



Application of LnCrTeO_6 oxides as new ceramic pigments of the type “green chromium”

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Abstract

The family of green mixed oxides LnCrTeO_6 ($\text{Ln}=\text{La}$, Nd , Gd , Dy , Er , Tm and Yb) was investigated as potential new green ceramic pigments. Prior to enamelling, they were fully characterized by XRD analysis and FTIR spectroscopy. The materials were tested by enamelling with transparent and opaque glazes, applied for single and double firings. The chromatic qualities of all the formulations, obtained in the thermal range 850–1000 °C, were evaluated. The colour performance is fairly maintained at 1000 °C, in the transparent frit, and a lighter green hue is achieved in the opaque frit. In the presence of a PbO -containing frit, a dark green yellowish shade is obtained. The colorimetric parameters a and b are within the range of typical pigments based on Cr_2O_3 in silicate and aluminate glazes. The homogeneity of the enamels was confirmed by SEM-EDX microscopy. These materials are promising for ceramic applications since a low amount of Cr-pigment would be necessary to achieve intense green coloration.

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1. Introduction

Chromium(III) compounds normally are green, but depending on its environment other shades are produced. The influence of the structural characteristic is far pronounced with Cr pigments giving rise to completely different colours [1]. Certain compounds of chromium are also used to provide chrome yellow and orange, besides the green inorganic pigments [2].

Historically, green pigmentation was obtained with Cr_2O_3 . This material however has only limited stability since it reacts with any zinc oxide or tin oxide, present in the most common frits. More satisfactory results are obtained if Cr is incorporated to a mixed oxide as to spinel- AB_2O_4 , due to the high thermal and chemical resistance of this type of structure, in conventional glazes [3].

Nowadays, several crystalline structures, mostly derived from chromium, give rise to the commercial green ceramic

pigments. Among them are the green spinels of cobalt chromate— Cr_2CoO_4 , cobalt titanate— Co_2TiO_4 , the green Victoria garnet— $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ and the green olivine of nickel silicate— NiSiO_4 [4]; and also the as known zircon green mixture, $\text{ZrSiO}_4\text{—Cr}_2\text{O}_3$, which produces green chromophores relatively inert in most common frits [5].

Other Cr-doped metal oxide materials, such as pink Cr-doped malayaite CaSnSiO_5 and the isostructural titanium analogue CaTiSiO_5 , have been investigated as ceramic pigments due principally to their thermal resistance. In the latter the brown shade obtained was attributed to the existence of Cr (VI), together with Cr_2O_3 [6].

Chromium, depending on the synthesis conditions can be found in different states of oxidation (II–VI) and these generate different properties, stability and coloration. The challenge is trying to maintain the Cr(III) cation from oxidising to Cr(VI) because of its negative environmental impact, since it will be segregated to the washing waters [7].

It is in this context that the investigation of mixed oxides containing Cr(III), as new sources, that could be applied as green ceramic pigment is relevant. In this context it seemed interesting

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to investigate a family of compounds of the type $\text{Ln}^{\text{III}}\text{Cr}^{\text{III}}\text{Te}^{\text{VI}}\text{O}_6$, in which Ln is a lanthanide cation, as potential ceramic pigments.

Forty years ago Blasse and De Pauw prepared a number of mixed oxide materials belonging to the PbSb_2O_6 structural type, including some tellurates of the type LaMTeO_6 (M=Al, Ga, Fe, and Rh) and BiMTeO_6 (M=Cr and Ga) [8]. As the number of lanthanide tellurates in general [9] and those of the type LnMTeO_6 in particular, remain relatively scarce, in a recent study it was reported the crystallographic and spectroscopic characterizations of LnFeTeO_6 (with the light lanthanides Ln=La, Pr, Nd, and Sm) [10]. On the other hand the similar series with Cr(III), LnCrTeO_6 , is known for all lanthanides between La(III) and Yb(III), including Y(III) [11].

The structure of these mixed oxides is particularly interesting because it involves the chromophore Cr(III) in an octahedral symmetry, surrounded by oxygen. In this structural environment it is possible to obtain a new palette of the “green chromium” type, by substitution of the Ln(III) cation. Due to the intense coloration of these materials and thermal resistance it could be possible to apply them as ceramic pigments in the industry.

In this paper the synthesis, structural, spectroscopic and microstructural characterizations of LnCrTeO_6 materials with Ln=La, Nd, Gd, Dy, Er, Tm and Yb, and the technological application as ceramic “chromium green” pigments are reported. The colour properties of the glazes prepared using transparent and opaque frits were determined.

2. Experimental details

The materials were prepared by heating well-ground stoichiometric mixtures of Ln_2O_3 , Cr_2O_3 and TeO_2 at 1000°C during 2 h, in air and using platinum crucibles. The reaction mixtures were removed from the furnace intermittently, ground and reheated in order to ensure reaction completion and phase purity. The colours of the synthesized powders vary from light-green (La) to dark-green (Yb).

The starting mixtures were homogenized in an agate mortar and fired in porcelain crucibles in a muffle electrical furnace for 2 h. The heating rate was $10^\circ\text{C}/\text{min}$ and the pigments were calcined at 1000°C . Reactions were carried out in air.

The synthesized mixed oxides were studied by XRD and FTIR analysis. X-ray diffraction patterns were obtained using a Philips PW 3710 diffractometer and monochromatic $\text{CuK}\alpha$ radiation. The infrared spectra were recorded on a Nicolet-Magna 550 FT-IR instrument, using the KBr pellet technique. Unit cell parameters were obtained using a minimum squared

procedure and refined with a locally modified version of the Werner PIRUM programme.

In an attempt to obtain more information on the interaction between the pigment and ceramic frits, test specimens were prepared by mixing these materials thoroughly. The composition of the frits employed is detailed in Table 1.

The mixtures of frits and pigment (5 wt%) were homogenized in an agate mortar and were wetted at $0.06\text{ kg H}_2\text{O}/\text{kg}$ dry solid. Cylindrical test specimens were formed with these powders by pressing at 416 MPa. The resulting materials were put onto ceramic biscuits and fired in a muffle electrical furnace. The thermal cycles consisted in heating up to 500°C at $25^\circ\text{C}/\text{min}$, keeping this temperature for 1 h and then raising it at $2^\circ\text{C}/\text{min}$ up to different maximum temperatures and maintaining these temperatures for another hour, as detailed in Table 2. All the specimens were finally milled and characterized by XRD and FTIR.

Individual samples of each of the pure frits were also fired at different temperatures for comparative purposes.

CIE Lab colour coordinates were obtained on glazed tiles, containing 5% LnCrTeO_6 pigments and different frits, with a Braive Super Chroma 20 mm colorimeter and a white standard as reference.

The microstructure of the materials was obtained by scanning electron microscopy (SEM) using a Microscope Jeol

Table 2

Pigment-frit batch formulations, treated at different maximum temperatures (T_{max}); and CIE Lab parameters.

Pigments	Frits	T_{max} [$^\circ\text{C}$]	<i>L</i>	<i>a</i>	<i>b</i>
LaCrTeO_6	C	850	42.26	-18.88	11.78
LaCrTeO_6	C	1000	56.36	-2.59	28.67
NdCrTeO_6	C	850	42.99	-12.61	12.36
GdCrTeO_6	C	850	29.83	-12.76	11.72
GdCrTeO_6	C	1000	41.01	-9.98	19.94
DyCrTeO_6	C	850	43.50	-9.87	6.47
ErCrTeO_6	C	1000	37.48	-10.67	13.92
TmCrTeO_6	C	850	38.12	-5.88	11.21
YbCrTeO_6	C	850	42.13	-8.91	15.87
YbCrTeO_6	C	1000	38.69	-11.98	15.49
NdCrTeO_6	B	900	63.82	-11.13	14.63
DyCrTeO_6	B	900	64.30	-4.68	27.99
TmCrTeO_6	B	900	60.11	-7.63	21.42
ErCrTeO_6	A	850	37.26	-1.18	46.48
YbCrTeO_6	A	850	33.00	-3.95	47.11

Table 1

Approximate composition of ceramic frits (in oxides (wt%)).

Oxides (wt%)	Na_2O	K_2O	CaO	PbO	ZnO	B_2O_3	Al_2O_3	SiO_2	ZrO ₂
Frit A	2–3	1–3	3–5	28–32	–	4–6	4–6	48–50	–
Frit B	2–4	0.5–1	9–12	–	1–4	15–18	5–8	44–47	10–15
Frit C	4–7	1–3	3–5	–	–	14–17	9–11	60–65	–

JSM-6460LV. The X-ray microanalysis was performed by an EDAX Genesis XM4-Sys 60, equipped with an EDAX mod EDAM IV multichannel analyser, with Zaffire Si(Li) detector and a ultra-thin Be window and software EDAX Genesis versión 5.11. The microstructure of the enamels were obtained on superficially polished gold-coated specimens

3. Results and discussion

3.1. Structural characterization of the pigments

The structure of $\text{Ln}^{\text{III}}\text{Cr}^{\text{III}}\text{Te}^{\text{VI}}\text{O}_6$ materials may be described as a superstructure of PbSb_2O_6 , one of the typical structural types of AB_2O_6 mixed oxides, with A and B cations octahedrally coordinated to oxygen. According to this in $\text{Ln}^{\text{III}}\text{Cr}^{\text{III}}\text{Te}^{\text{VI}}\text{O}_6$ the doubling of the c -parameter of the PbSb_2O_6 unit cell was reported with a long-range ordering of the Te(VI) and Cr(III) cations in the Sb(V) sublattice [9–11]. The XRD patterns shown in Fig. 1a and b were indexed,

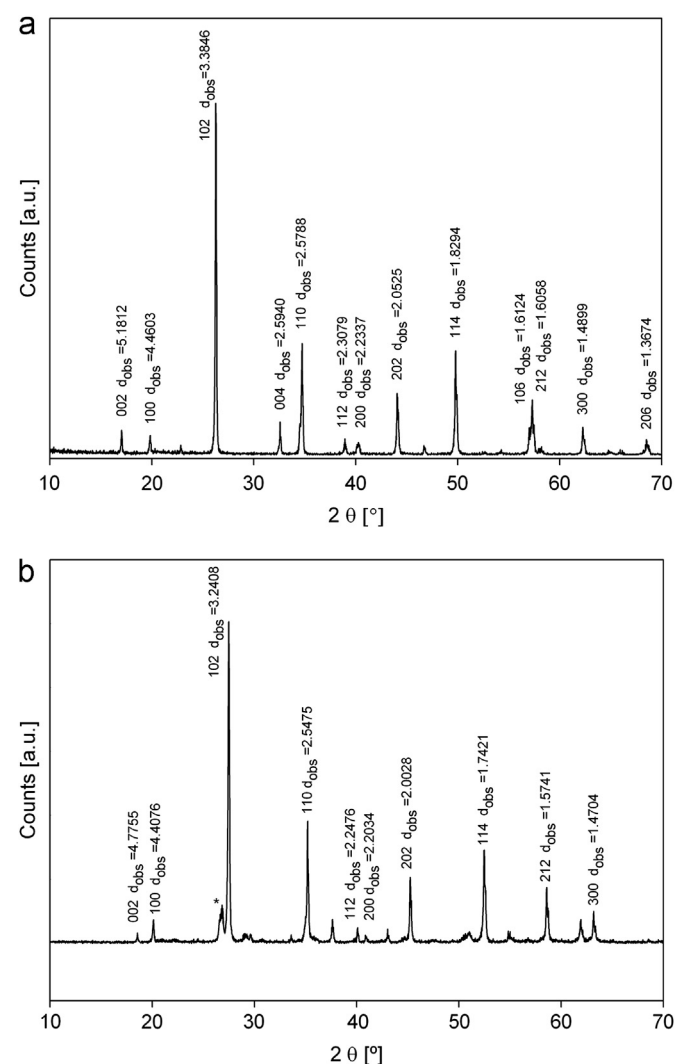


Fig. 1. (a) Indexed XRD pattern of LaCrTeO_6 showing d_{hkl} observed and (b) indexed XRD pattern of YbCrTeO_6 showing d_{hkl} observed, * impurity, probably Yb_2TeO_6 .

based on the hexagonal PbSb_2O_6 type and the space group of this superstructure $P3$ (Nr.147) with $Z=2$ was confirmed for all the samples [11].

The calculated and refined unit cell parameters of the synthesized $\text{Ln}^{\text{III}}\text{Cr}^{\text{III}}\text{Te}^{\text{VI}}\text{O}_6$ powders (with $\text{Ln}=\text{La}, \text{Nd}, \text{Gd}, \text{Dy}, \text{Er}, \text{Tm}$ and Yb) are detailed in Table 3. A decrease of the unit cell volumes from LaCrTeO_6 to YbCrTeO_6 is clearly observable. Since the structure is built up by stacking LnO_6 and $\text{CrO}_6/\text{TeO}_6$ units, alternately along the c -axis, the volume decreases almost linearly with the diminution of the ionic radii of the big interlaying Ln(III) cations, as also found in other related compounds belonging to the PbSb_2O_6 structure [12]. Besides, and also due to this stacking mode of the LnO_6 polyhedra, the c -parameters of the unit cell show a stronger dependence from the lanthanide size, than does the corresponding a -parameters.

3.2. Spectroscopic characterization of the pigments

Once the materials were fully characterized by XRD, the vibrational spectroscopy study was carried out. As an example of the IR spectra recorded for these materials, Fig. 2 shows the belonging to LaCrTeO_6 . The IR spectra of all the investigated materials are very similar in their general features, showing an

Table 3
Unit cell parameters of the LnCrTeO_6 investigated materials.

LnCrTeO_6 materials	r Ln(III) [Å]	a [Å]	c [Å]	V [Å ³]
LaCrTeO_6	1.2010	5.159(2)	10.368(6)	275.98(5)
NdCrTeO_6	1.1350	5.140(0)	10.117(7)	267.30(5)
GdCrTeO_6	1.0780	5.128(9)	9.877(0)	259.82(0)
DyCrTeO_6	1.0480	5.113(9)	9.742(2)	254.77(8)
ErCrTeO_6	1.0210	5.103(0)	9.647(0)	251.21(4)
TmCrTeO_6	1.0090	5.101(8)	9.600(2)	249.87(7)
YbCrTeO_6	0.9980	5.095(6)	9.540(2)	247.71(2)

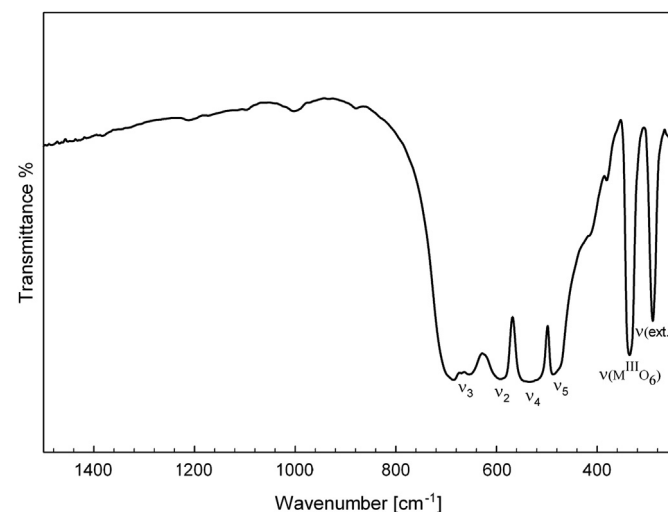


Fig. 2. FTIR spectrum of LaCrTeO_6 . Proposed assignment: $\nu_3(\text{TeO}_6)$, anti-symmetric Te–O stretching, $\nu_2(\text{TeO}_6)$, symmetric Te–O stretching; ν_4 and $\nu_5(\text{TeO}_6)$, antisymmetric deformations; $\nu(\text{M}^{\text{III}}\text{O}_6)$: $\nu(\text{Cr}^{\text{III}}\text{O}_6)/\nu(\text{La}^{\text{III}}\text{O}_6)$; $\nu(\text{ext.})$: external mode.

intense broad multiplet assigned to vibrations related to the TeO_6 coordination polyhedron, which is the highest charged cation involving Te–O bonds fairly covalent; and two defined absorptions in the low energy region, belonging to vibrations of Fe_2O_3 and Ln_2O_3 oxides, and to external modes [13].

The complete analysis of the vibrational modes of these tellurium (VI) mixed oxides was already reported [10]. In addition the IR spectra of LnCrTeO_6 compounds were carried out by comparison with the parent compounds LnFeTeO_6 . The approximate assignment can be seen in Table 4.

A weak but clear displacement to higher wavenumbers, in agreement with the decrease in the unit cell volumes from La to Yb, is observed [12]. This trend has been already observed in many other series of isostructural compounds of this type and implies the reinforcement of the Te–O bonds with the decrease of the unit cell dimensions [14].

3.3. Study of the enamels

The LnCrTeO_6 compounds were submitted to test by enamelling with three different transparent and opaque glazes.

These frits were provided by a local industry which manufactures roof and floor tiles. The glazes were selected to be representative of the double and single firing procedures currently applied in the plant.

The approximate compositions, expressed in equivalent oxide weight% are presented in Table 1, labelled as A, B and C. The common feature of A and C frits are the absence of ZnO in the glaze, which could react with chromium pigments. Chromium pigments are very sensitive to the presence of any ZnO [3]. The frit A, due to the high amount of lead, should be suitable for traditional double firing at rather low temperature ($\sim 850^\circ\text{C}$), as in overglaze applications. Furthermore the main feature of B and C is the significant amount of boron as flux and glass former. In addition the enamels prepared with frit C have higher SiO_2 content and give rise to transparent glaze. Whereas frit B contains some ZnO in the composition and ZrO_2 , as opacifier; and is characteristic of opaque glaze. For both B and C frits a high softening point is expected and confidently these materials could be used in single firing schedules due to the possibility to complete the ceramic biscuits reactions during the enamelling process.

In the case of frit A, at 850°C it was clearly softened whereas in the rest of the pellets made out of B and C, only

rounded borders are observed, in accordance with the respective compositions.

IR spectroscopy was applied to characterize the vitreous components present in each frit, prior to the preparation of the corresponding enamels.

As may be seen in Fig. 3, the spectrum of frit A is rather simple showing the strongest band centred in the $1070\text{--}1010\text{ cm}^{-1}$ range which can be assigned to Si–O antisymmetric stretching, and the medium intensity band observed around $475\text{--}400\text{ cm}^{-1}$ belonging to OSiO bending vibration modes, as in disordered SiO_4^{4-} tetrahedral groups present in amorphous SiO_2 and three-dimensional silicates [15,16].

In the case of frit C, as can be seen in Fig. 4, the main feature is the presence of additional bands in the high energy region, located at 1400 cm^{-1} , and the medium intensity absorption located around 700 cm^{-1} attributed to the borate units in these glasses. The strong band at 1400 cm^{-1} is a distinguishable feature of the chain anions of the type $(\text{BO}_2)_n^{n-}$, as in sodium metaborate and magnesium pyroborate [17,18].

When each glass is thermally treated within the range $850\text{--}1000^\circ\text{C}$, the same spectral pattern is obtained, suggesting that the structural arrangement and composition in these materials are maintained after firing and cooling, in absence of pigment.

The XRD diagrams of some of the enamels based on all the frits, obtained at the temperatures established in Table 2, were

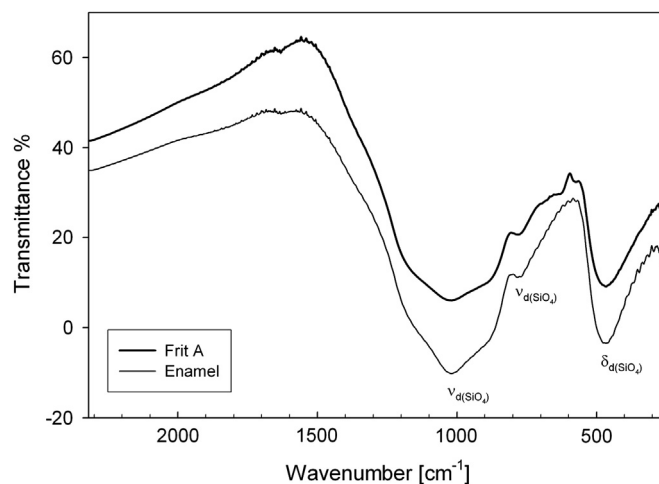


Fig. 3. FTIR spectra of LaCrTeO_6 pigment enamelled with frit A at 850°C ; $\nu_d(\text{SiO}_4^{4-})$: antisymmetric stretching SiO_4^{4-} and $\delta_d(\text{SiO}_4^{4-})$: antisymmetric deformation OSiO.

Table 4
Approximate assignment of the FTIR spectra of the investigated LnCrTeO_6 materials (band positions (cm^{-1})).

Materials	ν_3 (TeO_6)	ν_2 (TeO_6)	ν_4 (TeO_6)	ν_5 (TeO_6)	ν ($\text{M}^{\text{III}}\text{O}_6$)
LaCrTeO_6	685 vs, 654 sh	592 vs	534 vs, br	487 vs	335 s
NdCrTeO_6	689 vs, 672 sh, 663 sh	597 vs	538 vs	493 s	341 s
GdCrTeO_6	694 vs, 670 sh	619 vs, br	539 vs, br	495 vs	349 s
DyCrTeO_6	694 vs, 681 sh	604 vs, br	539 vs, br	483 s, 432 s	373 s
ErCrTeO_6	696 vs, 665 sh	612 vs	540 vs, br	500 vs, 439 s	345 s
TmCrTeO_6	696 vs, 665 sh	614 vs	541 vs	495 s, 456 m	351 m
YbCrTeO_6	692 vs, 680 sh	617 vs	561 vs, br	506 s, 443 s	345 m

vs: very strong; s: strong; m: medium; br: broad; sh: shoulder.

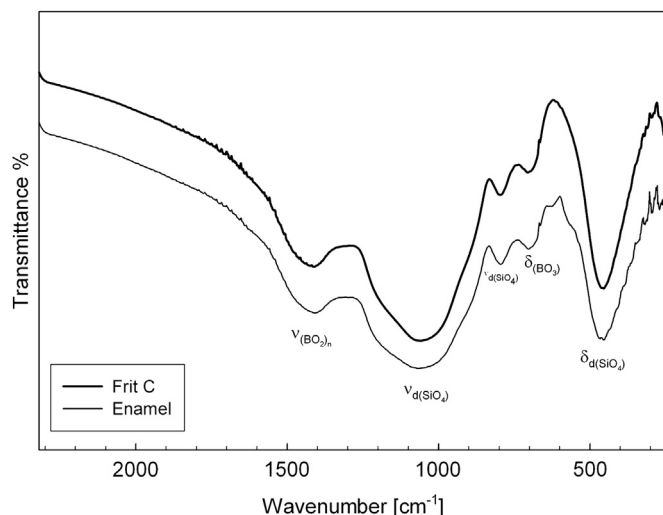


Fig. 4. FTIR spectra of GdCrTeO₆ pigment enamelled with frit C at 1000 °C; $\nu_a(\text{SiO}_4^{4-})$: antisymmetric stretching SiO_4^{4-} , $\delta_a(\text{SiO}_4^{4-})$: antisymmetric deformation OSiO and $\nu(\text{BO}_2)_n$: chain anions $(\text{BO}_2)_n^-$ vibration, $\delta(\text{BO}_3)$: deformation BO_3^{3-} units.

recorded. No diffraction peaks were detected over the broad “dome” located at around $2\theta=27^\circ$ and 23° , for A and C respectively, due to the amorphousness of the materials. The characteristic peaks belonging to the pigments were not observed suggesting that these particles loose their crystallinity by dispersion in the glassy silicate and boron-silicate matrices. Furthermore new crystalline phases, due to devitrifying, were not detected.

According to the FTIR study of the enamels, the main general features of the spectra are maintained during the enamelling process, as can be seen in Figs. 3 and 4. These evidences suggest that the boron and silicon glassy networks remain unchanged during the colour formation in the glazes.

This spectroscopic behaviour of the enamels is in total agreement with the diffractometric results, suggesting that new phases are not formed as a result of the interaction between pigment and frits by enamelling.

The colorimetric parameters measurements were made on white ceramic biscuits enamelled with transparent and opaque glazes, traditionally used in single firing (B and C) and double firing (A) processes, obtained at different temperatures. All the specimens and the resulting colorimetric values are detailed in Table 2. Both colorimetric parameters a and b are within the range of typical pigments based on Cr_2O_3 in silicate and aluminate glazes, according to CIELab diagram for reference pigments [3].

The colours of LnCrTeO_6 pigments darken from La to Yb. This indicates that the chromophore cation Cr(III) presents an intense crystal field splitting that increases with decreasing the lattice parameters from La to Yb. This feature is maintained when the pigment are glazed at high temperature, particularly with transparent frits.

The green hue and negative a values shown in Table 2 by all the glazes coloured by the pigments at the selected temperatures are undoubtedly attributed to the Cr(III) incorporated in the glaze matrixes.

In the case of enamels based on frit C the effect of the calcination temperature on the stability of the colours was also analyzed in some batches. As can be seen in Table 2 the CIELab colorimetric parameters of the enamels obtained at 850 °C using frit C to achieve a transparent glaze, the negative values of a , measured in the complete series of pigments, show an increase which parallels the diminution of the unit cell dimensions, due to the increase in the Ln(III) crystal radii from La towards the heavier lanthanides. Indeed, TmCrTeO_6 oxide displays the lowest green chroma. No general trend is observed for the values of b parameter, and a high value is noticeable for YbCrTeO_6 . Regarding the L parameters, the values show a slight variation throughout the series. In the case of GdCrTeO_6 which is the darkest enamel prepared, a very low lightness is achieved.

The values of Lab are fairly maintained upon firing but a higher lightness is observed at 1000 °C. Particularly in the case of YbCrTeO_6 the parameter b keeps almost constant. Nevertheless no general trend is observed. The green value of chroma decreases for the samples containing the light lanthanides La and Gd treated at 1000 °C, in comparison with the enamels obtained at 850 °C. In the La-glaze specimen the decrease in the intensity of the green chroma after firing is remarkable. Although for the pigment containing the heavier Yb cation, a more negative a value was found, when the temperature was raised. A similar a value was found for Er pigment. Both YbCrTeO_6 and ErCrTeO_6 , due to the low lightness displayed, are among the most intense green hues achieved with this family of pigments, using frit C.

The colouring performance of the formulations prepared with frit B which contains certain amount of ZnO and also ZrO_2 was analyzed. These are characterized, as can be seen in Table 2 by higher values of lightness, in comparison with the enamels prepared using frit C. L coordinates are over 60, while the chromatic a and b values are similar to those obtained employing the transparent frit C. This suggests that the colour is stable also in the opaque B matrix and a green pastel coloration is achieved. This behaviour seems to be responsible of the presence of the opacifier ZrO_2 which tends to shade the colour. Moreover a higher amount of pigment should be added in order to reach the hue intensity achieved by the transparent enamel. Nevertheless, these materials seem to be promising since the green hue is stable at 900 °C, in a glassy matrix containing ZnO. This behaviour is advantageous because Cr_2O_3 , traditionally used as green chromium pigment, is reactive in the presence of zinc oxide and the hue deteriorates during the thermal treatment.

On the other hand, in the matrix containing PbO in the composition, a high value of $+b$ coordinate, responsible for the yellow component, is noticeable. In this overglaze application, carried out at 850 °C, the presence of corrosive PbO as flux causes a damage of the pigment power. The most remarkable feature is the change of the green hue towards a yellowish colour and the darkening of the intensity.

The related materials LnFeTeO_6 oxides, whose colours vary from light-brown to dark-brown, with a reddish hue in some cases, were also investigated as ceramic pigments but the processing conditions affect the coloration, which vanishes

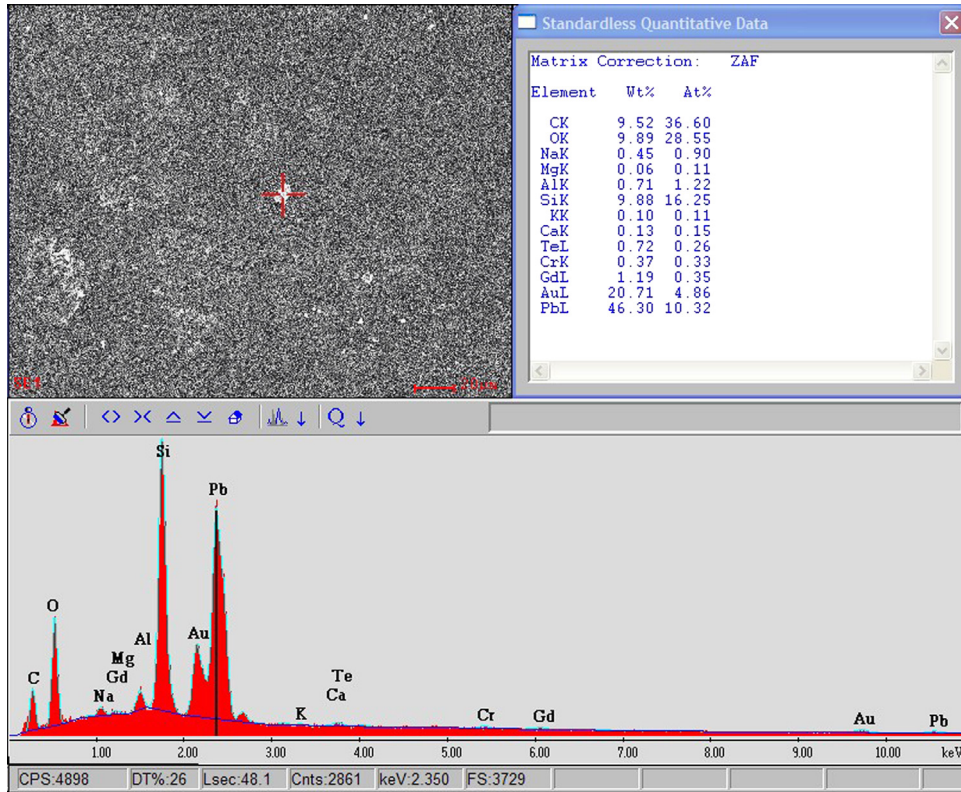


Fig. 5. SEM micrographs and element composition of GdCrTeO₆—frit A enamel.

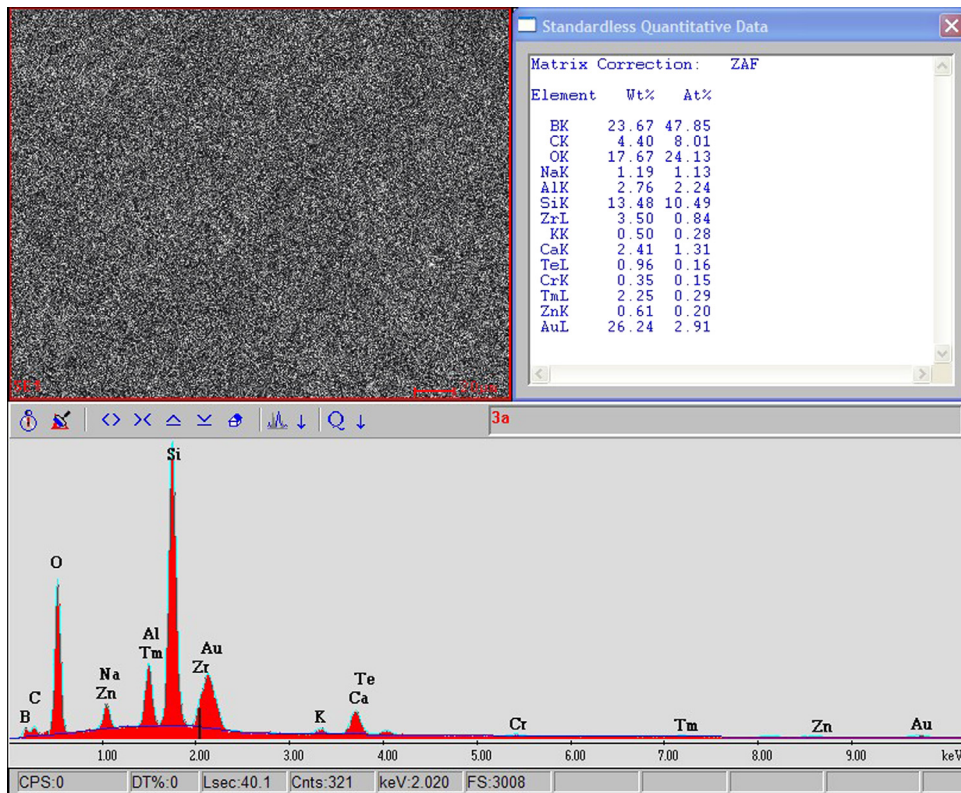


Fig. 6. SEM micrographs and element composition of TmCrTeO₆—frit B enamel.

upon calcination. These powders do not apply as ceramic pigments due to the decolorising effect by reaction with the glass of ceramic enamels. However these could be used as pigments for many materials.

The morphology of some representative enamel was analyzed by SEM-EDAX and the micrographs are shown in Figs. 5 and 6. The SEM images illustrated in these figures show a homogenous microstructure of the glazes obtained with double firing (A) and single firing (B) frits. Surface defects, as bubbles and cracks, are not observed in any of the enamels obtained. The EDAX scanning of the samples was registered in order to get a deeper insight into the atomic distribution on the surface of the glazes. The global elemental composition of both enamels is consistent with the chemical composition of the pigment-frit batches. According to SEM pictures and EDAX maps the pigments are incorporated into the amorphous matrix and the composition is homogenised during firing. In this way it was observed that the pigments are well dispersed in the glassy matrix, in accordance with diffractometric and spectroscopic evidences.

4. Conclusions

The colours of LnCrTeO_6 pigments darken from La to Yb. The chromophore cation Cr(III) presents an intense crystal field splitting that increases with decreasing the lattice parameters from La to Yb. This feature is maintained when the pigments are glazed at high temperature.

The colour performance of LnCrTeO_6 is maintained particularly for the heavier lanthanides, by calcination at 1000 °C, using a transparent frit, free of ZnO, keeping a strong colouring power. A palette of green hues is obtained by changing the Ln(III) cation in the pigment lattice.

In opaque matrixes the colours obtained at 900 °C tend to shade since the lightness is over 60, although the green hue $-a$ is achieved and the yellow $+b$ coordinate is higher than in the transparent glaze. The maintenance of the green hue at high temperature, in presence of ZnO is an advantage for these materials.

In presence of frits containing corrosive PbO, a dark green yellowish hue is obtained, 850 °C.

Surface defects, as bubbles and cracks or non-homogeneity, are not observed in any of the enamels obtained. Hence these materials are promising for ceramic applications, particularly in transparent glazes, in the thermal range up to 1000 °C.

Due to the intense coloration and thermal stability in transparent glazes, a small amount of pigment is necessary to obtain a green hue. A strong colouring power is achieved with a very low amount of pigment and hence a minimisation of chromium is possible.

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