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**COLOUR POSSIBILITIES OF RARE EARTH
ORTHOERRITE PIGMENTS**

Žaneta DOHNALOVÁ, Markéta VONTORČÍKOVÁ and Petra ŠULCOVÁ¹
Department of Inorganic Technology,
The University of Pardubice, CZ–532 10 Pardubice

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The paper deals with the preparation of the inorganic pigments of general formula $RE_{0.98}Ca_{0.02}FeO_3$, where $RE = La, Gd, Lu, Tm, Yb$ and Ho . The pigments were prepared by the conventional ceramic method, i.e. solid state reaction. As initial components were used Ln_2O_3 , $CaCO_3$ and two sources of Fe components, either Fe_2O_3 or $FeOOH$. The reaction mixtures were heated at the temperatures of 800, 900 and 1000 °C. The prepared pigments were applied to an organic binding system and their colour properties evaluated by measuring reflectance in the visible region of light. The most interesting colour properties were obtained by the preparation of the sample $Lu_{0.98}Ca_{0.02}FeO_3$. This pigment was prepared by the calcination of the reaction mixture containing $FeOOH$ and mineralizer LiF at the temperature of 900 °C. Generally, the mineralizer LiF affects the colour properties of all the pigments most significantly.

¹ To whom correspondence should be addressed.

Introduction

The perovskite-type mixed metal oxides have general formula ABO_3 . One of the typical characteristics of this group of inorganic compounds is the enormous variety of ionic substitutions that its crystallographic structure accepts. A represents a large cation, usually rare earth ion, while B is the smaller one. The perovskite structure can be described as a framework of corner-sharing BO_6 octahedron that contains A cations at 12-coordinate sites [1]. When B sites are occupied by Fe^{3+} cations, these oxides are called orthoferrites [2].

Recently, it has been found that the rare earth orthoferrites ($REFeO_3$) with perovskite-type structure are interesting materials for most of electronic applications because of their mixed conductivity. These materials display ionic and electronic defects [3], which make them important candidates for the development of solid-oxide fuel cells [4,5], active catalysis for oxidation or reduction of pollutant gases, oxygen sensor electrodes, gas diffusion electrodes, oxygen permeation membranes [6], chemical sensors for the detection of humidity, alcohol and gases, such as oxygen, CO, and NO_2 , as well as environmental monitoring applications [1,7,8] or inorganic pigments [9].

Research and development of environmentally friendly yellow, orange and red inorganic pigments have been of high interest for the last few decades due to high toxicity of lead, cadmium and chromate compounds. Therefore, we have been motivated to study the effect of divalent cation doping into $REFeO_3$ systems on the colour possibilities of these rare earth orthoferrites. The anticipated interesting optical properties of these compounds can be connected with their charge balances. According to Ahmed *et al.* [1]: depending mainly on the synthesis techniques and conditions and the difference in ionic radii between Ln^{3+} and M^{2+} ions in nine-fold coordination, the substitution of La^{3+} by Ca^{2+} in $LaFeO_3$ has at least two possibilities. First: the system $La_{1-x}Ca_xFeO_3$ consists of two or more phases; iron possesses an intermediate valence state that increases gradually from Fe^{3+} to Fe^{4+} with increasing x [10,11]. The second possibility is that the iron keeps its stable trivalent state and the oxygen deficiency appears in the lattice in order to neutralize the compound electrically.

The objective of this present work was to synthesize $RE_{0.98}Ca_{0.02}FeO_3$ perovskites, where RE = La, Gd, Lu, Tm, Yb and Ho, by solid state reaction and evaluate their colour properties and particle size distribution. Evaluation of the colour properties also covered the study of impact of mineralizers and heating temperature on the change in colour hue.

Experimental

Sample Preparation

$\text{Ln}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ perovskite pigments, where Ln = La, Gd, Lu, Tm, Yb and Ho, were prepared by the conventional ceramic method, i.e., the solid state reaction with a manual homogenization of initial compounds in a porcelain mortar and pestle. The initial components used were these compounds: Ln_2O_3 (99.5% purity, Indian Rare Earth Ltd., India), CaCO_3 (96 % purity, Sigma Aldrich) and two sources of Fe components — Fe_2O_3 and FeOOH (both Precheza a.s., CZ). The homogenized reaction mixtures were calcinated in corundum crucibles in an electric resistance furnace with the heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The heating temperatures 800, 900 and 1000 $^\circ\text{C}$ were maintained for two hours and then gradually decreased to room temperature. The obtained pigments were further hand-milled in an agate mortar in order to homogenize the agglomerates.

The change in the reaction conditions was studied by testing the presence of mineralizers (LiF , AlF_3 , Na_3AlF_6 , Na_2SiF_6 , NaF) in the reaction mixtures. The amount of 5 %wt. of mineralizer and stoichiometric ratios of initial components were well mixed, hand-milled using an agate mortar and transferred to the corundum crucibles for the heating procedure. Heating conditions were the same as above. The mineralizers were removed from the final products by decantation in 400 cm^3 hot distilled water.

The prepared pigments were applied into the organic binder system to evaluate their colour properties. Suspensions containing 1 g of pigment and 1.5 cm^3 of polyurethane binder were homogenized in an agate mortar. The colour layers were prepared by the deposition of slurries onto a white not absorbing paper by means of Birde applicator. Wet film thickness was 100 μm .

Measurement of Colour Properties

The colour properties of all the prepared pigments were objectively evaluated by the measurement of spectral reflectance with a spectrophotometer ColorQuerst XE (HunterLab, USA). For the description of colour, we used the color space CIE $L^*a^*b^*$. The measurement conditions were as follows: an illuminant D65, 10° complementary observer and measuring geometry $d/8^\circ$. The value a^* (the red-green direction) and b^* (the yellow-blue direction) express the colour hue. The value L^* represents the lightness or darkness of the colour as related to the natural grey scale. In the $L^*a^*b^*$ system, it is described by numbers from zero (black) to one hundred (white). The value C (Chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The total colour difference ΔE^*_{CIE} in the CIE $L^*a^*b^*$ system, which indicates the degree of colour

difference between two samples, is defined by the following equation: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔL^* , Δa^* , Δb^* are differences in L^* , a^* and b^* values between the colour sample and the colour standard, resp. The colour hue of pigments can also be expressed as the hue angle ($H^\circ = \arctan(b^*/a^*)$) [12].

Measurement of Particle Size Distribution

The particle size distribution of the samples was measured using a Mastersizer 2000/MU (Malvern Instruments, Ltd., UK). The equipment employs the scattering of incident light on particles. The pigments were ultrasonically homogenized in 800 cm³ solution of Na₄P₂O₇ ($c = 0.15 \text{ mol.dm}^{-3}$) for 90 seconds and measured. The particle size distribution was evaluated by red light (He-Ne laser with the wavelength of 633 nm) and blue diode. The signal was evaluated on the basis of Fraunhofer bending. Before the measurements, the samples were gently ground in an agate mortar.

Results and Discussion

The first examination of the pigment-application properties of the powders Ln_{0.98}Ca_{0.02}FeO₃, where Ln = La, Gd, Lu, Tm, Yb and Ho, showed that the most approaching orange colour is provided by the pigments Yb_{0.98}Ca_{0.02}FeO₃ and Tm_{0.98}Ca_{0.02}FeO₃ prepared from Fe₂O₃, which were heated at the temperature of 900 °C. Interestingly, an almost orange colour hue was also attained in the pigments Ho_{0.98}Ca_{0.02}FeO₃ and Lu_{0.98}Ca_{0.02}FeO₃ prepared from iron oxide and heated at the temperature of 900 °C. The colour of these pigments is the most vivid. Neither increasing temperature nor lanthanide ions used significantly affected the values of lightness (L^*) which are between 37 and 40. The shift of colour of pigments is from brick red to orange and sandy yellow, and it is caused by the increasing heating temperature from 800 to 1000 °C. Apart from the colour properties, also the particle size distribution of the pigments was measured. The most important value, that characterizes the particle size, is the value of d_{50} . The pigments prepared by calcination of the reaction mixture containing CaCO₃, Ln₂O₃ and FeOOH or Fe₂O₃, as the case may be, at the temperature of 800 °C had the value of d_{50} in range from 1.5 to 4 μm. A temperature increase of 100 °C caused a very slight increase in the value of median, about 1 μm. A further increase in temperature did not affect the change in median of particles. From the view of the effect of lanthanides on the particle size it can be concluded that the largest particles, i.e., agglomerates, were formed in pigments containing lanthanum, and the smallest particles were formed in Lu_{0.98}Ca_{0.02}FeO₃.

The most colouristically attractive pigments, i.e., Tm_{0.98}Ca_{0.02}FeO₃ and

Yb_{0.98}Ca_{0.02}FeO₃ prepared from Fe₂O₃ and Ho_{0.98}Ca_{0.02}FeO₃, Lu_{0.98}Ca_{0.02}FeO₃ prepared from FeOOH, were further investigated. The effect of mineralizers in the reaction mixtures on the change in colour properties of products was studied. The colour properties of the pigment Yb_{0.98}Ca_{0.02}FeO₃ prepared by heating at temperatures of 800 and 900 °C with the mineralizers are summarized in Table I. Addition of the mineralizers to reaction mixtures caused a shift of the colour hue to the orange tones. All the mineralizers with the exception of NaF positively affect the colour properties of the pigment Yb_{0.98}Ca_{0.02}FeO₃. All the samples prepared by heating at 800 °C have higher values of colour coordinates *a** and *b** and also higher values of chroma. The values of the total colour difference between the samples prepared with and without mineralizers ($\Delta E^*_{CIE} = 3-13$) clearly demonstrate the significant impact of the mineralizers on the colour properties. The most useful mineralizer seems to be LiF. The pigment prepared from the reaction mixture containing this compound had the most interesting colour properties. The almost orange hue of this pigment had the highest saturation and the highest value of lightness (*L**). Increase in the heating temperature from 800 °C to 900 °C brought very similar results. The mineralizer NaF is the least

Table I The colour properties of the pigment Yb_{0.98}Ca_{0.02}FeO₃ prepared from Fe₂O₃ with addition of mineralizers

<i>T</i> , °C	Mineralizer	<i>L</i> *	<i>a</i> *	<i>b</i> *	ΔE^*_{CIE}	<i>C</i>	<i>H</i> °
800	without mineralizer	38.09	19.79	14.25	-	24.39	35.76
	AlF ₃	41.09	21.47	20.10	6.79	29.41	43.11
	LiF	44.41	21.73	25.34	12.91	33.38	49.39
	Na ₂ SiF ₆	38.80	19.21	17.18	3.07	25.77	41.81
	Na ₃ AlF ₆	37.95	23.89	21.13	8.01	31.89	41.49
	NaF	36.57	15.85	11.55	5.01	19.61	36.08
900	without mineralizer	41.06	18.79	21.31	-	28.41	48.60
	AlF ₃	41.89	17.84	21.33	1.26	27.81	50.09
	LiF	45.46	17.53	27.70	7.86	32.78	57.67
	Na ₂ SiF ₆	43.77	20.35	24.83	4.71	32.10	50.66
	Na ₃ AlF ₆	42.39	17.86	23.87	3.03	29.81	53.20
	NaF	37.08	12.95	12.76	11.09	18.18	44.58

suitable for synthesis of this kind of perovskite pigments and, on the other hand, the mineralizer LiF brought very interesting optical properties of the sample. Increase in the temperature is connected with higher values of hue angle (H°) and chroma (C). The colour coordinate a^* , expressing the red direction, was almost unchanged but the colour coordinate b^* , that indicates yellow direction, significantly increased. The resulting colour of the samples is dark yellow to orange.

The second pigment, that was more closely studied, was $\text{Tm}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ prepared from Fe_2O_3 . The effect of mineralizers and the heating temperatures (800 °C and 900 °C) on the colour properties of the pigment $\text{Tm}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ are shown in Table II. The pigment with the addition of LiF provided the highest values of lightness (L^*), chroma (C) and yellow hue (b^*) at both calcining temperatures, which means the preparation of the pigment with the most orange colour. The highest value of the red hue (a^*) was caused by the mineralizer AlF_3 at the heating temperature of 900 °C and Na_3AlF_6 at the temperature of 800 °C. The colour of these pigments is more light brown than orange. Generally, the higher heating temperature stimulated the formation of lighter powders with higher saturation and with higher value of hue angle (H°). The colour of the sample was shifted from dark red to light brown and orange.

Table II The colour properties of the pigment $\text{Tm}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ prepared from Fe_2O_3 with addition of mineralizers

$T, ^\circ\text{C}$	Mineralizer	L^*	a^*	b^*	ΔE^*_{CIE}	C	H°
800	without mineralizer	38.63	16.48	13.31	-	21.18	38.63
	AlF_3	37.99	22.20	15.56	6.18	27.11	37.99
	LiF	44.67	19.81	25.85	14.31	32.57	44.67
	Na_2SiF_6	38.74	18.73	16.96	4.29	25.27	38.74
	Na_3AlF_6	39.37	24.51	18.55	9.62	30.74	39.37
	NaF	36.96	16.00	11.43	2.56	19.66	36.96
900	without mineralizer	39.92	15.56	18.32	-	24.04	49.66
	AlF_3	43.65	19.03	24.55	8.05	31.06	52.22
	LiF	46.06	17.92	28.29	11.94	33.49	57.65
	Na_2SiF_6	43.64	18.23	24.95	8.06	30.90	53.85
	Na_3AlF_6	41.54	16.48	21.67	3.83	27.22	52.75
	NaF	36.27	11.60	11.94	8.35	16.65	45.83

Apart from the measurement of colour properties, the particle size distribution of samples was analyzed. Granulometric composition of samples

$\text{Yb}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ and $\text{Tm}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$, which were prepared by heating at the temperature of 900 °C, are characterized by the optimum values of median (d_{50}) in the range of 2-8 μm (Table III). The synthesis of the pigments with the mineralizers LiF, Na_2SiF_6 and Na_3AlF_6 leads to the formation of powders of the same quality, from the granulometry point of view, as those of the pigment prepared without mineralizer. Conversely, using of the mineralizer AlF_3 makes the formation of coarser particles ($d_{50} = 7-8 \mu\text{m}$). Nevertheless, the results of the measurement of particle size distribution of the pigments showed that coarse grinding of the samples in an agate mortar after the heating process was sufficient for a potential application of pigments into organic binder or ceramic glaze. For applications of the samples into some other materials, for example plastics, it is needed to improve their granulometric composition by milling and obtain samples with particles less than two micrometers.

Table III The particle size distribution of pigments $\text{Yb}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ and $\text{Tm}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ prepared from Fe_2O_3 with addition of mineralizers (heating temperature 900 °C)

Mineralizer	$\text{Yb}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$			$\text{Tm}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$		
	$d_{10}, \mu\text{m}$	$d_{50}, \mu\text{m}$	$d_{90}, \mu\text{m}$	$d_{10}, \mu\text{m}$	$d_{50}, \mu\text{m}$	$d_{90}, \mu\text{m}$
without mineralizer	0.34	2.02	19.29	0.47	3.84	20.68
AlF_3	1.63	8.23	38.88	2.19	7.47	19.36
LiF	0.59	2.34	13.30	0.94	4.32	14.15
Na_2SiF_6	0.71	3.79	18.51	0.71	2.91	15.24
Na_3AlF_6	0.79	3.39	14.48	1.32	6.71	27.95
NaF	0.89	3.48	11.49	0.92	3.49	11.21

Table IV shows the effect of the mineralizers and calcination temperature on the colour properties of $\text{Ho}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ prepared from FeOOH . The addition of mineralizer LiF and calcining temperature 900 °C gives rise to the most interesting colour pigment. The pigment had the highest values of both colour coordinates a^* and b^* , lightness and also chroma. Attractive hues of the pigment were obtained also with the mineralizers AlF_3 and Na_3AlF_6 , nevertheless, their qualities are below the LiF. Sodium fluoride had the smallest impact on the change in optical properties of $\text{Ho}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$. Generally, lower firing temperature (800 °C) is connected with the formation of darker pigments with higher red direction (a^*) but lower saturation of hues.

The pigment $\text{Lu}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ was the last prepared sample with the presence of mineralizers in the reaction mixture. The iron precursor FeOOH was used for synthesis of the pigment. The results summarized in Table V showed the same conclusions like above-mentioned samples. In the comparison with the pigment

prepared without mineralizer, the mineralizer NaF made the resulting pigment the worst from the point of view of the colourity. A very good result was obtained from the synthesis of the pigment from the reaction mixture containing AlF_3 . This sample has almost the same values of co-ordinates a^* and b^* , that express the red and yellow direction. The values of hue angle is 45.43 (800 °C) or 48.21 (900 °C), and it means that the colour of the sample is light brown or very close to orange. The most orange sample was prepared by calcining the reaction mixture containing the mineralizer LiF at the temperature of 900 °C. The chroma (C) of the sample was almost 40 and was the highest value at all. Together with the value of hue angle $H^\circ = 52.02$ and lightness $L^* = 47.55$ it indicates that a vivid dark orange pigment was prepared. The remaining mineralizers (Na_2SiF_6 and Na_3AlF_6) caused rise of the pigment almost the same or slightly worse quality than without them.

Table IV The colour properties of pigment $\text{Ho}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ prepared from FeOOH with addition of mineralizers

$T, ^\circ\text{C}$	Mineralizer	L^*	a^*	b^*	ΔE^*_{CIE}	C	H°
800	without mineralizer	41.15	22.09	17.76	-	28.34	38.80
	AlF_3	42.45	22.20	21.39	3.86	30.83	43.94
	LiF	45.17	16.85	25.48	10.16	30.55	56.52
	Na_2SiF_6	41.13	23.13	20.38	2.82	30.83	41.38
	Na_3AlF_6	42.14	23.64	21.35	4.03	31.85	42.09
	NaF	36.34	15.33	11.34	10.49	19.07	36.49
900	without mineralizer	43.25	17.11	21.37	-	27.38	43.25
	AlF_3	43.47	20.94	24.19	4.76	31.99	43.47
	LiF	46.26	21.12	27.82	8.17	34.93	46.26
	Na_2SiF_6	39.30	19.59	19.74	4.94	27.81	39.30
	Na_3AlF_6	41.90	20.81	22.09	4.00	30.35	41.90
	NaF	36.80	11.51	13.82	11.40	17.99	36.80

The particle size distribution of the $\text{Ho}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ and $\text{Lu}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ powders, which were prepared from FeOOH , is summarized in Table VI. The median of all samples is in the range of 1.9-4.9 μm , and the width of the particle size distribution is closer in comparison with the samples prepared from Fe_2O_3 (Tab. III). The utilization of mineralizers in the reaction mixtures leads to the formation of coarser particles. While the median of samples prepared just from the initial reagents is less than 2 μm , all mineralizers caused the formation of powders with the median higher than 3 μm .

Table V Colour properties of pigment $\text{Lu}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ prepared from FeOOH with addition of mineralizers

$T, ^\circ\text{C}$	Mineralizer	L^*	a^*	b^*	ΔE_{CIE}^*	C	H°
800	without mineralizer	40.88	22.96	17.28	-	28.74	36.97
	AlF_3	44.78	25.78	26.17	10.11	36.74	45.43
	LiF	50.11	23.48	33.90	19.02	41.24	55.29
	Na_2SiF_6	39.84	23.01	18.72	1.78	29.66	39.19
	Na_3AlF_6	48.72	24.03	19.46	8.21	30.92	39.00
	NaF	37.89	19.17	14.89	5.39	24.27	37.84
900	without mineralizer	42.12	20.48	21.21	-	29.78	46.00
	AlF_3	43.05	24.66	27.59	7.68	37.00	48.21
	LiF	47.55	24.58	31.50	12.34	39.96	52.03
	Na_2SiF_6	40.92	20.61	20.80	1.27	29.28	45.26
	Na_3AlF_6	43.24	23.96	23.34	4.23	33.45	44.25
	NaF	36.05	13.33	14.011	11.82	19.34	46.42

Table VI Particle size distribution of $\text{Ho}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ and $\text{Lu}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ pigments prepared from FeOOH with addition of mineralizers (heating temperature 900°C)

Mineralizer	$\text{Ho}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$			$\text{Lu}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$		
	$d_{10}, \mu\text{m}$	$d_{50}, \mu\text{m}$	$d_{90}, \mu\text{m}$	$d_{10}, \mu\text{m}$	$d_{50}, \mu\text{m}$	$d_{90}, \mu\text{m}$
without mineralizer	0.36	1.90	17.10	0.39	1.94	17.10
AlF_3	0.98	3.74	15.22	0.89	4.18	18.01
LiF	0.97	4.49	17.58	0.99	3.86	14.94
Na_2SiF_6	0.92	3.80	13.52	0.91	4.02	17.01
Na_3AlF_6	1.19	4.48	14.03	1.13	4.90	26.84
NaF	1.01	3.76	11.02	0.91	3.27	9.61

Conclusion

The main aim of the present work was to synthesize the mixed metal oxide based on rare earth orthoferrite doped with calcium cations and describe their quality from the pigment-application point of view. The initial composition of pigments

was calculated according to the general formula $0.99\text{RE}_2\text{O}_3\text{-}0.02\text{CaO-Fe}_2\text{O}_3$. The pigments were synthesized by the conventional ceramic method, i.e., the solid state reaction with heating at high temperature (800-1000 °C). The main attention was focused on the measuring pigment-application properties.

Generally, the higher heating temperature stimulated the formation of lighter powders with higher saturation and with higher values of hue angle (H°). The colour of the samples was shifted from dark red (800 °C) to orange (900 °C) and light brown hue (1000 °C). The mineralizer NaF is the least appropriated for the synthesis of rare earth orthoferrites and the mineralizer LiF gives the best results of all. The most interesting colour properties were obtained by the preparation of the $\text{Lu}_{0.98}\text{Ca}_{0.02}\text{FeO}_3$ sample. This pigment was prepared by the calcination of the reaction mixture containing Lu_2O_3 , CaCO_3 , FeOOH and mineralizer LiF at the temperature of 900 °C.

Granulometric compositions of the samples prepared by heating at the temperature of 900 °C are characterized by the optimum values of median (d_{50}) in the range from 1.9 to 3.8 μm . The enlargement of the particle size distribution of powders and increase in median up to 8 μm caused the utilization of mineralizers in the reaction mixture.

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