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MECHANOACTIVATION AND COLOUR PROPERTIES OF MALAYAITES DOPED WITH LANTHANOIDS

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*The study deals with the preparation of the inorganic pigments of general formula $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$, belonging to the group of the malayaites, where Ln = La, Ce, Pr, Nd, Sm, Eu and Gd (LMREE). The malayaite samples were prepared in powdered form by the solid state reaction. As initial components were used the following basic raw materials: calcium carbonate, tin oxide, chromium oxide, silicon oxide, and oxide of the respective lanthanoid serving as the dopant. The reaction mixtures were homogenised and ground in the planetary mill for five hours. After mechanoactivation, they were calcinated at the temperatures from 1200 °C to 1450 °C in the electric furnace for four h. All the prepared pigments were applied / converted into a ceramic glaze P07410 and very interesting colours obtained: brown pink, deep burgundy, and red carmina shades.. The colour characteristics were described by CIE L*a*b* system (1976). From the*

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particle size distribution, it is evident that all three parameteres, d(0.1) µm, d(0.5) µm, and d(0.9) µm have increased with temperature. Finally, as confirmed experimentally, the mechanoactivation has led to very thin granules, increasing the brightness (L).*

Introduction

Malayaite is a natural calcium and tin silicate containing isolated SiO_4 tetrahedra with an additional oxygen (titanite group) usually found in skarns [1]. It is an important ceramic pigment with deep burgundy to pink shades. Colour of malayaite pigments depends on several factors, such as firing time, temperature, occurence of secondary phases, type and amount of mineralisers or codopants, and methods of preparation [2-7]. Malayaites are stable within a wide range of temperatures and, usually, being prepared by the solid state reactions between the given raw materials. Its crystal structure, first defined by Higgins and Ribbe [8], consists of a corner-sharing SnO_6 octahedra, forming slightly kinked chains parallel to a which are mutually connected *via* SiO_4 tetrahedra, so within the SnO_6–SiO_4 framework irregular CaO_7 polyhedra are defined [8-12]. Malayaite crystallises with monoclinic lattice and is topologically identical with titanite ($CaTiOSiO_4$), but truly isostructural only with the high temperature polymorph of chemically pure titanite [9-13]. Cr-doped malayaite contains Cr^{III} atoms in the octahedral coordination. Last studies seem to be in favour of tetravalent chromium, which has been suggested to be located in the tetrahedral positions of silicon in the malayaite lattice [14], in classification of DCMA is known under 12-25-5 register No. Actually, at this time, these pigments based on malayaite types could replace toxic inorganic pigments like those based on the cadmium base, selenium base, and other undesirable elements.

The lanthanide series of chemical elements comprises fifteen metallic chemical elements with atomic numbers 57-71; i.e., from lanthanum up to lutetium [15,16]. These fifteen light metals, along with the chemically similar scandium and yttrium are collectively known as the rare earth elements; in some reports, even “rare earths”. Those elements, in which the last electron enters one of the 4f-orbitals, are called 4f-block elements or first inner transition series. Lanthanoids could be divided into the three basic groups [17]; the first group being represented by La, Ce, Pr, and Nd elements and called “light lanthanoids, LREE”. Some other elements, namely: Sm, Eu, and Gd were placed in the second group and marked as “middle lanthanoids, MREE”. Finally, the third group includes heavy lanthanoids with Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y; HREE. In literature, we can sometimes find another division of lanthanoids comprising only two groups. The first one contains La, Ce, Pr, Nd, Sm, Eu, Gd (+ Sc), which means that the light and middle lanthanoids are gathered into one group, so-called LREE.

Heavy lanthanoids then form the second group, represented by the elements from Tb, Dy, up to Lu (+ Y), i.e.: HREE

In this study, we have selected the following septet of lanthanoids: La, Ce, Pr, Nd, Sm, Eu, and Gd; all in the form of powdered oxides. The work itself concentrates on the preparation of the malayaite pigment type, chemically $CaSnSiO_5$, offering the basic characterisation of its mechanoactivation with rating of the colour hue and satiety of Cr-doped malayaite pigments of the $CaSn_{0.855}Cr_{0.045}Ln_{0,1}SiO_{5\pm\delta}$ type, where Ln represents LMREE, i.e.: La, Ce, Pr, Nd, Sm, Eu, and Gd. The aim was to examine the effect of these doping elements, composition (x = 0.045), and calcination temperature (1200-1450 °C); all with respect to the colour properties. These measurements were then completed with the particle size distribution study and X-ray analysis of the pigment samples prepared.

Experimental

Materials and Methods

In order to prepare a pigment of the $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ type, the following basic raw materials were used: calcium carbonate, tin oxide, chromium oxide, silicon oxide and oxide of the respective lanthanoid. This basic mixture mixed in the stoichiometric ratio and homogenized in an agate bowl underwent the following reactions

$$CaCO_3 + SnO_2 + SiO_2 \rightarrow CaSnSiO_5 \quad (1)$$

$$CaCO_3 + 0.855\ SnO_2 + 0.0225\ Cr_2O_3 + 0.01\ Ln_2O_3 + + SiO_2 \rightarrow CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta} + CO_2 \quad (2)$$

where Ln symbol was marks the lanthanoid used as the dopand. This preparation representing a solid state reaction is the conventional ceramic method. The purity of these oxides and carbonate used was within the range of 98.5-99.9 % (specifically: $CaCO_3$ precipitated (98.5 %), Merck; SnO_2 (99 %), Shepherd Color Company, USA; SiO_2 ST9 (99.6 %) Sklopísek Střeleč, a. s., the Czech Republic; CeO_2 (99.5 %) ML Chemica, Troubsko, the Czech Republic; Cr_2O_3 (99.8 %) Lachema Brno, the Czech Republic and the oxides of the individual lanthanoids — La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3 and Gd_2O_3; (all 99.9 % in purity and purchased from Alfa Aesar & KG, Karlsruhe, Germany). As co-dopand, chromium was used giving rise to a colour shade to the natural pigment(s). After homogenisation, the basic compounds with stoichiometric mass were put into the agate mortars. The mechanoactivation process took place in the planetary mill. The process of calcination proceeded in the electric furnace at a heating gradient of 10 °min^{-1} in a temperature interval from 1200 °C to 1450 °C. The calcination of the samples lasted for 4 hours. The colour properties of the compounds tested were studied with respect to ceramic glaze; the temperature of glazing being 1050 °C and the glaze used the P07410 type (Glazura, the Czech Republic).

Instrumentation

The colour of studied pigments was characterised by using spectral reflectance in the visible region (400-700 nm) and a ColorQuest XE (HunterLab, USA) as the instrument of choice. The measurements were done under the following conditions: a D65 illuminant, 10° complementary observer and the *d*/8 measuring geometry. Description of the colour measured was made according to the CIE $L^*a^*b^*$ system (1976), where the two colour co-ordinates a^* and b^* define the respective colour hue and L^* lightness or darkness of the colour given (numbers from 0 meaning the black colour up to 100 for white colour). All samples were ground and pressed by hand into the cuvette. Richness of colour was calculated according to the formula $C = (a^{*2} + b^{*2})^{1/2}$, when the value of richness of colour could be used to define and select define the most convenient fire temperature. The particle size distribution (PSD) of all the pigments tested was measured using a Mastersizer device (model 2000/MU; Malvern Instruments, UK) operated in the mode of Miehe light scattering and Frauenhofer difraction. The PSD was evaluated with the aid of red light (He-Ne laser, 633 nm) and blue diode, when using the Frauenhofer bending for signal evaluation.

The mechanoactivation took place in agate mortar compartment of the planetary mill (model Pulverisette 6 ; Fritsch, Germany). The rotation speed was 200 rpm and the grinding time for 5 h. The final grinding effect was reached by the ball movement (with the material ground) around the inner side of grinding container and by striking the balls against the material at the opposite side. A hermetic sealing between the grinding container and its cover then ensured lossless grinding.

Results and Discussion

This work focuses on the assessment of colour hue and richness of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ after the mechanoactivation process. Seven lanthanoids (Ln … La, Ce, Pr, Nd, Sm, Eu, and Gd, belonging to the group of light and middle LEEs), served as dopands for the preparation of the respective compounds by solid state reaction followed by mechanoactivation and calcination at the temperature of 1200 °C. Afterwards, they were converted into the ceramic glaze P07410.

In Table I, we can see that the standard pigment, which contained only chromium as a co-dopant, is the darkest prepared pigment in this colour range because of the most pronounced brightness. A pigment, containing element of lanthanum has the biggest value of *a** coordinate and the second biggest value of *b** coordinate and the contributions of the red and yellow shades are the most significant. Its chroma is also the highest and the value of hue angle (*H*°) highest from all LMREE studied at this temperature. The values of *L*a*b** coordinates are quite similar and the colour shade of all samples is similar, too; its colour being carmine red. The lowest contribution of the yellow shade is evident for the $CaSn_{0.855}Cr_{0.045}Sm_{0.1}SiO_{5\pm\delta}$ pigment, a substance with the lowest value of *b**. Finally, the biggest value of *H*° has been found out for the pigment containing europium whose chroma is the second in the scale of intensity at this temperature of calcination.

Table II summarizes the results of *L*a*b** values of the $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment type which were prepared by heating at the temperature of 1250 °C. The colour properties of the pigment doped with lanthanum, $CaSn_{0.855}Cr_{0.045}La_{0.1}SiO_{5\pm\delta}$ are very interesting.

Table I Effect of the individual LMREEs selected as dopands on the properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment after its conversion into ceramic glaze P07410 at calcination temperature of 1200 °C and evaluated *via* the parameters *L**, *a**, *b**, *C*, and *H*°

Sample with	*L**	*a**	*b**	*C*	*H*°
La	47.21	20.16	2.25	20.29	6.37
Ce	51.07	16.93	1.49	17.00	5.03
Pr	49.20	16.84	1.81	16.94	6.14
Nd	51.70	16.24	1.44	16.30	5.07
Sm	49.69	16.07	1.27	16.12	4.52
Eu	49.77	18.39	2.50	18.56	7.74
Gd	51.17	16.49	1.37	16.55	4.75
standard	54.30	15.68	1.56	15.90	6.21

Its value of chroma and colour coordinate of *a**, expressing the red direction, are the highest whereas the value of *L** is the lowest. Other two similar samples are the pigments of $CaSn_{0.855}$ $Cr_{0.045}$ $Nd_{0.1}$ $SiO_{5\pm\delta}$ and $CaSn_{0.855}Cr_{0.045}Pr_{0.1}SiO_{5\pm\delta}$ type, where the increase in the temperature resulted in the lowest value of hue angle (*H*°) and the lowest *b** coordinate, expressing the

Table II Effect of the individual LMREEs selected as dopands on the properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment after its conversion into ceramic glaze P07410 at cacination temperature of 1250 °C and evaluated *via* the parameters L^*, a^*, b^*, C, and $H°$

Sample with	L^*	a^*	b^*	C	$H°$
La	44.58	18.80	2.71	18.99	8.2
Ce	45.31	15.51	1.15	15.55	4.24
Pr	47.71	15.48	2.13	15.63	7.83
Nd	47.25	16.10	2.34	16.27	8.27
Sm	47.40	15.29	1.04	15.33	3.89
Eu	51.19	15.11	1.17	15.16	4.43
Gd	50.24	15.86	0.91	15.89	3.28
standard	47.42	17.95	1.54	18.02	4.9

yellow direction by the pigment with the content of gadolinium. The highest value of L^* is then characteristic for the pigment with europium, being the darkest from all LMREEs in the colour range investigated.

The increase in heating of pigment of the $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm*}$ type in 50-degree steps up to a temperature of 1300 °C is demonstrated on the colour properties shown in Table III. From the respective data, it could be noticed that all the samples had a slightly reduced L^* value. The shades of the pigments prepared

Table III Effect of the individual LMREEs selected as dopands on the properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment after its conversion into ceramic glaze P07410 at calcination temperature of 1300 °C and evaluated *via* the parameters L^*, a^*, b^*, C, and $H°$

Sample with	L^*	a^*	b^*	C	$H°$
La	42.1	15.31	2.32	15.49	8.62
Ce	39.00	12.74	0.30	12.74	1.35
Pr	46.13	13.71	1.86	13.84	7.73
Nd	45.01	14.49	2.17	14.65	8.52
Sm	45.86	15.82	1.48	15.89	5.35
Eu	45.74	14.88	1.40	14.95	5.38
Gd	44.70	15.81	1.00	15.84	3.62
Standard	41.34	17.38	1.20	17.42	3.95

were a little bit darker than those at 1250 °C calcination. The lightest sample was the pigment with the formula $CaSn_{0.855}Cr_{0.045}Pr_{0.1}SiO_{5\pm\delta}$; its value of *L** being the highest and just opposite to the $CaSn_{0.855}Cr_{0.045}Ce_{0.1}SiO_{5\pm\delta}$, having been the darkest from all the LMREE-based pigments under testing.

This pigment is also characterised by the lowest *a** and *b** coordinates, as well as by the lowest values of chroma and colour hue. The very interesting pigment is the sample with La co-dopand ($CaSn_{0.855}Cr_{0.045}La_{0.1}SiO_{5\pm\delta}$) because of its attractive value of hue angle (*H*°) and value of *b** coordinate, being both the highest. The contribution of its yellow shade is very significant. The standard pigment sample had the highest value of chroma and one of the lowest value of lightness (*L**); therefore, it was the second darkest pigment prepared at the temperature of 1300 °C.

The colour properties of the samples of LMREE pigments prepared at calcination temperature of 1350 °C are documented in Table IV. As proved by experimental testing, the most remarkable change at this temperature is the observation that the $CaSn_{0.855}Cr_{0.045}Ce_{0.1}SiO_{5\pm\delta}$ pigment has exhibited the hightest value of the hue angle, which is an opposite phenomenon for temperatures of 1300 °C and below, because of negative sign for the *b** coordinate. Its contribution towads the yellow shade was too low also for the *a**, *C*, and *L** coordinates. Due to this, the pigment with addition of cerium was the darkest among all the LMREE samples tested.

Table IV Effect of the individual LMREEs selected as dopands on the properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment after its conversion into ceramic glaze P07410 at calcination temperature of 1350 °C and evaluated *via* the parameters *L**, *a**, *b**, C, and *H*°

Sample with	*L**	*a**	*b**	*C*	*H*°
La	40.53	14.10	1.66	14.20	6.72
Ce	37.38	11.12	–0.05	11.12	359.95
Pr	45.69	14.73	2.45	14.93	9.44
Nd	45.76	14.54	1.98	14.67	7.76
Sm	45.10	14.00	1.19	14.05	4.86
Eu	45.00	13.79	2.46	14.01	10.12
Gd	44.00	14.82	1.64	14.91	6.32
Standard	34.27	17.29	1.57	17.36	5.19

The highest value of chroma and *a** coordinate is seen for the standard (sample) characterised by the intensively dark shade forming a carmine colour. The other pigments studied in this colour range were somewhat lighter and their values of colouring factors approximately the same.

Table V summarizes the data for pigments containing the LMREE elements and calcinated at 1400 °C. The sample of $CaSn_{0.855}Cr_{0.045}Ce_{0.1}SiO_{5\pm\delta}$ is typical for the negative *b** coordinate being slightly lower than that obtained at 1350 °C. The value of *H*° (hue angle) is the highest for this sample and its colour characteristics of *L**, *a**, *b** and chroma coordinates attractive because of their lowest values in accordance with its brown red darkest shade. The standard $CaSn_{0.955}Cr_{0.045}SiO_{5\pm\delta}$ pigment is coloured by intense red carmina shade on the base of the highest value of chroma (*C*) and the *a** colour coordinate, corresponding to the contribution of the red shade. Its brightness is the lowest from all the pigments studied within this colour range. The contribution of the yellow shade is the second lowest for the sample with Pr co-dopand ($CaSn_{0.855}Cr_{0.045}Pr_{0.1}SiO_{5\pm\delta}$) and its value of angle hue (*H*°) the lowest, too. Approximately the same values of colour properties are also characteristic for samples with Nd, Sm, Eu and Gd co-dopands whose shade is little lighter. Among the pigments tested, only $CaSn_{0.855}Cr_{0.045}La_{0.1}SiO_{5\pm\delta}$ is darker.

Table V Effect of the individual LMREEs selected as dopands on the properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment after its conversion into ceramic glaze P07410 at calcination temperature of 1400 °C and evaluated *via* the parameters *L**, *a**, *b**, *C*, and *H*°

Sample with	*L**	*a**	*b**	*C*	*H*°
La	39.92	12.20	1.27	12.27	5.94
Ce	36.32	9.95	-0.55	9.97	359.45
Pr	41.94	10.92	0.04	10.92	0.21
Nd	44.02	13.11	1.86	13.24	8.08
Sm	46.64	14.60	1.34	14.66	5.24
Eu	46.16	13.93	2.23	14.11	9.1
Gd	44.29	14.87	1.64	14.96	6.29
Standard	33.16	16.54	1.32	16.59	4.56

The highest firing temperature applied after mechanoactivation proces was 1450 °C. In this case, all the pigments with LMREE ???coodopands??? are characterised by the same violet brown shades except for the standard (sample) with rich red carmina shade. The $CaSn_{0.855}Cr_{0.045}Ce_{0.1}SiO_{5\pm\delta}$ pigment is the most attractive with respect to the colour range, because of its highest value of *H*° (hue angle) caused by the lowest value of negative *b** coordinates and by its lowest contribution of the yellow shade. This sample seems to be like that from the darkest, because of its very low brightness (*L**). The sample with La co-dopand

Table VI Effect of the individual LMREEs selected as dopands on the properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment after its conversion into ceramic glaze P07410 at calcination temperature of 1450 °C and evaluated *via* the parameters L^*, a^*, b^*, C, and $H°$

Sample with	L^*	a^*	b^*	C	$H°$
La	40.70	9.87	0.06	9.87	0.35
Ce	40.37	10.74	–0.37	10.75	359.63
Pr	43.84	10.12	1.23	10.20	6.93
Nd	45.52	11.40	1.31	11.48	6.56
Sm	49.83	13.65	1.96	13.79	8.17
Eu	48.18	13.59	3.16	13.95	13.09
Gd	46.57	13.57	0.88	13.60	3.71
Standard	32.81	15.97	0.90	16.00	3.23

Table VII The colour properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment calcinated at 1200 °C and applied in the form of ceramic glaze P07410

Sample / 1200 °C	$d(0.1)$ µm	$d(0.5)$ µm	$d(0.9)$ µm
$CaSn_{0.855}Cr_{0.045}La_{0.1}SiO_{5\pm\delta}$	0.85	6.33	26.89
$CaSn_{0.855}Cr_{0.045}Ce_{0.1}SiO_{5\pm\delta}$	0.82	5.15	28.02
$CaSn_{0.855}Cr_{0.045}Pr_{0.1}SiO_{5\pm\delta}$	0.91	5.71	29.42
$CaSn_{0.855}Cr_{0.045}Nd_{0.1}SiO_{5\pm\delta}$	0.89	5.33	27.91
$CaSn_{0.855}Cr_{0.045}Sm_{0.1}SiO_{5\pm\delta}$	0.89	4.97	24.14
$CaSn_{0.855}Cr_{0.045}Eu_{0.1}SiO_{5\pm\delta}$	0.99	5.44	22.1
$CaSn_{0.855}Cr_{0.045}Gd_{0.1}SiO_{5\pm\delta}$	0.84	4.97	25.5
$CaSn_{0.955}Cr_{0.045}SiO_{5\pm\delta}$	1.25	7.67	32.84

is not so dark, its value of hue angle being the lowest from all LMREE pigments at this calcination temperature. The numerical values of the other colour coordinates like chroma, b^*, a^* and brightness are the lowest. Higher contribution of the red and of the yellow colour is observed for other co-dopands (Pr, Nd, Sm, Eu, Gd).

In Tables VII-IX, the results from studies on the particle size distribution (PSD) for $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ are summarized being obtained by measuring the samples at temperatures of 1200 °C, 1350 °C, and 1450 °C. It means that the individual values of PSD have been influenced by temperature. For the measurement of PSD, we used the particles which were manually spread in agate mortar. All three parameters, i.e., *d*(0.1) µm, *d*(0.5) µm, and *d*(0.9) µm increased with temperature and the granularity increased with temperature as well; for $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ varying from 0.82 to 74.50 µm in the temperature interval of 1200-1450°C. The similar situation is, for example, described for median of $CaSn_{0.855}Cr_{0.045}Pr_{0.1}SiO_{5\pm\delta}$ pigment, where the particle size varied from 5.71 to 22.51 µm. The polydisperse nature of the prepared samples is evident from the granularity of the standard with the median in the range of 7.67-21.83 µm over the whole interval of heating temperatures applied.

Table VIII The colour properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment calcinated at 1350 °C and applied in the form of ceramic glaze P07410

Sample / 1350 °C	*d*(0.1) µm	*d*(0.5) µm	*d*(0.9) µm
$CaSn_{0.855}Cr_{0.045}La_{0.1}SiO_{5\pm\delta}$	2.5	14.3	40.11
$CaSn_{0.855}Cr_{0.045}Ce_{0.1}SiO_{5\pm\delta}$	3.16	15.51	44.11
$CaSn_{0.855}Cr_{0.045}Pr_{0.1}SiO_{5\pm\delta}$	2.89	15.42	47.27
$CaSn_{0.855}Cr_{0.045}Nd_{0.1}SiO_{5\pm\delta}$	3.03	15.63	50.23
$CaSn_{0.855}Cr_{0.045}Sm_{0.1}SiO_{5\pm\delta}$	2.8	14.47	50.69
$CaSn_{0.855}Cr_{0.045}Eu_{0.1}SiO_{5\pm\delta}$	2.91	14.89	49.82
$CaSn_{0.855}Cr_{0.045}Gd_{0.1}SiO_{5\pm\delta}$	2.82	14.54	45.5
$CaSn_{0.955}Cr_{0.045}SiO_{5\pm\delta}$	1.88	12.15	41.41

Table IX The colour properties of $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$ pigment calcinated at 1450 °C and applied in the form of ceramic glaze P07410

Sample / 1450 °C	*d*(0.1) µm	*d*(0.5) µm	*d*(0.9) µm
$CaSn_{0.855}Cr_{0.045}La_{0.1}SiO_{5\pm\delta}$	2.54	21.53	63.55
$CaSn_{0.855}Cr_{0.045}Ce_{0.1}SiO_{5\pm\delta}$	1.51	17.59	60.45
$CaSn_{0.855}Cr_{0.045}Pr_{0.1}SiO_{5\pm\delta}$	3.27	22.51	67.73
$CaSn_{0.855}Cr_{0.045}Nd_{0.1}SiO_{5\pm\delta}$	2.79	22.17	58.17
$CaSn_{0.855}Cr_{0.045}Sm_{0.1}SiO_{5\pm\delta}$	0.87	6.86	36.16
$CaSn_{0.855}Cr_{0.045}Eu_{0.1}SiO_{5\pm\delta}$	0.94	7.95	40.91
$CaSn_{0.855}Cr_{0.045}Gd_{0.1}SiO_{5\pm\delta}$	0.88	7.69	38.36
$CaSn_{0.955}Cr_{0.045}SiO_{5\pm\delta}$	3.83	21.83	74.49

Conclusion

The main aim of this study was to synthesise the malayaite pigment structure based on LMREE (light and middle lanthanoids) and co-doped with chromium and to test the basic colour characteristics after the mechanoactivation process. All the samples tested were prepared at a stoichiometric ratio according to the general chemical formula $CaSn_{0.855}Cr_{0.045}Ln_{0.1}SiO_{5\pm\delta}$, when the respective synthesis proceeded *via* the solid state reaction. The samples prepared in the powdered form were ground in a planetary mill for five h and the heating temperature for the ultimate calcination varied from 1200 °C to 1450 °C.

The properties of the individual pigments were measured after application / conversion into ceramic glaze P07410. The colours obtained exhibited a very interesting brown pink, deep burgundy, and red carmina shades. From the results of the particle size distribution, it could de deduced that the sample was composed of several fractions with different size. All three parameteres $d(0.1)$ µm, $d(0.5)$ µm, and $d(0.9)$ µm used for evaluation have increased with temperature. Finally, the mechanoactivation has led to very thin granules, increasing the brightness (L^*).

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