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SYNTHESIS AND DESCRIPTION OF $SrSn_{0.6}Ln_{0.4}O_3$ PEROVSKITE PIGMENTS

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Inorganic pigments containing lanthanides based on pseudo cubic structure of $SrSnO_3$ have been prepared by solid state reaction between $SrCO_3$, SnO_2 and lanthanide oxides (Tb_4O_7, Pr_6O_{11}, CeO_2) in the temperature range 1300–1550°C. The resultant materials were characterised by XRD, TG-DTA and colourimetric techniques were used. The most interesting colour properties were provided by $SrTb_{0.4}Sn_{0.6}O_3$ prepared by firing at temperature 1500°C which has light yellow-green colour hue. The increase of temperature 1300–1500°C caused the creation of pigments with deeper and brighter colour hue. Colour properties of the samples prepared by calcination at 1550°C were of inferior quality due to structural changes from pseudo cubic to orthorhombic system.

Keywords: *DTA, optical properties, solid-state reaction, stannate pigments,* Tb_4O_7

Introduction

The compound $SrSnO_3$ belongs to the family of analogous alkaline-earth stannates, $MSnO_3$ (where M=Ca, Sr and Ba). Most often these compounds crystallize in the pseudo cubic system of perovskite structure [1]. Simple method of synthesis of these compounds is based on solid state reaction between SnO_2 and $SrCO_3$ or SrO [2, 3], but there are several different methods for the preparation of stannates. A novel preparative method called self-heat sustained (SHS) reaction technique has been reported [4]. The most attractive feature of SHS technique is the ability of highly exothermic reactions to be self-sustained and, therefore, energetically efficient. Preparation of strontium stannates ($SrSnO_3$ and Sr_2SnO_4) has been described by wet methods using coprecipitation [5, 6] and calcium stannate has also been prepared by polymeric precursor method, also known as the Pechini method [7].

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 [8]. The replacement of Sn^{4+} ions for the smaller Fe^{3+}/Fe^{4+} ions in perovskite $SrSnO_3$ shows that typical semiconductor may change from an electronic conductor to a fast ionic conductor by appropriate chemical substitution [9]. They are also important materials due to their wide application as humidity sensors [10]. Structural phase transitions in $SrSnO_3$ have also been studied from the viewpoint of photocatalytic and photoluminescence activities [11], especially luminiscence of Eu^{3+} ions in these host materials has been investigated [12].

The main interest of our research group was to prepared strontium stannate and find out whether the doped stannates by rare earth metals (Tb, Ce, Pr) can be used in ceramic industry as the high-temperature inorganic pigments.

Experimental

The compounds of general formula $SrSn_{0.6}Ln_{0.4}O_3$ were prepared by solid state reaction among SnO_2, $SrCO_3$ (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 (Indian Rare Earths Ltd., India). Raw materials were mixed in a porcelain mortar in order to obtain homogenous reaction mixture which was calcined at high temperature in an electric resistance furnace using heating rate of 10°C min^{-1} to the desired temperature, which in this study were 1300, 1400, 1500 and 1550°C and were maintained for 3 h. The pigments prepared were applied into organic matrix in mass tone and evaluated with respect to their colour properties by measurements of spectral reflectance in the visible region of light ColourQuest XE (HunterLab, USA) spectrophotometer. The measuring system uses colour space CIE $L^*a^*b^*$, where the 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 mathe-

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matical 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° [13].

Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (NETZSCH, Germany) in the temperature range 30–1400°C at heating rate 10 K 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 powder materials were studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using a Brucker (GB) diffractometer D8 (Bruker, GB) with a goniometer of 17 cm in the range 2θ of 10–80°. CuK_{α_1} (λ=0.15418 nm) radiation was used for angular range of 2θ<35° and CuK_{α_2} (λ=0.15405 nm) for range of 2θ>35. A scintillation detector was used.

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 pure $SrCO_3$ are shown in Fig. 1. Thermal decomposition of strontium carbonate is accompanied by reversible transformation from rhombic to hexagonal crystal structure [14]. This process is recorded on the DTA curve by endothermic effect with minimum at 937°C. The endothermic effect with minimum at 1240°C is connected with total thermal decomposition of $SrCO_3$ (Table 1). The decomposition is also detected on the TG curve by mass loss and total residual mass 70.23% is good agreement with theoretical value of residual mass (70.20%).

Table 1 Thermal decomposition data of $SrCO_3$ taken from Fig. 1

Temp. range/°C	Peak temp./°C	Mass change/%
30–1190	937; 1182	–16.25
1190–1280	1240	–13.52

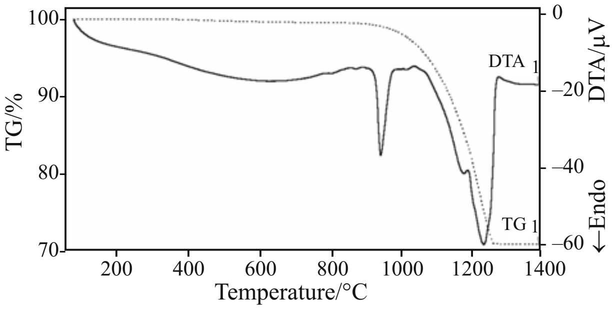

Fig. 1 DTA and TG curves of strontium carbonate

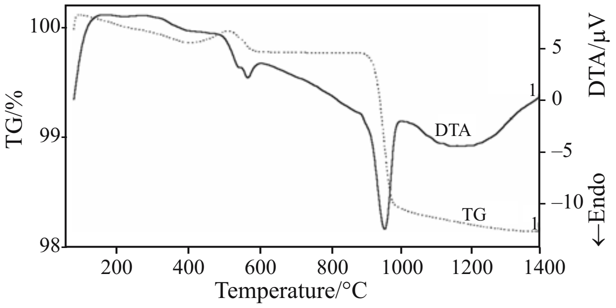

Fig. 2 DTA and TG curves of terbium oxide

Table 2 Thermal decomposition data of terbium oxide taken from Fig. 2

Temp. range/°C	Peak temp./°C	Mass change/%
30–370	–	–0.11
370–490	–	+0.12
490–520	517	–0.07
520–580	545	–0.14
580–1400	951	–1.79

Terbium oxide was next raw material studied by the thermal analysis (Fig. 2). Terbium ions are available in two oxidation states in this oxide mixture Tb_4O_7 ($Tb_2O_3{\cdot}TbO_{2-\delta}$) [15]. The first mass loss (0.11%) is detected on the TG curve in temperature range 30–370°C. This process corresponding to the loss of remaining moisture and is not detected on DTA curve. This region was also studied by DTG curve, but any presence of inflection peaks was not identified. Next process detected only on the TG curve is characterised by mass gain (0.12%). This process is the most probably connected with oxygen deficiency of the terbium oxide and hence, due to oxidation of terbium oxide $TbO_{2-\delta}$ to TbO_2. The next several endothermic effects that are connected with mass loss on the TG curve (2%) correspond to the loss of oxygen and formation of lower terbium oxides $Tb_2O_{3-\delta}$ (Table 2). The thermal analysis of the two raw materials of rare earth oxides (Pr_6O_{11} and CeO_2) have been published previously [16, 17].

Figure 3 describes the thermal behaviour of reaction mixture for preparation of sample $SrSn_{0.6}Tb_{0.4}O_3$.

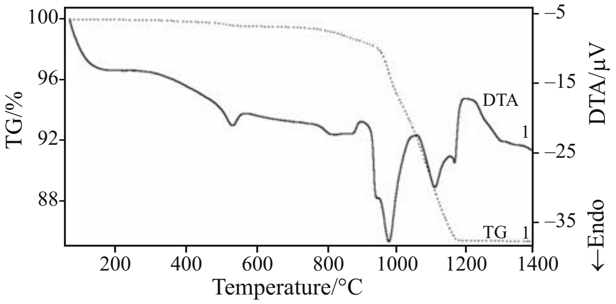

Fig. 3 DTA and TG curves of $SrSn_{0.6}Tb_{0.4}O_3$

Table 3 Thermal decomposition data of the synthesis of $SrSn_{0.6}Tb_{0.4}O_3$ taken from Fig. 3

Temp. range/°C	Peak temp./°C	Mass change/%
30–550	516	–0.29
550–880	892	–0.88
880–1010	937; 975	–4.08
1010–1200	1110; 1168	–8.72

There are several endothermic effects in the DTA curve (Table 3) that are connected with thermal decomposition of raw materials, particularly, phase transformation and decomposition of strontium carbonate and oxidation changes in terbium oxide. The formation of new phase of $SrSn_{0.6}Tb_{0.4}O_3$ is the most probably covered in temperature range 1200–1300°C.

On the basis of results of thermal analysis the reaction mixture containing rare earth elements were calcinated at temperature range 1300–1550°C. The basic compound strontium stannate was prepared by calcination at temperatures 1100 and 1200°C [4]. This powder material is of white colour and therefore our main goal was to modify strontium stannate with rare earth elements (Tb, Ce, Pr) to obtain powders with more interesting colour hue. The influence of calcining temperature on the colour properties of the samples was followed. Generally, the increase of temperature caused the creation of pigments with deeper and brighter colour hue (Table 4). The most interesting colour properties provided the compound $SrSn_{0.6}Tb_{0.4}O_3$ which is characteristic by light yellow-green colour hue. Increase of temperature from 1300 to 1500°C causes the increase of green colour hue ($-a^*$) and also the increase of yellow colour hue (b^*). The calcining at temperature 1550°C

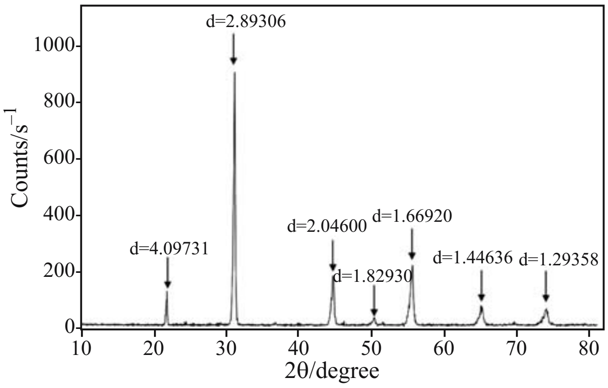

Fig. 4 X-ray diffraction pattern of $SrSn_{0.6}Tb_{0.4}O_3$ (T=1400°C)

Table 4 Colour properties of the pigments prepared

Pigment	T/°C	L^*	a^*	b^*	C
$SrSn_{0.6}Tb_{0.4}O_3$	1300	58.19	3.00	28.23	28.39
	1400	73.35	–4.60	55.50	55.69
	1500	77.30	–9.05	59.74	60.42
	1550	76.14	–8.12	56.60	57.18
$SrSn_{0.6}Tb_{0.2}Ce_{0.2}O_3$	1300	66.36	2.42	34.19	34.28
	1400	73.06	0.30	55.77	55.77
	1500	67.50	2.21	53.66	53.71
	1550	67.74	3.99	50.66	50.82
$SrSn_{0.6}Tb_{0.2}Pr_{0.2}O_3$	1300	44.17	–0.79	13.40	13.42
	1400	46.85	2.26	22.90	23.01
	1500	48.40	3.23	28.29	28.47

Table 5 Characterization of crystal structure of the prepared pigments

Pigment	T/°C	Structure	a/Å	b/Å	c/Å
$SrSnO_3$	1200	cubic	8.0682	–	–
$SrSn_{0.6}Tb_{0.4}O_3$	1400	cubic	8.1860	–	–
	1500	cubic	8.1650	–	–
	1550	orthorhombic	5.7920	5.7920	8.1850
$SrSn_{0.6}Tb_{0.2}Ce_{0.2}O_3$	1500	cubic	8.2190	–	–
	1550	orthorhombic	6.8940	6.8940	8.2320
$SrSn_{0.6}Tb_{0.2}Pr_{0.2}O_3$	1500	cubic	8.2360	–	–
	1550	orthorhombic	5.8140	5.8140	8.2150

brought again the diminution of both colour coordinates and then arising of pigment with worse colour properties. The modification of stannate by terbium and cerium at the same time caused the loss of green hue and the pigment prepared has dark yellow to ochre colour hue. The most appropriate calcining temperature for this type of pigment and for preparation of quite clear yellow hue of pigment is temperature 1400°C. The pigments containing praseodymium inside stannates structure are characteristic by significant decrease of brightness and chrome. The colour hue of this type of pigment is dark yellow-green. The most intensive colour, khaki green, brought calcining temperature 1500°C.

The crystal structure of prepared powder materials were studied by X-ray diffraction analysis. The only structural properties of samples prepared by calcining at higher temperature (1400–1550°C) were studied. One-phase systems have already been identified at the diffractograms of samples prepared by calcining at 1400°C (Fig. 4). The roentgen-diffraction analysis certifies that these new materials have pseudo cubic perovskite structure. The substitution of rare earth elements for Sn in these materials results in expansion of the volume of the elementary cell. The values of lattice parameters are summarized in Table 5. Raising the calcining temperature to 1550°C caused a phase transformation from cubic to orthorhombic crystal structure. This phase transformation is most likely to be responsible for the change in the colour properties of the pigments.

Conclusions

The main aim of the research was to prepare new stannate compounds which can be used as inorganic pigments. The pigments prepared were of yellow, yellow-green and khaki green colour. The most interesting colour properties were provided by the compound $SrSn_{0.6}Tb_{0.4}O_3$, prepared by firing at 1500°C, producing a light yellow-green colour hue. The increase of temperature caused the creation of pigments with deeper and brighter colour hue. Colour properties of the samples prepared by calcining at 1550°C were of inferior quality and due to structural changes from a pseudo cubic to an orthorhombic system. Generally, the modification of stannate by rare earth elements – terbium, cerium and praseodymium resulted in the expansion of the elementary cell.

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