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Study of Compounds Based on $SrM_xSn_{1-x}O_{3\pm x/2}$

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Abstract

Inorganic pigments of $SrM_xSn_{1-x}O_{3\pm x/2}$ type (where M = V, Cr), based on a pseudo cubic structure of $SrSnO_3$, have been prepared by the solid state reaction between $SrCO_3$, SnO_2 and oxides V_2O_5 or Cr_2O_3 in the temperature range 1300-1500°C with nominal compositions: x = 0.05, 0.1, 0.3. The resultant materials were characterised by XRD, TG-DTA, and colourimetric techniques were used. The pigments containing vanadium as chromophore give creamy, sand and yellow colour into an organic matrix. The increase of temperature caused the creation of pigments with deeper and brighter colour hue. The presence of chromium in compounds produces colour hues from reddish brown to brown. The compounds with higher content of chromium have the lower chroma colour hue.

Keywords: Stannate, Perovskite structure, Solid state reaction, Colour properties, Particle size

BADANIA NAD ZWIĄZKAMI OPARTYMI NA $SrM_xSn_{1-x}O_{3\pm x/2}$

Pigmenty nieorganiczne typu $SrM_xSn_{1-x}O_{3\pm x/2}$ (gdzie M = V, Cr), oparte na pseudo-regularnej strukturze $SrSnO_3$, o nominalnym składzie: x = 0,05, 0,1, 0,3, zostały przygotowane za pomocą reakcji w stanie stałym pomiędzy $SrCO_3$, SnO_2 i tlenkami V_2O_5 lub Cr_2O_3 w zakresie temperatury 1300–1500°C. Otrzymane materiały scharakteryzowano za pomocą metod XRD, TG-DTA, wykorzystano też technikę kolorymetryczną. Pigmenty zawierające wanad jako chromofor dają w organicznej matrycy kolory śmietankowy, piaskowy i żółty. Wzorst temperatury spowodował powstanie pigmentów o głębszym i jaśnieszym odcieniu. Obecność chromu w związkach wywoływała odcienie od brązowo-czerwonawego do brązowego. Związki z wyższą zawartością chromu miały odcień o mniejszym nasyceniu barwy.

Keywords: cyniany, struktura perowskitu, reakcja w stanie stałym, właściwości barwne, rozmiar cząstki

1. Introduction

Perovskite structures have a simple crystalline structure, which includes different symmetries, with cubic, tetragonal or orthorhombic unit cells, besides these distorted cells [1].

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 [2].

Simple method of synthesis of these compounds is based on the solid state reaction between SnO_2 and $SrCO_3$ or SrO [3, 4], 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 [5]. 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 [6, 7], and calcium stannate has also been prepared by polymeric precursor method, also known as the Pechini method [8].

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 [9]. 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 [10]. Strontium stannate, for instance, has been used as humidity sensor [11]. Structural phase transitions in $SrSnO_3$ have also been studied from the viewpoint of photocatalytic and photoluminescence activities [12], especially luminescence of Eu^{3+} ions in these host materials has been investigated [13].

In the present study, the new pigments having the formula $SrM_xSn_{1-x}O_{3\pm x/2}$ with various chromium and vanadium concentration levels have been prepared as potential ecological inorganic pigments. Their colour properties have been investigated.

2. Experimental

Our research is directed to perovskite compounds of $SrM_xSn_{1-x}O_{3\pm x/2}$ type where M = V and Cr. Samples in the doped strontium stannate, $SrV_xSn_{1-x}O_{3+x/2}$ and $SrCr_xSn_{1-x}O_{3-x/2}$, were prepared by solid state ceramic method. Mixed ox-

ides $SrM_xSn_{1-x}O_{3\pm x/2}$ with nominal compositions x = 0.05, 0.1 and 0.3 have been prepared. The compounds used for preparation of these materials were V_2O_5 or Cr_2O_3, SnO_2 and $SrCO_3$ (95% of purity). Stoichiometric amounts of respective compounds were mixed in a porcelain mortar. The mixtures were calcinated in corundum crucibles in an electric resistance furnace. The heating of the furnace was programmed with increasing temperature at a rate of 10°C·min^{-1} and the calcination temperature of 1300, 1400 or 1500°C was maintained for three hours.

The calcinated powder samples were applied to an organic matrix in mass tone. The final paints were evaluated for colour change by measuring spectral reflectance in the visible region of light (400–700 nm) using a ColorQuest XE (HunterLab, USA). The measurement conditions were following: illuminant D65, 10° complementary observer and measuring geometry *d*/8°. The colour properties are described in terms of CIE *L*a*b** system (1976). The value *a** (the red-green axis) and *b** (the yellow-blue axis) indicate the colour hue. The value *L** represents the lightness or darkness of the colour as related to the natural grey scale. In the *L*a*b** system, it is described by numbers from zero (black) to hundred (white). The value *C* (Chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The total colour difference ΔE^*_{CIE} in the CIE *L*a*b** diagram, which indicates the degree of colour difference between the two samples, is defined by the following equation: $\Delta E^*_{CIE} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, were ΔL^*, Δa^*, Δb^* are differences in *L**, *a**, and *b** values between the sample colour and the standard colour. It is also possible to express the colour of pigment as a hue angle ($H° = \text{arctg}\,(b^*/a^*)$) [9].

The crystal structures of the powder materials were studied by X-ray diffraction analysis. Diffractograms of the samples were obtained by using a Brucker (GB) diffractometer D8 Advance (Bruker, GB) with a goniometer of 17 cm in the 2Θ range of 10-80°. $CuK_{\alpha 1}$ (λ = 0.15418 nm) radiation was used for the angular range of 2Θ < 35° and $CuK_{\alpha 2}$ (λ = 0.15405 nm) for the range of 2Θ > 35°. A scintillation detector was used.

The particle size distribution of the samples was measured by equipment of Mastersizer 2000/MU (Malvern Instruments, GB). It is a highly integrated laser measuring system for analysis of a particle size distribution. The equipment uses the scattering of incident light on particles. The solids were homogenized for 90 s by ultrasonic devices and measured in solution of $Na_4P_2O_7$ (c = 0.15 mol·dm^{-3}). The signal was evaluated on the base of Fraunhofer bending.

Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (NETZSCH, Germany). The reaction mixtures of initial reagents before heating were studied by thermal analysis within the temperature range of 35–1300°C, under the air atmosphere, using corundum crucibles and the heating rate of 10 K·min^{-1}. α-Al_2O_3 was used as a reference material.

3. Results and discussion

Colour properties are the most important characteristic of inorganic pigments. The influences of heating temperature and used doping V and Cr ions on the colour properties of the samples were followed. Initially, the influence of the V content in the starting mixtures and calcination temperature on the colour hue of the pigment was studied. The prepared powder materials were applied to an organic matrix. Generally, the increase of temperature caused the creation of pigments with deeper and brighter colour hue (Table 1). Based on values *a** and *b** of pigments, it can be seen that the growing of heating temperature increases the colour value *b** (yellow hue) and the value *C* (Chroma). The value of brightness *L**, the value *a** and colour hue *H°* alternately falling and rising. It means that the samples change their colour hue from cream to bright yellow colour (1300–1500°C). Optical properties of the compounds and also their application preferences are determined by their particle size distribution (PSD). The values of d_{50} of the powder compounds are given in Table 1. The mean value of d_{50} increases from 5.16 μm to 17.19 μm in relation to the growing heating temperature that causes the mild sintering of samples, particularly, at the temperature of 1500°C. The size range (5.16–17.19 μm) predicts the effective utilization of the pigments for colouring of ceramic glaze or coating composition. In case of need to colour plastics, the particle size distribution has to be reduced. In that event the mean value of d_{50} should not exceed the limit of 2 μm.

The crystal structure of prepared powder materials were studied by X-ray diffraction analysis. Two - phase systems have been identified at the diffractograms of samples $SrV_{0.025}Sn_{0.975}O_{3+x/2}$ prepared by calcining at 1475°C (Fig. 1). All peaks of high intensity can be assigned to compound $SrSnO_3$, peaks of low intensity were identified as a compound $Sr_3(VO_4)_2$. The X-ray diffraction analysis certifies that these new materials have orthorhombic crystal structure. In the

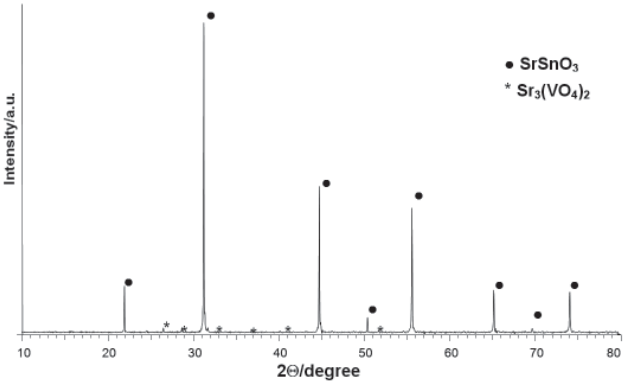

Fig.1. X-ray diffraction pattern of $SrV_{0.025}Sn_{0.975}O_{3+x/2}$ pigment calcinated at 1475°C.

Table 1. Colour properties of pigments $SrSn_{1-x}V_xO_{3+x/2}$ applied into organic matrix in mass tone.

T [°C]	x	d_{50} [μm]	*L**	*a**	*b**	*C*	*H°*
1300	0.05	5.67	88.97	-1.62	18.33	18.40	95.05
	0.1	5.19	86.79	-0,92	25.14	25.16	92.10
	0.3	5.16	82.09	2.38	26.95	27.05	84.95
1400	0.05	8.96	85.76	-0.24	37.95	37.95	90.36
	0.1	7.96	85.20	0.21	38.00	38.00	89.68
	0.3	9.11	90.65	3.24	32.68	32.85	84.33
1500	0.05	16.10	77.95	4.19	50.08	50.25	85.22
	0.1	17.19	79.49	1.83	44.26	44.30	87.63
	0.3	12.37	76.13	1.56	33.05	33.09	87.30

pigmentary field it is not always necessary to obtain single phase system but the conditions of synthesis have to be appropriate for the industrial occupancy.

The chromium ion forms the pigment of reddish brown colour in whole temperature range, but the increasing of temperature is reflected in formation of darker and less bright colour hue. The highest values of coordinates *a** (red hue), *b** (yellow hue) and the highest value of brightness *L** were obtained by heating at temperature 1300°C (Table 2). The increasing of heating temperature decreases the colour values *L**, *a**, *b** and the value *C* (Chroma). The most appropriate heating temperature for synthesis of the pigment and therefore, for preparation of reddish brown colour hue of pigment, is temperature 1300°C. The values of particle sizes of the prepared pigments are show in Table 2. The mean particle size of the samples is about from 2 μm to 7 μm, which is optimal for colouring of coating composition and ceramic glazes.

Table 2. Colour properties of pigments $SrSn_{1-x}Cr_xO_{3-x/2}$ applied into organic matrix in mass tone.

T [°C]	x	d_{50} [μm]	*L**	*a**	*b**	*C*	*H°*
1300	0.05	3.40	40.88	16.83	2.60	16.35	12.51
	0.1	3.46	35.36	15.49	3.04	14.32	12.17
	0.3	5.87	33.23	9.03	2.22	10.20	18.22
1400	0.05	2.61	38.37	13.23	1.24	15.72	12.49
	0.1	2.00	34.02	14.21	2.86	13.87	13.16
	0.3	6.99	28.97	8.24	1.72	8.00	15.51
1500	0.05	3.07	36.11	10.61	1.43	13.55	10.46
	0.1	2.08	33.17	11.22	1.69	11.68	12.66
	0.3	4.40	28.60	7.62	1.94	5.57	7.94

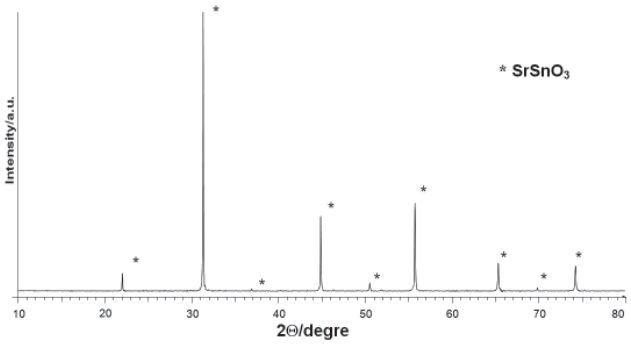

Fig. 2. X-ray diffraction pattern of $SrCr_{0.05}Sn_{0.95}O_{3-x/2}$ pigment calcinated at 1300°C.

The structure of the $SrSn_{1-x}Cr_xO_{3-x/2}$ pigment was also investigated by X-ray diffraction analysis. The X-ray pattern of this powdered material is given in Fig. 2. The structural properties of samples prepared by calcining at higher temperature (1300–1500°C) were studied. One-phase systems have already been identified at the diffractograms of samples prepared by calcining at 1300°C. Prepared samples have orthorhombic perovskite structure.

4. Conclusion

The main aim of the research was to prepare new stannate compounds which can be used as inorganic pigments. The compounds $SrM_xSn_{1-x}O_{3\pm x/2}$, where M = V and Cr, were synthesized. The presence of vanadium ions makes interesting hue of prepared solid solution. Calcination after firing at 1300°C gives the pigment with a creamy shade, but increasing of temperature changes the shade to bright yellow at 1500°C. The content of chromium ions forms the pigment of vinous, violet and reddish brown colour. The most interesting colour properties were provided by the compound $SrCr_{0.05}Sn_{0.95}O_{3-x/2}$, prepared by firing at 1300°C, producing a reddish brown colour hue. The increase of temperature caused the creation of pigments with deeper and brighter colour hue. Generally, prepared perovskite pigments are characterized by a high covering capacity, resistant to heat and represent potential inorganic pigments with interesting colour hues.

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