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Effect of Er^{3+} substitution on the quality of Mg–Fe spinel pigments

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ABSTRACT

Inorganic pigments containing erbium cations and based on the spinel structure of $MgFe_2O_4$ were prepared. This type of spinel compound provides pigments of red to brown colour; an increase in the content of trivalent erbium cations results in pigments of a light brown hue. The pigments displayed good resistance to sunlight but this was reduced as the content of erbium increased. Pigments prepared using mechanoactivation possessed good resistance to sunlight over a range of erbium cation content.

1. Introduction

Pigments with a spinel structure belong to the group of mixed metal oxide pigments. Mixed metal oxide pigments can be considered as a subcategory of complex inorganic, coloured pigments. The term mixed metal oxide, does not represent a real mixture as these pigments are solid solutions or compounds consisting of two or more metal oxides. Each pigment has a defined crystal structure which is determined by the host lattice. Other oxides interdiffuse at high temperature into the host lattice structure by forming either a solid-state solution or a new compound [1].

Spinel pigments have a common chemical formula AB_2X_4; structurally they have a cubic symmetry. Based on the ions A, B and X, the spinels can be divided into three categories [2]. Most often, the X ions represent oxygen anions. In classical spinels, the A ions occupy tetrahedral sites and the B ions occupy octahedral sites, $A^{tet}B_2^{oct}O_4$. In inverse spinels, the A ions and half of the B ions swap positions to give $B^{tet}[AB]^{oct}O_4$. Between both of these extremes there is a number of intermediate spinels [1]. The manner in which such sites are occupied depends on the calcination temperature [3,4].

Spinel pigments are widely used in ceramics for colouring porcelain, glass and glazes [5–8]. The pigments provide a wide range of colours. Many of them are thermally stable up to 1400 °C. Spinel compounds, especially ferrites, also have many technological applications due to their good electric and magnetic properties [9]. In recent years, close attention has been paid to the synthesis of ferrites doped by Ti^{4+} and Ln^{3+} [10–13] and the study of the structure, electrical and magnetic properties of the resulting solids.

The main aim of the present work was to study the spinel pigment of general formula $MgFe_{2-x}Er_xO_4$, where $x = 0$–0.5. The influence of the preparation method of spinel pigments and of the isomorphous substitution of Er^{3+} for Fe^{3+} on the quality of the pigments created was also studied.

2. Experimental

2.1. Preparation of samples

The pigments $MgFe_{2-x}Er_xO_4$ ($x = 0$; 0.05; 0.1; 0.2; 0.3; 0.4 and 0.5) were prepared by three methods of preparation. The first method represents a simulation of "Mixer Dryer Reactor" (MDR), under laboratory conditions [14]. This is a two-step method. The first step represents mixing the initial reagents, as suspensions, in a porcelain mortar. The suspension were then deposited on an alloy steel sheet and heated at 400 °C on an alloy steel sheet. The reaction mixture contained equimolar amounts of $MgCO_3$ (Lachema a.s., CR), Er_2O_3 (Indian Rare Earths Ltd., India) and $Fe_2(SO_4)_3 \cdot nH_2O$ (Lachema a.s., CR). The second step represents a classical calcination in an electric resistance furnace with an increase of temperature of 4 °C/min. The final temperature of the second step of synthesis, 900 °C, was maintained for 2 h. Then, the fired samples were decanted in hot water, filtered and dried.

The second method of preparation is based on the classical ceramic method (CM) [15]. The reagents $MgCO_3$ (Lachema a.s., CR), Er_2O_3 (Indian Rare Earths Ltd., India) and Fe_2O_3 (Precheza a.s., CR) were weighed in suitable molar proportions and subsequently ground manually in a porcelain mortar to obtain a "homogenous"

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reaction mixture. The reaction mixtures were heated at temperature 900 °C (4 h) in an electric resistance furnace. The heating rate was 4 °C/min. Corundum crucibles were used. The samples were gradually cooled to room temperature, ground in an agate mortar and heated again at 1200 °C for 5 h.

The third method of preparation (mechanoactivation) represents the classical ceramic method. Here, reagents were mechanochemically activated before heating [16]. The high energy milling process was carried out in a planetary ball mill Pulverisette 5 (Fritsch GmbH, Germany) for 6 h. The reaction mixture of $MgCO_3$, Er_2O_3 and Fe_2O_3 was ground together with agate balls (Ø 10 mm) in a ball-to-powder weight ratio of 20:1. The activated reaction mixtures were then heated at 900 °C (4 h) and then at 1200 °C (5 h). The products were gradually cooled to room temperature and subsequently ground in an agate mortar.

2.2. Characterisation of samples

The samples of pigments were formulated into an organic matrix in a mass tone format and evaluated with respect to their colour properties by measurements of the spectral reflectance. The measurement was carried out in the visible region (ColourQuest XE (HunterLab, USA)). The measuring system is CIE $L^*a^*b^*$ colour. Here, coordinate L^* expresses degree of brightness and coordinates a^* and b^* describe the colour hue. Thorough description of colour is done by recalculation of chroma extent C, according the formula $C = (a^{*2} + b^{*2})^{1/2}$ and the hue angle, $H^\circ = \text{arstan}\ a^*/b^*$. The next measurement conditions involved: illuminant D65 (6500 K), 10° complementary observer and the geometry of measurements being $d/8°$.

Determination of changes in colour properties after exposure of samples to daylight under glass was carried out. The samples were exposed to a xenon-arc light source in a Q-panel test chamber (Lab. Products, USA) for 360 h with an irradiance setting at 340 nm and 0.51 W m^2. The maximum black panel temperature was about 65 °C.

The particle size distribution of the samples was measured using a Mastersizer 2000/MU (Malvern Instruments, UK). The equipment employs the scattering of incident light on particles. The solids were ultrasonically homogenized for 90 s and measured in a solution with $Na_4P_2O_7$ ($c = 0.15$ mol/dm^3). The signal was evaluated on the basis of Fraunhofer bending. An electron microscope (JOEL JSM 5500 LV (JOEL Inc. USA)) was used to characterize the spinel pigments with respect to their particle size and their overall appearance.

The crystal structures of the powdered materials were studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using a Brucker (GB) difractometer D8 (Bruker, GB) with a goniometer of 17 cm in the range 2Θ of 10–80°. Cu $K_{\alpha 1}$ ($\lambda = 0.15418$ nm) radiation was used for angular range of $2\Theta < 35°$ and Cu $K_{\alpha 2}$ ($\lambda = 0.15405$ nm) for the range of $2\Theta > 35$. A scintillation detector was used.

Table 1
L^*, C, H° values for pigments of general composition $MgFe_{2-x}Er_xO_4$

x	CM method			MDR method			Mechanoactivation		
	L^*	C	H°	L^*	C	H°	L^*	C	H°
0	30.80	17.43	26.58	43.93	28.65	49.86	31.13	17.16	29.72
0.05	34.48	23.36	31.67	41.28	26.48	46.93	35.53	21.95	34.57
0.1	33.38	28.62	34.76	42.22	24.78	46.47	37.37	25.21	35.80
0.2	36.77	30.49	39.93	39.74	20.41	51.55	36.94	24.42	38.51
0.3	37.12	28.75	42.26	42.04	20.74	46.84	35.48	19.92	39.18
0.4	36.49	28.70	43.27	37.82	15.19	48.30	35.12	20.89	41.95
0.5	37.68	22.56	43.05	36.59	13.11	49.99	34.08	17.70	41.79

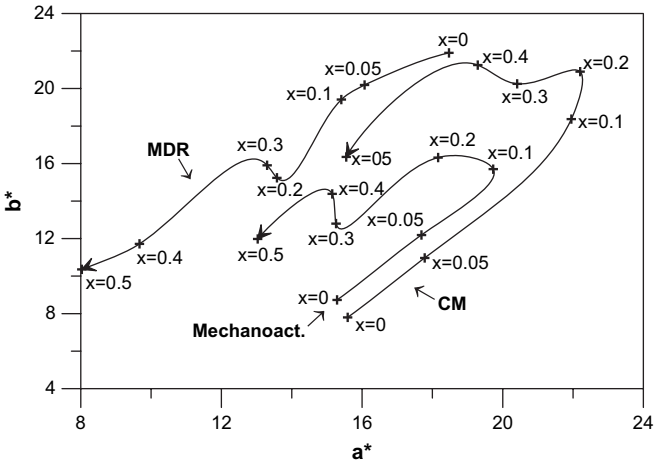

Fig. 1. The influence of the synthesis method and of the Er^{3+}/Fe^{3+} substitution on the red hue and on the yellow colour hue.

3. Results and discussion

The pigments of general formula $MgFe_{2-x}Er_xO_4$ are characterised by their deep brick red to brown colour. The pigments prepared by the classical ceramic method (CM) and by mechanoactivation show similar trends in the variation of the colour hue related to increasing amount of Er^{3+} to Fe^{3+} substitution. Values for the colour coordinates a^* and b^* and therefore the colour hue H°, of the samples prepared by the CM method are higher than the values of the colour hue H° of samples prepared by mechanoactivation. The chroma of the pigments prepared by the CM method increases up to the value of $x = 0.2$. Then the values of the chroma decrease (Table 1). The change of the red and yellow hues is clearly shown in Fig. 1. There is a considerable increase of the redness of samples containing not more than 10 mol% of erbium. Further increasing of Er^{3+} substitution leads to the loss of red hue that is expressed by lower values of colour coordinate a^*. The same trend comes through in the change of colour coordinate b^*. The extent of yellowness increases up to the content of erbium 10 mol% ($x = 0.2$). Between 10 and 20 mol% of erbium ($x = 0.2$–0.4), the amount of yellowness slightly varies. An increase of erbium to 25 mol% ($x = 0.5$) causes a decrease in the yellowness. The preparation of pigments by the CM method gave further interest in the clearer and richer colours that are achieved. Pigments prepared by MDR method proved wholly different colour properties depending on increase in the Er^{3+}/Fe^{3+} substitution. The sample, $MgFe_2O_4$, gave the highest values of both colour coordinates and therefore provides the most interesting red ochre colour hue (Fig. 1). The presence of erbium cations causes a slight decrease in the colour coordinates a^*, b^*. However, the colour hue expressed by the colour coordinate H° does not vary too much. The pigments have brown

Table 2
Particle size values of pigments $MgFe_2O_4$, $MgFe_{1.9}Er_{0.1}O_4$, $MgFe_{1.5}Er_{0.5}O_4$

Synthesis method	Milling time [min]	$MgFe_2O_4$	$MgFe_{1.9}Er_{0.1}O_4$	$MgFe_{1.5}Er_{0.5}O_4$
		d_{50} [μm]	d_{50} [μm]	d_{50} [μm]
CM	0	25.95	32.25	11.01
	20	2.08	2.86	4.23
	40	1.46	2.19	2.97
Mechanoactivation	0	48.53	29.30	19.07
	20	4.09	4.52	3.03
	40	3.42	1.82	1.87
MDR	0	4.89	7.56	8.30
	20	1.14	1.05	1.36
	40	0.88	1.05	1.20

Table 3
Effect of milling on the colour properties of the pigment $MgFe_2O_4$

Systhesis method	Mjilling time [min]	L^*	a^*	b^*	C	ΔE^*_{CIE}
CM	0	30.80	15.59	7.80	17.43	–
	20	35.73	16.60	11.48	20.18	6.23
	40	37.00	16.85	13.22	21.42	8.33
Mechanoactivation	0	31.13	15.29	8.73	17.61	–
	20	35.39	17.80	11.12	20.99	5.49
	40	38.28	18.60	12.80	22.58	8.87
MDR	0	43.93	18.47	21.90	28.65	–
	20	45.30	20.91	23.35	31.34	3.15
	40	47.11	22.72	25.70	34.30	6.53

colour hues that are characterised by the lesser richness of colour (Table 1). The pigments prepared by the MDR method gave increased darkness with increase in the erbium cation content.

The preparation method and the heating temperature affect not only the colour related properties, but also the particle size distribution (PSD). The PSD was measured after preliminary grinding in an agate mortar. Samples of pigments that were prepared by the CM method and by the mechanoactivation are characterised by higher mean values of particles in the number interval of d_{50} 11–49 μm. However, the mean values of the pigment particles that were prepared by the MDR method are in the number interval 5–9 μm (Table 2). The difference in PSD is particularly caused by the lower heating temperature of the MDR method. Better granulometric composition was obtained after wet milling at 20- and 40-min intervals. The mean values of d_{50} were decreased about 1–4 μm (Table 2). Reduction of particle size distribution affected the colour properties of the samples. Samples became brighter and the colour hue became richer. Values of the colour coordinates a^* and b^* are higher. A comparison of all of the colour coordinates of samples of $MgFe_2O_4$, before and after wet milling, is summarised in Table 3. The values of total colour difference between the samples, before and after milling, are greater than 3, meaning that the difference is visible to the human eye. A similar trend in the change of colour properties also applies to the samples of pigments containing the erbium cations. The total colour difference was calculated according to: $(\Delta E^*_{CIE} = ((L^*)^2 + (a^*)^2 + (b^*)^2)^{1/2})$.

Electron microscopy was used to characterize the spinel pigments with respect to their overall appearance and to confirm the results of the PSD as measured by laser diffractometry. Fig. 2(a) and (b) demonstrates the similar, almost spherical, shapes of particles that were prepared by the CM method and by the mechanoactivation. The powders predominantly consist of 1 μm particles. However, larger particles are also in attendance. The shape of the particles that were prepared by the MDR method is wholly different (Fig. 2(c)), probably explaining the divergence in colour properties of the samples prepared by the MDR method.

The light stability of formulations containing the spinel pigments $MgFe_2O_4$, $MgFe_{1.9}Er_{0.1}O_4$ and $MgFe_{1.5}Er_{0.5}O_4$, expressed as the total colour difference between the non-irradiated samples and the irradiated samples is given in Fig. 3. The samples were exposed

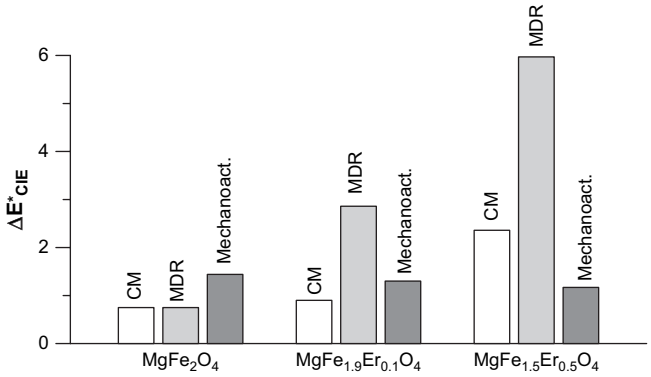

Fig. 3. The total colour difference of pigments after sunlight irradiation.

to a radiation load of 661 kJ/m^2. The samples that did not contain erbium cations were the most stable. Their colour change was almost imperceptible to the human eye. Increasing the erbium cation content causes degradation of pigment, particularly in the case of those pigments produced by the CM and MDR methods. Irradiation causes the pigments to become lighter and the yellow colour hue becomes more intensive. From the light stability point of view, the most suitable method of synthesis is mechanoactivation. This way allows the preparation of samples that are stable to sunlight and whose total colour difference (ΔE^*_{CIE}) after irradiation is less than 1.5. In this exact method of synthesis, the partial substitution of iron cations by erbium cations results in the better and sunlight resistant colour properties than are obtained using the spinel compound, $MgFe_2O_4$.

The colour fastness to irradiation could be associated with the phase composition of the samples. Results from the X-ray diffraction analysis demonstrate that the samples are not single phase systems (Table 4). The synthesis of the single phase red pigment, $MgFe_2O_4$, demonstrates that the MDR process is a suitable method for the preparation of this product. The MDR method provides a single phase system at 900 °C, a temperature that is lower (by about 300 °C) than other methods. On the other hand, the CM method seems to be inappropriate for the synthesis of spinel pigments. This is seen in the fact that the prepared sample is two phase system and also contains unreacted iron oxide. The pigment, $MgFe_2O_4$, has a cubic structure and value of lattice parameter a of 0.83873 nm. Systems containing erbium cations were not prepared as single phase systems. In the diffraction pattern of sample $MgFe_{1.9}Er_{0.1}O_4$ (composition calculated from the content of initial reactants) were identified the diffraction lines of $MgFe_2O_4$ and $ErFeO_3$ in the case of synthesis by the CM method or by mechanoactivation. An assumption that erbium cations replace the iron cations is based on the slight shift of the $MgFe_2O_4$ diffraction lines. Besides $MgFe_2O_4$ and $ErFeO_3$, unreacted erbium oxide was detected in the diffraction pattern of the sample $MgFe_{1.9}Er_{0.1}O_4$ that was prepared by the MDR method. The sample $MgFe_{1.5}Er_{0.5}O_4$ is two

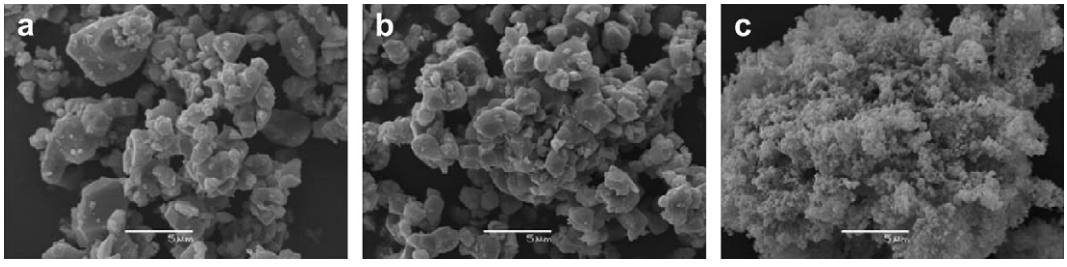

Fig. 2. SEM characterisation of the pigments $MgFe_2O_4$ prepared by: (a) the CM method; (b) the mechanoactivation method and (c) the MDR method.

Table 4
Phases composition of the pigments $MgFe_2O_4$, $MgFe_{1.9}Er_{0.1}O_4$, $MgFe_{1.5}Er_{0.5}O_4$

Systhesis method	Identified phases in pigments		
	$MgFe_2O_4$	$MgFe_{1.9}Er_{0.1}O_4$	$MgFe_{1.5}Er_{0.5}O_4$
CM	$MgFe_2O_4$	$MgFe_2O_4$	$MgFe_2O_4$
	Fe_2O_3	$ErFeO_3$	$ErFeO_3$
			Er_2O_3
Mechanoactivation	$MgFe_2O_4$	$MgFe_2O_4$	$MgFe_2O_4$
		$ErFeO_3$	$ErFeO_3$
MDR	$MgFe_2O_4$	$MgFe_2O_4$	$MgFe_2O_4$
		$ErFeO_3$	$ErFeO_3$
		Er_2O_3	Er_2O_3

phase system only in the case of synthesis by mechanoactivation. On the diffraction patterns were identified lines associated with $MgFe_2O_4$ and $ErFeO_3$. The shift of the diffraction lines and the value expansion of lattice parameter a of $MgFe_2O_4$ ($a = 0.8393$ nm) indicate the placing of erbium cations in the crystal lattice of $MgFe_2O_4$. Other ways of synthesis (the CM method and the MDR method) produced three phase systems and the samples of $MgFe_{1.5}Er_{0.5}O_4$ that resulted also contained $MgFe_2O_4$ and $ErFeO_3$ as well as unreacted erbium oxide.

4. Conclusion

The main aim of the research was to prepare spinel compounds that have application as inorganic pigments. The pigments, of general formula $MgFe_{2-x}Er_xO_4$, have deep red wine to light brown and ochre colour hues. The temperature of the spinel structure formation is affected by the method of preparation. The MDR method produced a single phase ochre pigment, $MgFe_2O_4$, at 900 °C. The mechanoactivation method and the CM method gave the synthesis of a wine red coloured pigment $MgFe_2O_4$ at a temperature of 1200 °C. $MgFe_2O_4$ based pigments show good resistance to sunlight. Increasing Er^{3+}/Fe^{3+} substitution leads to a change of colour hue. The pigments become darker and more brown than red. In the case of the CM method of synthesis and the MDR method of synthesis, the partial substitution of iron cations by erbium also affects the sunlight stability. Increasing contents of erbium cations caused a deterioration in the colour hue after sunlight irradiation. The opposite effect was seen in pigments that were prepared by mechanoactivation. The Er/Fe substitution stabilizes colour properties after sunlight irradiation.

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