THE EFFECT OF MINERALIZERS ON SYNTHESIS OF $Er_2Ce_2O_7$

Hablovičová B., Šulcová P.

University of Pardubice, Faculty of Chemical Technology, Department of Inorganic Technology, Studentská 95, 532 10 Pardubice, Czech Republic
blanka.hablovicova@student.upce.cz

Abstract

Pigment with pyrochlore structure $Er_2Ce_2O_7$ was prepared by mechanical activation. Mineralizers $CaCl_2$, $Na_2B_4O_7$, $FeCl_3$-NaCl, $CeCl_3$-KCl and $MgCl_2$-MgO were added in 5 wt. % before firing at temperature 1400 °C for 3 hours (heating rate 10 $°C \cdot min^{-1}$) in the electric furnace. Colour properties in the organic matrix in mass tone and ceramic glaze G 070 91 in 10 wt. %, particle size distribution and phase composition were investigated. Synthetized samples were visually pink or brown-orange in organic matrix and orange in the ceramic glaze. $Er_2Ce_2O_7$ was always created but samples were not single-phase mostly.

Introduction

Inorganic pigments are used for colouring e.g. plastics, paints or ceramics. But many of ceramic pigments contain toxic elements (Hg, Cd, As etc.) which are big ecology problem. Substitution of these problematic metals by lanthanides could be a solution[1]. Lanthanide oxides have been used in various fields of the industry due to their excellent physical and chemical properties (e.g. good phase stability, high thermal conductivity, excellent optical properties)[2]. Research is focused on the incorporation of the lanthanides into the pyrochlore structure because these compounds have also many interesting chemical and physical properties (used as dielectric materials, catalysts, thermal barrier coatings etc.)[3,4]. Pyrochlores have general formula $A_2B_2O_7$ in which cation A has charge 3+ (or 2+) and cation B has charge 4+ (or 5+)[5]. Many pyrochlore compounds with lanthanides as e.g. $Ln_2Ce_2O_7$, $Ln_2Zr_2O_7$, $Ln_2Ti_2O_7$ or $Ln_2Hf_2O_7$ were investigated in a lot of studies[6-10], but not for colour properties. The main aim of this research is the evaluation of colour properties of compound $Er_2Ce_2O_7$ prepared by mechanical activation with using of mineralizers. This procedure of synthesis was chosen on the basis of the previous research[11] which has been on the synthesis of single-phase pigment needed firing temperature 1600 °C. Mechanical activation in the mill is the simply method and arouses the interest of technologists due to mechanical and physical processes which extend during the milling[12]. Mineralizers are usually low-melting compounds. They act like the catalysts, assists formation of solid solutions, which help create more homogeneous products at the lower temperature and they can affect the colour properties[13,14].

Experiment

Compound with formula $Er_2Ce_2O_7$ was synthetized by mechanical activation. Stoichiometric amounts of oxides Er_2O_3 (99.9 %, Alfa Aesar) and CeO_2 (99.5 %, ML chemica, Czech Republic) were transferred to agate grinding bowl with 30 agate balls (diameter 1 cm). The closed bowl was placed in the planetary mill (Pulverisette 5, Fritsch, Germany) and the mixture was homogenized for 5 hours (200 rpm). Mineralizers were added to this pre-prepared mixture in 5 wt. %. Two salts ($CaCl_2$, $Na_2B_4O_7$) and three salt systems ($FeCl_3$-NaCl, $CeCl_3$-KCl, $MgCl_2$-MgO) were used as mineralizers. All mixtures (including without mineralizer) were put to corundum crucibles and were fired at temperature 1400 °C for 3 hours (heating rate 10 $°C \cdot min^{-1}$) in the electric furnace (Clasic, Clasic CZ s.r.o., Czech Republic). Prepared compounds were applied to the organic matrix (dispersive acrylic paint

Parketol, Balakom a.s., Czech Republic) in mass tone and into the ceramic glaze (G 070 91, Glazura s.r.o., Czech Republic) in 10 wt. %.

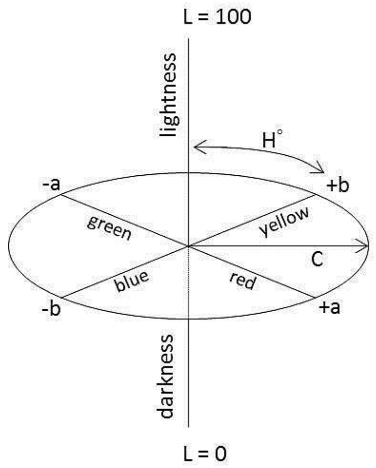
Colour properties for these applications were measured by spectrophotometer ColorQuest (HunterLab, USA) which used geometry d/8°, standardized day light with indication D65 and colour system CIEL*a*b* (Figure 1). L* represents lightness (from black = 0 to white = 100) and a* (red - green) and b* (yellow - blue) are colour coordinates (a* = 0 and b* = 0 → grey). Chroma C is degree of saturation (from grey to clear colour) and hue H° indicates degree of colour (350-0-35° = red, 35-70° = orange, 70-105° = yellow, 105-195° = green, 195-285° = blue, 285-350° = violet) and they are characterized by formulas $C = (a^{*2}+b^{*2})^{1/2}$ and $H^{\circ} = arctg(b^*/a^*)$. ΔE* represents colour difference between two colours. If it not exceeds value one the difference is imperceptible by human eye. Noticeable change can be observed when the ΔE* ≥ 1. It is calculated from equation $\Delta E^* = [(\Delta a^*)^2+(\Delta b^*)^2+(\Delta L^*)^2]^{1/2}$, e.g. Δa* means value a* of sample minus value a* of selected standard[15].

Particle size distribution of powder materials was measured by Mastersizer 2000/MU (Malvern Instruments, UK), which operating on the principle of laser diffraction on particles dispersed in liquid medium ($Na_4P_2O_7$ was used). Device contains red light (He-Ne laser, λ = 633 nm) and blue light (laser diode, λ = 466 nm). Fraunhofer bend was used for evaluating of the signal.

Phase compositions of powder samples were verified by diffractometer D8 Advance (Bruker AXS, UK) with the vertical goniometer. Measuring range 2θ was 10-80° and copper radiation was used.

Discussion and result analysis

Colour properties of all prepared compounds after application into the organic matrix in mass tone and into the ceramic glaze in 10 wt. % are shown in Figure 2 and in Table I (table also contains abbreviations of samples which are used in this paper). Sample without mineralizer E ($Er_2Ce_2O_7$) was selected as the standard for calculation of colour difference. Samples in organic matrix acquired pink shades except of EF ($Er_2Ce_2O_7$ + $FeCl_3$-NaCl) which is orange-brown (the highest values of both colour coordinates) due to iron ions. Colour properties recorded in Table I confirms this difference of EF (the lowest lightness 66.95, the highest chroma 33.60 and great colour difference 20.13). Against that the lowest contribution of red component (low a*) has sample EN ($Er_2Ce_2O_7$ + $Na_2B_4O_7$) which has the highest lightness 84.97, the lowest chroma 15.69 and the second highest colour difference 6.36. Other samples are similar. Hues of pigments are located in the orange area (57.89 - 58.34) even though they appear as a pink mostly (it is due to a higher contribution of the yellow component). Samples look almost identically in ceramic glaze except EF again (L* = 71.81, C = 32.98, ΔE*= 15.33), other five have similar chroma, lightness and colour differences are low (very similar colour EA ($Er_2Ce_2O_7$ + $CaCl_2$), EN, EC ($Er_2Ce_2O_7$ + $CeCl_3$-KCl) and EM ($Er_2Ce_2O_7$ + $MgCl_2$-MgO) with E). These results correspond with a*-b* diagram which shows increase of coordinate b* and decrease of coordinate a*. It is caused by glaze, lead inside glaze have the tendency to be yellowish themselves[16].



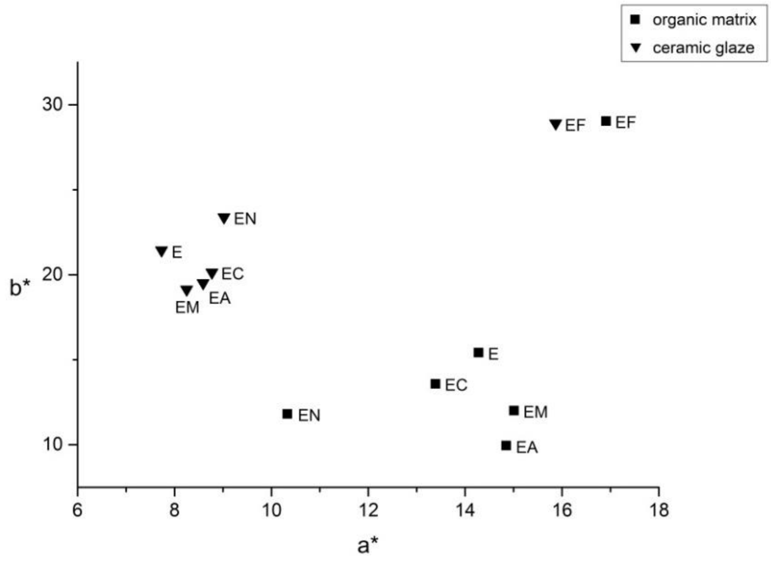


Figure 1. CIEL*a*b* colour space.

Figure 2. The effect of mineralizers and application on values of colour coordinates a* and b* (a*-b* diagram).

Table I
Colour properties of compound $Er_2Ce_2O_7$ without and with mineralizers applied into the organic matrix in mass tone and into the ceramic glaze in 10 wt. %.

Sample	Organic matrix				Ceramic glaze			
	L*	C	H°/°	ΔE*	L*	C	H°/°	ΔE*
E ($Er_2Ce_2O_7$)	81.54	21.02	58.12	---	82.44	22.79	58.52	---
EA ($Er_2Ce_2O_7$ + $CaCl_2$)	83.02	17.88	57.89	5.70	83.33	21.33	58.45	2.28
EN ($Er_2Ce_2O_7$ + $Na_2B_4O_7$)	84.97	15.69	58.15	6.36	81.62	25.07	58.50	2.48
EF ($Er_2Ce_2O_7$ + $FeCl_3$-NaCl)	66.95	33.60	58.34	20.13	71.81	32.98	58.36	15.33
EC ($Er_2Ce_2O_7$ + $CeCl_3$-KCl)	82.19	19.07	58.09	2.14	82.70	21.97	58.46	1.68
EM ($Er_2Ce_2O_7$ + $MgCl_2$-MgO)	82.45	19.22	57.97	3.60	83.15	20.84	58.46	2.46

Mean particle sizes (d_{50}) of samples are shown in Figure 3. The optimal particle size of inorganic pigments for applications into organic matrix (plastics) is about or less 2 μm and for applications into the ceramic glazes is located in interval 5 - 15 μm[17]. Mean particle sizes of samples have range between 6.9 - 14.9 μm. $Er_2Ce_2O_7$ without mineralizer has d_{50} = 9.3 μm. Samples with salt systems as mineralizers obtain larger mean particle sizes (EF = 14.9 μm, EC = 12.0 μm, EM = 11.2 μm), samples with one salt as mineralizer have smaller d_{50} (EA = 6.9 μm, EN = 8.3 μm).

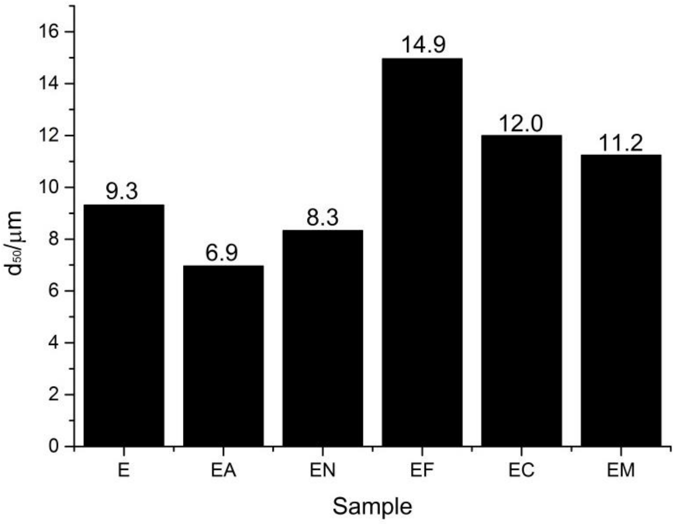


Figure 3. Mean particle sizes of compound $Er_2Ce_2O_7$ without and with mineralizers.

Phase composition of synthetized pigments was studied as next (Figure 4, Table II). One-, two- and three-phase compounds were prepared. All samples contain required pyrochlore structure of $Er_2Ce_2O_7$. EF is single-phased, E, EA, EC and EM include starting oxide Er_2O_3. EM moreover comprises MgO which remains in the compound due to very high temperature of melting point. Pigment EN with mineralizer borax contains $ErBO_3$.

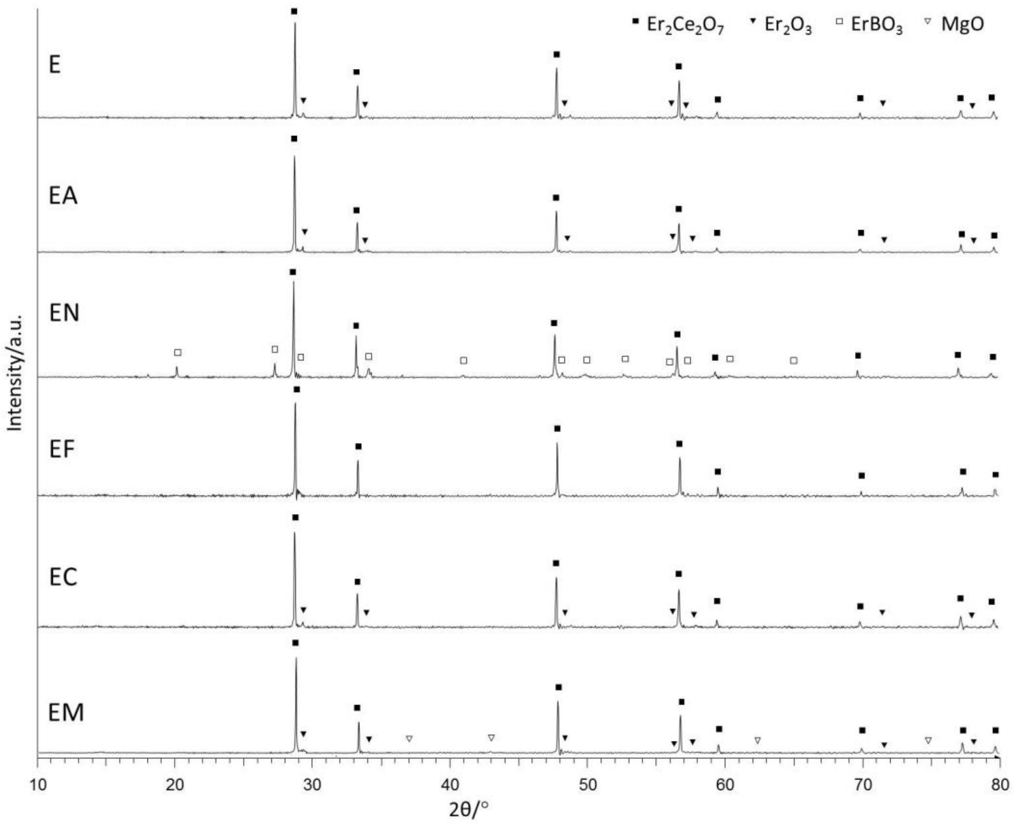


Figure 4. Phase composition of compound $Er_2Ce_2O_7$ without and with mineralizers.

Table II
Information about crystal structure and JPDF numbers of compound $Er_2Ce_2O_7$ without and with mineralizers.

	Phase composition	Crystal structure	JPDF number[18]
E	$Er_2Ce_2O_7$	cubic	04-012-6402
	Er_2O_3	cubic	04-015-0575
EA	$Er_2Ce_2O_7$	cubic	04-012-6402
	Er_2O_3	cubic	04-008-8242
EN	$Er_2Ce_2O_7$	cubic	04-012-6402
	$ErBO_3$	hexagonal	04-010-9114
EF	$Er_2Ce_2O_7$	cubic	04-012-6402
EC	$Er_2Ce_2O_7$	cubic	04-012-6402
	Er_2O_3	cubic	04-015-0575
EM	$Er_2Ce_2O_7$	cubic	04-012-6402
	Er_2O_3	cubic	04-008-8242
	MgO	cubic	00-045-0946

Conclusion

The inorganic pigment with pyrochlore structure $Er_2Ce_2O_7$ was prepared by mechanical activation, before firing at 1400 °C for 3 hours (heating rate 10 $°C \cdot min^{-1}$) in the electric furnace five mineralizers were added into this pre-prepared mixture. Synthetized powders were applied to the organic matrix in mass tone and ceramic glaze G 070 91 in 10 wt. %. Samples obtain pink and orange-brown colours in organic matrix and orange colour shades in the ceramic glaze. Compound without mineralizer was chosen as the standard for evaluation of colour difference. Colour properties have been most affected by mineralizer $FeCl_3$-NaCl due to iron ions. The lowest influence to colour difference has mineralizer $CeCl_3$-KCl. Synthetized powder materials are suitable for applications into the ceramic glazes according to mean particle sizes, but for applications into plastics and coatings particle size should be modified. $Er_2Ce_2O_7$ was created for all samples, but only $Er_2Ce_2O_7$ with $FeCl_3$-NaCl was single-phase. Probably, some substances are below the detection limit of diffractometer due to a small amount of added mineralizers so they were not revealed. Prepared compounds have potential to become environmental friendly inorganic ceramic pigments.

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