THE INFLUENCE OF PREPARATION CONDITIONS ON THE PROPERTIES OF $YFeO_3$ PIGMENTS

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Abstract

Inorganic pigments of type $YFeO_3$ were synthesized by mechanical activation in the liquid medium from the starting oxides Y_2O_3 and Fe_2O_3. Starting mixture was treated in the planetary mill for 5 hours and subsequently dried and homogenized. Prepared powders were fired in the electric furnace in two steps: for the first step temperature 700 °C for 6 hours was used. After homogenization pigments were fired in the temperature range 900 – 1300 °C for 6; 9 or 12 hours. $YFeO_3$ pigments were applied to the organic matrix in mass and diluted tone and also to the ceramic glaze G 02891. The objective of the present study is to compare differences in color properties, phase composition of pigments and particle size distribution of samples synthesized under various preparation conditions.

Introduction

Materials with general formula $RFeO_3$ are known as rare-earth orthoferrites where R represents trivalent rare-earth ion. The $YFeO_3$ has been studied mostly for its magneto-optical properties and catalytic activity [1]. $YFeO_3$-based catalysts have been investigated for photocatalytic oxidation of organic dyes, the selective catalytic reduction of NO_x to N_2 by propene. It is also used in optical switches, magneto-optical current sensors, cathodes in solid oxide fuel cells, environmental monitoring films, data storage devices, detectors of humidity and alcohols and material for magnetic resonance imaging (MRI) in biomedicine [2-7]. Pure $YFeO_3$ is a p-type indirect semiconductor with a band gap of 2.58 eV that is slightly wider than a band gap of Fe_2O_3 [3]. This compound crystallizes in either distorted orthorhombic (perovskite) or hexagonal ($YAlO_3$-type) structures, depending on synthesis conditions. The distortion is caused by the position of Y^{3+} ions while the position of Fe^{3+} ions remains octahedral. The investigation revealed that $YFeO_3$ is thermodynamically unstable and usually is partly transformed to thermodynamically more stable phase: Fe_3O_4 or $Y_3Fe_5O_{12}$ (Yttrium Iron Garnet – YIG). Therefore, preparation of this perovskite is a complex task [1; 5; 8-10]. $YFeO_3$ is often prepared using more efficient methods of synthesis than the simple classic solid state reaction. A number of reports are available on sol-gel, hydrothermal techniques, precipitation or microwave-assisted method usually followed by high-temperature calcination [4; 11; 12]. One of few studies that explore the possibility of using $YFeO_3$ as an inorganic pigment is a study of $YMn_xFe_{1-x}O_3$ prepared by modified citrate method [20]. The color of prepared samples is changing from blue-green to dark blue. Besides the chromatic properties NIR reflectance and thermal stability was investigated and phase composition was examined by XRD analysis.

Experiment

The pigments $YFeO_{3\pm\delta}$ were prepared by mechanical activation in liquid medium (volume ratio H_2O:C_2H_6O = 1:1). Reagents Y_2O_3 (99.99% purity, Alfa Aesar, Germany) and Fe_2O_3 (99% purity, Precheza a.s., Czech Republic) were weighed in molar proportions and homogenized in a mortar. Prepared mixtures were milled in a planetary mill (Pulverisette 5; FRITSCH, Germany) for 5 hours. The mass ratio of pigment and agate milling balls was 1:8.2 and as a liquid medium mixture of deionized water and ethanol in the volume ratio 1:1 was used. Powders were subsequently dried and re-homogenized. Reaction mixtures were fired in the electric furnace at 700 °C with the soaking time 6 hours in firs step and in the second step in the range 900 – 1300 °C for 6; 9 or 12 hours. Pigments were applied into an organic matrix (urethane-acrylate copolymer Parketol, Balacom, a.s., Czech Republic) in mass and diluted tone (mass ratio of pigment:TiO_2 = 1:1) and also to the ceramic glaze G028 91 (Glazura, s.r.o.; Czech Republic). The mixture of pigment in amounts of 10 % w/w and the glaze was glazed at 900 °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). The color properties were described in most used color system - the CIE *L*a*b**. The value *a** (the red-

green axis) and *b** (the yellow-blue axis) indicate the hue. The value *L** represents the lightness or darkness of the color. *L** is ranging from 0 (black) to 100 (white). From previous values it is possible to calculate the *C* (chroma), hue angle H° and color difference ΔE* according to the formulas:

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

$$H° = \text{arc tg}\,(b^*/a^*) \quad (2)$$

$$\Delta E^* = [(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} \quad (3)$$

C value represents saturation of the color and the hue angle *H°* expresses color using an angular position in the cylindrical color space. ΔE* is the color difference between standard and sample. The difference is perceptible when ΔE* is in the range from 1.5 to 3 and if it is greater than 3 the change of the color is significant.

Particle size distribution (PSD) was measured using Mastersizer 2000/MU (Malvern Instruments, Ltd. GB) which operates on the principle of diffraction of light on particles dispersed in liquid medium. 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 $Na_4P_2O_7$ (c = 0.15 g.l^{-3}). Device evaluates the PSD based on theory of the Fraunhofer bend.

Crystal structure was verified using diffractometer Empyrean (PANalytical; Netherlands) with a vertical goniometer (step size 0.0001°) and 2Θ geometry (10 – 100°). Cooper cathode is used as a source of X-ray radiation and photon counting detector is required for registration of X-ray signal.

Discussion and results

Color properties

Pigment $YFeO_{3\pm\delta}$ with soaking time 6 hours was prepared at first and serves as a standard for further comparison with the other samples. Color properties measured after application into the organics matrix in mass and diluted tone are shown in Table I. In mass tone the color ranges from red to brownish yellow with increasing temperature. The highest content of red has sample fired at 900 °C (a* = 20.00) because this temperature is not sufficient for complete reaction of starting Fe_2O_3. After raising the temperature yellow hue (b*) as well as lightness (L*) become more pronounced to level 1100 °C. This sample has also highest chroma C and hue angle is the most in the yellow region. Further increase of the temperature leads to the suppression of yellow and red colors, and also leads to darkening of the pigment. Application in diluted tone has expected effect – lightness values increase for all samples. In addition, there was a significant decrease in values of both color coordinates as well as chroma C. Final hue of these pigments ranges from pink to light brownish yellow.

Table I

Color properties of $YFeO_{3\pm\delta}$ pigment fired for 6 hours and applied into organics matrix.

Temperature	Mass Tone					Diluted Tone				
(°C)	L*	a*	b*	C	H°	L*	a*	b*	C	H°
900	38.51	20.00	12.37	23.52	31.74	54.06	17.47	7.85	19.15	24.20
1000	41.66	17.11	18.10	24.91	46.61	59.79	12.56	10.81	16.57	40.72
1100	43.19	17.08	24.40	29.78	55.01	66.10	10.28	14.21	17.54	54.12
1200	38.64	17.25	19.63	26.13	48.69	66.01	9.20	7.33	11.76	38.55
1300	34.52	12.53	10.32	16.23	39.48	71.45	5.77	4.30	7.20	36.69

Results of measurements of color properties for pigments with the soaking time 9 hours are in Table II. For the mass tone, there are not big differences between samples and standard ($YFeO_{3\pm\delta}$; 6 hours) in the temperature range 900 – 1100 °C. ΔE* values do not exceed the level 2.2 which means that the difference is for the human eyes very poorly recognizable. The color change is noticeable up to temperature 1200 °C. This sample has higher amount of red (a* = 21.77) and yellow (b* = 25.31) but it is also lighter (L* = 42.61). Total difference ΔE* = 8.27 is very well distinguishable. This sample has the highest content of red hue. Biggest ΔE* was achieved at 1200 °C. The a* value increased to 19.20 and b* to 18.19. Due to the brighter shade, the total difference ΔE* = 11.65. Hue angle is in the red and orange-yellow region which is confirmed by shade in mass tone varying from red to brownish yellow. In diluted tone the color of application is more saturated than standard ones. They have the highest amount of both red and yellow shade and their difference ΔE* ranging from 2.26 to 9.48 and samples can thus be visibly recognized from standards.

Table II
Color properties of $YFeO_{3\pm\delta}$ pigment fired for 9 hours and applied into organics matrix.

Temperature	Mass Tone						Diluted Tone					
(°C)	L*	a*	b*	C	H°	ΔE*	L*	a*	b*	C	H°	ΔE*
900	38.49	20.81	11.76	23.90	29.47	1.01	50.48	19.47	8.97	21.44	24.74	4.25
1000	41.34	17.30	17.09	24.32	44.65	1.08	58.57	13.15	12.62	18.23	43.82	2.26
1100	44.42	18.87	24.36	30.81	52.24	2.17	61.13	14.38	21.16	25.58	55.80	9.48
1200	42.61	21.77	25.31	33.38	49.30	8.27	67.38	12.83	12.64	18.01	44.57	6.58
1300	39.93	19.20	18.19	26.45	43.45	11.65	73.73	8.86	7.34	11.51	39.64	4.90

The next step of the synthesis was firing treatment for 12 hours. All results and comparison with standard samples are noted in Table III. Pigments applied in mass tone are very similar to previous ones fired for 9 hours. While the sample prepared at 900 °C is nearly identical with the standard, at the highest temperature the difference is significant and ΔE* = 11.85. The largest amount of red and yellow color has samples fired at 1200 °C. The final shade of these applications is changing from red to brownish yellow with increasing temperature. Greater difference was measured for the diluted tone of these pigments. The powder samples fired for the longest time have a better ability to color the achromatic environment of TiO_2. These applications are more saturated than standard ones and they have a bigger amount of red and yellow shade. The highest difference was measured for temperature 1200 °C (ΔE* = 11.33). The color is changing from pink to light brownish yellow.

Table III
Color properties of $YFeO_{3\pm\delta}$ pigment fired for 12 hours and applied into organics matrix.

Temperature	Mass Tone						Diluted Tone					
(°C)	L*	a*	b*	C	H°	ΔE*	L*	a*	b*	C	H°	ΔE*
900	38.07	20.68	11.90	23.86	29.92	0.94	52.78	18.52	8.14	20.23	23.73	1.68
1000	39.79	17.15	17.12	24.23	44.95	2.11	56.44	14.92	13.86	20.36	42.89	5.11
1100	44.73	19.43	25.89	32.37	53.11	3.18	61.93	13.97	21.07	25.28	56.45	8.84
1200	42.24	22.25	26.72	34.77	50.22	9.39	64.71	14.72	17.14	22.59	49.34	11.33
1300	40.05	19.20	18.41	26.60	43.80	11.85	72.75	9.20	7.68	11.98	39.85	4.99

All pigments were also applied into the ceramic glaze G 028 91 and measured data are shown in Table V. Already by examining the values of difference ΔE* it is obvious that the temperature or the firing time have a practically no influence on the results of color coordinates after application to ceramic glaze. All samples have dark reddish brown shade. The final hue is influenced more by type of glaze itself than the composition and color of applied pigment. Therefore, these pigments are not suitable for applications in this type of ceramic glaze.

Table IV
Color properties of $YFeO_{3\pm\delta}$ pigment applied into the ceramic glaze G 028 91.

Temperature	6 hours			9 hours				12 hours			
(°C)	L*	C	H°	L*	C	H°	ΔE*	L*	C	H°	ΔE*
900	36.97	10.31	33.37	36.14	10.38	24.12	1.86	36.30	8.92	26.94	1.88
1000	36.72	9.13	30.55	36.09	9.39	24.95	1.13	36.02	9.17	25.03	1.13
1100	37.66	11.82	33.19	37.19	12.26	29.68	0.98	37.23	12.02	30.32	0.76
1200	37.77	13.06	30.67	37.47	12.62	30.57	0.53	37.83	13.19	31.08	0.18
1300	37.08	14.28	32.62	38.26	15.24	34.63	1.60	37.90	16.00	33.97	1.94

Particle size distribution

The aim of the research was also to find out the effect of the firing temperature and time of treatment on the particle size distribution (Table V). With increasing temperature the values of median size d_{50} rising for all samples. The d_{50} of standard $YFeO_3$ (6 hours) ranges from 1.75 to 5.92 μm. Sample fired at 1300 °C was partly sintered which was reflected primarily on the d_{90} value (35.96 μm). Pigments fired for a longer time have maximums d_{50} lower approximately about one micrometer: 4.64 μm (9 hours) and 4.99 μm (12 hours). The

difference between all samples is small and have no significant consequence on further possible utilization. Due to medium particle size the prepared samples are more suitable for application to ceramic glazes. For use in another kind of organic binders, it will be necessary to reduce the d_{50} values below 2 µm by appropriate milling treatment.

Table V
Particle size distribution of $YFeO_{3\pm\delta}$ pigments.

Temperature	6 hours			9 hours			12 hours		
(°C)	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
900	0.58	1.75	5.16	0.55	1.66	6.40	0.45	1.47	6.06
1000	0.74	2.67	6.70	0.62	2.23	7.66	0.63	2.10	6.33
1100	0.99	3.58	8.33	0.71	2.96	7.36	0.74	3.00	7.83
1200	1.59	4.55	18.96	1.26	3.61	12.93	1.20	3.56	10.85
1300	1.80	5.92	35.96	1.65	4.64	32.04	0.86	4.99	30.02

X-ray diffraction analysis

To determine the reactions process in the system it needs to be evaluated by X-ray diffraction analysis. Phase composition was examined for all samples. At the temperature 900 °C system of standard $YFeO_{3\pm\delta}$ (6 hours) still contains non-reacted starting oxides Y_2O_3 (PDF No. 00-041-1105) [14] and Fe_2O_3 (PDF No. 01-079-1741) and desired product $YFeO_3$ (PDF No. 01-086-0170) is also created. At temperature 1000 °C sample is still not fully reacted but the amount of $YFeO_3$ increases. Both expected products are created during calcination at 1100 °C: $YFeO_3$ (PDF No. 01-086-0170) and thermally more stable $Y_3Fe_5O_{12}$ (PDF No. 00-043-0507). However, the sample still contains a small amount of Y_2O_3. The system is completely reacted at temperature 1200 °C and even after firing temperature increase to 1300 °C there are no more changes in the composition of this sample. Phase composition of samples fired for 9 hours is quite similar to the standard. Both non-reacted starting oxides are present in samples to the temperature 1100 °C and system is fully reacted at temperature 1200 °C when $YFeO_3$ (PDF No. 01-086-0170) and $Y_3Fe_5O_{12}$ (PDF No. 00-043-0507) are created. The structure does not change even when the temperature rises at 1300 °C. In the case of 12 hours treatment there is a little change during synthesis. At temperature 900 °C sample contains except Y_2O_3 and Fe_2O_3 product $YFeO_3$ also semi-product structurally adequate $Y_{12}Fe_{32}O_2$ (PDF No. 01-071-1040). By increasing of firing temperature the starting oxides and semi-product are consumed for the synthesis of products $YFeO_3$ and $Y_3Fe_5O_{12}$. Diffractograms of samples fired at 1300 °C are shown in Figure 1. Differences between samples are minimal and extension of firing time does not affect the final composition at elevated temperatures.

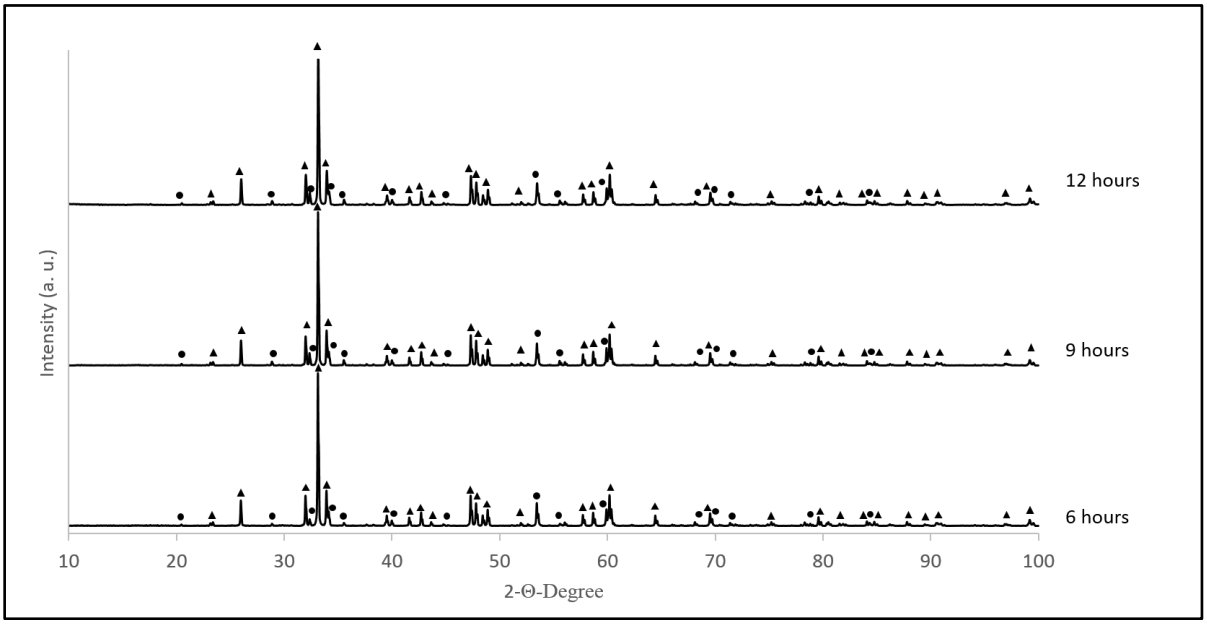

Figure 1. Diffractograms of $YFeO_{3\pm\delta}$ type pigments fired at 6; 9 and 12 hours – temperature 1300 °C [▲ $YFeO_3$ (PDF No. 01-086-0170); ● $Y_3Fe_5O_{12}$ (PDF No. 00-043-0507)].

Conclusions

Pigments of type $YFeO_{3\pm\delta}$ were prepared by mechanical activation in a liquid medium and fired in the temperature range 900 – 1300 °C for 6; 9 or 12 hours. The main aim of the research was to verify the effect of preparation conditions on color properties, phase composition and particle size distribution. Pigments were applied into the organic matrix in mass and diluted tone and also into the ceramic glaze G 028 91. Samples synthesised for 6 hours were used as a standard. In mass tone color is changing from red to brownish yellow and from pink to light brownish yellow in diluted tone. By extending the soaking time it was achieved the shift of color more to the red and yellow region and these samples were more saturated in the environment of TiO_2 in diluted tone. The difference between products fired at 9 or 12 hours is insignificant. The most appropriate firing temperature is 1200 °C because of the highest content of red color in prepared samples. The pigments proved to be not very suitable for application in the glaze G 028 91 which hue was dark reddish brown but neither temperature nor composition had affected the final hue. The median particle size d_{50} of synthesized samples ranges from 1.5 to 6 μm and with increasing temperature slightly decreases. XRD analysis confirms that soaking time has not significant effect to phase composition. The system always contains product $YFeO_3$ and more thermally stable compound $Y_3Fe_5O_{12}$ (Yttrium Iron Garnet).

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References

1. A. V. Racu, D. H. Ursu, O. V. Kuliukova, C. Logofatu, A. Leca, M. Miclau: Mater Lett 140 (2015) 107–110.
2. D. M. Gil, M. C. Navarro, M. C. Lagarrigue, J. Guimpel, R. E. Carbonio, M. I. Gómez: J Therm Anal Calorim (2011) 103: 889–896.
3. Y. Zhang, J. Yang, J. Xu, Q. Gao, Z. Hong: Mater Lett 81 (2012) 1–4.
4. F. Stevens, R. Cloots, D. Poelman, B. Vertruyen, C. Henrist: Mater Lett 114 (2014) 136–139.
5. W. Zhang, C. Fang, W. Yin, Y. Zeng: Mater Chem Phys 137 (2013) 877-883.
6. H. Sheni, J. Xue, A. Wu: J Rare Earths Vol. 28, No. 3 (2010) 416.
7. L. Jiang, W. Liu, A. Wu, J. Xu, Q. Liu, L. Luo, H. Zhang: J Sol-Gel Sci Technol 61 (2012) 527–533.
8. D. M. Gi, M. C. Navarro, M. C. Lagarrigue, J. Guimpel, R. E. Carbonio, M. I. Gómez: J Therm Anal Calorim 103 (2011) 889–896.
9. P. Tang, H. Chen, F. Cao, G. Pan: Catal Sci Technol 1 (2011) 1145–1148.
10. K. Bamzai, A. K. Razdan, P.N. Kotru: J Cryst Growth 121 (1992) 519 - 521.
11. T.Shen, C.Hu, W.L.Yang, H.C.Liu, X.L.Wei: Mat Sci Semicon Proc 34 (2015) 114–120.
12. L. J. Downie, R. J. Goff, W. Kockelmann, S. D. Forder, J. E. Parker, F. D. Morrison, P. Lightfoot: J Solid State Chem 190 (2012) 52–60.
13. A. Han, M. Ye, M. Zhao, J. Liao, T. Wu: Dyes and Pigments 99 (2013) 527-530.
14. Joint Committee on Powder Diffraction Standards, International Centre of Diffraction Data, Swarthmore, PA, USA.