

COLOR PROPERTIES OF PIGMENTS BASED ON YMnO_3

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Abstract

Inorganic pigments of the type $\text{YMn}_x(\text{CuSn})_{1-x}\text{O}_{3\pm\delta}$ and $\text{YMn}_x(\text{NiSn})_{1-x}\text{O}_{3\pm\delta}$, where $x = 0.9; 0.5, 0.1$, were prepared by wet mechanical activation. Influence of composition and calcination temperature on the color properties, particle size distribution and phase purity was examined. Pigments were applied into the ceramic glaze and organic matrix. With the calcination temperature increasing from 1000 °C to 1200 °C and with decreasing content of Mn the color of the powders is changing from black to dark green in case of (CuSn) and from black to dark brown in case of (NiSn). Particle size distribution (PSD) of samples varies in the interval suitable for pigment applications. A complete solid solution (hexagonal YMnO_3) was obtained only in the case of $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$. The effect of mineralizers (AlF_3 ; Na_3AlF_6 ; H_3BO_3 ; Na_2CO_3) on color properties and phase composition was also investigated. Prepared powders were compared with the industrially produced pigments.

Key words: perovskite structure; mineralizers, color properties; ceramic pigment; particle size distribution, XRD analysis

Introduction

Compounds with the general formula ABO_3 can exhibit a wide range of structure types including perovskite, corundum and ilmenite. In addition to this structural variability, many ABO_3 samples exhibit special physical properties such as superconductivity or magnetoresistivity [1]. One of the few classes of materials that exhibits both ferroelectricity and magnetic order is the RMnO_3 system ($R = \text{Ho-Lu}$, and Y) [2]. The hexagonal YMnO_3 is one of the most intensively studied manganates and may be considered the example of material, where the ferroelectricity is a secondary outcome of a structure, rather than an electronic instability. This structure type is relatively rare amongst ABO_3 oxides and attracts attention as a promising material with application potentials [3-5]. These new compounds can be an alternative to currently used pigments due to their lower impact on the environment and their stability [6]. The structure of YMnO_3 with the space group $\text{P6}_3\text{cm}$ is constituted by non-connected layers of MnO_5 , where each Mn ion is surrounded by three oxygen in plane and two apical oxygen ions forming a trigonal bipyramids, which are two dimensionally connected to each other through corners and separated by a layer of Y^{3+} ions [7-9]. Manganites with the general formula RMnO_3 , where R denotes rare-earth cation, can be found within two crystal symmetries: a perovskite orthorhombic structure, when the R cation has a large ionic radius, on the other hand, when the rare-earth has a small ionic radius ($R=\text{Ho-Lu}$, including Y and Sc),

manganites crystallize in a hexagonal structure [10,11]. In last few years, several attempts have been carried out to minimise the negative environmental effects of toxic elements in pigments. Therefore, the search for pigments with intense hue, which are environmentally benign and do not contain any volatile elements, is an important issue [9,12].

The aim of this research was to figure out an influence of calcination temperature and composition on color properties of pigments $YMn_x(MSn)_{(1-x)}O_{3\pm\delta}$ ($x = 0.9; 0.5; 0.1$; $M = Cu$ or Ni). All samples have been prepared by wet mechanical activation and besides the color properties particle size distribution (PSD), phase purity and the effect of mineralizers on these properties have been studied.

Experimental

The pigments $YMn_x(CuSn)_{1-x}O_{3\pm\delta}$ and $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$, where $x = 0.9; 0.5; 0.1$, were prepared by wet mechanical activation. The reagents Y_2O_3 (99.99% purity, Alfa Aesar, Germany), $MnCO_3$ (99% purity, Lachema Pliva a.s., Czech Republic), SnO_2 (99% purity, Sigma Aldrich, s.r.o., Czech Republic) and CuO (99% purity, Lachema Pliva a.s., Czech Republic) or NiO (99% purity, Lachema Pliva a.s., Czech Republic) were weighed in molar proportions and milled in the planetary mill (Pulverisette 5; FRITSCH, Germany) for 5 h. For milling in solution, mixture of deionised water and ethanol in volume ratio 1:1 as a medium was used. All homogenous reaction mixtures were fired successively in the first step at 700 °C with a soaking time of 6 h and in the second step at 1000 -1200 °C with a soaking time also 6 h. Prepared pigments were applied into an organic matrix (dispersive acrylic paint Parketol, Balakom, a.s., Czech Republic) in mass and diluted tone. Pigments were also applied into ceramic glaze G 073 91 (Glazura, s.r.o, Roudnice nad Labem, Czech Republic). The mixture of pigment in amounts of 10 % w/w a glaze was glazed at 1000 °C for 15 min. The applications of pigments into an organic matrix and ceramic glaze were evaluated by measuring of spectral reflectance in the visible region of light (400 - 700 nm) using a ColorQuest XE (HunterLab, USA). As the measurement conditions were used an illuminant D65, measuring geometry $d/8^\circ$ and 10° complementary observer. The color properties were described in the CIE $L^*a^*b^*$ system. The value a^* (the red-green axis) and b^* (the yellow-blue axis) indicate the color hue. The value L^* represents the lightness or darkness of the color. L^* is ranging from 0 (black) to 100 (white). The value C (chroma) represents saturation of the color and is calculated according to the formula:

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

From previous values it is also possible to calculate the color of pigment as a hue angle:

$$H^\circ = \arctg(b^*/a^*) \quad (2)$$

The hue angle H° expresses color using an angular position in the cylindrical color space ($H^\circ = 350-35^\circ = \text{red}$, $H^\circ = 35-70^\circ = \text{orange}$, $H^\circ = 70-105^\circ = \text{yellow}$, $H^\circ = 105-195^\circ = \text{green}$, $H^\circ = 195-285^\circ = \text{blue}$ and $H^\circ = 285-350^\circ = \text{violet}$).

Mastersizer 2000 MU (Malvern Instruments, Ltd. GB) was used for measurements of particle size distribution. The device uses the laser diffraction on particles dispersed in liquid medium and it allows evaluation of measured signal either based on Mie's

theory or Fraunhofer diffraction. As the source of light He-Ne laser (wavelength 633 nm) and blue light (466 nm) were used. The samples were ultrasonically homogenized for 90 s in a solution of $\text{Na}_4\text{P}_2\text{O}_7$ ($c = 0.15 \text{ mol.dm}^{-3}$) and measured. The crystal structures and phase purity of the powdered materials were studied by XRD analysis. The diffractograms of the samples were obtained by using a diffractometer D8 Advance (Bruker, GB) with a goniometer of 17 cm in the range 2θ of $10-80^\circ$. $\text{Cu K}\alpha_1$ ($\lambda = 0.15418 \text{ nm}$) radiation was used for angular range of $2\theta < 35^\circ$ and $\text{Cu K}\alpha_2$ ($\lambda = 0.15405 \text{ nm}$) for the range of $2\theta > 35$. A scintillation detector was used.

Results and discussion

Color properties in organic matrix

Table I demonstrates influence of calcination temperature on color properties of $\text{YMn}_x(\text{CuSn})_{1-x}\text{O}_{3\pm\delta}$ ($x = 0.9; 0.5; 0.1$) pigments applied into organic matrix in mass and diluted tone. Darkest samples were obtained for composition $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$. The values of color coordinates L^* , a^* , b^* decrease with growing temperature of calcination and color of this pigments became more blue and darker. Samples with $x = 0.5$ also turns darker with increasing temperature, however they have a lower proportion of blue color and higher content of red. Composition with $x = 0.1$ has the lightest hue and highest content of green color. The resulting color is dark green. Composition $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$ provides best color properties and the optimal temperature for preparing of this pigment is 1200°C because of highest content of blue hue ($b^* = -3.01$) and lowest brightness ($L^* = 20.02$). This pigment applied in organic matrix is darker and has higher proportion of blue tint than, for example industrially produced pigments based on copper chromite spinel: Black 1G [$L^* = 27.79$; $a^* = 0.41$, $b^* = (-1.65)$] or Black 430 [$L^* = 28.10$; $a^* = 0.44$, $b^* = (-1.93)$] both by The Shepherd Color Company; USA. Green and blue hues are amplified in diluted tone. Values a^* are in the interval from (-2.15) to (-5.11) and b^* from (-4.32) to (-8.98) . The brightness L^* significantly increased up to the point 70.27 ($T = 1200^\circ\text{C}$, $x = 0.1$). Final hues in diluted tone are ranging from grey to grey-blue.

Table I

The effect of calcination temperature on color properties of the $\text{YMn}_x(\text{CuSn})_{1-x}\text{O}_{3\pm\delta}$ pigments applied into organic matrix in mass and diluted tone.

x	$T [^\circ\text{C}]$	mass tone					diluted tone				
		L^*	a^*	b^*	C	H°	L^*	a^*	b^*	C	H°
0.9	1000	28.26	0.14	-2.66	2.66	273.01	49.63	-2.35	-7.89	8.23	253.41
	1100	28.06	-0.08	-2.78	2.78	268.35	53.25	-2.95	-8.98	9.45	251.81
	1200	20.02	-0.11	-3.01	3.01	267.91	54.26	-2.54	-8.48	8.85	253.33
0.5	1000	29.34	0.21	-1.98	1.99	276.05	52.59	-2.15	-7.58	7.88	254.16
	1100	28.42	0.04	-1.92	1.92	271.19	58.58	-2.60	-7.85	8.27	251.67
	1200	21.54	0.40	-1.61	1.66	283.95	67.02	-2.16	-5.96	6.34	250.08
0.1	1000	32.32	-1.98	-1.47	2.47	216.59	62.13	-3.33	-4.32	5.45	232.37
	1100	31.36	-4.46	-1.49	4.70	198.47	65.87	-5.11	-5.25	7.33	225.77
	1200	28.14	-3.02	-1.01	3.18	198.49	70.27	-3.85	-4.92	6.25	231.96

Results of measuring color coordinates of pigments $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$ are shown in Table II. With growing temperature the values of L^* mostly increase and opposite them a^* and b^* decrease, except for pigment with $x = 0.1$, where values a^* and b^* are rising. With increasing amount of Mn the colors of pigments are changing from black with a dash of blue hue ($x = 0.9; 0.5$) to dark brown ($x = 0.1$) Best color properties were measured for pigment with $x = 0.9$ prepared at the temperature 1200 °C, thanks to the highest proportion of blue color ($b^* = -2.20$) and one of the lowest L^* coordinate ($L^* = 27.15$). This sample was also compared with the industrially manufactured pigments and it also exhibits lower values of brightness and higher contribution of blue color than pigments Black 1G or Black 430. In diluted tone pigments $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$ provide grey and brown-grey hues. Brightness L^* and b^* values are significantly higher than in the mass tone. The colors of these applications are also affected by blue hues ($x = 0.9; 0.5$) or red tones ($x = 0.1$).

Table II

The effect of calcination temperature on color properties of the $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$ pigments applied into organic matrix in mass and diluted tone.

x	$T [^\circ C]$	mass tone					diluted tone				
		L^*	a^*	b^*	C	H°	L^*	a^*	b^*	C	H°
0.9	1000	29.26	1.53	-0.59	1.64	338.91	46.39	0.55	-5.34	5.37	275.88
	1100	27.94	0.12	-2.19	2.19	273.14	51.27	-2.20	-6.99	7.33	252.53
	1200	27.75	0.09	-2.20	2.20	272.34	52.06	-2.43	-8.36	8.71	253.79
0.5	1000	28.69	0.69	-0.83	1.08	309.74	49.43	-0.62	-5.49	5.52	263.56
	1100	27.42	0.42	-1.52	1.58	285.45	52.61	-1.42	-6.12	6.28	256.94
	1200	26.69	0.37	-1.75	1.79	281.94	52.46	-1.38	-5.54	5.71	256.01
0.1	1000	33.83	3.12	1.51	3.47	25.83	55.97	2.34	-1.60	2.83	325.64
	1100	34.60	3.52	2.17	4.14	31.65	57.93	1.96	-2.65	3.30	306.49
	1200	30.49	4.23	2.98	5.17	35.16	60.14	1.83	-2.64	3.21	304.73

Color properties in ceramic glaze

Table III implies the change of the color coordinates in dependence on the temperature of calcination and composition of both types of pigments $YMn_x(CuSn)_{1-x}O_{3\pm\delta}$ and $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$ applied into the ceramic glaze G 073 91. Composition with $x = 0.9$ provides dark brown colored glaze in case of both types of pigments. Samples (NiSn) are slightly darker with higher contribution of red hue. Reduction of the manganese content in the samples to limit $x = 0.5$ caused significant changes in color of glazes. (CuSn) type has brown-green hue and with increasing temperature of calcination samples became darker (L^* values mostly decrease). In case of (NiSn) samples color of the glaze is brown and opposite to previous they are brighter with rising temperature. The largest differences were observed for composition $x = 0.1$. Applications of pigment $YMn_{0.1}(CuSn)_{0.9}O_{3\pm\delta}$ have turquoise color with significant contribution of green hue (a^* axis) and decreasing values of brightness (L^* axis) with increasing temperature. After application into the ceramic glaze pigments $YMn_{0.1}(NiSn)_{0.9}O_{3\pm\delta}$ have beige hue. With rising temperature values L^* ; a^* ; b^* are gently decreasing. These results confirm that these pigments are not stable in aggressive environment of molten glaze and lose their original color.

Table III

The effect of calcination temperature on color properties of the $YMn_x(CuSn)_{1-x}O_{3\pm\delta}$ and $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$ pigments applied into the ceramic glaze G 073 91.

x	$T [^\circ C]$	$YMn_x(CuSn)_{1-x}O_{3\pm\delta}$					$YMn_x(NiSn)_{1-x}O_{3\pm\delta}$				
		L^*	a^*	b^*	C	H°	L^*	a^*	b^*	C	H°
0.9	1000	27.92	1.47	-0.63	1.60	336.80	26.71	1.70	-0.40	1.75	346.76
	1100	28.34	1.55	-0.76	1.73	333.88	27.57	1.75	-0.75	1.90	336.80
	1200	28.49	1.52	-0.95	1.79	327.99	27.52	1.42	-0.74	1.60	332.47
0.5	1000	35.33	-0.47	1.08	1.18	113.52	34.11	5.45	3.98	6.75	36.14
	1100	36.95	-0.05	2.85	2.85	91.01	34.15	5.04	3.48	6.12	34.62
	1200	33.57	0.32	2.31	2.33	82.11	35.95	5.85	5.53	8.05	43.39
0.1	1000	50.19	-15.39	-0.41	15.40	181.53	48.71	7.20	16.97	18.43	67.01
	1100	50.72	-14.59	2.07	14.74	171.92	47.68	6.87	16.63	17.99	67.55
	1200	47.43	-13.25	4.77	14.08	160.20	44.94	6.81	16.36	17.72	67.40

Particle size distribution (PSD)

The color properties of pigments may be strongly influenced by particle size distribution (PSD). Therefore, all samples were also investigated from this point of view (Table IV). The particle size distribution was measured for unmilled samples which were grinded in an agate mortar before measurement. Mechanical activation usually provides products with smaller particle sizes than for example classical ceramic method. PSD of $YMn_x(CuSn)_{1-x}O_{3\pm\delta}$ pigments mostly increases with rising temperature of calcination. In any case value d_{50} does not exceed limit of 15 μm and therefore these samples are suitable for applications in glazes. The lowest d_{50} (1.62 μm) was achieved for sample $YMn_{0.1}(CuSn)_{0.9}O_{3\pm\delta}$ (1000 $^\circ C$). $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$ pigments give values of d_{50} in the range 1.42 – 3.22 μm which enables effective utilization of the pigments without necessity of mechanical treatment. The lowest value of d_{50} (1.42 μm) was also gained by composition $x = 0.1$ and temperature of 1000 $^\circ C$. For applications in organic binders it would be appropriate to reduce the d_{50} value below 2 μm .

Table IV

Particle size distribution (PSD) of the $YMn_x(CuSn)_{1-x}O_{3\pm\delta}$ and $YMn_x(NiSn)_{1-x}O_{3\pm\delta}$

x	$T [^\circ C]$	$YMn_x(CuSn)_{1-x}O_{3\pm\delta}$			$YMn_x(NiSn)_{1-x}O_{3\pm\delta}$		
		$d_{10} [\mu m]$	$d_{50} [\mu m]$	$d_{90} [\mu m]$	$d_{10} [\mu m]$	$d_{50} [\mu m]$	$d_{90} [\mu m]$
0.9	1000	0.90	2.94	7.21	0.68	2.49	6.85
	1100	1.07	2.70	6.70	1.04	3.10	8.31
	1200	1.33	3.28	7.16	1.15	3.22	7.93
0.5	1000	0.51	1.83	5.56	0.57	2.12	6.73
	1100	0.72	3.24	8.93	0.55	2.20	6.08
	1200	1.95	7.17	18.07	0.67	2.50	7.64
0.1	1000	0.46	1.62	5.22	0.43	1.42	4.83
	1100	0.59	2.52	6.44	0.52	1.76	5.25
	1200	1.02	5.50	16.41	0.62	2.24	5.76

Influence of mineralizers

Influence of mineralizers AlF_3 ; Na_3AlF_6 ; H_3BO_3 and Na_2CO_3 on the color properties are shown in detail in Table V for $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$ and in Table VI for $\text{YMn}_{0.9}(\text{NiSn})_{0.1}\text{O}_{3\pm\delta}$. The best results were achieved using Na_2CO_3 in case of pigment $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$. After application to the organic binder the samples were darker and were characterized by a higher content of blue shade at temperatures of 1000 °C and 1100 °C. Mineralizers AlF_3 and Na_3AlF_6 provide very similar results. At temperature 1000 °C samples have a lower brightness value and a higher content of blue color; at 1100 °C are only darker and at 1200 °C have been measured worse results than for the sample without mineralizer. H_3BO_3 causes only darkening of the sample but the blue color of the samples is slightly fading.

For pigment $\text{YMn}_{0.9}(\text{NiSn})_{0.1}\text{O}_{3\pm\delta}$ is best to use a mineralizers Na_3AlF_6 or AlF_6 , because thus prepared samples have comparable or better color properties than powders prepared without mineralizer at all temperatures. Worse results were observed for Na_2CO_3 , where all samples give lower brightness values, but also lower content of blue color. Utilization of H_3BO_3 for this kind of synthesis was ineffective.

Table V

The effect of mineralizer (1 – AlF_3 ; 2 - Na_3AlF_6 ; 3 – H_3BO_3 ; 4 - Na_2CO_3) on color properties of the $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$ pigment applied into organic matrix in mass and diluted tone.

Min.	T [°C]	mass tone					diluted tone				
		L*	a*	b*	C	H°	L*	a*	b*	C	H°
1	1000	27.66	0.03	-3.12	3.12	270.55	51.51	-3.61	-9.57	10.23	249.33
	1100	25.44	0.44	-2.65	2.69	279.43	54.61	-2.44	-8.97	9.30	254.78
	1200	25.39	0.54	-2.30	2.36	283.21	61.87	-2.17	-8.53	8.80	255.73
2	1000	27.26	0.06	-3.31	3.31	271.04	47.73	-3.49	-9.33	9.96	249.49
	1100	25.47	0.45	-2.63	2.67	279.71	54.91	-2.51	-8.95	9.30	254.33
	1200	26.46	0.53	-2.24	2.30	283.31	61.63	-2.19	-8.60	8.87	255.71
3	1000	28.26	0.65	-2.28	2.37	285.91	48.78	-1.32	-7.37	7.49	259.85
	1100	27.47	0.41	-2.21	2.25	280.51	62.58	-2.14	-7.98	8.26	254.99
	1200	24.12	0.45	-2.15	2.20	281.82	72.59	-2.46	-5.97	6.46	247.61
4	1000	27.98	0.15	-2.73	2.73	273.14	52.69	-2.59	-8.42	8.81	252.90
	1100	27.17	0.15	-2.88	2.88	272.98	53.81	-2.89	-9.17	9.61	252.51
	1200	27.02	0.38	-2.32	2.35	279.30	58.33	-2.31	-8.07	8.39	254.03

Table VI

The effect of mineralizer (1 – AlF_3 ; 2 - Na_3AlF_6 ; 3 – H_3BO_3 ; 4 - Na_2CO_3) on color properties of the $\text{YMn}_{0.9}(\text{NiSn})_{0.1}\text{O}_{3\pm\delta}$ pigment applied into organic matrix in mass and diluted tone.

Min.	T [°C]	mass tone					diluted tone				
		L*	a*	b*	C	H°	L*	a*	b*	C	H°
1	1000	26.95	0.21	-2.78	2.79	274.32	48.21	-2.75	-8.13	8.58	251.31
	1100	26.48	0.27	-2.54	2.55	276.07	52.18	-2.85	-7.94	8.44	250.25
	1200	27.35	0.33	-2.06	2.09	279.10	57.41	-2.18	-8.01	8.30	254.78
2	1000	28.04	0.21	-2.41	2.42	274.98	47.15	-2.81	-7.97	8.45	250.58

	1100	26.39	0.24	-2.48	2.49	275.53	52.90	-2.75	-8.55	8.98	252.17
	1200	26.88	0.41	-2.11	2.15	281.00	59.33	-2.28	-8.11	8.42	254.30
3	1000	29.37	1.31	-0.58	1.43	336.12	45.24	0.45	-4.43	4.45	275.80
	1100	28.06	0.48	-2.02	2.08	283.37	50.85	-1.61	-8.36	8.51	259.10
	1200	26.74	0.44	-1.97	2.02	282.59	62.89	-2.13	-6.86	7.18	252.75
4	1000	29.06	1.62	-0.51	1.70	342.53	48.44	0.97	-3.75	3.87	284.50
	1100	27.86	0.19	-2.19	2.20	274.96	50.40	-2.17	-7.72	8.02	254.30
	1200	26.94	0.37	-2.02	2.05	280.38	58.60	-2.23	-8.06	8.36	254.53

XRD analysis

The powder pigments with $x = 0.9$ were also investigated by X-ray diffraction analysis. Pigment $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$ provides single phase X diffractograms (hexagonal YMnO_3 – PDF No. 04-011-9577) [13] already at 1100 °C, but the intensity of the crystalline phase is very low (Figure 1). The increase of intensity was achieved by using mineralizers. Synthesis in the presence of Na_2CO_3 ; AlF_3 ; Na_3AlF_6 provides also single phase products. It has been verified that all samples have perovskite structure. H_3BO_3 is ineffective as a mineralizer.

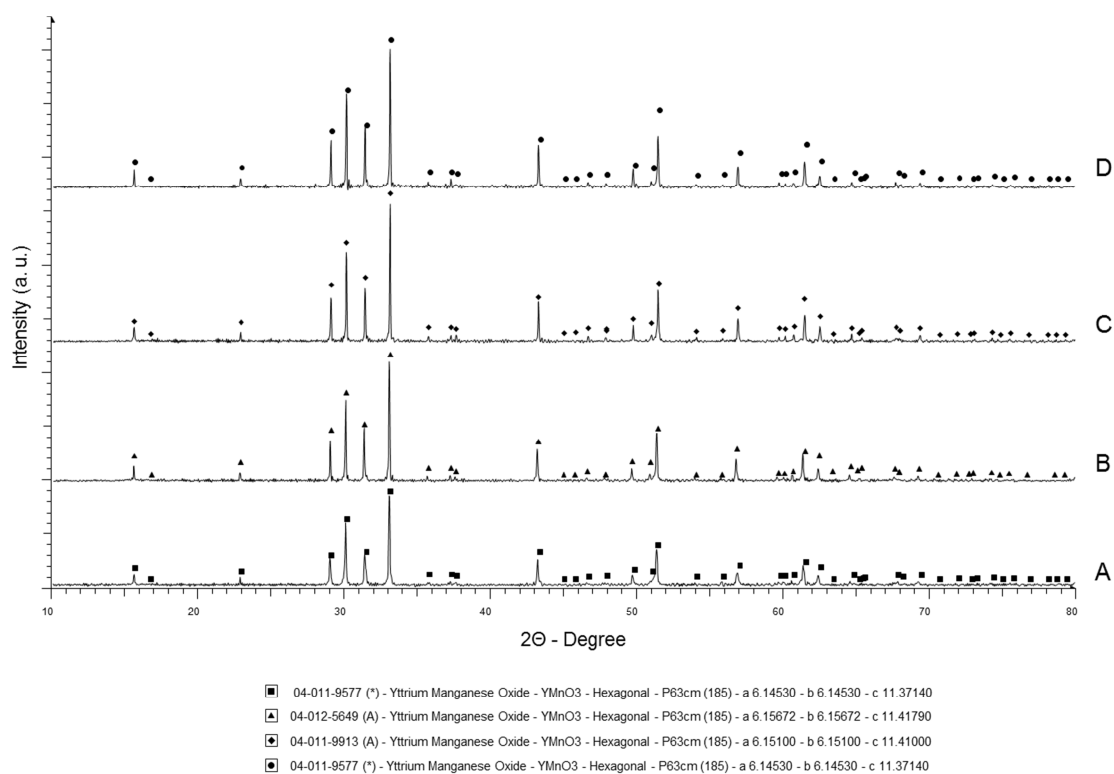


Figure 1. Diffractograms of pigment $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$; calcination temperature 1200 °C (A – without mineralizer, B – Na_2CO_3 , C – AlF_3 , D – Na_3AlF_6).

Even at the highest temperature 1200 °C $\text{YMn}_{0.9}(\text{NiSn})_{0.1}\text{O}_{3\pm\delta}$ provides only two-phased diffractogram (hexagonal YMnO_3 (PDF No. 04-011-9577); orthorhombic $\text{YMn}_{0.75}\text{Ni}_{0.25}\text{O}_3$ (PDF No. 04-015-1774) [13]) with low intensity of the crystalline

phase (practically amorphous). Mineralizers also help to create only multi-phases samples.

Conclusion

The aim of this research was to prepare pigments based on YMnO_3 doped by ions of Sn with general formula $\text{YMn}_x(\text{MSn})_{1-x}\text{O}_{3\pm\delta}$, where $x = 0.9; 0.5; 0.1$; and $M = \text{Cu}$ or Ni , and verify their color properties, phase purity, PSD and possible use of the mineralizers to improve these properties. The color shade is shifting from black to dark green for (CuSn) and from black to dark brown for (NiSn). The most interesting colors were obtained by pigments with $x = 0.9$ synthesized at $1200\text{ }^\circ\text{C}$. After application to ceramic glaze color of pigments change from dark brown to turquoise (CuSn) and from dark brown to beige (NiSn). The XRD analysis showed that pigment $\text{YMn}_{0.9}(\text{CuSn})_{0.1}\text{O}_{3\pm\delta}$ provides single-phase perovskite structure at $1100\text{ }^\circ\text{C}$. The use of mineralizers caused increase of intensity of the crystalline phase. Solid solution was not prepared in case of $\text{YMn}_{0.9}(\text{NiSn})_{0.1}\text{O}_{3\pm\delta}$. PSD of the prepared pigments is suitable for pigment applications.

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