SYNTHESIS AND POSSIBILITIES OF UTILIZATION OF ORTHOFERRITES WITH PRASEODYMIUM

Luxová J., Šulcová P.

University of Pardubice, Faculty of Chemical Technology, Department of Inorganic Technology, Doubravice 41, Pardubice 532 10, Czech Republic
jana.luxova@upce.cz

Abstract

In this study, the orthoferrite $PrFeO_3$ was prepared by calcination of initial mixture of raw materials Fe_2O_3 and Pr_6O_{11} at the temperature 1000-1400°C with the duration 3 h. The calcined products were investigated as inorganic pigments. The particle size distribution was measured by the device Mastersizer 2000/MU (Malvern Instr., GB). The phase composition was verified by the X-ray diffraction analysis using the apparatus D8 Advance (Bruker, GB). A heating microscope with automatic image analysis EM201-12 (Hesse-Instruments, Germany) was used for study of the thermal stability. The main attention was concentrated on assessment of colour properties. The colour properties were determined for powders and pigments applied into two binder systems. The acrylate matrix and the transparent leadless glaze P 07410 were selected. The compounds were dosed into binders in weight ratio in the mass tone, 10 wt. % respectively. The ColourQuest XE (HunterLab, USA) was used for characterization of colour properties.

Introduction

Currently, the great emphasis is given on the protection of environment. Therefore, based on not only of the environment protecting but also of human health, some materials containing elements, that have been identified as toxic or unsatisfactory, were eliminated. Utilization of the ceramic pigments was also affected by this ecological problem, when the pigments containing toxic metals were forbidden[1]. However, a space has been created for research and development of new pigments that would meet stringent environmental criteria. One of the promising options could be perovskite compounds containing lanthanides.

Mixed metal oxides with chemical formula AMO_3 belong to the great family of perovskite compounds, where A represents a large cation, while M is substituted by a small cation. Oxide perovskites have stoichiometry with a structure that consists a three-dimensional framework of corner sharing MO_6 octahedra. In the ideal perovskite structure the A cation sits a dodecahedral site surrounded by 12 oxide ions[2]. In case of orthoferrites the M sites are occupied by Fe^{3+} ions.

The rare-earth othoferrites with a general formula $RFeO_3$ (R-rare earth elements and yttrium) constitute a special subgroup of perovskites. These compounds have been investigated as materials with weak ferromagnetic ordering[3], semiconductors for detection of alcohol[4,5] or materials available on processing of the thin-films[6-9].

Rare-Earth orthoferrites crystalize in distorted perovskite structure with an orthorhombic unit cell. The distortion from the ideal perovskite is observed mainly in the position of rare earth ions, where the Fe^{3+} ions are surrounded by six oxygen ions giving octahedral coordination[10-12].

The research of orthoferrite compounds is also attractive in terms of preparation possibilities. The orthoferrites with orthorhombic structure with different properties in particular with interesting colour hues can be prepared by combination of different elements and using different methods and conditions of synthesis. They can be prepared by using solid state reaction[5,13], co-precipitation[9], sol-gel method or metal-organic processing[10], combustion method[14] or with using mechanical activation and subsequent sintering[15].

Otrhoferrite with chemical formula $PrFeO_3$ was prepared in this work. The main aim was to define the influence of firing temperature on the structural, optical, colour and application properties.

Experiment

For preparation of the $PrFeO_3$ the powders Fe_2O_3 (Precheza a.s., Přerov) and Pr_6O_{11} (Importer Trading Bochemie, s.r.o.) were used. The purity of used staring raw materials was about 99%. The homogenized initial mixture was calcinated at 1000-1400°C with the duration 3 hours on maximum temperature.

The main attention was focused on determination of influence of firing temperature on colour properties. The colour properties of the powder samples and pigments applied into 2 binding system – organic matrix in mass tone (Parketol, Akzo Nobel Coatings CZ, a.s., Opava, Czech Republic) and the middle-temperature transparent leadless ceramic glaze P 07410 in the weight ratio 10% (Glazura Roudnice, a.s., Czech Republic) were studied. The colour properties were measured in the visible region of the light (400-700 nm) using the

spectrophotometer ColourQuest XE (HunterLab, USA). The colour was evaluated in the system CIE L*a*b* (1976). In this system, the L* represents lightness or darkness of the pigment. The values a* and b* indicate the direction of the colour; +a* - the red colour; -a* – the green colour and similarly +b* – the yellow colour; -b* – the blue colour. Next colour characteristics have been calculated for better description of the colour, the chroma C and the hue angle H°. The chroma represents saturation of the colour, ranges from 0 (gray) to 100 (pure colour) and it is possible to calculate using the formula: $C=(a^{*2}+b^{*2})^{1/2}$. The hue angle H° is expressed in degrees and moves in the range within 0°- 360°C. The value of the hue angle can be found out from the formula: H°=arctg(b*/a*). The interval H° for this studied system of studied pigments is 35°-70° orange hue[16].
A heating microscope with automatic image analysis EM201-12 (Hesse-Instruments, Germany) was used for study of the thermal stability of orthoferrite. This apparatus enables to monitor the dilatometric behaviour of the powder compressed into a tablet depending on heating temperature. For investigating of thermal stability, the tablets of powders in shape of cylinder a diameter of 3 mm and height of 6 mm were prepared.
Particle size distribution was performed on device Mastersizer 2000/MU (Malvern Instruments, Ltd., GB). It is highly integrated laser measuring system for analysing of particle size distribution. Before own measuring, the all samples were ultrasonically homogenized in $Na_4P_2O_7$ solution (c=0.15 mol.dm^{-3}). The signal was evaluated based on the Fraunhofer bending.
Phase composition of the tested pigments were verified by RDX analysis using an equipment diffractometer D8 Advance (Bruker, GB) in range 2Θ from 10 to 80°. A scintillation detector was used.

Discussion and result analysis

The powders prepared by calcination at different temperatures were compressed into tablets and they were studied with the aim to verify their thermal stability. The heating microscopic curves as dependence of area changes of tablets on heating temperature are showed in Fig. 1. Only the temperature associated with the beginning of sintering was recorded for all the studied powders studied. The temperature of the start of sintering gradually increased with growing calcination temperature. The lowest value was recorded for the sample prepared at 1000°C (1223°C) and the highest (1391°C) for the sample calcined at the highest temperature - 1400°C. It can be seen from the graph that the gradual losses of tablet areas were observed at high temperatures. The smallest change in area was found in the 1400°C sample (19.5%), while the largest change was recorded for the 1200°C sample (34.3%). These changes are related to only the beginning of sintering of studied powders. Other characteristic temperatures associated with tablet degradation were not recorded, it means the orthoferrite $PrFeO_3$ is thermally stable up to the temperature 1200°C. In addition, the course of heating curves, which is unchanged up to 1200°C, indicated that commonly available glazes having a glazing temperature of up to 1150°C are suitable for application purposes.

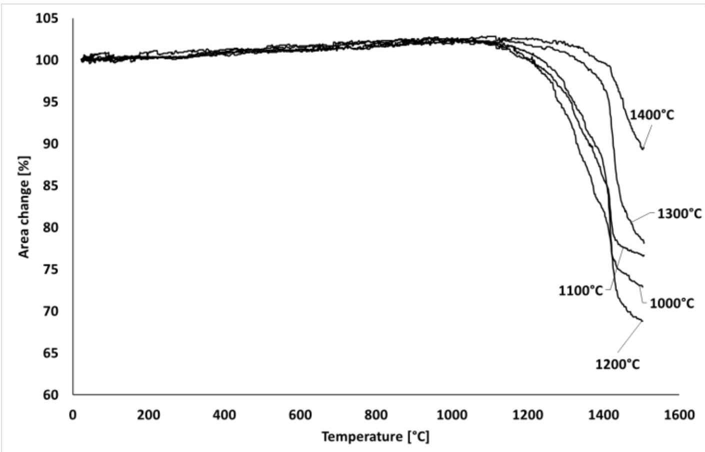

Figure 1. Records of microscopic curves of $PrFeO_3$ prepared at temperatures 1000-1400°C

The phase composition of orthoferrites in dependence on calcination temperature was investigated too and it is summarized in Table I. Because the start of formation of the orthoferrite compound found from the previous work[13] was above 995°C, the sample prepared at 1000°C was discarded from the RDX analysis from reason of the assumption of negative results. The RDX patterns identified an orthorhombic structure of $PrFeO_3$ with space group Pbnm(62), but only sample prepared at 1400°C was single-phase compound. The sample containing four compounds, next to major phase $PrFeO_3$ unreacted Fe_2O_3 and Pr_6O_{11}, but also non-identified compound was obtained by calcination at 1100°C. Increasing of calcining temperature on 1200°C and 1300°C was accompanied by the existence of a three-phase compound, which the composition is given in the Table I. From pigmentary point of view, it is not necessary to prepare pigment with single-phase composition. Nevertheless, for the industrial utilization appropriate the condition of pigment synthesis are the most important.

Table I
The phase composition of orthoferrites prepared at 1100-1400°C

	Calcination temperature [°C]			
	1100	1200	1300	1400
Identified phase-structure	$PrFeO_3$-orthorhombic Fe_2O_3-hexagonal Pr_6O_{11}-cubic Non-identified	$PrFeO_3$-orthorhombic Fe_2O_3-hexagonal Non-identified	$PrFeO_3$-orthorhombic Pr_6O_{11}-cubic PrO_2-cubic	$PrFeO_3$-orthorhombic

The dependence of mean particle size of $PrFeO_3$ on calcination temperature is shown in Table II and the growth of d_{50} with increasing firing temperature was demonstrated. At firstly the growth was gradual until 1200°C, where the values d_{50} ranged from 3.88 to 4.50 μm. However, another increase in the calcination temperature was accompanied by sudden jumping growth of d_{50}. The results of the particle size analysis showed that coarse grinding of the powders in agate mortar after the calcining process was sufficient for potential application of pigments into ceramic glaze, where an optimal particle size is recommended in range 5-15 μm. Nevertheless, the particle size of orthoferrites prepared at higher temperatures was for application into plastics unappropriated, because for this application the value of particle size d_{50} less than 2 μm is necessary[1].

Table II
The values of the band gap E_g, the mean particle size d_{50}, the lightness L*, the chroma C and the hue angle H° of powdered orthoferrties and the samples applied into organic binder

calcin. tem. [°C]	d_{50} [μm]	E_g [eV]	powder			application in organic matrix		
			L*	C	H° [°]	L*	C	H° [°]
1000	3.87	2.09	47.05	12.13	58.49	40.09	21.27	59.30
1100	3.88	2.08	47.13	11.61	57.16	40.86	21.72	56.05
1200	4.50	2.15	49.89	18.92	54.72	47.16	35.87	53.91
1300	6.07	2.01	43.75	7.23	46.59	31.41	14.15	45.26
1400	11.85	1.98	43.21	6.97	42.93	33.90	13.49	39.39

The band gap values E_g were calculated using the modified Kubelka-Munk function which is given by the equation $K/S=[F(R)h\nu]^2$, where K/S is the colour yield, R is reflectance and $h\nu$ is the photon energy. The value of the photon energy was substituted using formula: $h\nu$=1236/wavelength [nm]. The absorption edge was determined by the extrapolation of the linear part of the graph between the modified K/S and photon energy[17]. The thus obtained values E_g are summarized in Table II as well. The absorption edge grew until the calcification temperature 1200°C, and then it declined.

The main attention of this contribution was concentrated on determination of influence of firing temperature on colour properties of the orthoferrites. The values of lightness, the chroma and the hue angle of powders and after their application in organic binder in mass tone are showed in Table II. For both compared systems, a very similar trend was observed, a very small increase of L* and C values with a significant jump of both variables at 1200°C. But both characteristics were significantly reduced with the next calcination temperatures. These results are in completely conformity with colour coordinate values of the orthoferrite recorded in Fig. 2. The powder pigments had maintained the same trend as the compounds after application into the organic binder, i.e., the up growth until to 1200°C and subsequently the move to lower values. The hue angle H° describing the colour shade in the CIEL*a*b* space shifted from the orange-yellow shade towards the orange-red with increasing temperature. Based on the above results, it is possible to mark the best temperature 1200°C, at which the orthoferrite with the most interesting colour hue was prepared.

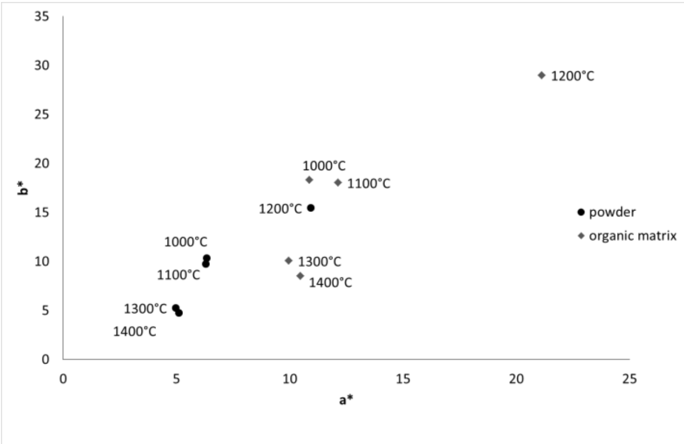

Figure 2. The influence of calcination temperature on the colour properties of the powdered $PrFeO_3$ and samples applied into organic matric in mass tone

It was found from the results of the thermal analysis, that the all samples had the thermal stability up to 1200°C and therefore they are applicable to commonly available glazes having a glazing temperature of about 1150°C. The middle-temperature glaze P 07410 with glazing temperature 1050°C was chosen for the purpose of this work. In Fig. 3, showing the colour direction of glazed samples, a grow in the values of the both colour coordinates up to 1100°C followed by a decrease the b* axis with the higher calcination temperature is observed.

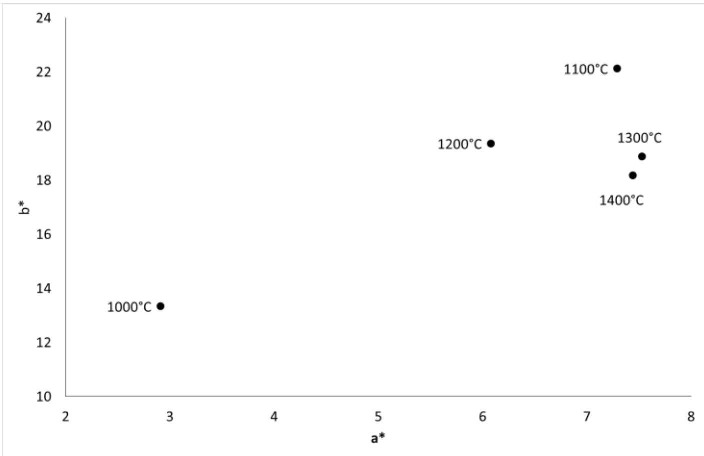

Figure 3. The influence of calcination temperature on the colour properties of the $PrFeO_3$ samples applied into the middle-temperature leadless glaze P 07410 in weight ratio 10%

Table III

The values of the lightness L*, the chroma C and the hue angle H° of the orthoferrites applied into glaze P 07410 in 10 wt.%

Calcination temperature [°C]	L*	C	H° [°]
1000	62.73	13.65	77.69
1100	60.61	23.30	71.77
1200	61.59	20.29	72.57
1300	59.68	20.33	68.26
1400	55.75	19.64	67.74

The colour characteristics obtained for the samples applied into the ceramic glaze are summarized in Table III. It was obvious from the brightness values, that the ceramic shards were very bright, but the L* values dropped with an increasing firing temperature and therefore the shards darkened. The chroma C, indicating colour saturation, in accordance with Fig. 3 grew with increasing temperature up to 1100°C and then dropped very slightly. The hue angle changed very little and it hinted that the ceramic shards had very similar shades. The best results for the pigment applied into the glaze P 07410 were obtained for the calcination temperature of 1100°C. Although the surface of the coloured ceramic shards had no visible defects, i.e. cracks or bubbles, the pigments applied to this type of glaze had an uninteresting beige colour. Therefore, it would be appropriate in further research to focus on improving of the colour quality in the ceramic glaze or to try another type of ceramic glaze.

Conclusion

The aim of this contribution was to prepare the compound $PrFeO_3$ with orthorhombic structure and further to assess the effect of firing temperature on the colour properties, particle size distribution and the phase composition of the pigment. The orthorhombic structure has been confirmed by X-ray diffraction analysis and it indicated that the higher calcination temperature (1400°C) is necessary for the formation of single-phase compound. The colour properties of the pigment were evaluated at powder and after application into two binder systems, namely in the acrylic matrix and in transparent leadless glazes P 07410. This glaze was chosen based on the results of thermal stability, which confirmed excellent heat resistance up to 1200°C. In the case of the organic binder, the firing temperature 1200°C may be designated as the most appropriate because for this temperature the best colour characteristics have been found, i.e. the highest values of the coordinates a*, b* and the highest value of chroma C. The best firing temperature 1100°C was evaluated for the ceramic leadless glaze. When assessing of the particle size, it can be stated that the pigment particles showed a gradual increase up to the calcination temperature 1200°C and with further calcinations occurred to the sudden growth of pigment particles, which it resulted in obtaining of the darker shades of $PrFeO_3$ compounds with the worse pigment optical properties.

Acknowledgement

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