synthesis was not improve and the pigmentary-application properties of the samples were measured.

Table 3 Intensities of the diffraction lines of the XRD patterns of samples No. 3, 6 and 9 (Fig. 2)

No.	Sample No. 3		Sample No. 6		Sample No. 9	
	d_{obs}/nm	I/I_0/%	d_{obs}/nm	I/I_0/%	d_{obs}/nm	I/I_0/%
1	0.400855	30	0.401934	27	0.395980	54
2	0.359006	7	0.359568	9	0.354507	5
3	0.288313	32	0.289249	29	0.284515	39
4	0.283310	100	0.287870	100	0.280130	100
5	0.278352	33	0.279503	35	0.272960	30
6	0.200416	25	0.201272	28	0.198125	27
7	0.181710	6				
8	0.179206	7	0.179927	12	0.179466	9
9	0.177044	4			0.177012	12
10	0.165401	9	0.165960	16	0.163198	18
11	0.161838	24	0.162703	37	0.160449	37
12	0.139368	4				
13	0.126780	7	0.127141	13	0.125201	8

Table 4 Colour properties of the samples

Sample No.	L^*	a^*	b^*	C
1	44.14	7.05	9.52	11.85
2	64.57	3.01	26.12	26.29
3	65.84	2.18	30.69	30.77
4	51.53	5.55	15.45	16.42
5	63.08	4.76	30.79	31.16
6	62.55	4.68	31.82	32.16
7	48.12	11.15	13.76	17.71
8	40.06	13.33	10.90	17.22
9	38.98	9.41	7.60	12.10

Table 5 Particle size distribution and values of specific surface area of the pigments prepared

Sample No.	d_{10}/μm	d_{50}/μm	d_{90}/μm	a/m^2 g^{-1}
1	1.25	5.99	25.57	2.22
2	3.51	12.24	37.96	1.20
3	4.71	16.54	45.11	0.99
4	1.34	6.90	25.62	2.04
5	3.01	11.50	32.47	1.31
6	5.11	17.40	38.36	0.95
7	1.01	5.66	25.54	1.01
8	2.59	9.50	31.97	1.43
9	3.62	17.14	48.86	1.05

Colour properties are the most important characteristic of the inorganic pigments. The influences of heating temperature and used doping Ln ions on the colour properties of the samples were followed. The terbium and praseodymium ions cause the formation of pigments with lighter (increase of L^*) and brighter (increase of C) colour hue with the increasing of temperature (Table 4). The increase of temperature from 1300 to 1500°C also causes the considerable increase of yellow colour hue (b^*) and at the same time, the less important change in value of coordinate a^*. It means that the samples change their colour hue from light brown to dark sandy colour (1300→1500°C). The cerium ion forms the pigment of brown colour in whole temperature range, but the increasing of temperature is reflected in formation of darker and less bright colour hue. The highest value of coordinate a^*, which describes the amount of red hue, was obtained by heating at temperature 1400°C. On the other hand, the sample prepared by heating at temperature 1300°C contains the highest amount of yellow colour hue (b^*). The most appropriate heating temperature for synthesis of the pigment No. 8 (Ca–Sn–Tb–Ce system) and therefore, for preparation of bright reddish brown colour hue of pigment, is temperature 1400°C.

Optical properties of the compounds and also their application preferences are determined by their particle size distribution (PSD). The values of d_{10}, d_{50} and d_{90} of the powder compounds are given in Table 5. The mean value of d_{50} increases from 5.5 to 17.5 μm in relation to increasing heating temperature that causes the mild sintering of samples, particularly, at temperature 1500°C. The effect of the present rare earth elements in the samples on the particle size distribution is not perceptible. The size range (5.5–17.5 μm) predicts the effective utilization of the pigments for colouring of ceramic glaze or coating composition. In case of need to colour plastics, the particle size distribution has to be reduced. In that event the mean value of d_{50} should not exceed the limit of 2 μm. The laser measuring equipment Mastersizer 2000/MU also provided the values of specific surface area (a) of the samples (Table 5). These values were not measured, but they were evaluated by equipment from particle sizes.

Conclusions

The main aim of the research was to prepare solid solutions of general formula $CaSn_{1-x}Ln_xO_3$ (Ln=Tb, Pr, Ce and x=0.4 respective 0.2) and tested their potential utilization as the inorganic pigments. The samples were prepared by solid-state reaction. The DTA analysis indicates the formation of stannates around of temperature 1200°C, but from the pigmentary – application point of view, it is better to synthesize the product at higher temperature, at least 1400°C. The pigments prepared were brown and sandy colour. The most interesting colour properties provided the sample that is expressed by composition of initial reagents: $CaSn_{0.6}Tb_{0.2}Ce_{0.2}O_3$. This sample, characteristic by reddish brown colour hue, was prepared by heating at temperature 1400°C. Although single phase systems were not prepared the shift of diffraction lines indicated the placing of the lanthanide ions into the stannates lattice.

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