Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 2, 559–563

SYNTHESIS AND CHARACTERIZATION OF $LnFeO_3$ PIGMENTS

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This work is focused on determination of the optimum firing temperature which leads to formation of the compounds $LnFeO_3$ with good pigment-application properties (*Ln*=Gd, La, Yb, Tm, Lu). Based on results of thermal analysis the compounds were prepared by the solid-state reaction at temperature 900 and 1000°C. Colours of pigments vary depending on type of used lanthanoid (from light sienna to dark brown) and also on the type of iron precursor. Generally, the compounds prepared from iron oxide have more interesting color properties. Colour of these compounds is brighter and deeper. Increasing of the calcination temperature from 900 to 1000°C causes the darkening of colour. The most problably, the darkening is connected with partial reduction of Fe^{3+} to Fe^{2+}.

Keywords: *heterometalic oxides, inorganic pigments, $LnFeO_3$, orthoferrites, thermal analysis*

Introduction

The rare earth orthoferrites of the general formula $LnFeO_3$ (where *Ln*=lanthanoids) are one of the most useful materials for the applications such as catalysis [1], electrode materials and solid electrolytes for fuel cells and gas sensors [2, 3]. These compounds and metal ion substituted ferrites crystallized in perovskite orthorhombic structure in which the FeO_6 octahedrons are distorted and the extent of distortion depends on the ionic size of the rare earth [4].

The most conventional method for the preparation of these heterometallic oxides is the solid-state reaction of Ln_2O_3 and Fe_2O_3 single oxides. However, this method is very difficult to control the powder quality and particle size [2]. Usual ceramic method proposed by Pechini was used for preparation of sample $LaFeO_3$ which was studied from the pigment application point of view [5]. Other methods capable for synthesis of orthoferrites encompass thermal decomposition of heteronuclear complexes [2], sol–gel method [6, 7].

In this presented work the rare earth orthoferrites were prepared by solid state reaction [8–10] and the influence of synthesizing method on the pigment-application properties was studied.

Experimental

The compounds of general formula $LnFeO_3$ (where *Ln*=Gd, La, Yb, Tm, Lu) were prepared by solid-state reaction among Fe_2O_3 (TP-303; Precheza, a.s., CR) or FeOOH (Heubach, GmbH, Germany) and Ln_2O_3 (99% of purity; Indian Rare Earths Ltd., India). Raw materials were mixing in a porcelain mortar in order to obtain homogenous reaction mixture which was calcinated at high temperature in an electric resistance furnace. The increase of temperature was set up on 10°C min^{-1}. The calcining temperatures 900 and 1000°C were maintained for 3 h. The pigments prepared were applied into organic matrix in mass tone and evaluated with respect to their colour properties by measurements of spectral reflectance in the visible region of light (400–700 nm) by equipment ColourQuest XE (HunterLab, USA). The measuring system uses colour space CIE $L^*a^*b^*$, where coordinate L^* expresses degree of brightness and coordinates a^* and b^* describe the colour hue. Thorough description of colour is done by recalculation of chrome extent *C* according to mathematical formula $C=(a^{*2}+b^{*2})^{1/2}$. The next measurement conditions were following: illuminant D65 (6500 K), 10° complementary observer and geometry of measurements *d*/8°.

The particle size distribution of the samples was measured by equipment of Mastersizer 2000/MU (Malvern Instruments, UK). It is a highly integrated laser measuring system for analysis of particle size distribution. The equipment uses the scattering of incident light on particles. The solids were measured in solution of sodium hexamethaphosphate (c=g l^{-1}). The signal was evaluated on the basis of Fraunhofer bending.

Simultaneous TG/DTA measurements were performed by STA Jupiter 449 equipment (Netzsch, Germany) in the temperature range 30–1150°C at heating rate 10°C min^{-1}. The analysis was carried out in a ceramic crucible under air and α-Al_2O_3 was used as a reference material.

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1388–6150/$20.00

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The crystal structures of the powder materials were studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using the equipment diffractometer D8 (Bruker, GB) with a goniometer of 17 cm in the range 2Θ of 10–80°. $CuK_{\alpha1}$ (λ=0.15418 nm) radiation was used for angular range of $2\Theta<35°$ and $CuK_{\alpha2}$ (λ=0.15405 nm) for range of $2\Theta>35$. A scintillation detector was used.

Results and discussion

Thermal behaviour of reaction mixtures containing raw materials Ln_2O_3 and Fe_2O_3 or FeOOH were followed by methods of thermal analysis. The TG and DTA curves of the first reaction mixture (La_2O_3 and FeOOH) are shown in Fig. 1. The first mass loss (0.47%) is detected on the TG curve in temperature range 30–250°C. This process corresponds to the loss of remaining moisture and this effect is represented by endothermic effect on DTA curve with minimum at 123°C. The next two endothermic effects with minimum at 337 and 414°C detected on DTA curve are connected to the thermal dehydration of FeOOH [11, 12] and also with first step of thermal decomposition of lanthanum carbonate. Previous results of thermal analysis of lanthanum oxide proved that the compound is the mixture of lanthanum oxide and carbonate and chemical composition of the compound is characterised by formula $La_2O_3{\cdot}0.125La_2(CO_3)_3$ [13]. Thermal decomposition of lanthanum carbonate is three steps process, but the final step of the decomposition was detected only by TG curve with mass loss 0.59%. Formation of lanthanum orthoferrite is presented by exothermic peak with maximum at 943°C. The thermal decomposition of the second reaction mixture containing raw materials La_2O_3 and Fe_2O_3 is described in Table 1. Exchange of raw material of iron caused the increase of forming temperature of the new compound $FeLaO_3$ from 942 to 971°C. Thermal behaviour of reaction mixtures containing raw materials Gd_2O_3 and Fe_2O_3 or FeOOH is shown in Table 2. Several endothermic peaks were recorded on the DTA curve. These effects are connected to the partial decomposition of raw materials; especially, with dehydration of FeOOH and loss of oxygen and formation of lower gadolinium oxides $Gd_2O_{3-\delta}$. The endothermic effects detected at temperature higher than 900°C the most probably correspond to the partial reduction of Fe^{3+} ions to Fe^{2+} ions. The exothermic effects are connected with oxidation of gadolinium oxides $Gd_2O_{3-\delta}$ to $GdO_{2-\delta}$ and with beginning of formation of gadolinium orthoferrite. Thermoanalytical measurements show that formation of $GdFeO_3$ is under way at 820°C.

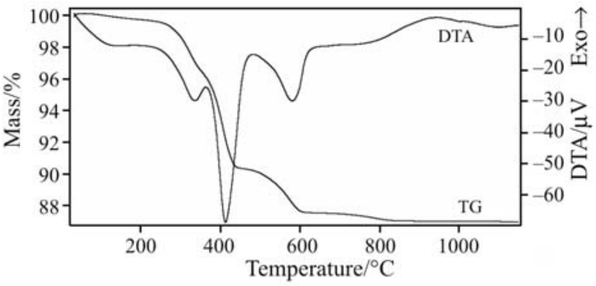

Fig. 1 DTA and TG curves of the decomposition of reaction mixture containing La_2O_3 and FeOOH (285.200 mg)

Table 1 Thermal decomposition of reaction mixtures La_2O_3+FeOOH (Fig. 1) and La_2O_3+Fe_2O_3

La_2O_3+FeOOH			La_2O_3+Fe_2O_3		
T_{range}/°C	Peak temperature/°C	Mass change/%	T_{range}/°C	Peak temperature/°C	Mass change/%
30–250	123	–0.47	30–300	–	–0.14
250–350	337	–2.96	300–440	402	–5.87
350–450	414	–6.27	440–600	560	–2.87
450–600	581	–2.74	600–850	780	–0.57
600–850	–	–0.59	–	–	–

Table 2 Thermal decomposition of reaction mixtures Gd_2O_3+FeOOH and Gd_2O_3+Fe_2O_3

Gd_2O_3+FeOOH			Gd_2O_3+Fe_2O_3		
T_{range}/°C	Peak temperature/°C	Mass change/%	T_{range}/°C	Peak temperature/°C	Mass change/%
30–200	145	–0.35	30–200	144	–0.31
200–400	335	–4.17	200–450	402	–1.10
400–800	410; 768	–0.91	450–800	768	–0.59
800–860	820; 849	–1.37	800–930	805; 925	–1.50
860–1000	923	–2.76	–	–	–

Table 3 Colour properties of the samples $LnFeO_3$ prepared by calcining at 1000°C

	Reaction mixture Ln_2O_3 and FeOOH				Reaction mixture Ln_2O_3 and Fe_2O_3			
	*L**	*a**	*b**	*C*	*L**	*a**	*b**	*C*
$LaFeO_3$	47.07	22.39	29.31	36.88	49.43	17.66	32.92	37.36
$GdFeO_3$	50.22	21.85	31.51	38.34	52.23	18.77	35.75	40.38
$YbFeO_3$	40.23	18.51	15.10	23.89	42.45	16.92	17.79	24.55
$TmFeO_3$	41.72	19.38	17.87	26.36	41.73	16.81	17.89	24.55
$LuFeO_3$	40.85	19.08	16.16	25.00	42.27	17.68	18.05	25.27

Colours of pigments vary depending on type of used lanthanoids and also on the type of iron precursor from light sienna and light brown to reddish brown (Table 3). Generally, the compounds prepared from iron oxide are brighter (*C*) and deeper (*L**), but on the other hand, pigments prepared from FeOOH contained bigger amount of red hue (*a**) and this characteristic makes them more interesting. On the basis of colour properties the pigments can be divided into two groups. In the first group of sienna pigments are compounds which contain lanthanide with bigger ionic radius; $LaFeO_3$ and $GdFeO_3$. Lanthanoids with smaller ionic radius, around 0.8 Å (Yb^{3+}, Tm^{3+} and Lu^{3+}), form pigments of reddish brown colour. Increasing of the calcination temperature from 900 to 1000°C causes the darkening of colour. The most problably, the darkening is connected with partial reduction of Fe^{3+} to Fe^{2+}. The compound $GdFeO_3$, which was prepared by calcinig of rection mixture containing gadolinium oxide and iron hydroxide oxide at temperature 1000°C, provides the most interesting colour properties.

The calcining temperature also affects the particle size distribution of the pigments. While the d_{50} values of the pigments prepared at 900°C are in range 2.0–3.5 μm, the pigments prepared at 1000°C have d_{50} values in range 2.0–7.0 μm. From the pigment-application point of view is useful when the values of mean particle size (d_{50}) are less than 2 μm. This is connected with wider possibilities of practical usage and also smaller particles usually provide more interesting colour properties. This reason lead to the procedure of grinding. Compounds $LaFeO_3$ (1000°C) and $GdFeO_3$ (1000°C) were ground in planetary mill in presence of zirconium corpuscles and ethanol medium for 10 and 20 min. Decreasing of particle size distribution of the compound $LaFeO_3$ prepared from reaction mixture containing FeOOH and La_2O_3 is clearly visible in Fig. 2. The mean particle size of the compound was reduced from value 3.42 to 1.66 μm after 20 min of grinding. This significant reduction of particle size distribution did not reflect on the changes in colour properties (Table 4). Gentle increasing of amount of yellow hue (*b**) and decreasing of red hue (*a**) caused the increasing of chrome (*C*). Total colour difference between unground and 20 min ground samples was caunted according to a formula $\Delta E^*_{CIE} = (\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}$. Value $\Delta E^*_{CIE} = 1.3$ gives mathematical express of almost unperceptible colour difference. In the second case (reaction mixture Fe_2O_3 and La_2O_3), the best granulometric composition was obtained after 10 min of grinding (Fig. 3). The mean particle size was reduced from 2.34 to 1.42 μm and the grinding next 10 min was not effective. The colour properties of the ground samples were changed significantly. The value of coordinate *L** (brightness) decreased and it means the formation of darker colour hue. Also the coordinate expressing amount of yellow hue (*b**) decreased and it subsequently caused the formation of less rich colour. The value of total colour difference between unground and 10 min ground sample is 5.0. This value expresses the big colour difference which is perceptible by human eye.

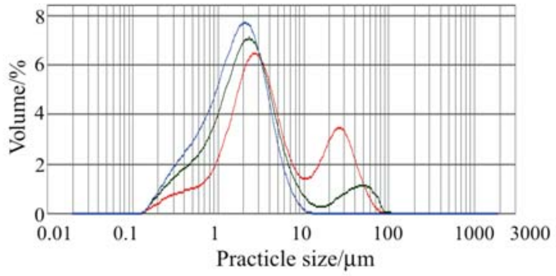

Fig. 2 Particle size distribution of the samples $LaFeO_3$ (reaction mixture: La_2O_3+FeOOH); 1 – $LaFeO_3$; 2 – $LaFeO_3$ (10 min of grinding); 3 – $LaFeO_3$ (20 min of grinding)

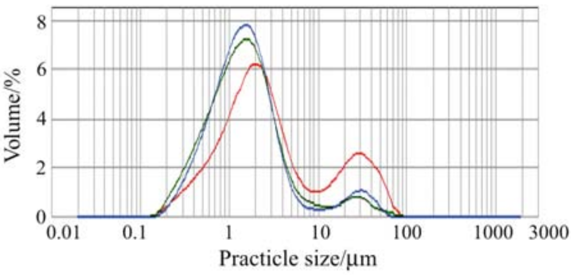

Fig. 3 Particle size distribution of the samples $LaFeO_3$ (reaction mixture: La_2O_3+Fe_2O_3); 1 – $LaFeO_3$; 2 – $LaFeO_3$ (10 min of grinding); 3 – $LaFeO_3$ (20 min of grinding)

Table 4 Colour properties of the samples $LaFeO_3$ after grinding

Reaction mixture	Grinding time/min	*L**	*a**	*b**	*C*	ΔE^*_{CIE}
La_2O_3+FeOOH	0	47.07	22.39	29.31	36.88	–
La_2O_3+FeOOH	10	46.63	22.25	28.11	35.85	1.29
La_2O_3+FeOOH	20	47.83	23.25	29.94	37.91	1.31
La_2O_3+Fe_2O_3	0	49.43	17.66	32.92	37.36	–
La_2O_3+Fe_2O_3	10	47.22	17.74	28.44	33.52	5.00
La_2O_3+Fe_2O_3	20	46.65	17.37	28.05	32.99	5.62

Table 5 Colour properties of the samples $GdFeO_3$ after grinding

Reaction mixture	Grinding time/min	*L**	*a**	*b**	*C*	ΔE^*_{CIE}
Gd_2O_3+FeOOH	0	50.22	21.85	31.51	38.34	–
Gd_2O_3+FeOOH	10	50.71	21.35	32.21	38.64	0.98
Gd_2O_3+FeOOH	20	50.54	21.34	32.17	38.60	0.90
Gd_2O_3+Fe_2O_3	0	52.23	18.77	35.75	40.38	–
Gd_2O_3+Fe_2O_3	10	51.01	17.40	32.67	37.01	3.59
Gd_2O_3+Fe_2O_3	20	50.80	17.30	31.95	36.33	4.32

The similar results were obtained by grinding of $GdFeO_3$. The mean particle size of the product prepared from Gd_2O_3 and FeOOH was written down from 2.42 to 1.70 μm after 20 min of grinding (Fig. 4). The reduction of particle size distribution did not elicit strong change of colour properties (Table 5). Values of colour coordinates *L** and *a** almost did not shift and value of coordinate *b** (yellow hue) was slightly increased. It also caused the increasing of chrome (*C*). The grinding of the $GdFeO_3$, prepared from Gd_2O_3 and Fe_2O_3, has a negative effect on the colour properties. Values of all colour coordinates decreased with the decreasing of particle size distribution (Table 5). Grinding of the sample caused the change of mean particle size from 1.98 to 1.40 μm (Fig. 5) and formation the darker pigment with less amount of red (*a**) and yellow (*b**) hue and therefore with less chrome (*C*).

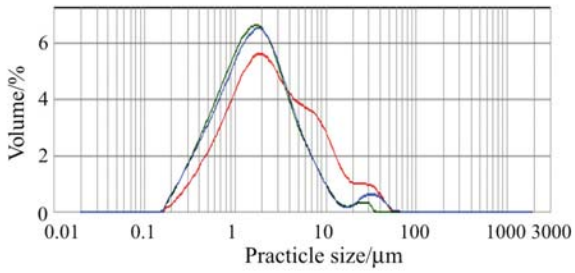

Fig. 4 Particle size distribution of the samples $GdFeO_3$ (reaction mixture: Gd_2O_3 + FeOOH); 1 – $GdFeO_3$; 2 – $GdFeO_3$ (10 min of grinding); 3 – $GdFeO_3$ (20 min of grinding)

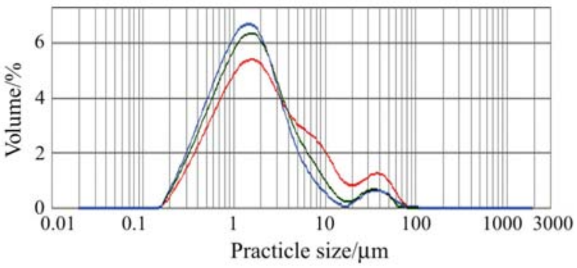

Fig. 5 Particle size distribution of the samples $GdFeO_3$ (reaction mixture: Gd_2O_3+Fe_2O_3); 1 – $GdFeO_3$; 2 – $GdFeO_3$ (10 min of grinding); 3 – $GdFeO_3$ (20 min of grinding)

Structure of samples was studied by X-ray diffraction analysis. Samples prepared by calcining at 900°C are two-phases and contain next to the phase of rare earth orthopherrite unreacted rare earth oxide. Compounds $LnFeO_3$ crystallize in orthorhombic symmetry and values of lattice parameters of $GdFeO_3$ are a=5.349 Å; b=5.610 Å and c=7.667 Å. Values of lattice parameters of $LaFeO_3$ are a=5.553 Å; b=5.563 Å and c= 7.862 Å.

Conclusions

The main aim of the research was to prepare and study pigmentary-application properties of the rare earth orthopherrites of general formula $LnFeO_3$. Adding Ln^{3+} ions to Fe_2O_3 change the colour of the pigment due to formation of perovskite compounds. Formation of new compounds with perovskite structure begins at temperature around 800°C in case of solid state reaction of oxide precursors. Ions of lanthanum and gadolinium form pigments of sienna or orange colour. Adding Lu^{3+}, Tm^{3+} and Yb^{3+} to Fe_2O_3/FeOOH forms pigments with dark reddish brown colour. The increase of temperature from 900 to 1000°C causes the creation of pigments with darker colour hue probably due to reduction of Fe^{3+} to Fe^{2+}. Colours of pigments also vary depending on type of used iron precursor. Pigments prepared from iron oxide are brighter and deeper, but pigments prepared from FeOOH contain bigger amount of red hue and they are more appropriate for applications that require main particle size less than 2.0 μm.

Acknowledgements

This work has been supported by the Ministry of Education, Youth and Sports of the Czech Republic under project MSM No. 0021627501 and by the Grant Agency of the Czech Republic by grant No. 104/05/2081.

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Received: July 12, 2007
Accepted: July 19, 2007
OnlineFirst: October 13, 2007

DOI: 10.1007/s10973-007-8636-0