Journal of the European Ceramic Society 23 (2003) 429–435

www.elsevier.com/locate/jeurceramsoc

Influence of crystallinity on chromatic parameters of enamels coloured with malayaite pink pigments

V. Harisanov[a], R.S. Pavlov[b,*], I.T. Marinova[b], V. Kozhukharov[a], J.B. Carda[b]

[a]*Department of Silicate Technology, University of Chemical Technology and Metallurgy, Sofia, Bulgaria*
[b]*Department of Inorganic and Organic Chemistry, University of Jaume I, Castellón, Spain*

Received 20 September 2001; received in revised form 21 March 2002; accepted 1 April 2002

Abstract

Chromium-doped malayaite ceramic pigments, $CaSnSiO_5$:Cr were obtained by solid state reaction using $CaCO_3$, SnO_2, SiO_2 and $PbCrO_4$ as precursors. The synthesis process was studied by means of thermal analysis and mass spectroscopy, the results evidencing the volatilization of carbon dioxide and lead in a large temperature range. The major aim of the study was to evaluate the dependence of the pigment colour and crystallinity from the soaking time at a maximum synthesis temperature fixed at 1400 °C. X-ray diffraction data indicate a nearly linear tendency of crystallinity increase with increasing soaking time. The colour of glazes prepared with the pigments, which was monitored by measuring their chromatic coordinates, presents a clear tendency of improvement with increasing crystallinity. This was interpreted in terms of decreasing solubility of the pigments as their crystallite size is increased. SEM and EDX studies confirm that hypothesis, evidencing very small dissolution of the highly crystallized pigments in the glaze. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: $CaSnSiO_5$; Crystallinity; Malayaite; Pigments

1. Introduction

The mineral malayaite having the chemical formula $CaSnSiO_5$ is a rare variety, which can be considered as the mineral sphene ($CaTiSiO_5$), in which the titanium atoms are completely substituted by tin atoms. Both malayaite and sphene are monoclinic and belong to the space group A2/a (No.15), thus a complete series of solid solutions can be formed between them.[1] Groat et. al.[2] reported very complete crystallographic information about the malayaite, which is resumed in Tables 1 and 2.

According to Higgins et al.[3,4] the structure is built up of distorted octahedra of tin surrounded by oxygen, which are linked by vertex sharing and form chains, which on their behalf are bridged by isolated SiO_4 tetrahedra. The larger calcium is accommodated in the remaining gaps, its coordination number being seven. A model of the structure (Fig. 1) was created introducing the data from Tables 1 and 2 in the program Diamond 2.1 as shown in Fig. 1.[5]

The malayaite has a very good thermal stability and it is therefore a very good candidate for a host lattice of ceramic pigments. Several d- and f- elements [6–8] have been introduced in the malayaite lattice and checked as chromophores but up to now the interest has been focused mainly on the chromium-doped structure. It is the base of one of the few pink pigments produced industrially and it is catalogued under number 12-25-5 in the DCMA classification.[9]

There are fairly good proofs that the chromium enters preferentially the octahedral positions in the structure in the form of Cr(III). However, there are indications, although not very convincing, that certain portion of Cr(IV) enters also the tetrahedral SiO_4 sites.[10] Data from Mösbauer spectroscopy demonstrate that the substitution of the Sn(IV) for the relatively smaller Cr(III) provokes an increase in the symmetry of the distorted octahedral site by stretching the two axial bonds and contracting the four longer equatorial bonds.[6] The same experiments indicate that practically all the tin is in oxidation state four. This excludes the hypothesis that the compensation of the lower charge of chromium(III) is realised by reduction of tin(IV) to tin(II).

The ceramic method is usually preferred for the synthesis of malayaite as it is for the majority of the ceramic pigments due to its simplicity. It consists of mixing the starting materials, usually oxides and carbo-

---

[*] Corresponding author.
E-mail address: al023657@alumail.uji.es (R.S. Pavlov).

PII: S0955-2219(02)00090-0

nates, in stoichiometric proportion, followed by grinding in a ball mill in a liquid medium, drying and then firing at 1200–1400 °C. Sometimes it could prove necessary to fire on a few stages with intermediate grindings in order to increase the homogeneity of the system and enhance better reactivity through increasing the active surface of the particles.

Generally, many reports point out that the formation of the malayaite does not occur directly from the starting materials but $CaSnO_3$ is formed first and further it reacts with the silica to form the malayaite.[11,12] Even an attempt was done to calculate the activation energy of the process.[11]

A question, which is particularly interesting, is the influence of different mineralizers on the reaction mechanism and the quality of the final product. Experiments with diferent mineralizers ($Na_2B_4O_7.10H_2O$, H_3BO_3, NaF, Li_2CO_3, $LiBO_2$, KNO_3, B_2O_3) and their mixtures have been carried out [6,12–14] and $LiBO_2$ has been reported to be the most benefitial one for the colour.[13] Other investigators[15] indicate that the addition of 1% B_2O_3 to the reaction mixture leads to nearly 100% yield of malayaite on heating at 1250 °C while the value is 30% even at 1400 °C if no mineralizer is used. However, there are evidences that phase purity is not an indispensable requisite for obtaining an intense pink colour.

There are also reports about alternative methods of malayaite synthesis,[16,17] however, they are more expensive and the results obtained by them up to now do not suggest any benefits justifying their use.

The malayaite pink pigments present a problem which is related to their behaviour when introduced in different enamels.[18–20] This problem consists in a drastic change of the colour towards paler shades or in the appearance of a bluish hue. It can be attributed to the formation of $BaSnSi_3O_9$ in the case of barium-rich and calcium-poor glazes or brown chromium spinels in the case of frits containg ZnO, MgO or BaO.[20] The formation of these undesired compounds is facilitated by dissolution of the pigment particles in the fused glaze. The crystallite size can be expected to be a crucial factor determining the dissolution rate. However, up to now there are no studies on this effect in the malayaite structure. The present study is an attempt to establish the relation between the crystallinity of the malayaite pigments and the colour parameters of the glazes obtained with them.

Table 1
Unit cell parameters

Parameter	Value
Cell edges (Å)	$a = 7.1535(6)$
	$b = 8.8933(8)$
	$c = 6.6674(6)$
Angle between axes a and c (°)	$\beta = 113.342(7)$
Cell volume (Å^3)	$V = 389.50$
Number of formula units per unit cell	$Z = 4$

2. Experimental

2.1. Raw materials

The raw materials used for the preparation of the samples are shown in Table 3. The industrial precursors were analysed in our laboratory previously. The $PbCrO_4$ was synthesized by precipitation of aqueous solutions of $Pb(NO_3)$ and K_2CrO_4. Both salts were with quality "pure for analysis", 98% from Merck.

2.2. Preparation procedure

Using the above precursors, a pigment composition was prepared in which the molar proportion between the component oxides was $CaO:SnO_2:SiO_2:Cr_2O_3 = 1:1:1:0.036$. This proportion was selected as being the optimal one required in order to obtain a good colour according to previous studies. The raw materials were mixed, micronized and homogenized in acetone media using a planetary ball mill. After drying at 110 °C, a second homogenization was carried out, this time without the use of dispersing media, in order to eliminate possible heterogeneity due to different sedimentation rate of the ingredients. The as prepared precursor was divided into several portions, put in corundum crucibles and fired in air atmosphere in an electrical furnace (Nannetti). The thermal cycles consisted of heating up to 1100 °C with 10 °C/min, retaining 1 h at this temperature, and then

Table 2
Atomic positions and anisothropic thermal parameters. Note: U_{ij} values are multiplied by 10^{-5}

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	0.25	0.66262(4)	0.5	1289(4)	3240(10)	486(8)	753(7)	0	−129(6)	0
Sn	0.5	0.5	0	663(8)	362(6)	417(6)	494(5)	−18(1)	143(4)	4(4)
Si	0.75	0.68196(4)	0.5	685(12)	409(8)	420(10)	476(7)	0	151(5)	0
O1	0.75	0.58681(4)	0	944(8)	540(10)	570(10)	1340(10)	0	470(9)	0
O2	0.91140	0.56776(3)	0.67552(4)	883(8)	956(9)	797(10)	561(8)	298(7)	154(6)	154(6)
O3	0.37224(4)	0.71195(3)	0.89032(4)	895(8)	910(10)	600(10)	758(9)	252(6)	414(7)	72(6)

up to 1400 °C with 4 °C/min. After retaining at the maximum temperature, which was varied in the range of 4–10 h, the samples were left to cool freely. The references of the samples prepared with the different retention times are shown in Table 4.

2.3. Glazing tests

The pigmenting power of the materials introduced in glazes was evaluated. For this purpose, suspensions of 5 wt.% pigment with an industrial frit in water were prepared and deposited on double firing wall tile bodies. The frit whose approximate composition is shown in Table 5 was chosen following the criteria pointed out in the introductory part and after realizing several comparative tests with other similar frits. The thermal cycle used for the glazing had the form shown in Fig. 2.

2.4. Characterization techniques

The following equipment and characterization techniques were employed in the present work. Thermal analysis (TG/DTA) and masspectroscopy: A METTLER TOLEDO STAR^e balance coupled with a BALZERS QUADSTAR^{TM} 422 was used. The samples were put in 70 μl platinum crucibles in quantity of 70–80 mg. The thermogravimetric and differential curves were obtained using cycles reproducing the heat treatment for the synthesis of sample S3. The masspectra were obtained for fixed values of $M/e = 12$, 22, 69, 103.5, which correspond to the ions C^+, CO_2^{++}, Pb^{+++} and Pb^{++}.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX): The samples were characterized microstructurally using an electron microscope LEO 440 coupled with energy dispersive X-ray analyser (Link Pentaset; Oxford Instruments). The backscattered electron images were obtained at 20 kV acceleration voltage and 200 pA probe current. The samples were fixed on aluminium supports using graphite conducting stickers and a thin graphite layer was deposited on them in order to attain good electrical conductivity. The EDX analyzes were performed with probe current 2000 pA and counting time 100 s.

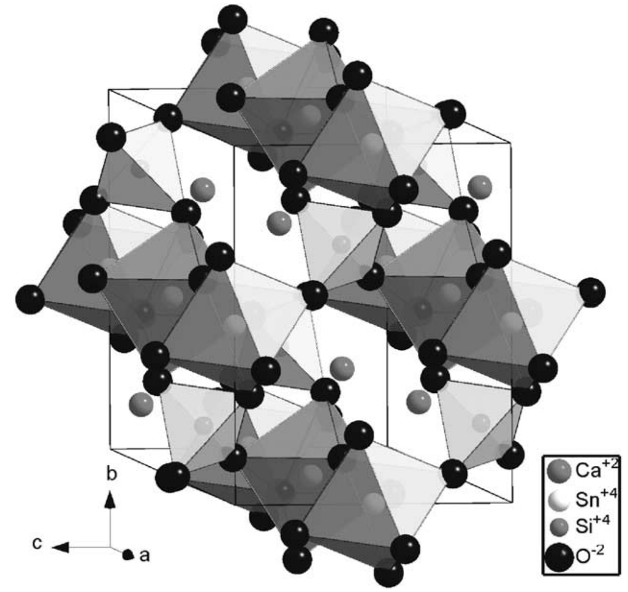

Fig. 1. A model of the malayaite structure created with the program Diamond 2.1d.

X-ray diffraction (XRD): all the samples were characterised by X-ray diffraction using a diffractometer SIEMENS D5000 and software SIEMENS DIFRACT Plus. The measurements were performed in the range of 20–80° 2θ with a goniometer speed of 0.05°2θ/s and an impulse collection time of 1 s/step using Cu-K_α radiation.

The colour coordinates of the enamels coloured with the pigments were measured using a Perkin Elmer Lambda 19 spectrophotometer.

3. Analysis and discussion

3.1. Pigment samples

3.1.1. Thermal analysis and masspectroscopy

As can be seen in Fig. 3, there are several sudden weight losses, all of them accompanied by endothermal effects. The comparison with the mass spectra presented

Table 3
Raw materials

Precursor	Provider	Grade
$CaCO_3$	Esmaltes SA	Industrial, 99%
SnO_2	Esmaltes SA	Industrial, 99.9%
SiO_2	Esmaltes SA	Industrial, 98.5%
$PbCrO_4$	Synthesized	–

Table 4
Sample references

References	Retention time
S1	1400 °C/4 h
S2	1400 °C/6 h
S3	1400 °C/8 h
S4	1400 °C/10 h

Table 5
Composition of the frit, represented as oxide content

Oxides	SiO_2	Al_2O_3	B_2O_3	CaO	BaO	MgO	K_2O	Na_2O
wt.%	55–65	10–15	5–15	5–10	0–5	0–5	5–10	0–5

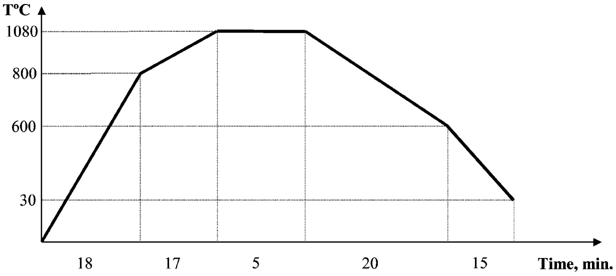

Fig. 2. Glazing thermal cycle.

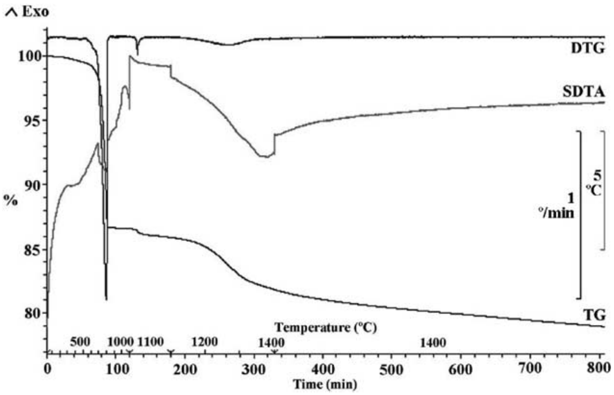

Fig. 3. TG, DTG and SDTA curves of the precursor.

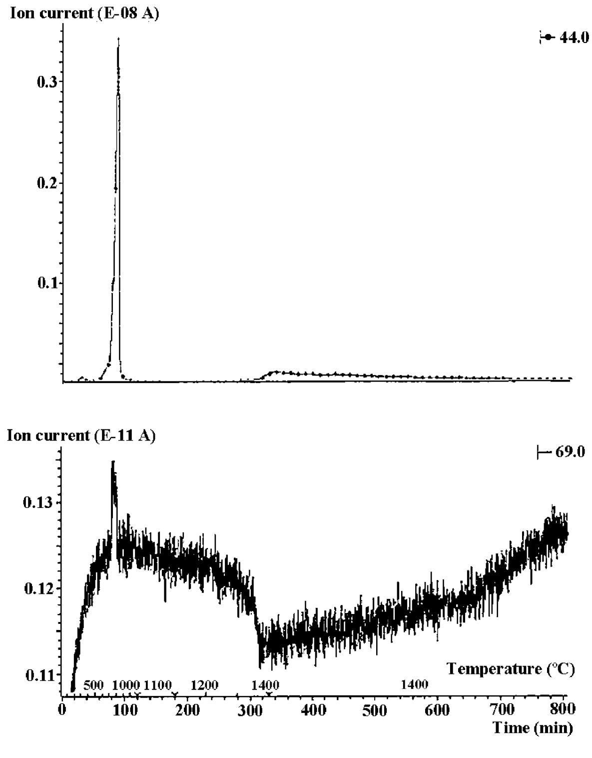

Fig. 4. Mass spectra of ions with M/e ratios 44 (CO_2^{++}) and 69 (Pb^{+++}).

in Fig. 4 indicate that the strong weight loss at around 800 °C (−13.4%) is due to elimination of carbon dioxide.

There is a second strong weight loss, which starts at about 1200 °C and it is also accompanied by an endothermal effect. This weight loss could be attributed to emission of CO_2 confined in a PbO-based glass phase. The process is probably eased by a simultaneous crystallization of the malayaite phase. The hypothesis that lead is liberated above the melting point of $PbCrO_4$ (m.p. = 844 °C) was checked by measuring the ion current corresponding to the mass numbers $M(Pb)/e = 207/3 = 69$ and $M(Pb)/e = 207/2 = 103.5$. A small increase of the ion current corresponding to the mass number 69 is observed at around 800 °C and during the retention at 1400 °C despite the low signal-to-noise ratio of the spectrum. Thus the weight loss of approximately 2% throughout the plateau at 1400 °C could be attributed to volatilization of lead-based glass and the rest of the gasses (CO_2).

3.1.2. *Electron microscopy and energy dispersive X-ray analysis*

The microstructure of the pigments was studied by SEM and EDX. Two micrographs corresponding to the samples S2 and S4 are shown in Figs. 5 and 6, respec-

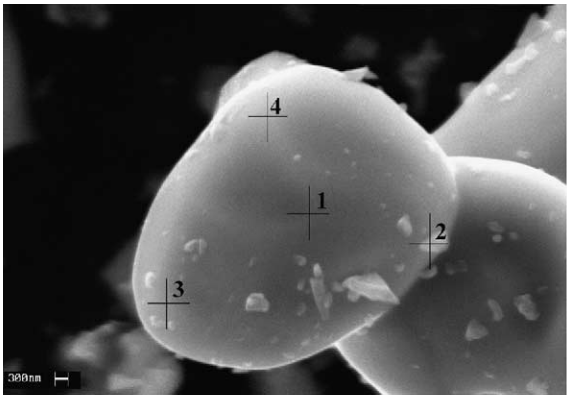

Fig. 5. SEM micrography of a grain of sample S2.

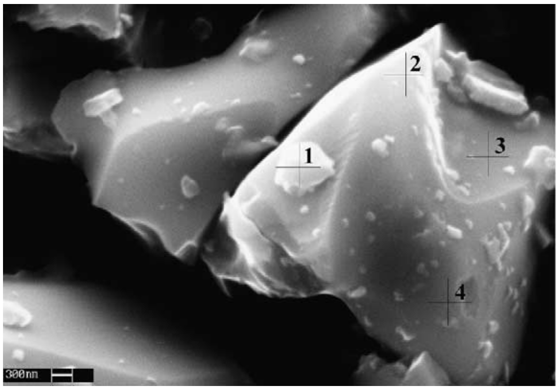

Fig. 6. SEM micrography of a grain of sample S4.

tively. A slight difference is observed between the two samples consisting in that the particles of sample S2 are rounder than the particles of sample S4. This could be attributed to the presence of a comparatively large quantity of glass phase in the case of sample S2 and on the other hand to increazed crystallinity of the pigment particles of sample S4.

Table 6
Composition (in wt.%) obtained by EDX point analysis of sample S2, fired at 1400 °C/6 h

	Point 1	Point 2	Point 3	Point 4
SiO_2	24.08	23.89	26.06	25.89
CaO	19.32	19.85	18.69	18.56

Table 7
Composition (in wt.%) obtained by EDX point analysis of sample S4, fired at 1400 °C/10 h

	Point 1	Point 2	Point 3	Point 4
SiO_2	19.97	8.52	26.54	24.71
CaO	13.88	22.65	19.63	18.85
Cr_2O_3	0.73	0.81	0.26	0.44
SnO_2	65.43	68.02	53.57	56.00
PbO	–	–	–	–

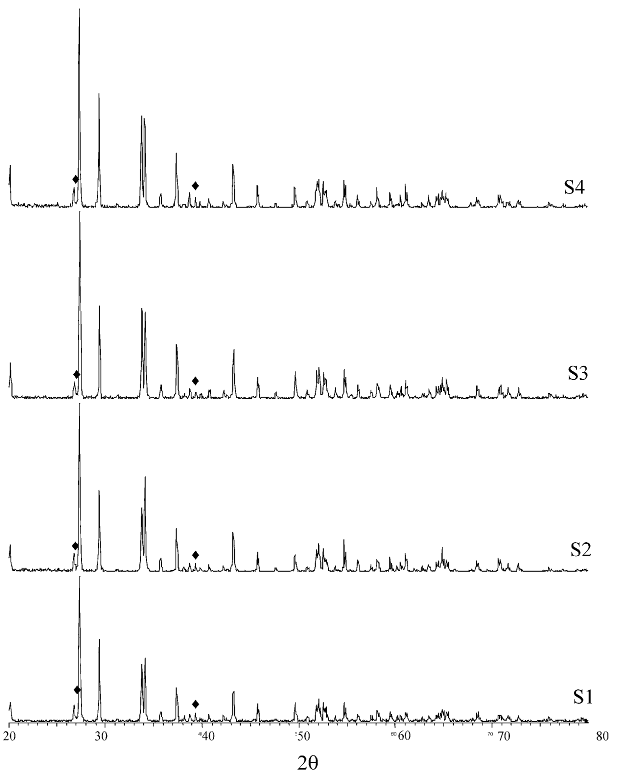

Fig. 7. X-ray diffraction patterns of the samples; ◆ stands for cassiterite, the rest of the peaks belong to the malayaite.

The EDX analysis realized at different points on the grains (shown as crosses in Figs. 5 and 6) indicates that there is no lead in sample S4 while in sample S2 it is still present (see Tables 6 and 7). Thus, it can be suggested that the lead from the $PbCrO_4$ forms a glass (probably consisting mainly of PbO and SiO_2) in the samples fired for relatively short times (4–6 h). The samples obtained by longer soaking time cycles contain practically no lead because as evidenced also by the thermal analysis and the mass spectra it is evaporated.

3.1.3. X-ray diffraction

As can be seen from the diffraction patterns of the samples shown in Fig. 7, there is a small quantity of cassiterite (SnO_2, JCPDF 41–1445) besides the main malayaite phase ($CaSnSiO_5$; JCPDF 25-0176).

Table 8
Intensities of the strongest malayaite and cassiterite peaks

Sample	Time (h)	I_m (cps)	I_c (cps)
S1	4	370	49
S2	6	440	50
S3	8	487	49
S4	10	520	55

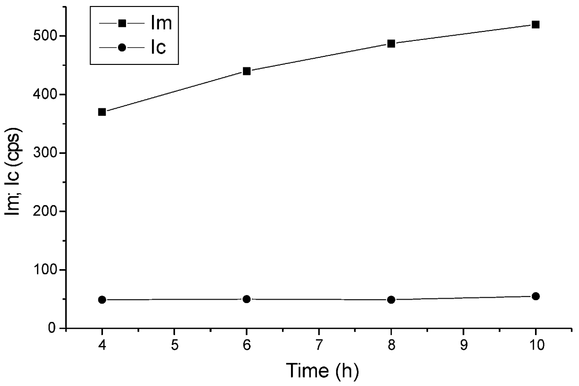

Fig. 8. Crystallinity as a function of soaking time at 1400 °C.

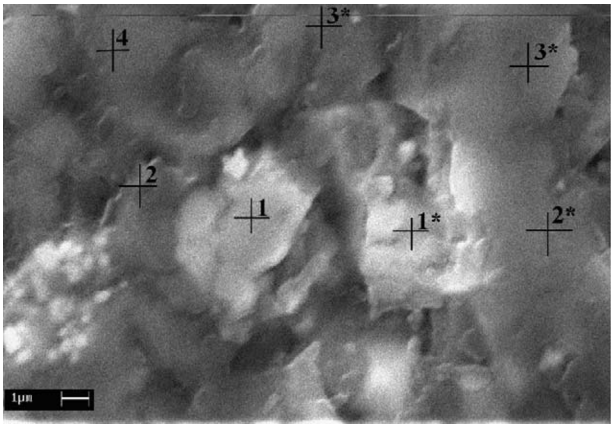

Fig. 9. SEM image of a pigment S2 grain within the glaze.

As the retention at the maximum temperature of the synthesis is increased, the intensities of the reflections also increase. This can be interpreted also in terms of increase of sample cristallinity as the peak intensity is proportional to the crystallite size. The intensities I_m of the most intense malayaite peak (200), as well as those of the most intense cassiterite peak (110), I_c, are compared in Table 8. The plot of the values in Fig. 8, shows a nearly linear tendency of increase in I_m, while I_c remains constant.

3.2. Pigmented glazes

3.2.1. Electron microscopy and energy dispersive X-ray analysis

Two SEM images corresponding to the glazed pigment samples S2 and S4 are shown in Figs. 9 and 10 respectively. Despite the low contrast of the images, the pigment particles are distinguishable as white spots within the glaze. Several EDX measurements were performed at different points around them in order to study the dissolution of the pigments in the glaze. The points are marked with crosses on the micrographs and the corresponding concentration values of SnO_2 and Cr_2O_3 are presented in Table 9.

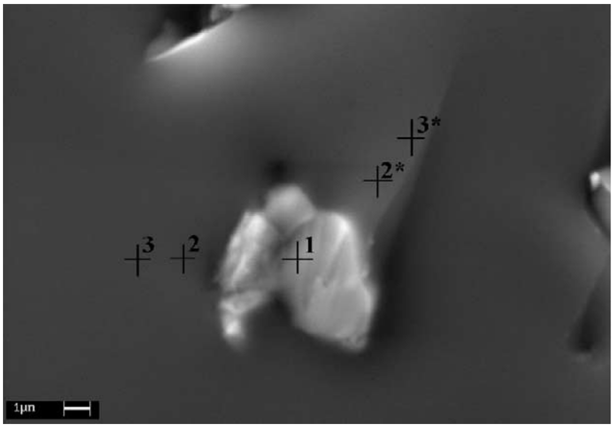

Fig. 10. SEM image of a pigment S4 grain within the glaze.

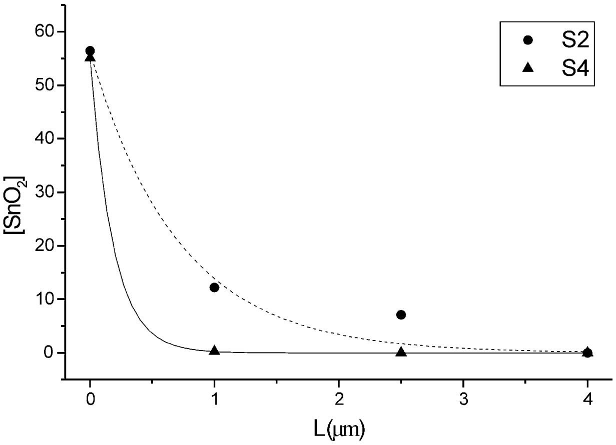

Fig. 11. Concentration of SnO_2 vs. distance (L) from the grain surface.

The tin was selected in order to trace the dissolution of the pigment particles as it is a major component of the pigments and it is not present in the glaze. The tin concentration (expressed as wt.% SnO_2) is plotted in Fig. 11 as a function of the distance from the pigment particle surface. It is evident from the figure that the tin concentration decreases faster with the distance in the case of S4, than in the case of S2. This indicates that the solubility of the pigment S4 in the glaze is lower than the solubility of the pigment S2. These results as well as the results from the other methods already discussed confirm that the increased crystallinity of S4 inhibits its dissolution in the glaze.

Table 9
Composition (in wt.%) around and within grains of samples S2 and S4 as determined by EDX

	Point number	1	2	3	4
Sample	Distance (μm)	0	1	2.5	4
S2	SnO_2	56.59	12.23	8.70	–
	Cr_2O_3	0.38	0.10	–	–
S4	SnO_2	55.07	0.24	–	–
	Cr_2O_3	0.51	–	–	–

The concentration values are taken as the average from two points at each distance.

Table 10
CIE Lab colour coordinates of the glazes

	$L*$	$a*$	$b*$
S1	39.21	23.55	5.27
S2	37.5	23.94	5.31
S3	37.81	24.31	5.61
S4	37.65	25.51	6.79

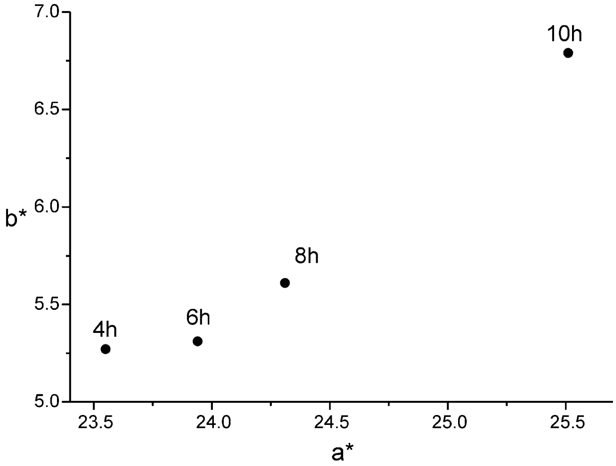

Fig. 12. Plot of the CIE Lab colour coordinates of the pigmented glazes.

3.2.2. Chromatic coordinates

The chromatic coordinates CIE Lab of the glazes prepared with the pigments S1 to S4 are represented in Table 10 and Fig. 12.

An obvious trend of increase in the coordinates $a*$ and $b*$ is observed when comparing the glazes prepared with the pigments S1 to S4. This tendency can be interpreted also as increasing chromatic purity. Actually, a gradual improvement of the colour is observed even comparing the samples visually.

4. Conclusions

Pink chromium-doped malayaite ceramic pigments were obtained by solid state reaction using $PbCrO_4$ as a precursor for the chromium. This chromate exhibits also a mineralizing action through the formation of PbO, which is a typical flux. The crystallinity of the malayaite phase was found to increase when increasing the soaking time at the maximum temperature during the synthesis. Simultaneously, a process of decrease in the quantity of a glass phase caused by the presence of PbO was observed. Both processes determine the colour and stability of the pigments in the glaze. The solubility of the pigments in the glaze decreases proportionally to the increase of their crystallinity and as a result their chromatic parameters are improved.

Acknowledgements

V. Harizanov acknowledges the grant provided to him by an ERASMUS project of the EC for the realization of an investigation work in the University of Jaume I. Also, R. Pavlov and I. Marinova are grateful for the PhD grants provided to them by AECI (Sociedad Española de Cooperación Internacional).

References

1. Takenouchi, S., Hydrothermal synthesis and consideration of the genesis of malayaite. *Mineral Deposita*, 1971, **6**, 335–347.
2. Groat, A., Kek, S., Bismayer, U., Schmidt, C., Krane, H., Mayer, H., Histor, L. and Tendeloo, G., A Synchrotron radiation HRTEM, X-ray powder diffraction, and Raman spectroscopic study of malayaite, $CaSnSiO_5$. *Am. Mineral.*, 1996, **81**, 592–602.
3. Higgins, J. B. and Ribbe, P. H., The structure of malayaite, $CaSnSiO_5$, a tin analog of titanite. *Am. Mineral.*, 1977, **62**, 801–806.
4. Higgins, J. B. and Ross, F. K., The crystal structure of malayite: $CaSnSiO_5$. *Cryst. Struct. Comm.*, 1977, **6**, 179–182.
5. DIAMOND—Visual Crystal Structure Information System CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn.
6. Sanghani, D. V., Abrams, G. R. and Smith, P. J., A structural investigation of some tin-based coloured ceramic pigments. *Trans. J. Br. Ceram. Soc.*, 1981, **80**, 210–214.
7. Carda, J., Escribano, P., Monros, G., Rodrigo, M. D. and Alarcon, J., Co-SnO_2–CaO–SiO_2 based ceramic pigments. *Interceram.*, 1990, **39**(3), 22–24.
8. Niemeier, D., Mehner, H., Bismayer, U. and Becker, K. D., A temperature-dependent ^{119}Sn and ^{57}Fe Mössbauer study of malayaite, $CaSnSiO_5$:Fe, *Phys. Stat. Sol. (b)* 1999, **211,** 581–594.
9. *DCMA classification and chemical description of the mixed metal oxide inorganic pigments*, 2nd edn. Metal Oxides and Ceramic Colors Subcommittee, Dry Color Manufacturer's Ass., Washington, DC, 1982.
10. Heyens, A. M. and Harden, P. M., Evidence for the existence of Cr(IV) in chromium-doped malayaite, Cr^{4+}:$CaSnSiO_5$: a resonance Raman study. *J. Phys. Chem. Solids*, 1999, **60**, 277–284.
11. Solc, Z., Trojan, M. and Kuchler, M., Formation of ceramic pigments of Sn–Cr type. A study using thermal analysis methods. *Thermochim. Acta*, 1985, **88**, 421–424.
12. Stefani, R., Longo, E., Escribano, P. and Carda, J., Study of malayaite synthesis $CaSnSiO_5$. *Key Eng. Mater.*, 1997, **132–136**, 277–280.
13. Cordoncillo, E., Del, Rio., Carda, F. and Escribano, J. P., Influence of some mineralizers in the synthesis of sphene-pink pigments. *J. Eur. Ceram. Soc.*, 1998, **18**, 1115–1120.
14. Stefani, R., Longo, E., Escribano, P. and Carda, J., Devolping a pink pigment for glazes. *Am. Ceram. Soc. Bull.*, 1997, **76**(9), 61–64.
15. Airey, A. and Roberts, W., Advances in ceramic colors. *Ceram. Eng. Sci. Proc*, 1987, **8**(11–12), 1168–1175.
16. Antonic, S., Dimitrijevic, R. Petrovic, L., Sol-gel novel method of ceramic pigments synthesis. In *13th Conference of Glass and Ceramics*. Varna, Bulgaria, 1999.
17. Georgieva, L., Samuneva, B. and Ivanova, Y., Ceramic pigments obtained by the sol-gel method, In *11th Conference of Glass and Ceramics*. Varna, Bulgaria, 1993.
18. Blachere, S. T., Chrome-tin pink glazes. *Ceram. Eng. Sci. Proc.*, 1989, **10**(1–2), 65–68.
19. Eppler, R. A. and Eppler, D. R., Color in lead-free glazes. *Ceram. Eng. Sci. Proc.*, 1992, **13**(1–2), 338–357.
20. Byrne, C. J., Kutney, S. T. and Pipoly, R. A., How glaze composition affects chrome-tin pink. *Am. Ceram. Soc. Bull.*, 1994, **73**, 46–49.