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Synthesis and investigation of perovskites

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Abstract

The presented dissertation thesis was focused on the study of perovskite brown pigments based on $SrSnO_3$ structure. In this structure, part of tin ions was replaced by manganese ions. For preparation of pigments with formula of $SrSn_{1-x}Mn_xO_3$, where substitution x took on values of 0.1 – 0.5, four methods of preparation were used: classical ceramic method, dry mechanoactivation, wet mechanoactivation and precipitation method. The aim of the thesis was to find optimal method for preparation of perovskite pigments and then described their synthesis conditions in detail. The prepared pigments were evaluated by laboratory techniques such as X – ray diffraction analysis, VIS – spectrophotometry, particle sizes distribution, diffuse reflectance in near infrared region and scanning electron microscopy.

Abstrakt

Předkládaná disertační práce byla zaměřena na studium perovskitových hnědých pigmentů se strukturou $SrSnO_3$. V této struktuře byla část cíničitých iontů byla nahrazena ionty manganu. K přípravě pigmentů $SrSn_{1-x}Mn_xO_3$, kde substituce x nabývala hodnot 0,1 – 0,5, byly použity čtyři metody přípravy: klasická keramická metoda, suchá mechanoaktivace, mokrá mechanoaktivace a metoda srážení. Cílem bylo nalézt optimální metodu pro přípravu perovskitových pigmentů a detailně popsat jejich podmínky syntézy. Dále byly připravené pigmenty hodnoceny laboratorními technikami jako jsou rentgenová difrakční analýza, VIS spektrofotometrie, měření distribuce velikosti částic, difúzní odrazivost v blízké infračervené oblasti a elektronová mikroskopie.

Keywords

Ceramic pigments, perovskites, $SrSnO_3$, colour properties, NIR reflectivity, particle size distribution, brown pigment, phase composition

Klíčová slova

Keramické pigmenty, perovskity, $SrSnO_3$, barevné vlastnosti, odrazivost v blízké infračervené oblasti, distribuce velikosti částic, hnědý pigment, fázové složení

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1 INTRODUCTION

Inorganic pigments are powder materials, which are used for colouring of ceramic glazes, plastics, painting colours and for another application. These pigments are divided into basic and special group of pigments. The ceramic pigments belong to the group of special inorganic pigments, which is characterized with high thermal stability and chemical resistance. The pigments are consisting of thermal stable crystal structure, which it is incorporated the colouring chromophore element, for example Mn^{4+}, Fe^{3+}, La^{3+}. For this reason, ceramic pigments are suitable for colouring of ceramic glazes, building materials. Commercially produced ceramic pigments with brown colour hue are based on the hematite, rutile, or spinel structure. The structure of rutile and spinel are associated with the theoretically problematic chromophore element of Cr^{3+} and hematite structure has thermally labile particles of Fe_2O_3. The ecological problem with element of Cr^{3+} lies in its a production, which is based on carcinogenic compounds of dichromate. Therefore, new ways and new possibilities of preparation of ecological brown pigments are being sought. The perovskite compounds with suitable chromophore elements (Mn^{4+}, Fe^{3+}, et.al) are promising candidates for investigation as ceramic brown pigments.

2 THE AIM OF THESIS

The aim of this work was to prepare high temperature perovskite pigments with a high solar reflectance in near infrared region. Prepared pigments were described by chemical formula of $SrSn_{1-x}Mn_xO_3$, where substitution x moved in range of 0.1 – 0.5. The main attention was focused on possibilities of preparation of these perovskite compounds. Powders were prepared by solid state reaction of preparation such as classical ceramic method, dry mechanoactivation and wet mechanoactivation. Subsequently, impact of synthesis methods on the pigmentary application properties and its colour characteristics were evaluated. Furthermore, effect of preparation method on the phase composition, particle size distribution, particle morphology and diffuse reflectance in near infrared region were also investigated. In order to lower preparation temperature, precipitation method was used as a wet way of synthesis. Impact of precipitation method was also investigated as with mentioned in dry methods.

3 THEORETICAL PART

Ceramic pigments belong to the group of special inorganic pigments, which are characterised by high thermal stability and chemical resistance. The host lattice is formed of a highly stable mineral (rutile, cassiterite, spinel, hematite, et. al) and in pure form is colourless. Coloured pigments are obtained by incorporation of chromophore elements into the host lattice. This incorporation is conditioned by high calcining temperature of raw materials (up to 1600 °C) [1, 2]. Oxides, or compounds, which turn into oxides (hydroxides, carbonates, oxalates) at high temperatures are used as raw materials. The chromophores are ions with unfilled d- or f-orbitals (transition metals or lanthanides) [3].

Perovskites belong to the group of ceramic materials and derive to the mineral of $CaTiO_3$, which is describes as double oxide titanium-calcium. The general formula of perovskite compounds is ABX_3, where B is usually a transition metal, cation A is an alkaline earth metal or a rare-earth metal, and X is the most often O^{2-} [4, 5]. Larger cation A have 12- fold coordination with anion X and is located on the edge of framework structure. Cation B reside in corner-sharing octahedron of X anions [6]. The basic structure of perovskite compounds is given in Fig.1. The last few decades, perovskite compounds with ABO_3 structure are intensively studied due to their optical, catalytic, optoelectronic, photoluminiscent and magnetic properties [7, 8, 9]. The powder materials based on $SrSnO_3$ host lattice are the most common ferroelectric oxides with the perovskite ABO_3 structure, which are also used for production of catalysts, lithium ions batteries, cool pigments, and humidity sensors [10, 11].

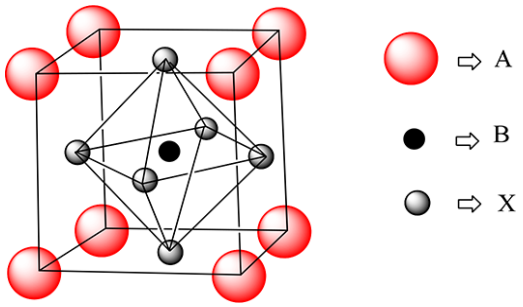


Figure 1: Crystal structure of perovskite compounds of ABX_3 [13]

The commercially available brown inorganic pigments are based on the spinel, hematite, or rutile structure. Hematite structure is thermally labile due to the particle of Fe_2O_3. Rutile and spinel structure are based on the colouring chromophore of Cr^{3+} [13, 14]. Production of Cr^{3+} ions is harmful for environment due to toxicity of raw materials containing Cr^{6+} ($Cr_2O_7^{2-}$ and CrO_4^{2-}) [15]. Therefore, it is appropriate to look for substitutes in the form of nontoxic and thermally stable pigment materials. Recent studies of the brown pigments focus on perovskite structure of $SrSnO_3$ and $BiFeO_3$. These pigments can be suitable for a commercial production [16, 17, 18].

4 EXPERIMETAL PART

4.1 SYNTHESIS OF PEROVSKITE PIGMENTS

The perovskite pigments with chemical formula $SrSn_{0.9}Mn_{0.1}O_3$ were prepared by four different approaches of preparation. The first three methods of preparation were based on dry way of synthesis. For the synthesis of this way, SnO_2 (99 % purity, Shepherd Color Company, USA), $SrCO_3$ (99.9 % purity, Sigma–Aldrich, Italy) and MnO_2 (99 % purity, Lachema Brno, Czech Republic) were used as raw materials. The first method was the classical ceramic method (CCM). The starting materials were weighed in suitable molar ratios and homogenized in a porcelain mortar. The homogenous mixtures were placed into corundum crucibles and then calcined in an electric furnace. The calcining process was carried out at the temperatures of 950 °C, 1050 °C, 1200 °C, 1300 °C and 1400 °C with a heating rate of 10 °C/min for 4 hours followed by natural cooling to ambient temperature.

The second method of dry way was innovated by the dry mechanochemical process prior to the calcination (DMA). The homogenous mixture was mechanochemically activated in the planetary mill Pulverisette 5 (Fritsch, Germany) for five hours with a spinning rate of 200 rpm using agate balls in a ball-to-powder weight ratio of 10:1. The mechanochemically activated mixture was exposed to the same calcining process as in the classical ceramic method.

The third method of synthesis was carried out by wet mechanochemically activated of starting materials (WMA). The activated milling process was performed in a planetary mill Pulviresette 5. The initial reagents were ground in solution of ethanol with agate balls in a ball-to-powder ration 10:1. Milling process was performed for five hours at a rotational velocity of 200 rpm. The activated reaction mixture was dried in electric dryer at temperature of 70 °C to the constant weight. Calcining process was carried out as in the previous method.

The last technique of synthesis was precipitation method (PM), which belongs among the wet way of synthesis. As initial reagents in this case were used $Na_2SnO_3 \cdot 3H_2O$ (95 % purity, Sigma-Aldrich, USA), $Sr(NO_3)_2$ (99.9 % purity, Sigma-Aldrich, India) and $Mn(NO_3)_2 \cdot 4H_2O$ (99,5 % purity, Lach-Ner, Czech Republic). Firstly, $Sr(NO_3)_2$ was dissolved in 400 ml distilled water and then stirred. Subsequently, $Mn(NO_3)_2$ was dissolved into the solution of $Sr(NO_3)_2$ and intensively stirred for 10 minutes. Solution of nitrate was adjusted the pH to 10 by 5M solution of sodium hydroxide. Secondly, $Na_2SnO_3 \cdot 3H_2O$ was dissolved in 300 ml distilled water, then added to the nitrate solution. The reaction was kept for a further 10 minutes. The obtained precipitate was filtered, decantated in 800 ml distilled water and then dried in electric dryer at temperature of 80 °C. The dried precipitate was homogenized and calcined at

temperature of 700 °C, 800 °C, 950 °C and 1050 °C with the rate of temperature increase 10 °C/min and duration of 4 hours [19].

The final dry powders were milled in planetary mill Pulviresette 5 for 10 minutes and then analysed in terms of pigmentary properties.

4.2 CHARACTERIZATION TECHNIQUES

For the identification of phase composition, powder X-ray diffraction (XRD) measurements were performed on all prepared samples using a MiniFlex 600 X-ray diffractometer (Rigaku, Japan) with a vertical goniometer of 15 cm. The device was equipped with Cu anode (U = 40 kV, I = 15 mA) and semiconductor detector D/TEX Ultra High Speed 1D. The patterns were recorded in the range of 2θ 10 – 80 ° with a step size of 0.02 ° 2θ and scanning speed of 10°/min and subsequently, evaluated with the aid of database PDF2.

Mastersizer 2000/MU (Malvern, GB) was used for investigation of particle size distribution. This device provides volumetric distribution and uses the laser diffraction on particles dispersed in a liquid medium. The apparatus is equipped with two lasers: a red-light laser with wavelength of 633 nm and a blue light laser with wavelength of 466 nm. All samples were homogenized in the solution of $Na_4P_2O_7$ with concentration 0.15 mol/L. The measured signal was evaluated by Mie theory [20].

For assessment of the colour properties, the pigments were applied into the dispersive acrylic binder in a mass tone. The testing suspensions were prepared by mixing of 0.5 g of the pigment and 0.85 – 0.9 g of binder then converted into a dense flowing paste using a pestle and agate mortar. The paste was applied on the white non-absorbing paper. The coating layer was created by pulling the Bird applicator. Prepared coating films were kept drying in a laboratory temperature. The colour properties of the prepared films were examined by a spectrophotometer UltraScan VIS (HunterLab, USA). The device operates with a wavelength interval record of 10 nm and in the visible region 400 – 700 nm. An illuminant D65, measuring geometry d/8° and complementary observer 10 ° were used as the measurement conditions. The CIE L*a*b* system (1976) was used for description of the colour properties (Fig. 2). The value L* describes the lightness or darkness of a colour and it can reach values in the range of 0 – 100, where number “0” represents black and number “100” represents white. The values a* (the axis of red - green) and b* (the axis of yellow-blue) indicate the colour hue. The value C (chroma) represents saturation of the colour and calculated according to following formula [21]:

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

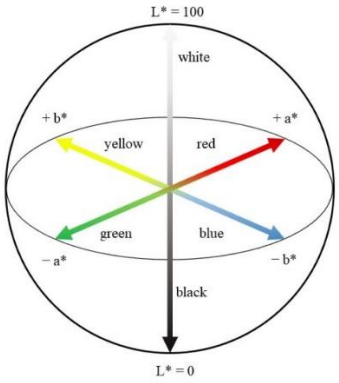


*Figure 2: CIE L*a*b* colour space [21]*

Thermal analysis of the initial mixtures was carried out using an STA 449 F1 Jupiter (Netzsch, Germany). Powder specimens were weighted in range of 80 – 100 mg. Measurements were performed in an air atmosphere with a flow of 50 ml/min and corundum crucibles with a heating rate of 10 °C/min. The measuring range was set to 25–1250 °C. The α-Al_2O_3 was used as a reference material.

The diffuse reflectance of pigments in the wavelength range of 700 – 1650 nm was measured with a spectrophotometer UV-3600 Plus (Shimadzu, Japan). The device was equipped with a white integrating sphere of ISR-603 and semiconductor detector of InGaS. Calibration of reflectance was performed using by a standard of $BaSO_4$. The measured results were used to calculate the solar reflectance R* according to the standard of ASTM G173-03. The solar reflectance was calculated by the following formula:

$$R^* = \frac{\int_{700}^{1650} r\,(\lambda)\cdot i\,(\lambda)\cdot d\lambda}{\int_{700}^{1650} i\,(\lambda)\cdot d\lambda} \qquad (2)$$

where r (λ) is the experimentally obtained reflectance and i (λ) is the standard solar spectrum ($Wm^{-2}\,mm^{-1}$) determined from ASTM Standard G 173-03 [22].

The morphological properties of powders were studied by scanning electron microscopy (SEM). The analysis were taken in an ultra-high vacuum apparatus of Lyra 3 (Tescan, Czech Republic). An accelerating voltage 10 kV was used for the measurements and a thin film of gold (15 nm) were sputtered on the samples.

5 RESULTS AND DISSCUSION

5.1 THERMAL ANALYSIS

Thermal behaviour of reaction mixture containing SnO_2, $SrCO_3$ and MnO_2 for the preparation of $SrSn_{0.9}Mn_{0.1}O_3$ pigment by CCM method is showed in Fig. 3. On the DTA curve, the first endothermic peak at a minimum of 86 °C is connected a loss of adsorbed water on the surface. This effect is also indicated on the TG curve and relates to a small weight change (Δm = -0.21 %). The subsequent peak with a minimum at 665 °C and small peak at 789 °C are accompanied by weight change (Δm = -1.35 %) and is connect with a decomposition of MnO_2 to Mn_2O_3 according to Equal 1 [23]. The third slight endothermic peak with minimum at 938 °C can be associated with decomposition of Mn_2O_3 to Mn_3O_4 (Eq. 2) or the phase transformation of $SrCO_3$ (orthorhombic → hexagonal structure). Three endothermic peaks with minimums at 998 °C, 1043 °C and 1078 °C is probably associated with decomposition of $SrCO_3$ [24] and formation of the new perovskite phases $SrSnO_3$ (Eq. 3) and $Sr_7Mn_4O_{15}$ (Eq. 4) and mixed oxide Sr_2SnO_4 (Eq. 5). The last endothermic effect is connected with reaction of mixed oxide Sr_2SnO_4 with SnO_2 yielding $SrSnO_3$ (Eq. 6) [25, 26]. The total mass change which is given on the TG curve is Δm = -15.10 %.

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2 \quad (1)$$

$$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2 \quad (2)$$

$$SrCO_3 + SnO_2 \rightarrow SrSnO_3 + CO_2 \quad (3)$$

$$21SrCO_3 + 4Mn_3O_4 + 4O_2 \rightarrow 3Sr_7Mn_4O_{15} + 12CO_2 \quad (4)$$

$$2SrCO_3 + SnO_2 \rightarrow Sr_2SnO_4 + 2CO_2 \quad (5)$$

$$Sr_2SnO_4 + SnO_2 \rightarrow 2SrSnO_3 \quad (6)$$

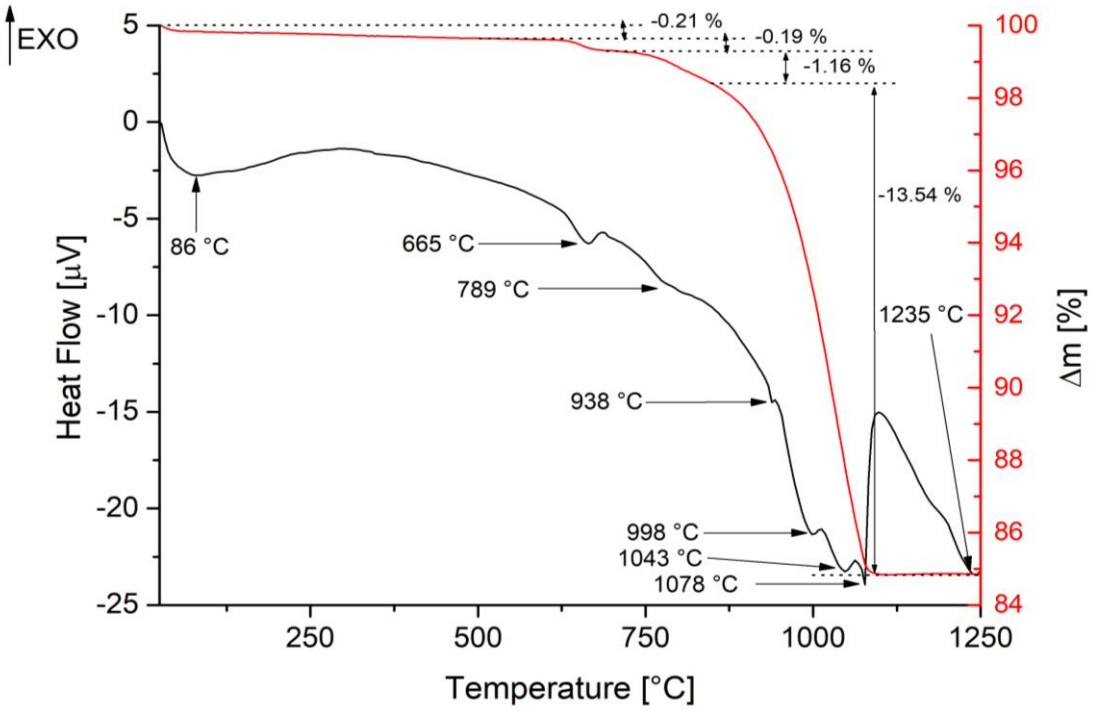


Figure 3: DTA/TG curve of reaction mixture of CCM $SrSn_{0.9}Mn_{0.1}O_3$ (mass weight 93.41 mg)

Thermoanalytical curves of reaction mixture for the preparation of $SrSn_{0.9}Mn_{0.1}O_3$ pigment by dry mechanochemical method are given in Fig. 4. The first endothermic peak with a minimum at 87 °C is related to loss of residual moisture. This effect is also evident on the TG curve (Δm = -0.65 %). On the DTA curve, the next effect corresponds with the decomposition of MnO_2 to Mn_2O_3 with a minimum at 686 °C. An endothermic effect at 801 °C is accompanied with the formation of perovskite phase $SrSnO_3$. The next two endothermic effects with minimums at 952 °C and 1034 °C represented decomposition of $SrCO_3$ and formation a new perovskite phase of $SrMnO_3$. The incorporation of $SrMnO_3$ phase into the $SrSnO_3$ perovskite is not recorded on the DTA/TG curve, but the results of phase composition showed that at temperature of 1200 °C, the single-phase product forms [25].

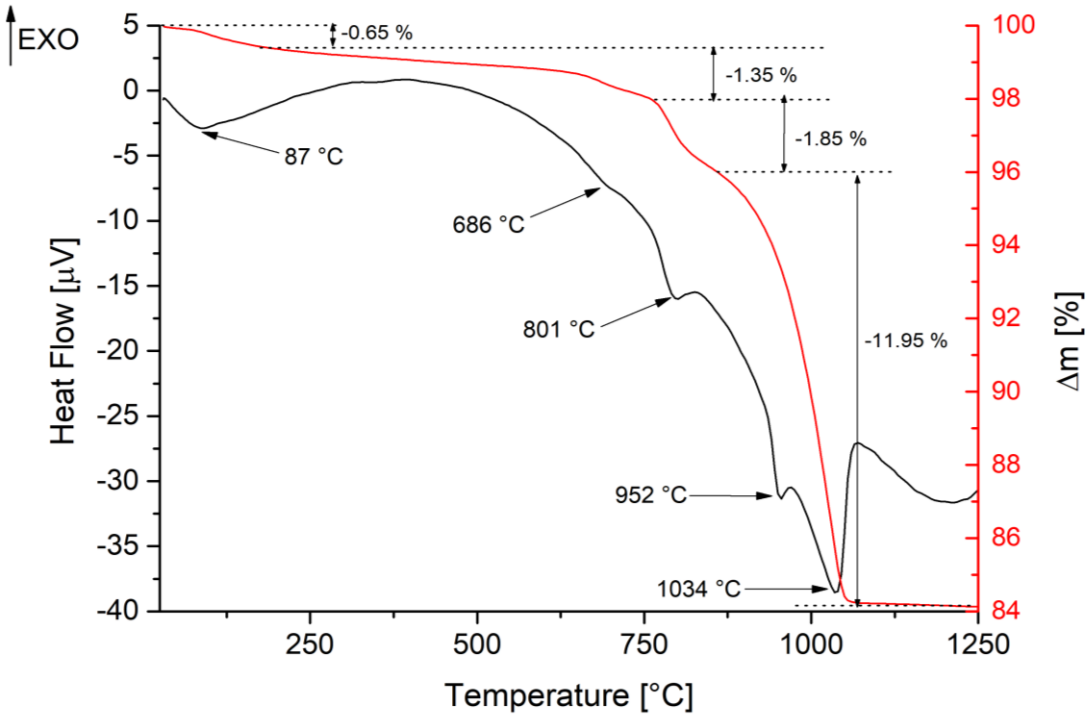


Figure 4: DTA/TG curve of reaction mixture of DMA $SrSn_{0.9}Mn_{0.1}O_3$ (mass weight 102.73 mg)

5.2 PHASE COMPOSITION

The phase composition of $SrSn_{0.9}Mn_{0.1}O_3$ was studied by XRD analysis. The results of XRD analysis are shown in Table 1 and XRD patterns of samples prepared by different methods are given in Figure 5. According to these results, the samples prepared by solid state reactions (CCM, DMA, WMA) provide a single-phase product at high calcining temperature. Four phases are detected at all methods at the temperature of 950 °C and identify as unreacted SnO_2, Sr_2SnO_4 mixed oxide and two perovskite phases of $SrMnO_3$ and $SrSnO_3$. The samples prepared by CCM and WMA methods at 1050 °C contain three phases which are identified as $SrSnO_3$, SnO_2 and Sr_2SnO_4. In cause of DMA method, three phases are also detected which are describe as $SrSnO_3$, SnO_2 and $SrMnO_3$. The only major phase corresponding to $SrSnO_3$ is detected at temperature 1200 °C and in samples prepared by CCM and DMA methods. At the temperature 1200 °C, the method of WMA does not still provide single phase product. The sample consisted of $SrSnO_3$ and unreacted phase of SnO_2. All methods based on solid state reactions form single-phase products by calcination at the temperature of 1300 °C and higher. In cause of precipitation method (PM), single phase product is detected at temperature of 700 °C. The phase corresponds to the structure of $SrSnO_3$. The results of single-phase product were not confirmed at the higher temperatures of 800 °C and 950 °C. In these temperatures, XRD patterns show two-phase products which are

identified as phase of $SrSnO_3$ and $SrMnO_3$. The calcining temperature of 1050 °C already produces the same phase composition as that at 700 °C.

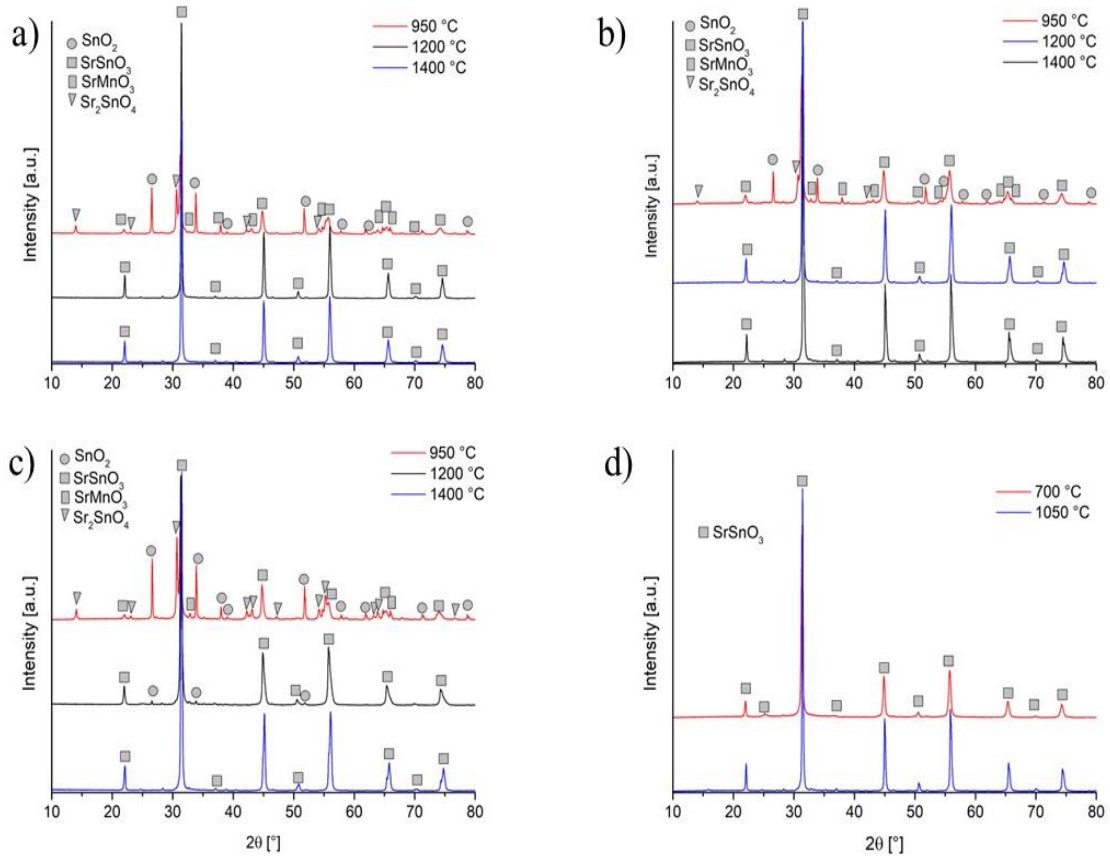


Figure 5: XRD patterns of calcined samples $SrSn_{0.9}Mn_{0.1}O_3$: a) CCM; b) DMA; c) WMA; d) PM

Table 1: Phase composition of the $SrSn_{0.9}Mn_{0.1}O_3$ perovskite pigments

Method of preparation	Calcining temperature [°C]	Detected phases
CCM	950	$SrSnO_3$, SnO_2, Sr_2SnO_4, $SrMnO_3$
	1050	$SrSnO_3$, SnO_2, Sr_2SnO_4
	1200	$SrSnO_3$
	1300	$SrSnO_3$
	1400	$SrSnO_3$
DMA	950	$SrSnO_3$, SnO_2, Sr_2SnO_4, $SrMnO_3$
	1050	$SrSnO_3$, SnO_2, $SrMnO_3$
	1200	$SrSnO_3$
	1300	$SrSnO_3$
	1400	$SrSnO_3$
WMA	950	$SrSnO_3$, SnO_2, Sr_2SnO_4, $SrMnO_3$
	1050	$SrSnO_3$, SnO_2, Sr_2SnO_4
	1200	$SrSnO_3$, SnO_2
	1300	$SrSnO_3$
	1400	$SrSnO_3$
PM	700	$SrSnO_3$
	800	$SrSnO_3$, $SrMnO_3$
	950	$SrSnO_3$, $SrMnO_3$
	1050	$SrSnO_3$

5.3 COLOUR PROPERTIES

The impact of synthesis methods on the colour properties of the perovskite pigments upon application into the organic matrix is summarized in Table 2. The obtained results show that the colour coordinates of L*, a* and b* are changing in the dependence of the way of synthesis and the calcination temperature. For CCM, DMA and WMA methods, values L* decrease with increasing calcining temperature and pigments become darker. The value of L* increases with growing calcining temperature in sample prepared by PM method and samples become lighter. The values of L* move in the range of 29 – 38. The values of a* have irregular character with growing temperature in sample prepared by solid state reactions. When using the PM, the obtained values of a* have increasing character with the ascending temperature. The colour coordinates of b* have decreasing character with increasing temperature in sample prepared by CCM, WMA and DMA methods. In case of PM method, values of b* have opposite character. The best colour results are obtained in sample prepared by PM method and at the calcination temperature of 1050 °C. This sample provide the highest value of chroma (C = 12.9) and is characterized by interesting brown hue.

Table 2: Colour characteristics of $SrSn_{0.9}Mn_{0.1}O_3$ pigments applied into the organic binder

Method of preparation	Calcining temperature [°C]	L*	a*	b*	C
CCM	1200	33.1	6.7	7.9	10.4
	1300	29.4	5.6	5.4	7.8
	1400	29.4	6.1	4.4	7.5
DMA	1050	37.6	4.3	10.1	11.0
	1200	31.7	6.9	7.6	10.3
	1300	31.3	6.0	6.8	9.1
	1400	31.0	4.8	5.6	7.4
WMA	1050	36.7	4.3	8.4	9.4
	1200	32.4	5.7	6.9	8.9
	1300	30.8	6.3	5.8	8.5
	1400	29.0	5.6	4.2	7.0
PM	700	34.9	2.5	6.2	6.7
	800	36.0	3.9	8.4	9.3
	950	36.6	5.4	9.9	11.3
	1050	38.0	6.1	11.4	12.9

5.4 SOLAR REFLECTANCE

The values of solar reflectance R* of the prepared samples $SrSn_{0.9}Mn_{0.1}O_3$ in powder form are depicted in Table 3. The values of solar reflectance move in the range from 25 % to 44 %. The highest values are obtained in samples prepared by PM method. Their measured reflectance and calculated solar spectra are shown in Figure 6. All methods of synthesis provide values of R* higher than 20 %, which is a limit for considering samples as cool pigment. The high solar reflectance values clearly highlight the potential for the utility of the pigment in colouring of roof and façade painting coats.

Table 3: Total solar reflectance of $SrSn_{0.9}Mn_{0.1}O_3$ pigments

Method of preparation	Calcining temperature [°C]	R* [%]
CCM	1200	40.2
	1300	34.2
	1400	31.9
DMA	1050	40.8
	1200	35.9
	1300	31.5
	1400	24.7
WMA	1050	39.7
	1200	31.4
	1300	32.8
	1400	31.0
PM	700	34.1
	800	39.2
	950	43,5
	1050	42,0

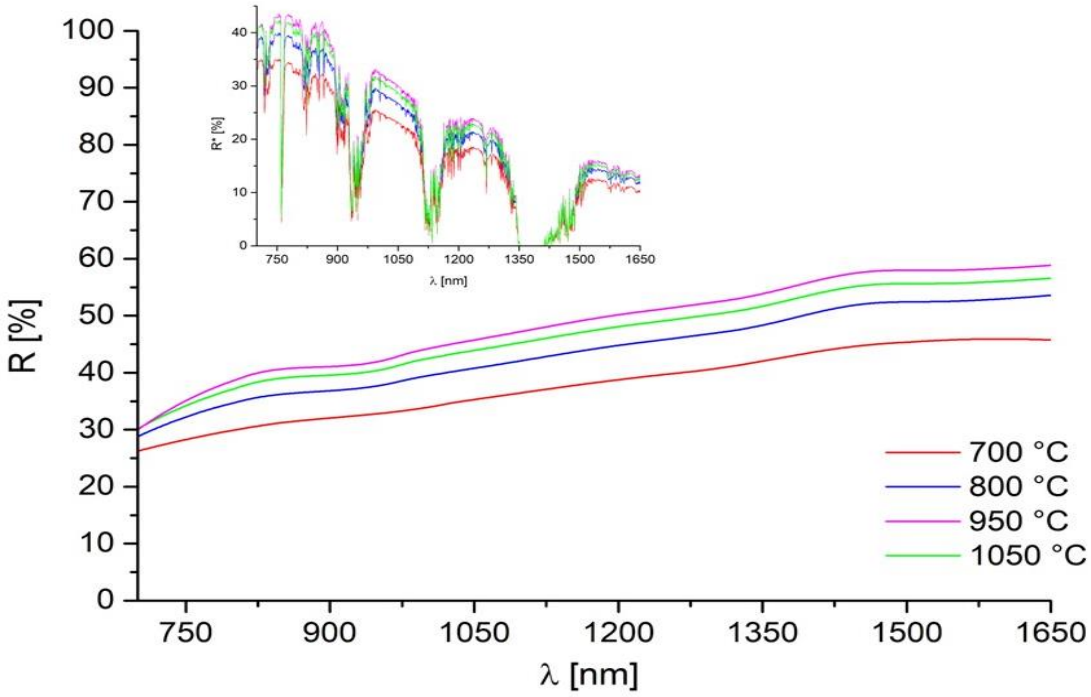


Figure 6: NIR reflectance and solar reflectance spectra of $SrSn_{0.9}Mn_{0.1}O_3$ prepared by precipitation method

5.5 PARTICLE SIZE DISTRIBUTION

Particle size characterization belongs to the one of the most important properties of powder pigments. The most important value, which characterizes particle size, is the value of d_{50}. The results of particle size distribution of $SrSn_{0.9}Mn_{0.1}O_3$ samples prepared by four different methods and after 10 minutes of milling process in planetary mill are given in Table 4. The values of d_{50} of all pigments does not exceed limit of 3.5 μm and moves in a range from 1.0 to 3.5 μm. The highest values are recorded for samples prepared by the dry mechanochemical activation method. It was caused by the sintering of powder during the calcination process. The recommended values of d_{50} for their potential use in painting coats are approximately 2 μm. Most of samples after milling process meet given range of the mean particle size d_{50} but in case of the samples prepared DMA method, it would be suitable to extend a milling time.

Table 4: Particle size distribution of the perovskites $SrSn_{0.9}Mn_{0.1}O_3$

Method of preparation	**Calcining temperature [°C]**	**After milling process (10 minutes)**		
		d_{10} [μm]	d_{50} [μm]	d_{90} [μm]
CCM	1200	0.52	1.42	7.14
	1300	0.91	1.80	4.39
	1400	0.89	2.15	9.16
DMA	1050	0.47	1.38	6.10
	1200	0.65	2.18	9.19
	1300	0.82	2.96	10.70
	1400	0.82	3.51	13.46
WMA	1050	0.57	1.15	10.90
	1200	0.41	1.06	5.56
	1300	0.52	1.25	3.33
	1400	0.77	1.89	4.47
PM	700	0.71	2.20	9.76
	800	0.69	1.91	8.06
	950	0.68	1.82	6.55
	1050	0.72	1.91	5.57

5.6 MORPHOLOGICAL PROPERTIES

SEM microphotographs of calcined samples of $SrSn_{0.9}Mn_{0.1}O_3$ obtained by CCM, DMA, WMA and PM method are shown in Figure 7. The sample prepared of CCM can be characterized as elongated particles with a small number of spherical particles. It is clear from the micrograph of the DMA sample that particles are sintered during the calcination process. Clusters of the particles prepared by DMA have irregular shapes. The particles obtained by WMA method are smaller than the particles obtained by the

other methods. The particle size distribution results in the previous chapter match this fact. The PM method provides elongated particles with matchstick shapes.

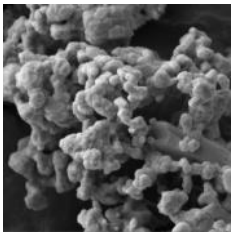
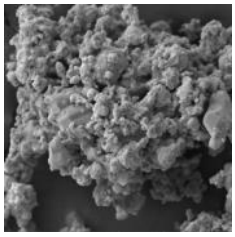
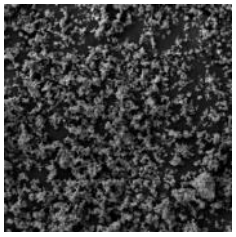
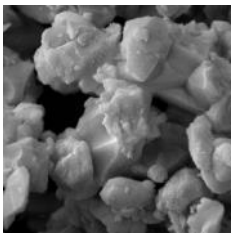
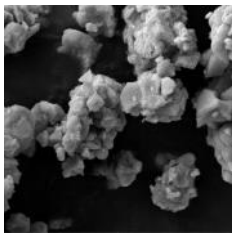
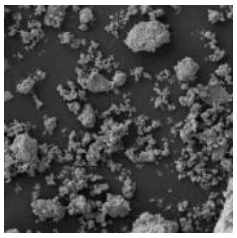
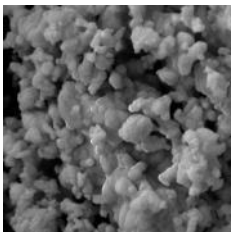
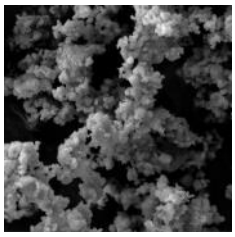
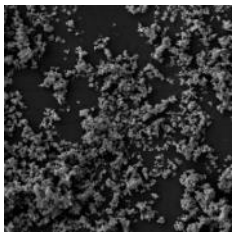
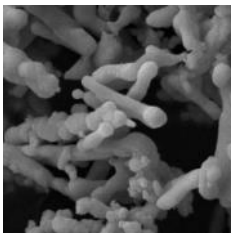
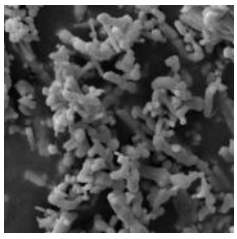
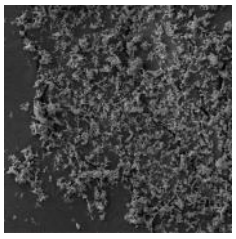
Method of preparation	Field of view		
	5 μm	10 μm	100 μm
CCM 1200 °C			
DMA 1200 °C			
WMA 1200 °C			
PM 1050 °C			

Figure 7: SEM photographs of perovskite samples of $SrSn_{0.9}Mn_{0.1}O_3$

6 CONCLUSION

The main goal of the dissertation work was to prepare brown pigments of general formula $SrSn_{1-x}Mn_xO_3$, where x = 0.1 – 0.5, and found out the impact of synthesis method on their phase composition, colour properties, granulometric composition and solar reflectance in near infrared region. The pigments were synthesised by classical ceramic method, dry mechanochemical activation, wet mechanochemical activation and precipitation method. Firstly, the thermoanalytical methods were used for description of thermal behaviour of initial reagents for obtaining the optimal calcining temperature necessary for the formation of perovskite structure of $SrSn_{0.9}Mn_{0.1}O_3$. From the results of DTA/TG analysis, it found out that the dry mechanochemical activation shifted all processes to a lower temperature (approximately at 800 °C). Initial mixture for classical ceramic method and wet mechanochemical activation formed the perovskite structure of $SrSnO_3$ in temperature range of 950 – 1000°°C. On the basis of obtained results, the calcination temperatures used for preparation of the pigments were in the range of 950 °C – 1400 °C. The resulting calcination temperatures for the precipitation method, 700 °C – 1050 °C, were chosen on the basis of information from the literature [19]. High calcining temperatures had a positive effect on phase composition, the single-phase products $SrSn_{0.9}Mn_{0.1}O_3$ were found out at higher temperatures. In case of preparation of the pigments by ways based on solid state reactions, higher calcining temperatures also caused the formation of darker powders with lower values of chroma C. The positive effect of the growing calcining temperature on the colour properties were found in samples prepared by precipitation method, when the values of chroma C ascended. The milling process, 10 minutes in planetary mill, is necessary to obtain the particles with size of d_{50} moved in the range of 1.0 – 3.5 μm. Most of the samples meet required range of the mean particle size d_{50} less than 2 μm, which is a necessary condition for the pigments to be applicable into the organic matrix. The samples prepared by dry mechanochemical activation require the longer milling time. All pigments exhibited high solar reflectance in near infrared region and their values lied in range of 25 – 45 %. From the technological and ecological point of view, the precipitation method is the most suitable method for preparation of brown perovskite pigment $SrSn_{0.9}Mn_{0.1}O_3$, which can be used as cool pigments.

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