COMPARISION OF THE COLOR PROPERTIES OF COMPOUNDS $Ln_2Ce_2O_7$ AND Ln_2CeZrO_7

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Pyrochlore type pigments $Ln_2Ce_2O_7$ and Ln_2CeZrO_7 (Ln = Nd, Sm, Gd, Dy, Er, Yb and Y) prepared by solid-state reaction were investigated. Effect of rare earths and zirconium ions and calcination temperature (1400, 1500 and 1600°C for $Ln_2Ce_2O_7$ and 1400, 1450 and 1500°C for Ln_2CeZrO_7) on their color properties in organic matrix and ceramic glazes, particle size distribution and phase composition were evaluated. The most interesting shades achieve compounds with the highest calcination temperature. Their colors depend on used rare earth ions (shades change from green, cross yellow to pink in organic mass and from green, cross yellow-green to orange in ceramic glazes), while compounds without zirconium have better color properties. Pigments $Ln_2Ce_2O_7$ calcined at 1600°C are single-phase (except $Yb_2Ce_2O_7$).

INTRODUCTION

Natural inorganic pigments have been known since prehistoric times. Natural ocher was used in Ice Age over 60 000 years ago as coloring material. About 2000 BC this ocher was burnt to producing red, violet and black pigments for pottery. First pigment with pyrochlore structure was Naples yellow [1]. Many of ceramic pigments used in ceramic industry contain transition and heavy metals. Interest of environmental pigments without toxic elements (such as e.g. Pb, Hg, Cd, Sb, As or Cr) is growing for this reason. These are mainly materials where transition elements are exchanged by lanthanides [2].

We try to synthetized new environmentally friendly pigments in authors workplace. These compounds could replace existing toxicological unsuitable pigments in the future. Compounds with formula $Ln_2Ce_2O_7$ and Ln_2CeZrO_7 could be considered as such pigments.

Pyrochlore minerals may be represented by formula $NaCa(Nb,Ta)_2O_6(OH,F)$ [3]. So, where in this formula is chlorine? Nowhere. Name of pyrochlore originates from Greek words for “fire” and “green”, because when it is ignited, it turns green [4]. Pyrochlore group has general formula $A_{2-x}B_2O_6(O,OH,F)_{1-y}\cdot pH_2O$ and three subgroups based on atomic proportion of B atom: pyrochlore, microlite and betafite [5]. However, $A_2B_2O_7$ indicates as general formula for pyrochlores mostly [6-8]. Element A has oxidation state 2+ or 3+ and element B has oxidation state 5+ or 4+ for charge neutrality [9]. Crystal structure of pyrochlores is anion deficient fluorite structure (Fm3m, Z = 8) [3, 7].

Lanthanide zirconates with pyrochlore structure were studied in most of works [8, 10-12], but not for pigment properties. Rare earth oxides (lanthanide oxides) have excellent physical and chemical properties as good phase stability, fluorescent performance etc. so they have specially attention in various fields. Lanthanide oxides can occur in three crystalline types below temperature 2000°C: A, B and C; above 2000°C they are indicate as H and X [13]. Rare earth oxides are stable on composition Ln_2O_3 except CeO_2, Pr_6O_{11} and Tb_4O_7. These are white to cream colored powders (Er_2O_3 is pink, Nd_2O_3 is blue-violet). Melting points of Ln_2O_3 is ranging around 2400°C [14] and refractive indexes are in interval from 1.90 to 1.99 [15]. Zirconium oxide exists in three modifications by temperature: monoclinic (m-ZrO_2) is stable to 1170°C, tetragonal (t-ZrO_2) occurs in range 1170 - 2370°C and cubic (c-ZrO_2) is stable above 2370°C [16]. Refractive index of zirconium oxide is about 2.19 for t-ZrO_2 and c-ZrO_2 and 2.24 for m-ZrO_2 [17].

The aim of this work is evaluating the influence of compounds $Ln_2Ce_2O_7$ and Ln_2CeZrO_7 (Ln = Nd, Sm, Gd, Dy, Er, Yb and Y) synthetized by solid-state reaction. Color properties, particle size distribution and phase composition were measured.

EXPERIMENTAL

Compounds with general formula $Ln_2Ce_2O_7$ and Ln_2CeZrO_7 (Ln = Nd, Sm, Gd, Dy, Er, Yb, Y) were prepared by solid-state reaction. Stoichiometric amounts of Nd_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3, Yb_2O_3 or Y_2O_3 (all 99.9 %, Alfa Aesar) and CeO_2 (99.9 % Alfa Aesar) were homogenized for $Ln_2Ce_2O_7$. ZrO_2 (98.5 %, Glazura s.r.o., CZ) was extra added to previous oxides for compounds Ln_2CeZrO_7. Mixtures were transfered to corundum crucibles after homogenization. Compounds $Ln_2Ce_2O_7$ were calcined at temperatures 1400, 1500 and 1600°C for 3 hours (heating rate 10°C·min^{-1}) in air atmosphere. Only calcination temperatures differed for compounds Ln_2CeZrO_7, they were 1400, 1450 and 1500°C, because there would be sintering at higher temperatures. All synthesized pigments were applied to organic matrix, dispersive acrylic varnish Parketol specifically (Balakom a.s., CZ), in mass tone. Selected pigments were applied to ceramic glazes G 050 91 and G 070 91 (both Glazura s.r.o., CZ) in 10 wt. %, calcined at 1000°C for 15 min (heating rate 10 °C·min^{-1}).

Color properties were evaluated by spectrophotometer ColorQuest XE (HunterLab, USA), which used color system CIE L*a*b* for measurements. L* represents lightness (0 = black, 100 = white) and coordinates a* and b* describe color hue. Coordinate a* indicates color hue from green (–a*) to red (+a*), while b* means hue from blue (–b*) to yellow (+b*). Chroma and degree of color tone were calculated from equations (1 and 2). H° has interval from 0° to 360° (350-0-35° = red, 35-70° = = orange, 70-105° = yellow, 105-195° = green, 195-285° = = blue, 285-350° = violet) [18].

$$C = (a^{*2} + b^{*2})^{1/2} \quad (1)$$

$$H^\circ = arctg\,(b^*/a^*) \quad (2)$$

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. 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 signal. Solution $Na_4P_2O_7$ (0.15 g·l^{-1}, 40 ml) was added to the sample (about 0.3 - 0.5 g). Suspension was given to ultrasonic bath for 90 s. Meanwhile solution $Na_4P_2O_7$ (3 g·l^{-1}, 4.8 ml) was added to distilled water (800 ml) as background, which was measured. Suspension was poured into this solution immediately after dispergation (max. concentration 12.5 ± 0.5 %). Then the measurement was started.

Phase composition of the most interesting compounds was studied by difractometer D8 Advance (Bruker AXS, UK) with vertical goniometer θ-θ (radius 217.5 mm). Measuring range of 2θ was 10 - 80° (with step 0.020°). Radiation Cu $K_{\alpha 1}$ (λ = 0.15418 nm) was used for angular range 2θ < 35° and Cu $K_{\alpha 2}$ (λ = 0.15405 nm) for range 2θ > 35° (X-ray tube with Cu anode, X-ray of copper, secondary graphite monochromator, scintilation NaI counter).

RESULTS AND DISCUSSION

Color properties in organic matrix

All prepared pigments were applied into organic matrix in mass tone at first. Color properties of compounds $Ln_2Ce_2O_7$ are shown in Table 1. Pigments doped by neodymium have green shades, which prove color coordinates (coordinate a* from –9.62 to –9.10, decreasing with increasing temperature) and degree of color tone H° (values 118.81° - 125.54°). Color of compounds with erbium is pink, due to coordinates a*, which have the highest value of all compounds (10.77 - 14.82) and degree of color tone H° has the smallest ones (21.61° - 23.62°). $Gd_2Ce_2O_7$ is yellow and other pigments are characterized by yellow-green shades, because coordinates a* are negative. All compounds have positive color coordinate b* (no blue shade). Pigments calcined at 1600°C achieve the best color properties. Color properties of compounds Ln_2CeZrO_7 are shown in Table 2. Color shades of these pigments are very similar as shades of $Ln_2Ce_2O_7$, but degrees of color tones are higher generally. The best color properties give pigments calcined at the highest temperatures. All synthetized pigments have very high values of lightness, higher than 80 except compounds doped by neodymium (L* = = 75.05-78.75). Conversely, chroma of all pigments is very low (below 24).

Table 1. Color properties of $Ln_2Ce_2O_7$ applied to organic matrix in mass tone.

Ln	1400°C					1500°C					1600°C				
	L*	a*	b*	C	H°	L*	a*	b*	C	H°	L*	a*	b*	C	H°
Nd	77.99	-9.10	12.74	15.66	125.54	75.71	-9.40	15.74	18.33	120.85	75.05	-9.62	17.49	19.96	118.81
Sm	89.75	-0.35	15.21	15.21	91.32	90.04	0.02	20.77	20.77	89.95	89.33	-0.46	22.44	22.44	91.17
Gd	89.71	1.56	15.68	15.76	84.32	87.40	1.78	19.51	19.59	84.79	87.90	1.56	19.83	19.89	85.50
Dy	91.68	-0.86	11.46	11.49	94.29	90.80	-1.76	17.36	17.45	95.79	89.61	-1.23	22.12	22.15	93.18
Er	87.11	10.77	4.71	11.75	23.62	84.80	14.82	6.36	16.13	23.23	85.61	13.96	5.53	15.02	21.61
Yb	90.78	0.82	9.33	9.37	84.98	92.25	-1.05	9.55	9.61	96.27	91.74	-1.46	12.49	12.58	96.67
Y	90.67	1.36	10.10	10.19	82.33	91.79	-0.90	8.59	8.64	95.98	91.15	-0.83	15.78	15.80	93.01

Table 2. Color properties of Ln_2CeZrO_7 applied to organic matrix in mass tone.

Ln	1400°C					1450°C					1500°C				
	L*	a*	b*	C	H°	L*	a*	b*	C	H°	L*	a*	b*	C	H°
Nd	78.75	-7.95	9.03	12.03	131.36	75.73	-8.29	11.69	14.33	125.34	78.49	-8.74	10.63	13.76	129.43
Sm	90.75	-0.84	14.95	14.97	93.22	89.43	-0.99	20.60	20.62	92.75	90.67	-1.35	17.45	17.50	94.42
Gd	87.29	2.35	19.47	19.61	83.12	89.60	0.26	18.60	18.60	89.20	86.17	2.88	23.05	23.23	82.88
Dy	91.54	-1.25	15.18	15.23	94.71	91.39	-2.52	16.94	17.13	98.46	91.23	-1.74	19.14	19.22	95.19
Er	85.85	12.41	7.42	14.46	30.88	86.93	11.96	7.32	14.02	31.47	86.22	12.61	6.97	14.41	28.93
Yb	91.75	-0.67	9.06	9.08	94.23	91.34	-1.35	11.98	12.06	96.43	92.61	-1.33	11.12	11.20	96.82
Y	90.90	-0.17	12.37	12.37	90.79	91.34	-0.96	13.60	13.63	94.04	91.39	-1.26	9.44	9.52	97.60

Color properties in ceramic glazes

Samples with the best color properties (calcinated at the highest temperatures: 1600°C for $Ln_2Ce_2O_7$ and 1500°C for Ln_2CeZrO_7) were applied to ceramic glazes labeled G 050 91 with 34.3 % PbO (Table 3) and G 070 91 with 52.6 % PbO (Table 4) in 10 wt. %. Transparent lead glazes have tendency to be yellowish themselves [19] and this is the reason of high values of coordinate b* for all samples (from 16.06 to 32.09). The lowest coordinates a* and b* own pigments doped by neodymium, which are green visually, but by degrees of color tone H° = = 94.02 - 100.71 and by color coordinates (-a*, +b*) are yellow-green. Compounds with erbium gained orange shades (H° below or about 70, coordinate a* positive) through the color of glazes. Other pigments have yellow-green (yellow visually) shades due to negative values of color coordinate a*, which prove large degrees of color tone with interval 90.31 - 94.38, except Sm_2CeZrO_7 applied to G 070 91 (a* = 0.24, H° = 89.57), which have yellow color. Different composition of compounds in application to same glaze is not very reflected. Better glaze for these samples is glaze with higher content of lead G 070 91 for two reasons. First, chroma acquired higher values (applied pigments have better color properties). Second, glaze G 050 91 with samples creates fissures and bubbles, which are undesirable (influence on functionality, bad visual impression).

Particle size distribution

Particle size distribution was measured for all synthetized powder samples. The optimal particle size of inorganic pigments for applications into organic matrix (plastics) is about or less 2 μm and for ceramic glaze applications is located in interval 5 - 15 μm [20]. Mean particle sizes of synthetized pigments are shown at Table 5; there are growing with incresing calcination temperature mostly. The highes particle sizes achieve

Table 3. Color properties of pigments applied to glaze G 050 91 in 10 wt. %.

Ln	$Ln_2Ce_2O_7$ (1600°C)					Ln_2CeZrO_7 (1500°C)				
	L*	a*	b*	C	H°	L*	a*	b*	C	H°
Nd	76.66	-2.46	16.06	16.25	98.71	76.29	-1.18	16.78	16.82	94.02
Sm	83.90	-0.41	25.42	25.42	90.92	82.92	-0.15	27.69	27.69	90.31
Gd	84.44	-0.13	22.22	22.22	90.33	84.07	-0.53	25.20	25.21	91.20
Dy	84.64	-0.96	24.01	24.03	92.29	84.65	-1.00	25.12	25.14	92.28
Er	81.15	8.87	19.54	21.46	65.59	81.08	7.69	21.07	22.43	69.95
Yb	86.51	-1.32	20.98	21.02	93.60	85.97	-0.93	22.39	22.41	92.38
Y	86.09	-0.69	20.40	20.41	91.94	85.66	-1.06	23.29	23.31	92.61

Table 4. Color properties of pigments applied to glaze G 070 91 in 10 wt. %.

Ln	$Ln_2Ce_2O_7$ (1600°C)					Ln_2CeZrO_7 (1500°C)				
	L*	a*	b*	C	H°	L*	a*	b*	C	H°
Nd	77.00	-3.56	18.82	19.15	100.71	74.40	-1.65	19.88	19.95	94.74
Sm	84.60	-0.99	29.44	29.46	91.93	83.27	0.24	32.09	32.09	89.57
Gd	84.09	-0.77	29.44	29.45	91.50	84.05	-0.55	30.27	30.27	91.04
Dy	85.42	-1.88	28.32	28.38	93.80	84.31	-1.03	29.69	29.71	91.99
Er	80.16	9.84	26.28	28.06	69.47	81.03	8.13	26.20	27.43	72.76
Yb	86.12	-2.19	28.62	28.70	94.38	85.00	-1.39	28.48	28.51	92.79
Y	85.88	-1.89	28.04	28.10	93.86	85.17	-1.02	27.66	27.68	92.11

Table 5. Mean particle sizes of compounds $Ln_2Ce_2O_7$ and Ln_2CeZrO_7.

Ln	$Ln_2Ce_2O_7$			Ln_2CeZrO_7		
	1400°C d_{50} (μm)	1500°C d_{50} (μm)	1600°C d_{50} (μm)	1400°C d_{50} (μm)	1450°C d_{50} (μm)	1500°C d_{50} (μm)
Nd	4.04	4.84	6.81	3.59	5.01	7.48
Sm	4.63	4.89	5.05	5.68	6.24	6.42
Gd	3.79	5.61	5.52	4.20	5.39	5.28
Dy	4.22	5.86	5.56	3.93	5.01	5.31
Er	4.93	8.99	10.17	6.69	7.31	8.36
Yb	4.73	6.46	8.20	5.88	6.34	6.05
Y	5.70	8.86	6.67	6.06	7.06	8.5

pigments with erbium at all temperatures in both types of compounds generally. Mean particle sizes of compounds $Ln_2Ce_2O_7$ have range between 3.79 - 5.70 μm for calcination temperature 1400°C, 4.84 - 8.99 μm for temperature 1500°C and 5.05 - 10.17 μm for 1600°C. The smallest size difference between the lowest and the highest temperatures has pigment doped by samarium (only 0.42 μm), while the biggest change achieves compound with erbium between temperatures 1400°C and 1500°C (from 4.93 to 8.99 μm). Range of mean particle sizes for compounds Ln_2CeZrO_7 is between 3.59 - 6.69 μm for temperature 1400°C, 5.01 - 7.31 μm for 1450°C and 5.28 - 8.50 μm for the highest calcination temperature. Mean particle size increases with growing temperature generally. Most of prepared pigments are suitable for applications to ceramic glazes, but particle sizes for applications to organic matrix should be modified (e.g. milling).

X-ray powder diffraction analysis

All compounds $Ln_2Ce_2O_7$ calcined at 1600°C have crystalline character (intensities located in range from 800 to 1300 a.u.) and they are single-phase except $Yb_2Ce_2O_7$, which has two phases: $Yb_2Ce_2O_7$ and Yb_2O_3 (Figure 1). Pigments $Nd_2Ce_2O_7$, $Gd_2Ce_2O_7$, $Dy_2Ce_2O_7$, $Er_2Ce_2O_7$, $Yb_2Ce_2O_7$ and $Y_2Ce_2O_7$ gained cubic fluorite structure with space group Fm3m and $Sm_2Ce_2O_7$ (and Yb_2O_3) received cubic bixbyite structure with space group Ia3. Intensities of Ln_2CeZrO_7 calcined at 1500°C have values between 250 and 365 a.u. (low values), which means non-crystalline character generally and obtained from two to four phases (Figure 2). All these pigments contain unreacted ZrO_2 as monoclinic baddeleyite (formed during cooling [21]). Starting oxides Ln_2O_3 remained in compounds Er_2CeZrO_7, Yb_2CeZrO_7 and Y_2CeZrO_7 and perovskite structure was identified

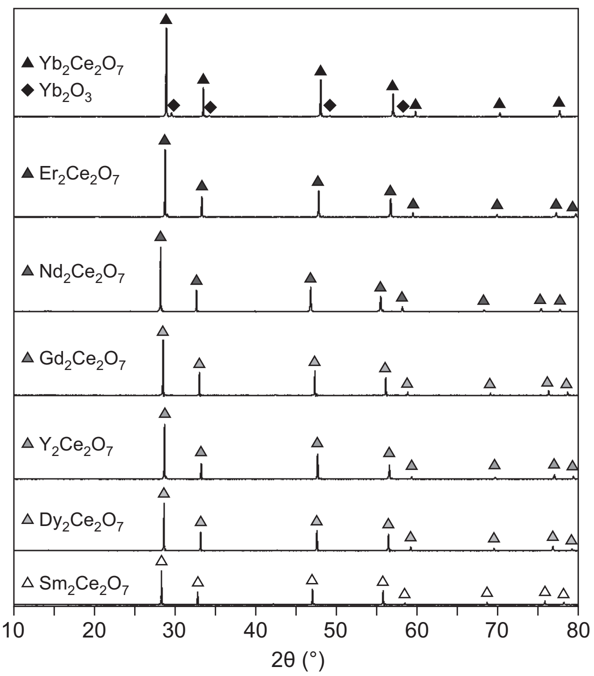

Figure 1. Phase composition of pigments $Ln_2Ce_2O_7$ calcined at temperature 1600°C.

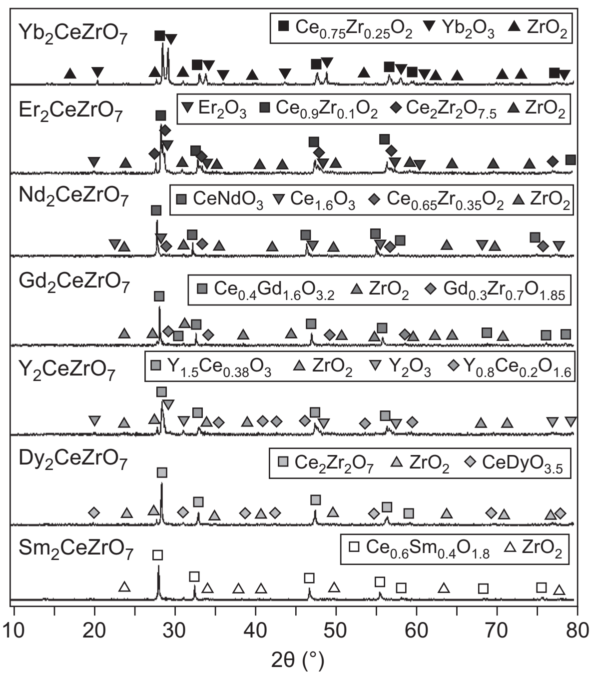

Figure 2. Phase composition of pigments Ln_2CeZrO_7 calcined at temperature 1500°C.

for pigments Nd_2CeZrO_7 ($CeNdO_3$) with Dy_2CeZrO_7 ($CeDyO_{3.5}$) as one of phase. Other phases are mixed oxides, while pyrochlore structure was created in compounds Er_2CeZrO_7 as $Ce_2Zr_2O_{7.5}$ (F43m) and Dy_2CeZrO_7 as $Ce_2Zr_2O_7$ (Fm3m).

CONCLUSION

Pyrochlore pigments $Ln_2Ce_2O_7$ and Ln_2CeZrO_7 (Ln = Nd, Sm, Gd, Dy, Er, Yb and Y) were synthetized by solid-state reaction at firing temperatures 1400, 1500, 1600 °C for $Ln_2Ce_2O_7$ and 1400, 1450, 1500°C for Ln_2CeZrO_7 from oxides. Color properties in organic matrix and ceramic glazes, particle size distribution and phase composition were evaluated. All prepared pigments have very high values of lightness in both applications (L* = 76.66 - 92.61). Color transition reaches green (very low a*), yellow-green, yellow and pink (high a*) shades in organic matrix, while presence of zirconium was not approved from view of color properties (and phase composition); and green, yellow-green and orange shades in ceramic glazes, while better color properties have pigments applied to ceramic glaze G 070 91. Synthetized pigments are suitable for applications to ceramic glazes by mean particle sizes mostly, which ranged from 3.59 to 10.17 μm, compounds are necessary to mill for applications into plastics. Phase composition of pigments calcined at the highest temperatures was measured. $Ln_2Ce_2O_7$ samples were single-phase (created required structure) except $Yb_2Ce_2O_7$ and Ln_2CeZrO_7 have from two to four phases, when one of them was always ZrO_2. Prepared compounds have potential to become environmental friendly inorganic ceramic pigments.

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