INFLUENCE OF RAW MATERIALS ON OPTICAL PROPERTIES OF Bi-DOPED PrFeO3

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Abstract

In this work, the orthoferrites based on $PrFeO_3$ doped by Bi were investigated as inorganic pigments. The samples with chemical formula $Bi_xPr_{1-x}FeO_3$ (x=0-0.3) were synthetized by solid state reaction and an influence of different raw material source of Fe^{3+} (Fe_2O_3 and FeOOH) was studied. Calcination process was performed at 1000°C and 1100°C with maintaining for 3 hours. 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 Miniflex 600 (Rigaku, Japan) and the phase identification of studied powders was achieved with a program that using matching of the diffraction patterns with data by the ICDD-PDF2 database. A heating microscope with automatic image analysis EM201-12 (Hesse-Instruments, Germany) was used for study of the thermal stability. The greatest attention was focused on determination of the colour properties. Colour properties of the powders and pigments applied into organic binder were studied with using device ColorQuest XE (HunterLab, USA). The results have shown that the utilization of a suitable Fe^{3+} raw material has a significant effect on the colour properties of the orthoferrites. Pigments prepared from FeOOH were significantly darker with a lower contribution of the red colour. Shades were brown to red-brown. In contrast, pigments prepared from Fe_2O_3 showed brighter orange to reddish orange shades.

Introduction

Oxide compounds with perovskite-type structure have a general formula ABO_3. In this compound A is formed by a large cation and a smaller one is placed on B side. Oxide perovskites have a stoichiometry with a structure that consists a three-dimensional framework of corner-sharing BO_6 octahedron that contains A cations at 12-coortinate sites[1,2]. In case of the A^{3+}-B^{3+} or (3-3) type perovskites (in their orthorhombic forms), the displacement of different A^{3+} cations from ideal position appears to decrease with increasing the size of A^{3+} with the same B^{3+} cation[1,3].

When Fe^{3+} ions are on the place B, the compounds are called orthoferrites[4]. The orthoferrites doped by Ln are also interesting from point of view of research of inorganic pigments. Rare earth elements with not completely filled f orbitals offer an opportunity to tune the colour response through manipulation of energy and delocalization phenomenon in conduction and valence bands, which can affects the optical properties of materials[5].

Result of the colour of the orthoferrites is very dependent on condition of the preparation[2] and also on used starting Fe^{3+} materials and rare earth oxides[6]. Based on determination of colour properties of $LnFeO_3$ (when Ln=La, Gd, Yb, Tm and Lu), the pigments can be divided into two groups. The first one is represented by pigments with the bigger ionic radius (La^{3+} and Gd^{3+}), which forms pigments with sienna colour. Second group presents orthoferrites with smaller ionic radius (Tm^{3+}, Lu^{3+} and Yb^{3+}) forming compounds with reddish brown colours[6].

Bismuth ferrite oxide ($BiFeO_3$) is an one of the most studied multiferroic materials. That's because it is the only material known to exhibit magnetic and ferroelectric order at room temperature[7]. $BiFeO_3$ is distinguished by its extremely high magnetic and ferromagnetic transition temperatures, it has a rhombohedrally distorted structure and possesses a large polarization[8,9]. Synthesis of single-phase bismuth ferrite prepared by solid state reaction can be very difficult. For synthesis of pure $BiFeO_3$ from oxides, ultrapure starting oxides are necessary to used. However, when the $BiFeO_3$ is prepared from materials about analytical purity, secondary phases, the mullite with orthorhombic structure ($Bi_2Fe_4O_9$) and the sillenite ($Bi_{25}FeO_{40}$) with cubic structure next to $BiFeO_3$ can be formed[10].

Currently, inorganic pigments are mostly produced from simple oxides. However, more alternative raw material sources can be used for production of pigments. Therefore, the knowledge of the fundamental pigmentary properties with respect to the different raw material sources is one of the primary necessity of an inorganic producer.

In this work the orthoferrites based on $PrFeO_3$ doped by Bi were prepared and an influence of different raw material sources of Fe^{3+} was studied. The primary pigmentary properties (a particle size distribution, a phase composition, a thermal stability and colour properties) of $Bi_xPr_{1-x}FeO_3$ pigments prepared from Fe_2O_3 and FeOOH were compared in this contribution.

Experiment

The commercially available components Fe_2O_3 and FeOOH (Precheza a.s., Přerov), Bi_2O_3 (Pliva Lachema, a.s. Brno) and Pr_6O_{11} (importer: ML Chemica, Troubsko) with analytical purity were used for preparation of the orthoferrite compounds. The $Bi_xPr_{1-x}FeO_3$ pigments were prepared by calcination of homogenised initial mixture in stoichiometric ratio. The calcination was performed at 1000 and 1100°C with the duration 3 hours on maximum temperature. Heating rate of calcination process was $10°Cmin^{-1}$.

All powder samples were milled by using planetary mill Pulverisette 5 (Fritsch, DEU) due to improve particle size distribution. Conditions of milling: speed – 200 rpm; time: 20 min; milling bowl: agate; milling balls: zircon balls with diameter 1.1-1.2 mm; ball-to-power weight ratio: 8:1; wet milling: in ethanol.

For characterisation of prepared samples some techniques have been used.

A heating microscope with automatic image analysis EM201-12 (Hesse-Instruments, DEU) was used for study of the thermal stability. 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 Miniflex 600 (Rigaku, Japan) in range 2Θ from 10 to 80° with 1D D/teX Ultra silicon strip detector an K_β filter. The Cu K_α radiation was used for this analysis. More precisely, Cu $K_{\alpha 1}$ (λ=0.15418 nm) radiation was used for range 2Θ < 35°, and Cu $K_{\alpha 2}$ (λ=0.15405 nm) for range 2Θ > 35°. The phase identification of studied powders was achieved with a program that using matching of the diffraction patterns with data contained in the JCPDS database.

Density of powdered compounds was obtained with using equipment AutoPycnometer (Micrometrics, USA). A principle of the measurement is based on the gas displacement method to measure volume accurately. Helium as the displacement medium was used. Based on knowledge of the exact volume and weight of the sample density of powders is calculated.

The main attention was focused on comparison of colour properties of the samples prepared from different raw materials. The colour parameters were studied for the powdered samples and for samples applied in organic matrix in mass tone (Parketol, Akzo Nobel Coatings CZ, a.s., Opava, Czech Republic). The colour properties were measured in the visible region of the light (400-700 nm) using the spectrophotometer ColorQuest 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, the hue angle H° and for observing of colour changes the total colour difference ΔE^*_{CIE}. The total colour difference can be found out from formula: $\Delta E^*_{CIE}=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2}$, where ΔL^* - brightness difference between the standard and given sample, Δa^*, Δb^* - difference of the colour coordinates a* and b* between the standard and the given sample. The standard sample ($PrFeO_3$) and the $Bi_xPr_{1-x}FeO_3$ (x=0.1-0.3) samples have been compared. 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 following: 350°-35° red hue, 35°-70° orange hue, 70°-105° yellow hue[11].

Discussion and result analysis

Thermal stability is one of the basic properties of inorganic pigments[12]. Therefore, the studied powders prepared by calcination from different starting components were compressed into tablets and they were subjected to verify their thermal stability. The results of this analysis are summarized in Table I and it is obvious that only start of sintering (t_1) and deformation temperatures (t_2) were detected. The temperature of sintering was decreased

with growing amount of Bi in $Bi_xPr_{1-x}FeO_3$ for all measured samples. But deformation temperature (t_2) in case of samples prepared from Fe_2O_3 was detected only for samples x=0.2 and 0.3 which were heated at 1000°C. It was found that powders prepared from the FeOOH had in comparing with samples from Fe_2O_3 lower sintering temperature values and the deformation temperature was detected for most of samples. From the point of view of thermal stability, the Fe_2O_3 can be recommended as a starting material for the preparation of Bi - doped orthoferrites. Powders prepared from this raw material have greater thermal stability and lower area losses. The lower stability of samples from FeOOH is probably due to the presence of more side-compounds and unreacted raw materials, as it was confirmed by XRD analysis.

Table I
Table of detected characteristic temperatures (t_1- start of sintering temperature; t_2 – deformation temperature) and decreases of area in dependence on calcination temperature, raw material and partial substitution of Bi in $Bi_xPr_{1-x}FeO_3$

| | Samples prepared from Fe_2O_3 | | | | | | Samples prepared from FeOOH | | | | | |
| | 1000°C | | | 1100°C | | | 1000°C | | | 1100°C | | |
x	t_1 [°C]	t_2 [°C]	decr. of area [%]	t_1 [°C]	t_2 [°C]	decr. of area [%]	t_1 [°C]	t_2 [°C]	decr. of area [%]	t_1 [°C]	t_2 [°C]	decr. of area [%]
0.0	1050	-	41.0	1050	-	26.7	1040	-	37.0	990	1333	27.7
0.1	980	-	34.6	995	-	21.6	960	1381	32.3	970	-	23.2
0.2	982	1442	38.4	970	-	30.0	970	1330	41.9	950	1396	36.9
0.3	931	1431	38.6	960	-	35.9	940	1332	41.7	930	1321	38.4

• $PrFeO_3$ + $Bi_xPr_{1-x}FeO_3$ ◆ $Bi_2Fe_4O_9$ △ Fe_2O_3
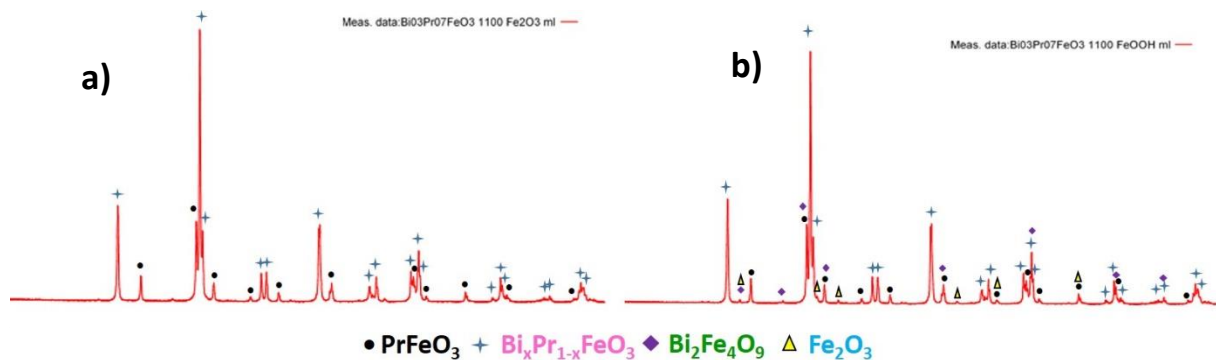
Figure 1. XRD patterns of $Bi_{0,3}Pr_{0,7}FeO_3$ calcinated at 1100°C and prepared form: a) Fe_2O_3; b) FeOOH

The phase composition of the powders was verified by XRD analysis and the identification of the individual phases was realized by matching of obtained diffraction patterns with the data in the ICDD-PDF2 database. $PrFeO_3$ (with $2\Theta \approx 22.7°$, 25.5°, 32.0°, 32.4° and 32.6°) was identified as the major phase for all samples. Nevertheless, the diffraction lines at position $2\Theta \approx 22.2°$, 32.0°, 32.4° and 32.6° were found and responded to $BiFeO_3$. Based on results of XRD, there a superposition of diffraction lines assigned to $PrFeO_3$ and $BiFeO_3$ was proven and it shown formation of $Bi_xPr_{1-x}FeO_3$ solid solutions for both sets of samples. A single-phase composition was detected for only samples prepared from Fe_2O_3 at 1100°C. In the other samples, unreacted compounds (Fe_2O_3 and Pr_6O_{11}) were found. However, in addition to the unreacted compounds, samples prepared from FeOOH also contained impurity - $Bi_2Fe_4O_9$ with mullite structure.

Density is from next primary properties of the pigments. It is also an important indicator for assessing the type and purity of the pigment under investigation. A theoretical density can be counted from crystallographic parameters[12]. The theoretical density values of $Bi_xPr_{1-x}FeO_3$ compounds shifted from 6.82 gcm^{-3} to 7.36 gcm^{-3} with increasing amount of Bi. The measured densities of orthoferrites prepared from Fe_2O_3 were very close to theoretical values and they indicated that the studied compounds were probably pure. It was confirmed by XRD analysis. Conversely, large differences between theoretical and determined density were registered for pigments synthesized from FeOOH. The determined densities of these orthoferrites were in interval 6.52-6.80 $g.cm^{-3}$. Large

deviations from the theoretical density values were probably caused by presence of unreacted compounds and impurities, which it was again consistent with the results with XRD analysis.

Information about particle size distribution belongs to the fundamental pigmentary properties[13]. Obtained results of particle size are summarized in Table II. The d_{50} values of powders prepared from Fe_2O_3 were around 1 μm for calcinations 1000°C without a visible trend of the effect of doping ion. However, very slight growth of particles with increasing amount of dopant is noticeable in samples prepared from Fe_2O_3 at 1100°C. A similar dependence was found for orthoferrites prepared from FeOOH. By comparing the results for both investigated materials, larger particles were proven for pigments prepared from FeOOH. Generally, the studied pigments had a suitable particle size especially for application to an organic binder (where a mean particle size of about 2 μm is recommended).

Table II
The particle size distribution of studied samples

| | Samples from Fe_2O_3 | | | | Samples from FeOOH | | | |
| | 1000 °C | | 1100 °C | | 1000 °C | | 1100 °C | |
x	d_{50} [μm]	d_{10} - d_{90} [μm]	d_{50} [μm]	d_{10} - d_{90} [μm]	d_{50} [μm]	d_{10} - d_{90} [μm]	d_{50} [μm]	d_{10} - d_{90} [μm]
0.0	0.92	0.37 – 2.11	1.08	0.40 – 2.88	1.00	0.38 – 2.30	1.08	0.42 – 2.36
0.1	0.91	0.35 – 2.16	1.25	0.33 – 3.40	0.89	0.40 – 1.83	1.09	0.33 – 2.75
0.2	0.91	0.35 – 2.22	1.28	0.31 – 3.55	1.06	0.43 – 2.47	1.22	0.31 – 3.45
0.3	1.00	0.36 – 2.64	1.59	0.33 – 4.33	1.16	0.43 – 2.75	2.12	0.38 – 5.62

The main aim of this work was study of colour properties of Bi-doped orthoferrites which were prepared from different starting materials. The colour properties were investigated for powders and for pigment after their application in organic binder in mass tone. The dependence of a*b* coordinates on the starting raw materials, the calcination temperature and the amount of substitution is shown in Fig. 1. A two-dimensional a*b* graph (Fig. 2a) summaries the influence of raw material of colour properties of powdered samples and it is shown that pigments prepared from FeOOH had lower values of colour coordinates. The biggest a*b* values were obtained for pigments prepared from Fe_2O_3. In addition, there is a trend of growth colour coordinates with increasing Bi content in $Bi_xPr_{1-x}FeO_3$. This character was for both investigated raw material sources. However, the increasing calcination temperature from 1000 to 1100°C had a negative character to the colour properties. Pigments prepared at this temperature had lower colour coordinate values and had darker shades of orange-brown. The same character observed for powder pigments was also obtained for pigments after their application in an organic matrix (Fig. 2b).
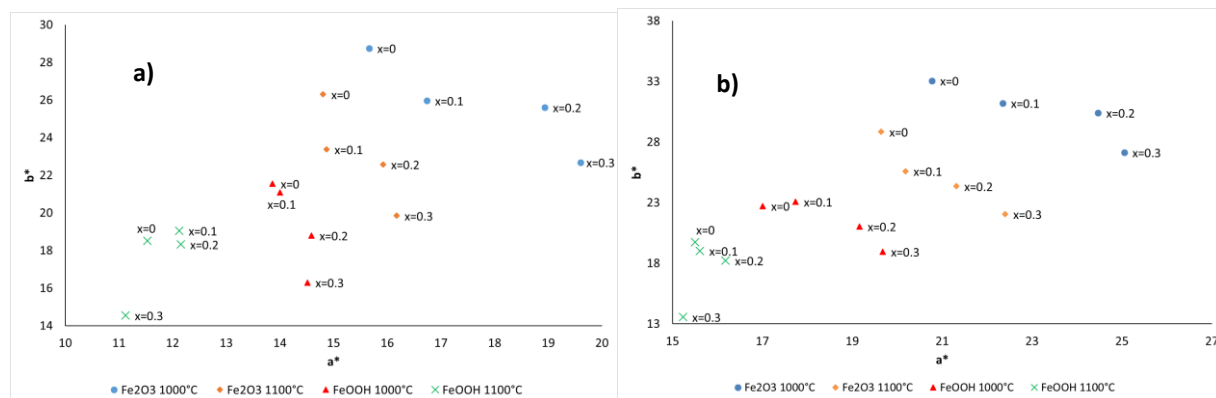

Figure 2: Colour properties of $Bi_xPr_{1-x}FeO_3$ prepared from different iron raw materials: a) powdered samples; b) pigments applied into acrylate binder in mass tone

The resulting colour of the pigments depends on the starting materials. By comparing the colour characteristics (Table III), it was found that brighter and lighter pigments were prepared from Fe_2O_3. The values of chroma C and brightness L* were for pigments from Fe_2O_3 greater. According the hue angle values, the all pigments were placed in the orange region. The decreasing character of coordinate L* with increasing Bi substitution in Bi_xPr_{1-}

$_x$FeO$_3$ compounds was found for both studied sets. This is consistent with visual appearance of samples, where the darkening of compounds from x = 0 to x = 0.3 was highly visible to the naked eye. The biggest value of the chroma was detected for pigment with substitution Bi x=0.1. The shift from orange to red-orange region with increasing Bi in Bi$_x$Pr$_{1-x}$FeO$_3$ is noticeable. The colour change can also be evaluated based on the total colour difference. In this case the standard (PrFeO$_3$) and the sample with different Bi amount were compared. For sample x = 0.1 prepared from FeOOH, the ΔE^*_{CIE} value close to 1 was found and it belongs to the barely perceptible colour difference ($0.5 \leq \Delta E^*_{CIE} \leq 1.5$). However, for the same sample but prepared from Fe$_2$O$_3$, the lowest ΔE^*_{CIE} was also detected, which in this case belongs to the area of perceptible colour difference ($1.5 \leq \Delta E^*_{CIE} \leq 3$). If the values are greater than 3, ΔE^*_{CIE} belongs to the area of large colour differences and it is very well perceptible by a human eye.

Table III: Comparison of the values of L*, C, h° and ΔE^*_{CIE} for the pigments Bi$_x$Pr$_{1-x}$FeO$_3$ applied into organic acrylate binder in mass tone

x	Samples from Fe$_2$O$_3$							
	1000°C				1100°C			
	L*	C	h° [°]	ΔE^*_{CIE}	L*	C	h° [°]	ΔE^*_{CIE}
0.0	48.98	39.03	57.85	-	46.44	34.88	55.74	-
0.1	47.61	38.38	54.38	2.79	44.10	32.59	51.74	4.03
0.2	47.08	39.03	51.17	4.93	43.67	32.35	48.80	5.53
0.3	44.83	36.93	47.28	8.40	42.72	31.42	44.54	8.22
x	Samples from FeOOH							
	1000°C				1100°C			
	L*	C	h° [°]	ΔE^*_{CIE}	L*	C	h° [°]	ΔE^*_{CIE}
0.0	42.71	28.38	53.18	-	40.85	25.09	51.85	-
0.1	42.71	29.09	52.43	0.81	40.25	24.60	50.61	0.94
0.2	41.43	28.45	47.66	3.02	40.22	24.36	48.38	1.78
0.3	40.59	27.31	43.09	5.09	37.92	20.39	41.66	6.84

Generally, the results have shown that the utilization of a suitable Fe^{3+} raw material has a significant effect on the colour properties of the orthoferrites. Pigments prepared from FeOOH were meaningly darker with a lower contribution of the red colour. Shades were brown to reddish-brown. In contrast, pigments prepared from Fe$_2$O$_3$ showed brighter orange to reddish orange shades.

Conclusion

In this work, the orthoferrites based on PrFeO$_3$ doped by Bi were investigated as inorganic pigments. The samples with chemical formula Bi$_x$Pr$_{1-x}$FeO$_3$ (x=0-0.3) were synthetized by solid state reaction and the influence of different raw material sources of Fe^{3+} (Fe$_2$O$_3$ and FeOOH) on pigmentary properties was studied. By comparison of results was found, that:

- the particle size distribution: larger particles were prepared using the raw material FeOOH.
- the thermal stability: more thermally stable pigments were prepared from Fe$_2$O$_3$.
- the phase composition: the results indicated the formation of Bi$_x$Pr$_{1-x}$FeO$_3$ solid solutions in both cases. However, the powders prepared from FeOOH containing more secondary products or unreacted components.
- the colour properties: observed colour properties and other parameters confirmed that more attractive shades of brown-red colour were prepared from Fe$_2$O$_3$.

Based on all results, for the preparation of orthoferrite compounds doped with Bi, the Fe$_2$O$_3$ as the starting raw material can be recommended.

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