

PREPARATION OF TRANSITION METALS DOPED SrSnO₃

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Present work deals with the synthesis and evaluation of physical and chemical properties of SrSn_{1-x}A_xO₃ perovskite pigments, where A represents doping elements - Fe, Mn, V. These compounds were prepared by modified solid state synthesis at high temperature. The main attention was focused to observing the colour properties of the prepared compounds and their sun light resistance. Also thermal stability, particle morphology and granulometric composition of the pigments were analysed.

Keywords: *perovskite, ceramic pigments, solid state reaction*

Introduction

In recent years, legislation and society have placed great emphasis on the environmental aspects of chemical productions. The production of inorganic pigments is no exception and their ecological and hygienic safety is being examined. Current worldwide research in the field of inorganic pigments is directed by three basic directions that are characterized by 3E: efficiency, economics and ecology [1]. The quality of inorganic pigments is dictated by their properties and characteristics, which are collectively referred to as pigment application properties [2,3]. The most important characteristics in terms of use of powder materials as inorganic pigments are physico-chemical and technological properties. An important parameter is their colour. Some other physical properties, such as particle size and shape, refractive index, and others are also related to colour properties. Particularly useful in terms of dispersibility of pigments for different application environments, particle size distribution, specific gravity and critical volume concentration of pigments are important indicators. From the application point of view, thermal stability determining the suitability of pigments for high temperature applications in ceramic glazes and enamels [4] and resistance to sunlight and weather conditions are also important indicators [5].

For a long time, the research of the Department of Inorganic Technology of the University of Pardubice has focused on the environmentally safe synthesis routes and at the same time on the synthesis of thermally and chemically stable inorganic pigments that could replace the previously used pigments with not very attractive environmental impacts. In the present work new mixed metal oxides with perovskite structure were synthesized by solid state reaction and their potential use as the inorganic pigments were tested.

Experimental part

The perovskite compounds of general formula SrSn_{1-x}A_xO₃ (where A = Fe, Mn, V and x = 0.05-0.2) were prepared by modified solid-state reaction at high heating temperatures using SrC₂O₄, SnC₂O₄ and dopants in form of Fe₂O₃, V₂O₅, MnCO₃ as initial materials [6]. In a typical synthesis initial reagents and surfactant polyethylene glycol (PEG)-400 were put in a mortar grinder (Pulverisette 2, Fritsch GmbH, Germany), and the mixture was fully ground for 30 min. The reaction mixture gradually became damp, and then a paste formed quickly. The reaction mixture was kept at room temperature for 24 h. Nanocrystalline powders with perovskite structure were obtained via calcining at 950 -1300 °C for 12 hours.

The phase composition of the calcination products was studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using a MiniFlex 600 diffractometer (Rigaku, Japan) working in Bragg-Brentano ($\theta/2\theta$) geometry with 1D d/teX Ultra: silicon strip detector and K β filter. The data were collected within 2 θ angle from 10-80 ° at a step size of 0.02 ° and speed of 10 °.min⁻¹ using CuK α line. CuK α_1 ($\lambda=0.15418$ nm) radiation was used for the angular range of 2 θ < 35° and CuK α_2 ($\lambda=0.15405$ nm) for the range of 2 θ >35 °. The identification of individual phases was based on the matching of the obtained diffraction patterns with the data contained in the JCPDS database [7].

The thermal stability of final pigments was tested using a heating microscope EM201-15 (Hesse Instruments, Germany). The samples in form of tablets were gradually heated from room temperature to 1500 °C and a change of sample areas were detected. The heating rate was 10 K.min⁻¹.

Particle size distribution of the samples was measured using a Mastersizer 2000/MU (Malvern Instruments, UK). The equipment employs a scattering of incident light on particles. The signal was evaluated on the basis of Mie theory. Specific surface area was evaluated based on BET isotherm by equipment NOVA 1200e (Quantachrome Instruments, Germany).

The colour properties of all prepared pigments were objectively evaluated by measuring of spectral reflectance using a spectrophotometer ColourQuerst XE (HunterLab, USA). The measurement conditions were the following: an illuminant D65, 10° complementary observer and measuring geometry d/8°. The colour properties of the samples were estimated in terms of the CIE L*a*b* system.

The assessment of resistance to day light of coloured pigments was tested according to the general methods of the test for pigments described in ISO standard 787-15:1986. The samples were exposed to simulated sunlight in a Q-Sun Xenon Test Chamber, model Xe 1 (Lab. Products, USA) for 456 h at 0.51 W.m⁻²@ 340 nm.

Results and discussion

The results of XRD analysis of the samples SrSn_{0.95}A_{0.05}O₃ (A=Fe, Mn, V) after calcination at 950 °C indicate that solid state reaction between initial reagents does not result in a single-phased system (Table 1). The SrSn_{0.95}Fe_{0.05}O₃ powder after calcination at 950 °C contains rest of the unreacted reagent such as SnO₂ and besides the perovskite SrSnO₃ phase contains also spinel phase Sr₂SnO₄. Increase the calcining temperature at 1200 °C is connected with the decomposition of spinel

phase and formation of SrSnO₃ type solid solution. Although diffraction lines of any Fe compound were not detected at the diffractograms, it is supposed that the Fe ions were built into the perovskite structure. Lattice parameters of the solid solution SrSn_{0.95}Fe_{0.05}O₃ after calcination at 1300 °C are: a = 0.57000 nm, b = 0.80608 nm and c = 0.57002 nm. In the case of synthesis of the SrSn_{0.95}Mn_{0.05}O₃, the situation was almost analogous. While the calcining temperature 950 °C brought synthesis of two perovskite phases SrSnO₃ and SrMnO₃ (Table 1), increase of temperature at 1200 °C caused formation of single phase solid solution SrSn_{0.95}Mn_{0.05}O₃ with lattice parameters a = 0.57010 nm, b = 0.80625 nm a c = 0.57013 nm. Partial substitution of Sn ions by V ions in perovskite structure of strontium stannate led to the formation of two or three phase systems (Table 1).

Table 1 The effect of calcining temperature on phase composition of powders

Pigment	Temperature [°C]	Detected phases
SrSn _{0.95} Fe _{0.05} O ₃	950	SnO ₂ , Sr ₂ SnO ₄ , SrSnO ₃
	1200	SrSnO ₃ type solid solution
	1300	SrSnO ₃ type solid solution
SrSn _{0.95} Mn _{0.05} O ₃	950	SrSnO ₃ , SrMnO ₃
	1200	SrMnO ₃ type solid solution
	1300	SrMnO ₃ type solid solution
SrSn _{0.95} V _{0.05} O ₃	950	SrSnO ₃ , Sr ₂ VO ₄ , VO ₂ and SnO ₂
	1200	SrSnO ₃ , VO ₂
	1300	SrSnO ₃ , Sr ₃ V ₂ O ₇ , Sr ₂ VO ₄

The results of colour parameters of powdered pigments (after calcination at 1300 °C) and the effect of sunlight irradiation on their change are summarised in Table 2. Light stability of pigments is defined as the resistance of materials to discoloration caused by the action of direct sunlight. The change of the colour properties of the powders is expressed by values of total colour difference after exposition to a radiation load of 315 kJ.m⁻², respective 664 kJ.m⁻². Colour of SrSn_{0.95}Fe_{0.05}O₃ pigment is khaki green. An exposition of the powder to sunlight irradiation caused its darkening, decrease amount of green colour hue and increase of yellow colour hue. The total colour difference of powder (ΔE^*_{CIE}) after irradiation is higher than 1.5 and it expresses that the colour change is easy visible. Colour of the pigment SrSn_{0.95}Mn_{0.05}O₃ is dark brown. The colour of this pigment is very resistant to sunlight action and its change after irradiation is not perceptible by human eye. The total colour difference value after exposure to sunlight radiation (ΔE^*_{CIE}) is less than 0.5. The less attractive colouration of host perovskite structure was obtained by partial substitution of tin ions by vanadium ions. Colour of the powder is very light yellow-beige and its resistant to sunlight irradiation is also very bad ($\Delta E^*_{CIE} > 6$). The

origin of less attractive colour properties of vanadium doped perovskite SrSnO₃ is its multi-phase composition. In the past, SrSn_{0.95}V_{0.05}O₃ pigment was prepared by classical ceramic route and subsequent calcination of initial reaction mixture (SrCO₃, SnO₂ and V₂O₅) at high temperature. Colour of the pigment prepared by such route was intense yellow [8].

Table 2 The effect of sunlight irradiation on the change of colour parameters of powders

Pigment	Time [h]	H [kJ.m ⁻²]	L*	a*	b*	ΔE* _{CIE}
SrSn _{0.95} Fe _{0.05} O ₃	0	0	68.25	-2.18	13.12	—
	216	314.7	67.07	-1.42	14.14	1.74
	456	664.20	66.28	-1.08	14.10	2.46
SrSn _{0.95} Mn _{0.05} O ₃	0	0	50.47	10.26	14.09	—
	216	314.7	50.12	10.54	13.93	0.48
	456	664.20	50.15	10.47	13.91	0.42
SrSn _{0.95} V _{0.05} O ₃	0	0	86.00	-0.53	6.69	—
	216	314.7	79.68	1.28	7.43	6.62
	456	664.20	79.18	1.47	7.33	7.14

Technological important properties such as particle size, specific surface area and thermal stability of powder are summarised in Table 3. Particle sizes of pigments less than 10 μm is optimum for applications of pigment to organic binder system and also for application into ceramic glazes. Wider particle size distribution of V doped SrSnO₃ can be done by the multi-phase composition of sample. Thermal stability of powders was measured by heating microscope. The sintering of powders started at temperature higher than 1250 °C. High thermal stability of pigments predicts that the powders SrSn_{0.95}Fe_{0.05}O₃ and SrSn_{0.95}Mn_{0.05}O₃ can be used for colouration of ceramic glazes.

Table 3 Granulometric composition, specific surface area and thermal stability of powders

Pigment	d ₅₀ [μm]	d ₁₀ - d ₉₀ [μm]	S _{BET} [m ² .g ⁻¹]	T _{sint} [°C]
SrSn _{0.95} Fe _{0.05} O ₃	0.60	1.77-9.91	3.46	1270
SrSn _{0.95} Mn _{0.05} O ₃	0.63	2.34-9.24	2.04	1250
SrSn _{0.95} V _{0.05} O ₃	0.91	5.30-33.70	0.77	1260

Conclusion

Present work contains results related to the synthesis of perovskite pigments based on structure of SrSnO₃ in which a part of Sn⁴⁺ ions was substituted by iron, manganese and vanadium ions. The pigments were synthesized by modified solid state reaction between strontium and tin oxalates and transition metal oxides in the presence of surfactant polyethylene glycol. Formation of single phase solid solution in the case of Fe and Mn substitution was detected after calcination at 1200 °C.

Colour of $\text{SrSn}_{0.95}\text{Fe}_{0.05}\text{O}_3$ powder is khaki green and pigment $\text{SrSn}_{0.95}\text{Mn}_{0.05}\text{O}_3$ is dark brown. Preparation of $\text{SrSn}_{0.95}\text{V}_{0.05}\text{O}_3$ perovskite pigment by this synthesis route was not successful. Thermal stability and particle size distribution of powders are suitable for testing of pigments for colouration of ceramic glazes.

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