

Perovskite pigments based on $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$

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The aims of this research were to monitor the phase composition, colour properties, and morphology of perovskite pigments SrSnO_3 in which a part of tin(IV) atoms have been substituted by manganese(IV). The composition of the perovskite powders prepared is described by general formula $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$, where $x = 0.1–0.5$. Pigments were prepared by solid state reaction at calcining temperature in a range of 1200–1500 °C. The powders of interest have been studied with respect to their use in ceramic industry as the inorganic pigment(s).

Keywords: Perovskite pigments; solid state reaction, colour properties.

Introduction

Perovskites are the type of mixed oxides that have a general formula ABO_3 , where B is usually a transition metal and A is a cation of alkaline earth metal or rare-earth metal [1]. Cation A is larger and located on the edge of framework structure. In the centre of octahedron, cation B is located, being smaller [2]. Perovskites attract attention due to their properties: electric, optical, piezo-electric, photoluminescent, optoelectronic, and catalytic [3–4]. Perovskite based on SrSnO_3 could be used as pigments [5], for the production of solar cells [6], lithium-ion batteries or components of humidity sensors [7].

Perovskites are highly desirable pigments which have no toxic effects [8] and which can be classified as ceramic pigments [9]. Ceramic pigments are inorganic compounds offering good thermal and chemical stability [10]. The structure of ceramic pigments contains chromophores that colour the system.

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By partial replacement of Sn^{4+} ions with suitable chromophores one can achieve the desired colour change in the originally colourless system [11]. Due to the relatively larger radius of Sn^{4+} ion (0.069 nm, [12]) than Mn^{4+} ion (0.054 nm [13]), it is then possible to easily incorporate the chromophore ions into the SrSnO_3 crystal lattice.

This work deals with synthesis and characterization of $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$ pigments, where $x = 0.1\text{--}0.5$, and the main attention is paid to the monitoring of morphology, colour properties, and phase composition of samples.

Materials and methods

Synthesis

Pigments $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$ (where $x = 0.1, 0.2, 0.3, 0.4, 0.5$) were prepared by classical ceramic method – solid state reaction. The perovskites were prepared from oxides SnO_2 (99.9% purity, Alfa Aesar, Karlsruhe, Germany), MnO_2 (99% purity, Lachema, Brno, Czech Republic) and strontium carbonate SrCO_3 (99.9% purity, Sigma-Aldrich, Milan, Italy). The starting materials were weighed at suitable molar ratios and then homogenized in a porcelain mortar. The homogenized mixtures were calcinated in corundum crucibles in an electric resistance furnace with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ at temperatures of 1200, 1300, 1400, and 1500 $^\circ\text{C}$ for 4 hours. The powders were characterized by scanning electron microscopy (SEM), X-ray photoelectron microscopy (XPS), X-ray diffraction analysis (XRD), by means of colour properties and via particle size distribution (PSD).

Characterization of powders

The colour properties of synthesised perovskites applied in an organic binder (dispersive acrylic paint Luxol, AkzoNobel Coatings CZ, Opava, Czech Republic) were measured within a visible region of light using an UltraScan VIS spectrometer (HunterLab, Reston, VA, USA). The measuring conditions were: standard illuminant D_{65} (6500 K), 10° complementary observed, geometry of measurements $d/8^\circ$. The colour properties were described in terms of the CIE- $L^*a^*b^*$ system (1976). In this system, L^* is described by numbers from 0 (black) to 100 (white), whereas the values a^* and b^* represented the colour hue from $+a^*$ (red) to $-a^*$ (green) and from $+b^*$ (yellow) to $-b^*$ (blue).

The phase composition of samples was determined by diffractometer (Miniflex 600, Rigaku, Tokyo, Japan) equipped with Cu-anode ($U = 40\text{ kV}$, $I = 15\text{ mA}$), 1D detector D/TeX Ultra. Data acquisition was realized in the 2θ range $10\text{--}80^\circ$ with a scan step of 10° min^{-1} .

The chemical composition was determined by X-ray photoelectron spectroscopy (XPS) carried out in an ultra-high vacuum apparatus ESCA 2SR (Scienta-Omicron, Taunusstein, Germany) with a base pressure below $1 \cdot 10^{-9}$ mbar and by using monochromatic X-ray source (Al $K\alpha$, 1486.6 eV). Charging of samples was compensated by a low energy electron source (flood gun). Survey spectra and high-resolution spectra were collected using the pass energy 150 eV and 50 eV, respectively. The binding energy scale was referenced to the adventitious carbon (284.8 eV). The quantitative analysis was based on sensitivity factors provided by the manufacturer.

The morphological properties were studied by scanning electron microscopy (SEM) realized in an ultra-high vacuum apparatus Tescan Lyra 3 (Tescan, Brno, Czech Republic). An accelerating voltage 5 kV was used for the measurements and a thin film of gold (15 nm) sputtered on the samples.

The particle size distribution of the synthesised pigments was measured using a Mastersizer 2000/MU equipment (Malvern Instruments, Worcestershire, UK). This device ensures a volumetric distribution by using the laser diffraction on particles dispersed in a liquid medium. The particle size distribution was analysed by two lasers – red light (He-Ne laser with wavelength of 633 nm) and blue light (laser diode with wavelength of 466 nm). The signal was evaluated on the basis of Mie theory. The measurement is performed in three steps and results automatically calculated as the average presented as d_{10} , d_{50} , d_{90} and span values.

$$\text{span} = \frac{d_{90} - d_{10}}{d_{50}}$$

Results and discussion

Colour properties

All synthesised pigments were applied in the organic binder (dispersive acrylic paint Luxol, AkzoNobel Coatings CZ). The colour properties of $\text{SrSn}_{0.5}\text{Mn}_{0.5}\text{O}_3$ in the dependence of calcining temperature are summarized in Table 1. The powders of dark-chocolate brown hue were obtained by calcination at the temperature of 1200 and 1300 °C. The pigments prepared by calcination at temperature higher than 1300 °C are black. The values L^* have irregular dependence on the calcining temperature and may vary in the range 26.59–28.78. It is evident that the increasing temperature has affected the values of lightness, but not in a wider range. The coordinates a^* and b^* have a slowly decreasing character with increasing calcining temperature (Table 1). The highest values of a^* and b^* parameters were found for the temperature of 1200 °C ($a^* = 1.50$ and $b^* = 1.12$). The effect of partial substitution of stannic ions by manganese ions for

calcining temperature 1500 °C is shown in Table 2. From the data in this table, it is evident that the coordinates L^* are only slightly affected by the increasing range of substitution. The pigment with substitution $x = 0.1$ has a brown chocolate hue and the highest values of colour coordinates. The values of colour parameters a^* and b^* are $a^* = 4.08$ and $b^* = 2.97$. The values a^* and b^* had a decreasing character with the increasing amount of manganese ions and the powders became black.

Table 1 Colour parameters of the $\text{SrSn}_{0.5}\text{Mn}_{0.5}\text{O}_3$ applied in the organic matrix

Calcining temperature [°C]	L^*	a^*	b^*
1200	28.78	1.50	1.12
1300	26.90	0.75	0.34
1400	27.41	0.30	-0.02
1500	26.59	0.10	-0.12

Table 2 The effect of substitution on the colour properties of pigments $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$ calcinated at 1500 °C and applied in organic matrix

Calcining temperature [°C]	Substitution x	L^*	a^*	b^*
1500	0.1	25.38	4.08	2.97
	0.2	25.46	0.69	0.27
	0.3	26.47	0.16	-0.09
	0.4	26.51	0.14	-0.06
	0.5	26.59	0.10	-0.12

XRD analysis

The phase composition of the prepared powders with a general formula of $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$ in dependence on the calcining temperature from 1200 °C to 1500 °C was studied. An impact of calcining temperature on the phase composition of perovskite compounds doped by manganese ions is shown in Fig. 1. From this figure, it is evident that synthesis of perovskite pigments $\text{SrSn}_{0.5}\text{Mn}_{0.5}\text{O}_3$ at all calcining temperatures did not result in the formation of single-phase product. The sample calcinated at temperature of 1200 °C contains of SrSnO_3 as a major phase and SrMnO_3 with $\text{Sr}_4\text{Mn}_3\text{O}_{10}$ as two minor phases. Thus, it can be seen that this temperature is not satisfactory for the formation of single-phase perovskite, $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$. The calcining temperature of 1300 °C produces the same phase composition as that at 1200 °C, when the latter temperature is still not satisfactory

for preparation of perovskite compounds with good phase composition. The single-phase product was not obtained during the calcining temperatures 1400 and 1500 °C and the SrMnO₃ compound became major phase. The two-phase product was formed at these temperatures because the Sr₄Mn₃O₁₀ phase is decomposed. From a pigmentary point of view, it is not necessary to obtain a pigment with single-phase composition, but important are conditions of synthesis that can be used in the industry. The identified phase composition, the corresponding structure, and the JPDF numbers are shown in Table 3. The SrSnO₃ and SrMnO₃ phases have an orthorhombic structure; Sr₄Mn₃O₁₀ phase exhibits a cubic structure.

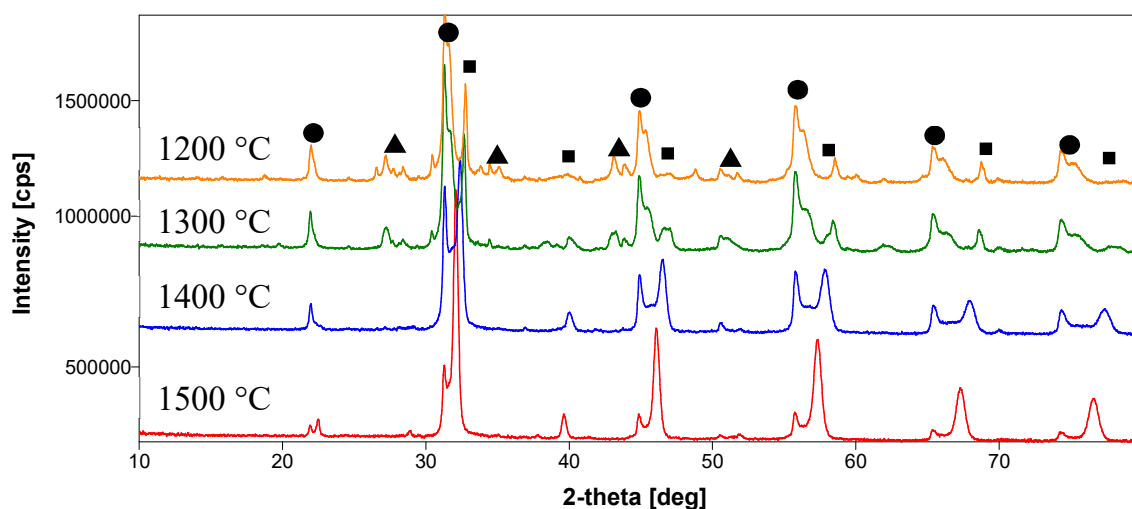


Fig. 1 XRD diffractograms of perovskite SrSn_{0.5}Mn_{0.5}O₃ with phases labelled as follows: SrSnO₃ (●), SrMnO₃ (■), Sr₄Mn₃O₁₀ (▲)

Table 3 The impact of calcining temperature on phase composition of SrSn_{0.5}Mn_{0.5}O₃

Calcining temperature [°C]	Detected phases	Structure	JPDF number
1200	SrSnO ₃	Orthorhombic	01-070-4389
	SrMnO ₃	Orthorhombic	01-075-9937
	Sr ₄ Mn ₃ O ₁₀	Cubic	01-089-6885
1300	SrSnO ₃	Orthorhombic	01-070-4389
	SrMnO ₃	Orthorhombic	01-075-9937
	Sr ₄ Mn ₃ O ₁₀	Cubic	01-089-6885
1400	SrSnO ₃	Orthorhombic	01-070-4389
	SrMnO ₃	Orthorhombic	01-075-9937
1500	SrSnO ₃	Orthorhombic	01-070-4389
	SrMnO ₃	Orthorhombic	01-075-9937

XPS analysis

The XPS image (see Fig. 2) shows the XPS spectrum of powder after thermal treatment at temperature of 1300 °C. Spectra do not differ with calcining temperature, therefore only one spectrum of perovskite is given in this work. The core lines of the elements (Mn 2p, O 1s, Sn 3d, Sr 3d) and Auger electrons of the perovskite $\text{SrSn}_{0.5}\text{Mn}_{0.5}\text{O}_3$ are also shown in the image, when the Auger electrons have a binding energy for Sn MNN 1057.8 ± 0.3 eV, O KLL 983.6 ± 0.3 eV and Mn LMM 904.6 ± 0.3 eV. The cover lines were then found for tin – Sn 3d with a binding energy 484.8 ± 0.3 eV, for manganese – Mn 2p 641.2 ± 0.3 eV, for strontium – Sr 3p 279.8 ± 0.3 eV and for oxygen – O 1s 531.7 ± 0.3 eV.

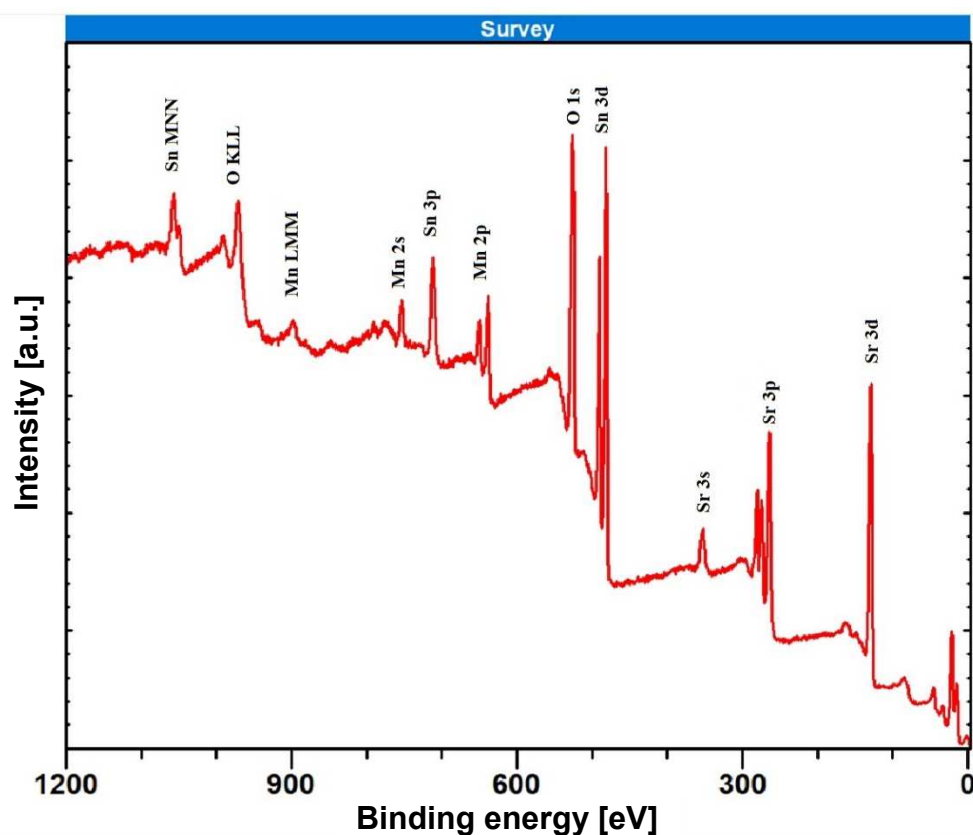


Fig. 2 XPS spectrum for perovskite $\text{SrSn}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (firing temperature of 1300 °C)

SEM analysis

The SEM images of perovskites $\text{SrSn}_{0.5}\text{Mn}_{0.5}\text{O}_3$ are given in Fig. 3 and Fig. 4. Scanning electron microscope showed changes in the morphology of perovskite occurring with the increasing temperature. Elongated particles with a small amount of orthorhombic particles were formed at calcining temperature of 1200 and 1300 °C.

It was found out that the amount of elongated particles were reduced and amount of orthorhombic particles were formed with the increasing temperature, which was also associated with the phase composition of perovskite.

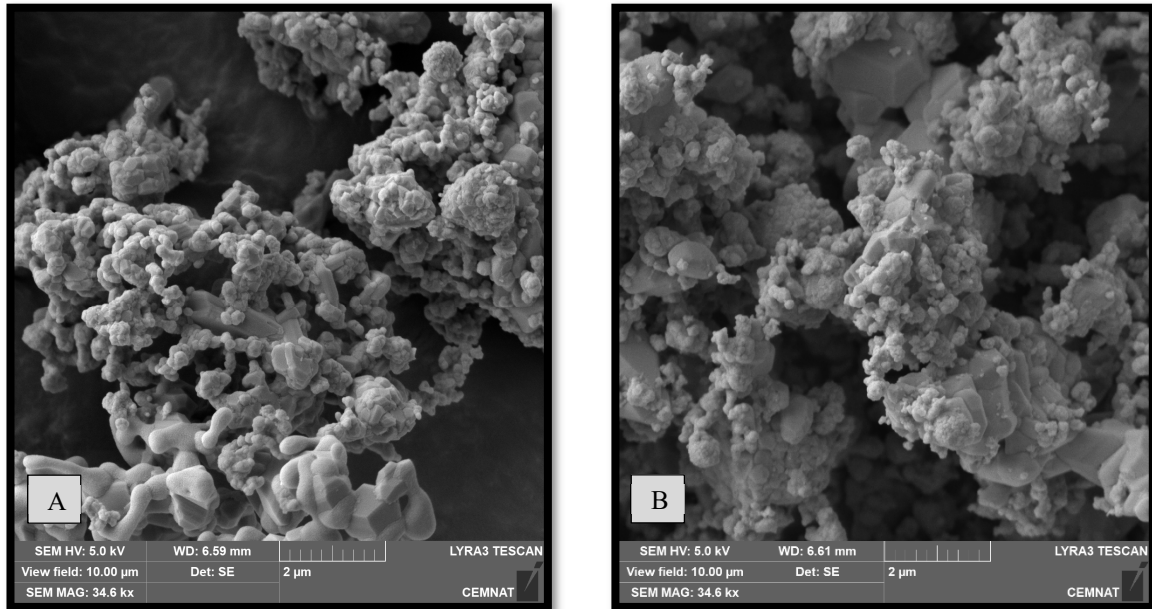


Fig. 3 SEM images of SrSn_{0.5}Mn_{0.5}O₃ for firing temperature of 1200 °C (A) and of 1300 °C (B)

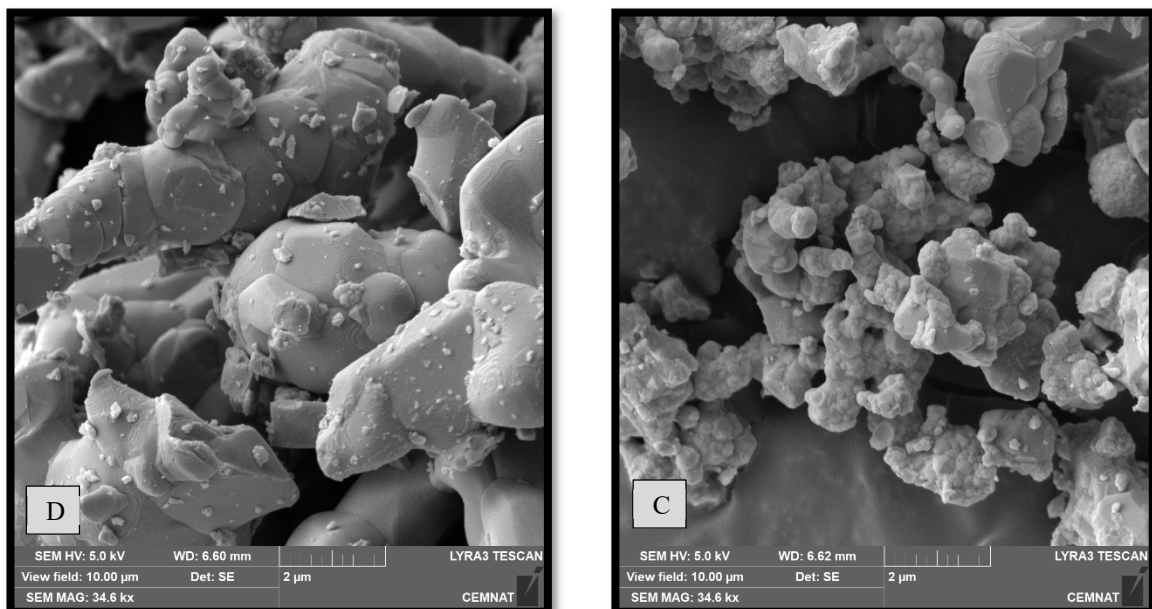


Fig. 4 SEM images of SrSn_{0.5}Mn_{0.5}O₃ for firing temperature of 1400 °C (C) and of 1500 °C (D)

Particle size distribution

All prepared pigments were subjected to the measurement of the particle size distribution in dependence on the calcining temperature and a range of substitution of stannic ions. Particle size characterization belongs to the one of the most significant properties measured of powder pigments.

The most important value, which characterizes particle size, is the value d_{50} . The values in Table 4 show that particle size d_{50} of pigments grows with the increasing calcining temperature. The values of d_{50} are in a range from 1.95 to 5.83 μm . The parameter span moved within a range 2.38–4.15, which means that the particle size distribution was wider with increasing calcining temperature. From Table 5, it is evident that with the increasing range of stannic ions substitution, the mean particle size also grows. The values of d_{50} are located in a narrow interval from 3.94–5.83 μm ; the parameter span lying in range 2.86–6.37. Such particle sizes are sufficient for the potential application of perovskites in the organic binder and ceramic glaze.

Table 4 Effect of calcination temperature on the particle size distribution of $\text{SrSr}_{0.5}\text{Mn}_{0.5}\text{O}_3$

Temperature [$^{\circ}\text{C}$]	d_{50} [μm]	span
1200	1.95	3.48
1300	2.66	2.38
1400	4.41	4.15
1500	5.83	4.09

Table 5 The impact of stannic ions substitution on the particle size distribution for 1500 $^{\circ}\text{C}$

Temperature [$^{\circ}\text{C}$]	Substitution x	d_{50} [μm]	span
1500	0.1	3.94	6.37
	0.2	4.35	4.61
	0.3	4.22	2.86
	0.4	5.26	4.35
	0.5	5.83	4.09

Conclusions

The main aim of the research was to synthesise and analyse Mn-doped perovskite pigments. Perovskites of $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$ were prepared by classical ceramic method from SrCO_3 , SnO_2 and MnO_2 in the range calcining temperature from 1200 to 1500 °C. The X-ray diffraction analysis has proved that single-phase product could not be prepared, but the increasing calcining temperature positively affects the phase composition. At the calcining temperature of 1200 and 1300 °C, SrSnO_3 is formed as the major phase with a small amount of SrMnO_3 and $\text{Sr}_4\text{Mn}_3\text{O}_{10}$, when the phase of SrMnO_3 is dominant with the increasing temperature. Morphology of perovskite is changed with increasing calcining temperature. Yet another finding was that the value of d_{50} for powder $\text{SrSr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ had moved in range 1.95–5.83 μm in dependence on the calcining temperature; the median value having increased according to the increasing substitution of stannic ions and has had the highest value at $x = 0.5$ (5.83 μm). Such particle sizes of pigments are suitable for applying pigment in the organic binder and ceramic glaze. The prepared pigments have also had interesting colours in a brown hue and black hue. Finally, the synthesised pigments $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$ are environmentally friendly as they do not contain toxic elements.

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