

## Brown pigments with perovskite structure of $\text{SrSnO}_3$ : The role of mineralizers

Jan Hroch\* and Žaneta Dohnalová

Department of Inorganic Technology, The University of Pardubice,  
CZ–532 10 Pardubice, Czech Republic

Received: May 28, 2020; Accepted: June 26, 2020

*Ceramic pigments of the type  $\text{SrSn}_{0.8}\text{Mn}_{0.2}\text{O}_3$  were prepared by classical method. Solid-state reaction of initial components was supported by molten salts that had played role of mineralizers. The selected mineralizers ( $\text{Li}_2\text{CO}_3$ ,  $\text{NaF}:\text{NaCl}$  (1:1),  $\text{KCl}$ ,  $\text{KCl}:\text{K}_2\text{CO}_3$  (1:1), and  $\text{Na}_3\text{AlF}_6$ ) in an amount of 5 % (w/w) were used. Effect of the type of mineralizer and the calcining temperature on the colour properties, particle size distribution, morphological properties and phase composition was studied. The single-phase product was obtained at calcining temperature of  $1200^\circ\text{C}$  and above. A particle size of  $d_{50}$  was varied in the range  $1.1\text{--}6.5\ \mu\text{m}$ . The pigments prepared were applied into the organic matrix. With a higher calcining temperature, the brown colour of application became darker. The most interesting brown colour of pigment was eventually obtained by calcination of the reaction mixture containing the  $\text{NaF}:\text{NaCl}$  mixture.*

**Keywords:** Colour measurement; Ceramic pigments; Brown hue; Mineralizers

### Introduction

Ceramic oxides with the  $\text{ABO}_3$  structure are intensively studied due to their optical, catalytic, and magnetic properties [1–3]. The powder materials based on  $\text{SrSnO}_3$  host lattice are most ordinary ferroelectric oxides with the perovskite  $\text{ABO}_3$  structure that are also used for production of thermistors, semiconductors, and humidity sensors [4–5]. The interesting properties of these materials are associated with structural changes, due to the specific slope of the  $\text{SnO}_6$

---

\* Corresponding author, ✉ jan.hroch@student.upce.cz

octahedron incorporated in [6]. This slope is also related to the width of the band gap that is equal  $E_g = 4.1$  eV [7]. The changes of band gap energies can be achieved by doping of the  $\text{SrSnO}_3$  structure by the elements of transition metals (Cu, Mn, Fe) [8].

The commercially available brown inorganic pigments are based on the spinel or rutile structure, in which the colouring element is chromium [9–10]. Production of  $\text{Cr}^{3+}$  ions is problematic in terms of starting materials ( $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$ ) [11]; for example, rutile *Brown 24* (Cr-Ti-Sb) [12]. A brown pigment based on  $\text{Fe}_2\text{O}_3$  belongs to the most often used inorganic pigments in construction industry for colouring the building materials. Although, it is characterized by low thermal stability, it has found application as “cool pigment” because of a high NIR reflectivity [13]. This type of pigments reduces the surface temperature of roofs and walls of buildings [14].

A lack of the high-temperature stable brown inorganic pigments is one of the actual problems of the research of inorganic pigments. Therefore, it is appropriate to look for the respective substitutes in the form of nontoxic and pigment materials with high thermal stability. New studies of pigments deal with the research of brown pigments based on perovskite structure of  $\text{SrSnO}_3$  [15] and  $\text{BiFeO}_3$  [16–19]. These pigments can be suitable for commercial production.

In this work, the impact of mineralizers on the preparation of  $\text{SrSn}_{0.8}\text{Mn}_{0.2}\text{O}_3$  brown pigment has been studied and their effect on the quality of pigment from pigmentary properties point of view discussed.

## Materials and methods

### Synthesis

The perovskite pigments  $\text{SrSn}_{0.8}\text{Mn}_{0.2}\text{O}_3$  were prepared by classical ceramic method by using mineralizers. The starting materials, namely  $\text{SnO}_2$  (99 % w/w, Alfa Aesar, Karlsruhe, Germany),  $\text{SrCO}_3$  (99.9 %, Sigma-Aldrich, Milan, Italy), and  $\text{MnO}_2$  (99 %, Lachema, Brno, Czech Republic) were weighed in the molar ratio and homogenized with 5 % (w/w) mineralizers ([20–21],  $\text{Li}_2\text{CO}_3$ , NaF:NaCl (1:1), KCl,  $\text{K}_2\text{CO}_3$ :KCl (1:1), and  $\text{Na}_3\text{AlF}_6$ ) in a mortar (Pulverisette 2; Fritsch, Idar-Oberstein, Germany) for 10 min. Then, homogeneous mixtures were heated in electric furnace. The calcining process was carried out at temperatures of 950, 1050, 1200, and 1300 °C, with a heating rate of 10 °C  $\text{min}^{-1}$  for 4 hours and, then, gradually cooled down to laboratory temperature. Afterwards, the obtained pigments were further hand-milled in an agate mortar to homogenize the remaining agglomerates. Finally, the mineralizers were removed from the final products by decantation in 400 mL of hot distilled water (with conductivity 6.2–6.5  $\mu\text{S cm}^{-1}$  at laboratory temperature). The final dry samples were characterized in terms of pigmentary properties.

## Characterization of powders

The phase composition of powders was studied by X-ray diffraction analysis (XRD); the proper analysis being performed using by diffractometer (MiniFlex 600, Rigaku, Tokyo, Japan) equipped with a vertical goniometer of 15 cm, X-ray tube with Cu anode ( $U = 40$  kV,  $I = 15$  mA) and semiconductor detector D/TEX Ultra High Speed 1D. The range of  $2\theta$  was set in an interval of  $10$ – $80^\circ$  with a step scan of  $10^\circ \text{ min}^{-1}$ . The final diffractograms were evaluated with the aid of database PDF2.

For measurements of the particle size distribution (PSD), mastersizer 2000/MU (Malvern Instruments, Worcestershire, UK) was used. This apparatus enables to perform a volumetric distribution, when using laser diffraction on particles dispersed in a liquid medium. The device is equipped by two lasers: red light (He-Ne laser with wavelength of 633 nm) and blue light (laser diode with wavelength of 466 nm). The powders were homogenized in the solution of  $\text{Na}_4\text{P}_2\text{O}_7$  ( $c = 0.15 \text{ mol L}^{-1}$ ) in an ultrasonic bath for 120 s and with ultrasonic power  $0.89 \text{ W cm}^{-2}$ . The signal was evaluated based on Mie theory [22].

The colour properties of pigments were measured after their application into the dispersive acrylic binder (Luxol, Akzonobel coatings CZ, Opava, Czech Republic) in the mass tone. The mixture containing 0.4 g of the sample and  $1 \text{ cm}^3$  of binder was homogenized and transformed to a dense fluid-like paste. Coloured thin films were prepared by application of the paste on white non-absorbing glossy paper by using the Bird applicator with a slit width of  $100 \mu\text{m}$ . The colour parameters of the films were evaluated by measuring the spectral reflectance in the visible region (400–700 nm) by using a spectrometer UltraScan VIS (HunterLab, Reston, VA, USA). The measuring conditions were as follows: standard illuminant  $D_{65}$ ,  $10^\circ$  complementary observer, geometry of measurements  $d/8^\circ$ . The results were described in terms of CIE  $L^*a^*b^*$  system [23]. The value  $L^*$  represents the lightness or darkness of the colour and it is described by numbers from 0 (black) to 100 (white). In this system, a value of  $L^* = 50$  corresponds to the grey hue. The values  $a^*$  (the axis red-green) and  $b^*$  (the axis yellow-blue) then indicate the colour hue. The value  $C$  (Chroma) represents a saturation of the colour, determines the colour purity being expressed by the eqn. (1):

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

The total colour difference  $\Delta E_{\text{CIE}}^*$ , which indicates the degree of colour difference between the two samples, is defined by the following formula (2):

$$\Delta E_{\text{CIE}}^* = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} \quad (2)$$

where  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$  are differences in  $L^*$ ,  $a^*$  and  $b^*$  values between the colour sample and colour of standard.

The morphological properties were studied by scanning electron microscopy (SEM) realized in an ultra-high vacuum apparatus 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 chosen for SEM imaging.

## Results and discussion

### Colour characteristics

The impact of mineralizers on the colour properties of the perovskite pigments were studied based on their application into an organic binder (see Table 1). The pigment prepared without mineralizer (standard sample) had not the desired brown hue at calcining temperatures of 950 and 1050 °C caused by high values of the coordinate  $b^*$ . An interesting brown colour was achieved by calcination at a temperature of 1200 °C and higher. The colour coordinates  $a^*$  moved in the range of 2–7; the highest value being obtained by calcination at 1050 °C. The colour coordinates  $b^*$  had a decreasing intensity with the growing calcining temperature. The pigment synthesised in the presence of  $\text{Na}_3\text{AlF}_6$  and  $\text{NaF}:\text{NaCl}$  gave rise to a dark brown colour hue at all calcining temperatures. The use of  $\text{Na}_3\text{AlF}_6$  led to the formation of an interesting brown hue at the calcining temperature of 1050 °C and, in the case of  $\text{NaF}:\text{NaCl}$ , already at 950 °C. Mineralizer of  $\text{Li}_2\text{CO}_3$  formed different colour hue related to phase composition. This mineralizer exhibited the highest colour values  $a^*$  (21.6),  $b^*$  (34.7) and chroma  $C$  (40.1), when these values caused an orange-saturated colour hue. The mineralizers of  $\text{KCl}$  and  $\text{K}_2\text{CO}_3:\text{KCl}$  then provided very similar results. In the case of  $\text{KCl}$  and  $\text{K}_2\text{CO}_3:\text{KCl}$  mixture, a brown hue was formed at the temperature of 1050 °C and higher. From the Table 1, it is evident that the values of lightness  $L^*$  had decreased with the increasing temperature and it means that the pigments became darker. Also, the colour parameters  $a^*$  and  $b^*$  had a decreasing character with growth of the calcining temperature and they moved to the centre of colour cross, indicating that their colour shifted to a nearly black. The total colour difference between the pigments prepared with mineralizers in the reaction mixtures and without them is expressed by  $\Delta E_{\text{CIE}}^*$  values. For all the samples, high values of  $\Delta E_{\text{CIE}}^*$  occurred at temperatures of 950 and 1050 °C; here, caused by the high values of  $a^*$  and  $b^*$  coordinates of the standard sample. Pigments with  $\text{Li}_2\text{CO}_3$  provided of the highest value of the total colour difference  $\Delta E_{\text{CIE}}^*$  (35.1).

**Table 1** The effect of mineralizer on colour properties of the powders applied into the organic binder in mass tone

Mineralizer	$T$ [°C]	$L^*$	$a^*$	$b^*$	$C$	$\Delta E_{CIE}^*$
Standard pigment	950	51.32	3.30	16.42	16.73	–
	1050	36.66	7.41	10.91	13.17	–
	1200	29.31	3.43	3.63	4.95	–
	1300	27.66	2.45	2.08	3.19	–
$\text{Na}_3\text{AlF}_6$	950	31.32	3.80	6.86	8.68	21.78
	1050	29.81	4.50	6.49	7.91	8.64
	1200	28.20	4.71	4.42	6.44	1.89
	1300	26.88	3.24	2.13	3.83	1.12
$\text{NaF}:\text{NaCl}$ (1:1)	950	28.96	4.61	4.32	6.30	25.46
	1050	28.45	4.76	4.04	6.22	11.04
	1200	26.09	2.67	1.77	3.20	3.77
	1300	26.32	1.64	0.66	1.77	2.11
$\text{Li}_2\text{CO}_3$	950	56.15	21.06	32.44	38.68	24.41
	1050	59.09	20.12	34.72	40.13	35.10
	1200	41.67	14.67	19.43	24.35	23.03
	1300	31.02	5.27	5.44	7.57	5.54
$\text{KCl}$	950	38.50	4.09	8.73	12.42	13.67
	1050	33.29	4.43	8.06	9.20	5.31
	1200	28.56	3.90	3.54	5.27	0.90
	1300	26.97	1.70	0.73	1.85	1.69
$\text{K}_2\text{CO}_3:\text{KCl}$ (1:1)	950	31.11	4.69	7.37	7.91	22.60
	1050	29.95	4.00	4.57	6.07	9.83
	1200	27.46	3.05	3.08	4.33	1.95
	1300	26.83	2.07	1.73	2.70	0.97

### Particle size distribution

The colour properties of pigments are influenced by particle size distribution. Therefore, all the pigments prepared were investigated in terms of particle sizes; the most important characteristic of the particle size being the value  $d_{50}$ . From Table 2, it is evident that the calcining temperature and type of mineralizer affect both the particle size distribution. Value of  $d_{50}$  of all samples does not exceed limit of 6.5  $\mu\text{m}$ .

The results have shown that the lower values were achieved for a sample prepared without mineralizer at 1050 °C (1.32  $\mu\text{m}$ ) and sample prepared with the mixture KCl:K<sub>2</sub>CO<sub>3</sub> at a temperature of 1200 °C (1.15  $\mu\text{m}$ ). The biggest value of  $d_{50}$  was found out for the sample with Li<sub>2</sub>CO<sub>3</sub> (6.5  $\mu\text{m}$ ) which was caused by the sintering of powder during the calcination process and a reduction of parameter  $d_{50}$  by milling will thus be necessary. In general, the increase of calcination temperature enhances the  $d_{50}$  values, as well as the width of the particle size distribution. The pigments prepared from the reaction mixtures containing KCl mineralizer have the optimal particle size, more or less like standard pigments. The recommended values of  $d_{50}$  are *ca.* 2  $\mu\text{m}$  for application of the pigments into the organic matrix.

**Table 2** Particle size distribution of the pigments

Mineralizer	$T$ [°C]	$d_{10}$ [ $\mu\text{m}$ ]	$d_{50}$ [ $\mu\text{m}$ ]	$d_{90}$ [ $\mu\text{m}$ ]
standard pigment	950	0.48	1.52	12.50
	1050	0.49	1.32	11.78
	1200	0.59	1.51	5.48
	1300	0.89	1.87	4.06
Na <sub>3</sub> AlF <sub>6</sub>	950	0.74	1.93	8.71
	1050	0.84	2.10	9.04
	1200	1.03	2.63	8.49
	1300	1.17	3.23	8.99
NaF:NaCl	950	0.79	1.94	4.66
	1050	0.80	1.97	5.43
	1200	0.99	2.30	5.54
	1300	1.05	2.53	6.22
Li <sub>2</sub> CO <sub>3</sub>	950	0.66	2.58	16.07
	1050	0.66	2.55	18.64
	1200	0.82	4.02	28.41
	1300	0.92	6.49	28.39
KCl	950	0.59	3.04	11.76
	1050	0.53	2.58	11.46
	1200	0.56	1.92	12.86
	1300	0.62	1.56	14.06
K <sub>2</sub> CO <sub>3</sub> :KCl	950	0.50	1.78	9.34
	1050	0.48	1.53	8.42
	1200	0.47	1.15	3.48
	1300	0.64	1.63	5.49

## X-ray diffraction analysis

The results of phase composition of all calcined reaction mixtures are shown in Table 3. From the surveyed data, it is evident that the standard sample has not provided a single-phase product even at the highest calcining temperature. At temperatures of 950 °C and 1050 °C, four phases were detected in the standard sample: unreacted SnO<sub>2</sub> (JPDF 00-021-1250), SrMnO<sub>3</sub> (JPDF 00-024-1213), Sr<sub>2</sub>SnO<sub>4</sub> (JPDF 01-073-9233) and SrSnO<sub>3</sub> (JPDF 01-081-2514). At the temperatures 1200 °C and 1300 °C, the sample is composed only from two phases: SrSnO<sub>3</sub> as a major phase and SrMnO<sub>3</sub> as a minor constituent.

**Table 3** The influence of the mineralizer on phase composition of the pigments

Mineralizer	<i>T</i> [°C]	Detected phases
standard pigment	950	SnO <sub>2</sub> , Sr <sub>2</sub> SnO <sub>4</sub> , SrSnO <sub>3</sub> , SrMnO <sub>3</sub>
	1050	SnO <sub>2</sub> , Sr <sub>2</sub> SnO <sub>4</sub> , SrSnO <sub>3</sub> , SrMnO <sub>3</sub>
	1200	SrSnO <sub>3</sub> , SrMnO <sub>3</sub>
	1300	SrSnO <sub>3</sub> , SrMnO <sub>3</sub>
Na <sub>3</sub> AlF <sub>6</sub>	950	SrSnO <sub>3</sub> , SnO <sub>2</sub> , SrMnO <sub>3</sub>
	1050	SrSnO <sub>3</sub> , SnO <sub>2</sub> , SrMnO <sub>3</sub>
	1200	SrSnO <sub>3</sub>
	1300	SrSnO <sub>3</sub>
NaF:NaCl (1:1)	950	SrSnO <sub>3</sub> , SrMnO <sub>3</sub>
	1050	SrSnO <sub>3</sub> , SrMnO <sub>3</sub>
	1200	SrSnO <sub>3</sub>
	1300	SrSnO <sub>3</sub>
Li <sub>2</sub> CO <sub>3</sub>	950	SrSnO <sub>3</sub> , Li <sub>2</sub> MnO <sub>3</sub>
	1050	SrSnO <sub>3</sub> , Li <sub>2</sub> MnO <sub>3</sub>
	1200	SrSnO <sub>3</sub>
	1300	SrSnO <sub>3</sub>
KCl	950	SnO <sub>2</sub> , SrSnO <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub> , SrMnO <sub>3</sub>
	1050	SnO <sub>2</sub> , SrSnO <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub> , SrMnO <sub>3</sub>
	1200	SrSnO <sub>3</sub>
	1300	SrSnO <sub>3</sub>
K <sub>2</sub> CO <sub>3</sub> :KCl (1:1)	950	SnO <sub>2</sub> , SrSnO <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub> , SrMnO <sub>3</sub>
	1050	SnO <sub>2</sub> , SrSnO <sub>3</sub> , Mn <sub>3</sub> O <sub>4</sub> , SrMnO <sub>3</sub>
	1200	SrSnO <sub>3</sub>
	1300	SrSnO <sub>3</sub>

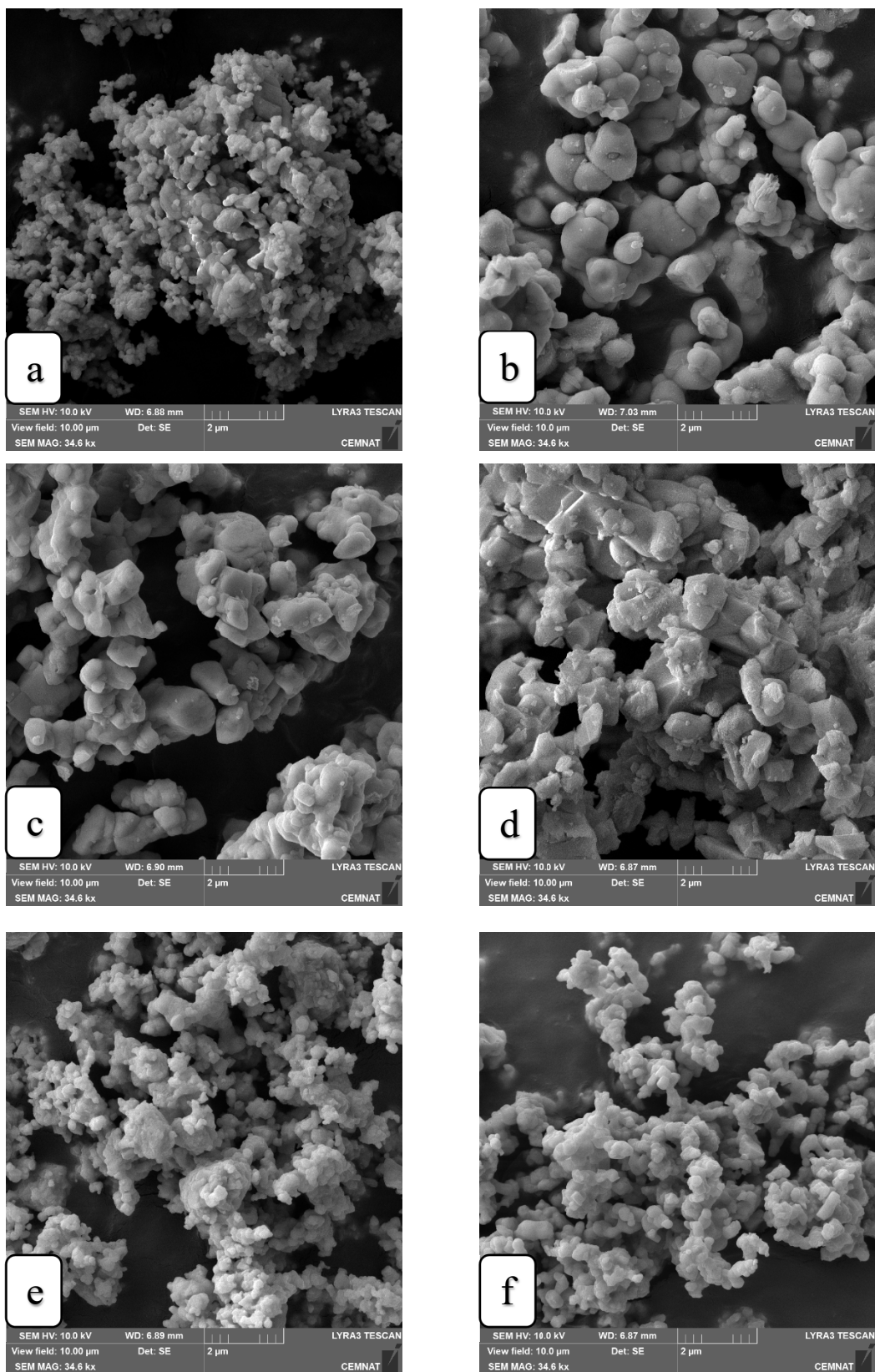
The sample  $\text{Na}_3\text{AlF}_6$  contains three phases at temperatures of 950 °C and 1050 °C (Table 3). The following phases were found out: unreacted  $\text{SnO}_2$  (JPDF 00-021-1250),  $\text{SrMnO}_3$  (JPDF 00-024-1213), and  $\text{SrSnO}_3$  (JPDF 01-081-2514). The sample  $\text{NaF}:\text{NaCl}$  provided two-phase systems at a temperature of 950 and 1050 °C respectively consisting of  $\text{SrSnO}_3$  and  $\text{SrMnO}_3$  phases. The pigment synthesised from  $\text{Li}_2\text{CO}_3$  contained also two phases at a temperature of 950 °C and 1050 °C, respectively, but the phase of  $\text{SnMnO}_3$  is missing. The main phase was  $\text{SrSnO}_3$ , whereas the second phase corresponded — rather surprisingly — to  $\text{Li}_2\text{MnO}_3$  (JPDF 01-081-1953).  $\text{KCl}$ -based mineralizer and the mixture of  $\text{K}_2\text{CO}_3:\text{KCl}$  gave rise to the same phase composition at all temperatures used. Four phases were detected at the temperature 950 and 1050 °C identified as unreacted  $\text{SnO}_2$ ,  $\text{SrSnO}_3$ ,  $\text{Mn}_3\text{O}_4$  (JPDF 01-080-0382), and  $\text{SrMnO}_3$ .

Finally, all mineralizers formed one-phased systems by calcination of the reaction mixtures at the temperatures 1200 °C and 1300 °C. It can be concluded that these high temperatures enable the entrance of manganese ions into the lattice of  $\text{SrSnO}_3$ .

## SEM analysis

Fig. 1 illustrates that the type of mineralizer influenced the morphology of the prepared pigments. The standard sample (see image 1a) can be characterised as elongated particles from which a small amount has exhibited irregular shape, whereas clusters with spherical particles occurred in the sample of  $\text{Na}_3\text{AlF}_6$  (Fig. 1b). Preparation with  $\text{NaF}:\text{NaCl}$  (Fig. 1c) then provided orthorhombic and spherical particles and irregular clusters of particles were observed in the sample with  $\text{Li}_2\text{CO}_3$  (Fig. 1d) forming distinct aggregates. A similar morphology as the standard sample was found in the samples with  $\text{KCl}$  (Fig. 1e) and  $\text{K}_2\text{CO}_3:\text{KCl}$  (1f).





**Fig. 1** SEM images of the pigments after calcination at 1200 °C  
a) standard pigment, b)  $\text{Na}_3\text{AlF}_6$ , c)  $\text{NaF}:\text{NaCl}$ , d)  $\text{Li}_2\text{CO}_3$ , e)  $\text{KCl}$ , f)  $\text{K}_2\text{CO}_3:\text{KCl}$

## Conclusions

The main aim of the research reported in this article was to prepare the  $\text{SrSn}_{0.8}\text{Mn}_{0.2}\text{O}_3$  perovskite pigment and verify the effect of mineralizer in the reaction mixture on its colour properties, phase composition, and particle size distribution. The X-ray diffraction analysis showed that mineralizers had a positive impact on the formation of single-phase product at the temperatures of 1200 °C and 1300 °C. The standard sample prepared without mineralizers had multiphase composition at all the calcination temperatures applied, when the phase composition itself affects the different colour of the prepared pigments.

The experimental observations can be summarised as follows. The mineralizer  $\text{Li}_2\text{CO}_3$  caused the highest contribution of red hue in the final colour, as well as the highest contribution of yellow hue. In the dependence of the growing calcining temperature, the final colour hue turns from a bright orange to bright brown. The use of mineralizers of  $\text{NaF}:\text{NaCl}$  and  $\text{Na}_3\text{AlF}_6$  gave rise to the formation of dark brown pigment at all calcining temperatures. Also  $\text{KCl}$  and  $\text{K}_2\text{CO}_3:\text{KCl}$  provided a brown hue at a temperature of 1050 °C and above.

From the results obtained, it can be concluded that higher calcination temperature stimulates the formation of generally darker powder pigments. Most of samples meet a given range of the mean particle size  $d_{50}$ , which is a necessary condition for the pigments to be applicable into the organic matrix. Samples prepared with  $\text{Li}_2\text{CO}_3$  is then necessary to mill.

In addition, it can be stated that the use of mineralizers in the synthesis of the  $\text{SrSn}_{0.8}\text{Mn}_{0.2}\text{O}_3$  perovskite pigment reduces the required calcining temperature when forming an interesting dark brown pigment of the single-phase composition. The mineralizer of choice for the synthesis of the  $\text{SrSn}_{0.8}\text{Mn}_{0.2}\text{O}_3$  pigment seems to be the mixture of  $\text{NaF}:\text{NaCl}$  and the calcining temperature of 950 °C. These reaction conditions allow one the formation of the pigment of attractive brown hue with low particle size values ( $d_{50}$  and  $d_{90}$ ).

## Acknowledgement

*This research has been supported by University of Pardubice, Czech Republic under the project SGS\_2020\_008. Also, the authors appreciate financial support from the Ministry of Education, Youth and Sports of the Czech Republic (project No. LM2018103) and from the European Regional Development Fund-Project “Modernization and Upgrade of the CEMNAT” (No. CZ.02.1.01/0.0/0.0/16 013/0001829).*

## References

- [1] Lu L., Ni S., Liu G., Xu X.: Structural dependence of photocatalytic hydrogen production over La/Cr doped perovskite compound  $\text{ATiO}_3$  (A = Ca, Sr, Ba). *International Journal of Hydrogen Energy* **42** (2017) 23539–23547.
- [2] Zhang F.W., Yin Z., Zhang S.M., Du L.Z., Chen C. W.: Roles of defects and grain sizes in photoluminescence of nanocrystalline  $\text{SrTiO}_3$ . *Journal of Physics: Condensed Matter* **11** (1999) 5655–5660.
- [3] Lobo M.T., Lebullenger R., Bouquet V., Guilloux-Viry M., Santos I.M.G., Weber I.T.:  $\text{SrSnO}_3\text{:N}$  – nitridation an evaluation of photocatalytic activity. *Journal of Alloys and Compounds* **649** (2015) 491–494.
- [4] Zhang F.W., Tang J., Ye J.: Photoluminescence and photocatalytic properties of  $\text{SrSnO}_3$  perovskite. *Chemical Physics Letter* **418** (2006) 174–178.
- [5] Souza C.S., Santos G.M.I., Silva S.R.M., Cassia-Santos M.R., Soledade L.E.B., Souza A.G., Lima S.J.G., Longo E.: Influence of pH on iron doped  $\text{Zn}_2\text{TiO}_4$  pigments. *Journal of Thermal Analysis and Calorimetry* **79** (2005) 451–454.
- [6] Alves F.C.M., Souza C.S., Lima H.H.S., Nascimento M.R., Silva M.R.S., Espinosa J.W.M., Lima S.J.G., Longo E., Pizani P.S., Soledade L.E.B., Souza A.G., Santos I.M.G.: Influence of the modifier on the short and long range disorder of stannate perovskites. *Journal of Alloys and Compounds* **476** (2009) 507–512.
- [7] Mizoguchi H., Eng W.H., Woodward M.P.: Probing the electronic structures of ternary perovskite and pyrochlore oxides containing  $\text{Sn}^{4+}$  or  $\text{Sb}^{5+}$ . *Inorganic Chemistry* **43** (2004) 1667–1680.
- [8] Melo D., Marinho R.M.M., Vieira F.T.G., Lima S.J.G., Longo E., Souza A.G., Maia A.S., Santos I.M.G.: Influence of Cu (II) in the  $\text{SrSnO}_3$  crystallization. *Journal of Thermal Analysis and Calorimetry* **106** (2011) 513–517.
- [9] Ozel E., Unluturk G., Turan S.: Production of brown pigments for porcelain isulator applications. *Journal of the European Ceramic Society* **26** (2006) 735–740.
- [10] Matteucci F., Cruciani G., Dondi M., Raimondo M.: The role of counterions (Mo, Nb, Sb, W) in Cr-, Mn-, Ni- and V-doped rutile ceramic pigments: Part 1. Crystal structure and phase transformations. *Ceramics International* **32** (2006) 385–392.
- [11] Shanker K.A., Cervantes C., Loza-Tavera H., Avudainayagam S.: Chromium toxicity in plants. *Environment International* **31** (2005) 739–753.
- [12] Dohnalová Ž., Bělina P., Šulcová P., Gorodylova N., Vlček M.: Brown pigments based on perovskite structure of  $\text{BiFeO}_{3-\delta}$ . *Journal of Thermal Analysis and Calorimetry* **133** (2018) 421–428.
- [13] Thongkanluang T., Limsuwan P., Chirakanphaisarn N.: Preparation of NIR reflective brown pigment. *Procedia Engineering* **32** (2012) 895–901.
- [14] Yuan L., Han A., Ye M., Chen X., Yao L., Ding C.: Synthesis and characterization of environmentally benign inorganic pigments with high NIR reflectance: Lanthanum-doped  $\text{BiFeO}_3$ . *Dyes and Pigments* **148** (2018) 137–146.
- [15] Hroch J., Dohnalová Ž.: Perovskite pigments based on  $\text{SrSn}_{1-x}\text{Mn}_x\text{O}_3$ . *Scientific Papers of the University of Pardubice, Series A* **25** (2019) 65–74.

- [16] Luxová J., Šulcová P.: The Effect of partial substitution of Bi on colour properties and thermal stability of  $\text{Bi}_x\text{Pr}_{1-x}\text{FeO}_3$  pigments. *Journal of Thermal Analysis and Calorimetry* **138** (2019) 4303–4312.
- [17] Opuchovic O., Kreiza G., Senvaitiene J., Kazlauskas K., Beganskiene A., Kareiva A.: Sol-gel synthesis, characterization and application of selected sub-microsized lanthanide (Ce, Pr, Nd,Tb) ferrites. *Dyes and Pigments* **118** (2015) 176–182.
- [18] James V., Prabhakar P.R., Sameera S., Divya S.: Multiferroic based reddish brown pigments:  $\text{Bi}_{1-x}\text{M}_x\text{FeO}_3$  (M=Y and La) for colouring applications. *Ceramics International* **40** (2014) 2229–2235.
- [19] Liu L., Han A., Ye M., Zhao M.: Synthesis and characterization of  $\text{Al}^{3+}$  doped  $\text{LaFeO}_3$  compounds: a novel inorganic pigment with high near-infrared reflectance. *Solar Energy Materials and Solar Cells* **132** (2015) 377–384.
- [20] Dohnalová Ž., Šulcová P., Vontorčíková M.: Colour possibilities of rare earth orthoferrite pigments. *Scientific Papers of the University of Pardubice, Series A* **18** (2012) 105–115.
- [21] Dohnalová Ž., Šulcová P., Gorodylova N.: Study of ceramic pigments based on cobalt doped  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  system. *Journal of Thermal Analysis and Calorimetry* **116** (2014) 647–654.
- [22] de Boer G.B.J., de Weerd C., Thoenes D., Goossens H.W.J.: Laser diffraction spectrometry: Fraunhofer diffraction versus Mie scattering. *Particle Characterization* **4** (1987) 14–19.
- [23] Völz H.G.: *Industrial color testing: Fundamentals and techniques*, Second edition. Wiley-VCH, Weinheim 2002.