STUDIUL COMPORTĂRII PIGMENȚILOR ROZ CU STRUCTURĂ DE MALAYAIT ÎN COLORAREA GLAZURILOR PENTRU FAIANȚĂ DE MENAJ ▲

MALAYAITE PINK PIGMENTS BEHAVIOR IN COLOURING SOME TABLEWARE FAIENCE GLAZES

SILVANA BORCĂNESCU*, IOAN LAZĂU, RADU IOAN LAZĂU, CORNELIA PĂCURARIU

Universitatea "Politehnica" Timişoara, Piața Victoriei Nr. 2, 300006, Timişoara, România

Thermoresistant pigments interaction with molten glazes often restricts the use of some pigments in obtaining the desired glaze nuances.

Major difficulties arise when the nuance of the glaze colored with the dispersed pigment in the vitreous matrix is different from the ionic color generated by the pigment dissolution. As a common situation, $CaSnSiO_5$ pink malayaite pigments with chromium as chromophore often undergo a color change from pink to green after structure deterioration by the molten glaze and inclusion of the chrompohore in the glass matrix, as Cr^{3+}.

The obtained results show that in the case of tableware faience glazes, annealed at temperatures between 1150÷1190°C, the glaze aggressiveness can be controlled within certain limits by taking action on the chemical composition, and adding wollastonite, quartz or ZnO during the milling process.

Interacțiunea pigmenților termorezistenți cu topiturile generatoare de glazuri, în care se introduc pentru a le colora, condiționează succesul obținerii glazurilor de culorile dorite.

Dificultățile majore intervin atunci când culoarea glazurii colorată cu pigmentul dispersat în matricea vitroasă diferă esențial de culoarea glazurii colorată ionic de către cromoforul din pigment, eliberat în urma acțiunii dizolvante a topiturii asupra pigmentului. Un caz frecvent de acest tip este oferit de pigmenții roz cu structură de malayait, $CaSnSiO_5$, când prin cedarea cromoforului şi includerea lui în matricea vitroasă (Cr^{3+}), aceşti pigmenți suferă o alterare a culorii, cu viraj spre verde.

Rezultatele obținute arată că agresivitatea glazurilor pentru faianța de menaj, arse la temperaturi de 1150÷1190°C, poate fi controlată în anumite limite prin acțiuni asupra compoziției chimice, respectiv adaos la măcinare de: wollastonit, cuarț sau ZnO.

Keywords: *faience glazes, UV-VIS spectroscopy, malayaite, pigment-glaze interaction*

1. Introduction

For obtaining faience tile glazes, with colors varying from pink to purple-red, the malayaite structure pigments are the most used [1-8]. These pigments can be obtained by including chromium as chromophore in the malayaite $CaO·SnO_2·SiO_2$ ($CaSnSiO_5$) crystalline network. The malayaite structure with monoclinic symmetry consists of chained [SnO_6] tetrahedra, bonded by [SiO_4] tetrahedra, respectively [CaO_7] polyhedra [9].

The former literature data states [1, 2, 10] the chromophore Cr^{3+} in the malayaite structure is octahedrally coordinated. Yet, VIS absorbance spectra of these pigments are essentially different from the typical spectra of octahedrally coordinated Cr^{3+} in case of pink pigments with ruby, spinel or cordierite structure [11, 12].

Recent studies about the pink pigments with malayaite structure lead to the conclusion that most of the chromium cations are tetravalent [13 - 15]; Cr^{4+} substitute octahedrally coordinated Sn^{4+}, but $Si^{4+} \rightarrow Cr^{4+}$ substitution in tetrahedral coordination is also possible, which explains the different spectra of ruby, spinel or cordierite chromium pigments.

The presence of Cr^{4+}, which substitutes Sn^{4+} is also sustained by the obtaining possibility of purple pigments with $Sn_{1-x}Cr^{4+}{}_xO_2$, cassiterite structure, where is no other possibility of cation substitution.

It needs to be mentioned that during the obtaining of usual pink pigments with malayaite structure it has to work with a SnO_2 excess so that the present phases in the pigment are malayaite and cassiterite, admitting the chormophore Cr^{4+} presence in the structure of both phases.

Colouring the ceramic glazes with pink pigments where chromophore is Cr^{4+} or Cr^{3+} is usually made difficult by the glaze-pigment interaction: if the melt formed during the glaze annealing partially dissolves the dispersed pigment, the chromophore is transferred and included in the vitreous matrix as Cr^{3+}, resulting a green colour. This alters the glaze colour, which is totally inacceptable in practice. The glaze-pigment inter-

* Autor corespondent/*Corresponding author,*
Tel.: + 4 072 442 45 10, e-mail: lazau_ioan@yahoo.co.uk

▲ Lucrare prezentată la / *Paper presented at:* Consilox XI

action is influenced by the pigments characteristics, glaze composition and annealing conditions.

The aim of the experimental studies consists in the synthesis, characterization and testing of some pink pigments with malayaite structure in colouring of some ceramic glazes for faience tableware.

To follow the effect of the glaze chemical composition on the pigments behavior during the annealing, glazes with 10 wt % wollastonite, quartz and ZnO addition were prepared starting from the basic glaze. Glazes were applied on the ceramic tiles and annealed at temperatures between 1150ºC and 1190ºC.

2. Experimental

In the experimental section two receipes have been tested for pigment 1 and 2 respectively, as presented in Table 1.

For the obtaining of the malayaite structure pigments a $CaO:SnO_2:SiO_2$=1:1.2:1.0 molar ratio was used. These pigments were obtained by classical synthesis route and the raw materials used were: $CaCO_3$ (calcite Băița-Bihor), SnO_2 (Colorobia) and quartz as SiO_2 source. The Cr_2O_3 sources were: in pigment 1- $(NH_4)_2Cr_2O_7$ and in pigment 2 - $K_2Cr_2O_7$. Based on the previous results of the authors [16], Li_2CO_3 was used as mineralizing agent.

The raw materials mixtures were dosed for obtaining 0.1 moles of final product. After the dosage the raw materials were wet homogenized in a ball mill for 30 minutes and dried in a drying oven. The samples were loaded in the crucibles and annealed at 1200ºC and 1300ºC respectively, for three hours. After annealing and cooling the samples were washed with distilled water for removing of unbounded chromium (soluble Cr^{6+}) – which colours in yellow the rinsing water. Afterwards, the washed samples were dried in a drying oven.

A reference pigment noted Ref. manufactured by a traditional producer was used to compare the obtained results.

The phase composition of the powders was established by X-ray diffraction, using a Rigaku Ultima IV instrument operating at 40 kV and 40mA. The X-ray diffraction patterns were recorded using the monocromated CuK_α radiation. Crystallite size was calculated using the whole pattern profile fitting method (WPPF) and the instrument influence has been subtracted using the diffraction pattern of a Si standard recorded in the same conditions.

Malayaite pigments structure characterization from the colorimetric point of view was done by diffuse reflectance spectrophotometry – using a VARIAN CARY 300 spectrophotometer with integrating sphere (D65 illuminant, 10°angle). The trichromatic coordinates were established using Varian Cary Win UV Color 3.1 software.

The two pigments obtained by classical synthesis method annealed at two different temperatures and also the reference pigment, were tested in colouring of ceramic glazes. The basic glaze oxide composition is presented in Table 2. The optimal annealing temperature for this glaze situates around 1150-1160ºC.

3. Results and discussion

3.1. Pigments characterisation

The XRD pattern of the pigments obtained by classical method and annealed at 1200°C respectively at 1300°C and XRD pattern of the reference sample (Ref.) are presented in Figure 1.

On the XRD patterns of the samples 1a, 1b, 2a and 2b there are no differences one may observe in all the samples malayaite is the main phase, alongside cassiterite, in accordance with the projected phase composition ($CaO{\cdot}1.2SiO_2{\cdot}SiO_2$). This means that the 1200ºC temperature with 3 hours soacking time and 3 % Li_2CO_3 are sufficient for the formation of the projected phases, in case of chromium introduction as $(NH_4)_2Cr_2O_7$ (1a and 1b) and also in the case of chromium introduced as $K_2Cr_2O_7$ (2a and 2b).

In case of the XRD pattern of the reference pigment, malayaite is the main phase, alongside cassiterite–similar to the case of the pigments obtained in the laboratory conditions. Alongside these phases, the weak diffraction

Table 1

The composition of the pigments obtained by the classical method / *Compoziția pigmenților obținuți prin metoda clasică*

Sample No *Nr. probă.*		Molar ratio *Raportul molar*	Cr_2O_3 addition *Adaos de Cr_2O_3* [wt %]		Mineralizer *Mineralizator* [wt %]	Annealing temperature *Temperatura de calcinare* [°C]
			$(NH_4)_2Cr_2O_7$	$K_2Cr_2O_7$	Li_2CO_3	
1.	a.	$CaO{\cdot}1.2SnO_2{\cdot}1.0SiO_2$	0.75	-	3	1200°C
	b.	$CaO{\cdot}1.2SnO_2{\cdot}1.0SiO_2$	0.75	-	3	1300°C
2.	a.	$CaO{\cdot}1.2SnO_2{\cdot}1.0SiO_2$	-	0.75	3	1200°C
	b.	$CaO{\cdot}1.2SnO_2{\cdot}1.0SiO_2$	-	0.75	3	1300°C

Table 2

The oxide composition of the glazes / *Compoziția oxidică a glazurilor*

Glaze *Glazura*	Oxides / *Oxizi* (wt %)										
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	R_2O	ZnO	BaO	B_2O_3	ZrO_2	PbO
G.0	59.48	0.18	11.46	12.5	2.28	3.44	-	7.70	1.50	1.46	-

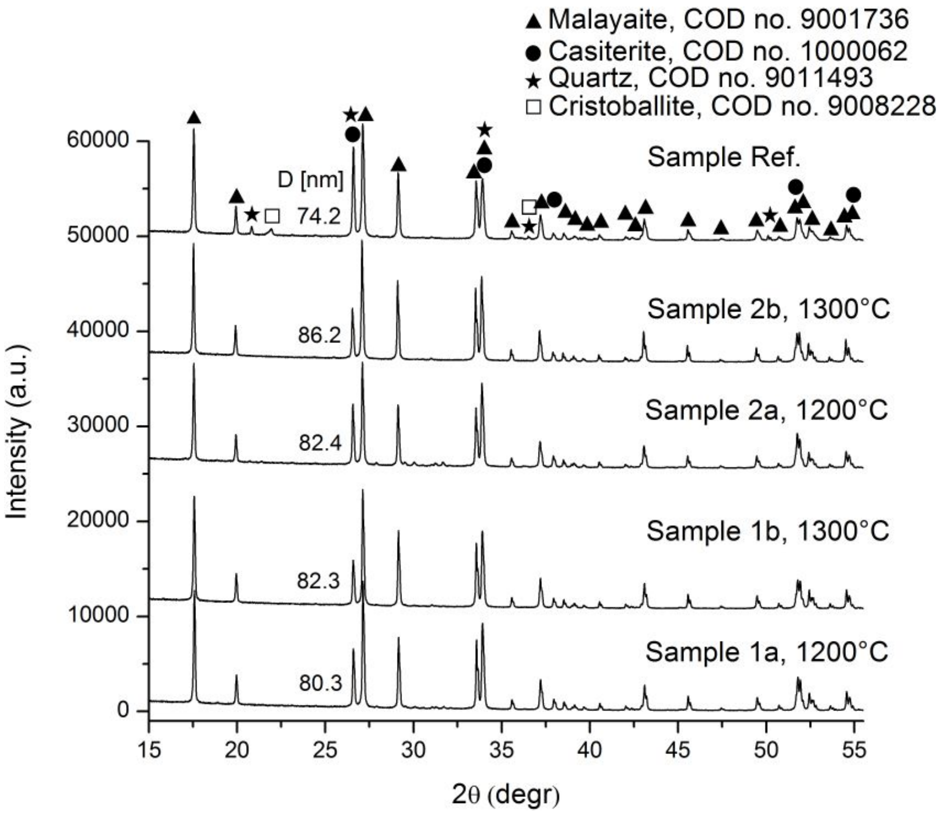

Fig.1 - *XRD patterns of the pigments Ref., 1a and 2a annealed at 1200ºC and 1300ºC /* Spectrele de difracție RX ale pigmentului de referință Ref., respectiv ale pigmenților 1a şi 2a calcinați la 1200°C şi 1300°C.

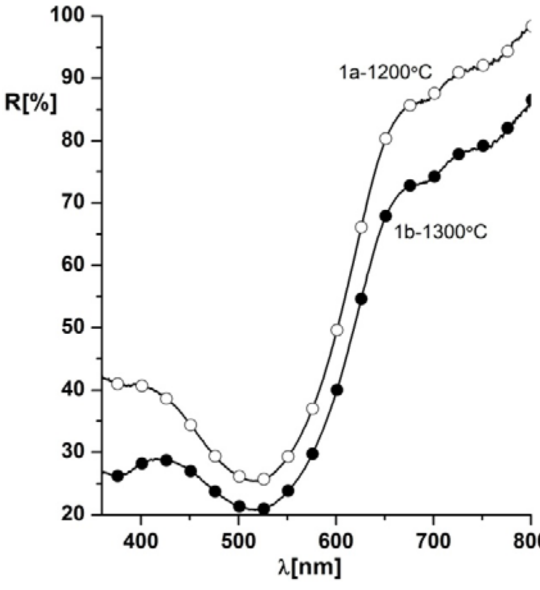

Fig.2 - The VIS reflectance spectra of the pigment 1a and 1b
Spectrele de reflexie difuză VIS ale pigmentului 1a şi 1b.

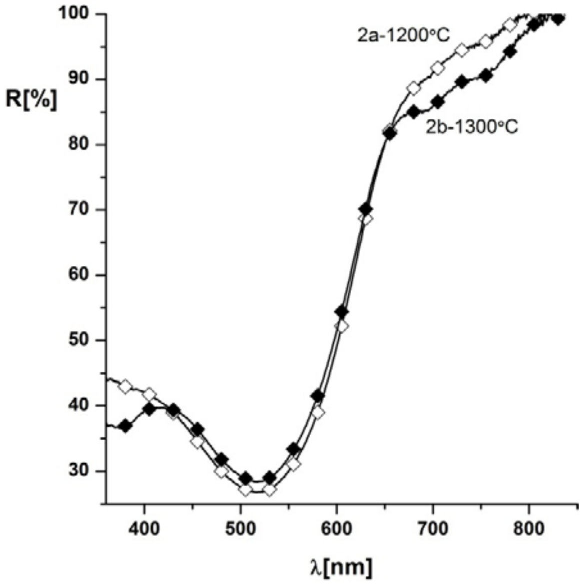

Fig.3 - The VIS reflectance spectra of the pigment 2a and 2b
Spectrele de reflexie difuză VIS ale pigmentului 2a şi 2b.

maxima of quartz and cristobalite (less intense) can be noticed. The industrial producer worked with a SiO_2 (quartz) excess related to the malayaite stoichiometry.

To assess the crystallization degree of the main phase in the pigments (malayaite phase) the crystallites size (D) was established. The obtained values are presented in Figure 1. It can be noticed that:

- although the differences between the crystallites size are not very significant, there is an increase in the crystallites size by increasing the temperature from 1200ºC to 1300ºC in both compositions 1 and 2. Regarding the Cr_2O_3 addition, in case of sample 2, as $K_2Cr_3O_7$, the crystallites size are a little larger compared to sample 1 annealed at the same temperature. This difference can be assigned to the K_2O fondant

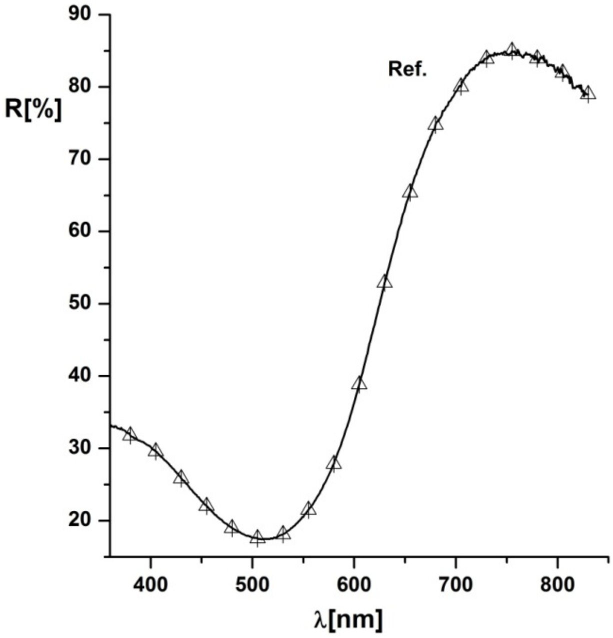

Fig.4 - The VIS reflectance spectrum of the Ref. pigment / *Spectrul de reflexie difuză VIS al pigmentului de referință (Ref.).*

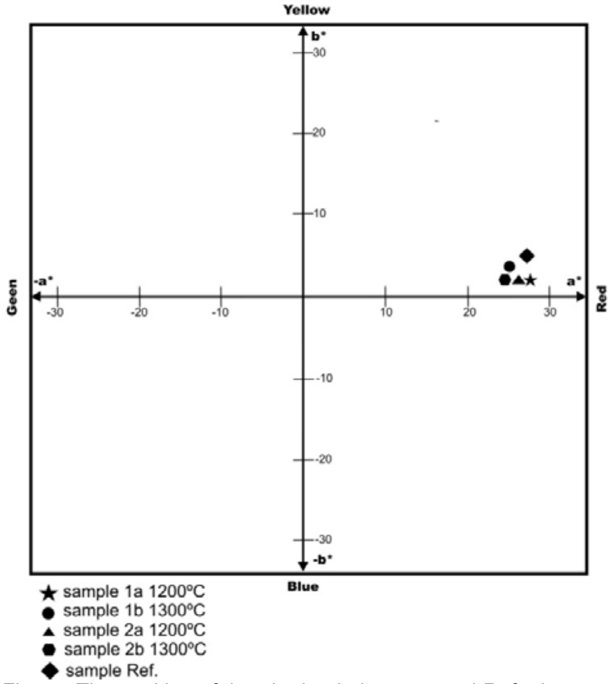

Fig. 5 - The position of the obtained pigments and Ref. pigment in the color diagram / *Poziția pigmenților obținuți şi a pigmentului de referință în diagrama culorilor.*

effect, which generates a liquid phase enhancing the malayaite ordering-crystallization processes. This effect intensifies by increasing the temperature from 1200ºC to 1300ºC.

For the colorimetric characterisation the VIS reflectance spectra of the obtained pigments and Ref. pigment were recorded. Diffuse reflectance curves are presented in Figures 2-4.

It can be noticed a great similarity between the diffuse reflectance curves of the pigments 1 and 2 obtained at 1200ºC and 1300ºC, and that of the reference pigment. In all the cases an absorption band specific for these pigments is present between 450-570 nm.

In case of the pigments obtained at 1300ºC (1b and 2b) a weak band is present below 400 nm. Visually, the colour of the pigments obtained in the laboratory conditions is practically identical with the colour of the reference pigment.

Trichromatic coordinates (L*a*b*) of the studied pigments are presented in Table 3 and the position of the pigments in the colour diagram is shown in Figure 5.

The *a** (red) and *b** (yellow) values situate all the pigments in the red-orange field. Pigments 2a and 2b show higher lightness (*L** value).

3.2. Pigments testing in the colouring of ceramic glazes

Starting from the basic glaze (G.0) with the composition presented in Table 2, coloured glazes were prepared by using a proportion of 5 wt % of the studied pigments.

The glazes annealed at 1180ºC and 1190ºC were overfired. Justification for these temperatures is the need to highlight the differences in the

Table 3

CIELAB trichromatic coordinates of the 1a, 1b, 2a, 2b and Ref. pigments
Coordonatele tricromatice CIELAB ale pigmenților 1a, 1b, 2a, 2b şi Ref.

Sample no. *Nr. probă*	L*	a*	b*
1a-1200°C	66.3446	27.4056	2.4038
1b-1300°C	60.8606	25.1729	4.1782
2a-1200°C	68.9486	26.1959	2.0395
2b-1300°C	68.3986	24.9976	2.8993
Ref.	57.7950	27.0051	5.1756

L - lightness (L* = 0 yields black and L* = 100 indicates diffuse white) / L* - luminozitatea (L* = 0 indică negru and L* = 100 indică alb);*

+ a - positive values indicate red; -a* - negative values indicate green / + a* - valorile pozitive indică roşu; -a* - valorile negative indică verde;*

+b - positive values indicate yellow; -b* - negative values indicate blue / +b* - valorile pozitive indică galben; -b* - valorile negative indică albastru;*

pigments behavior (resistance) against the chemical aggression of the different glazes compositions, at different temperatures. The studied glazes composition (different additions) and the observations made on the pigments behavior at different temperatures are presented in Table 4.

The observations regarding the obtained glaze colors with different additions (wollastonite, quartz, ZnO) and annealed at temperatures between 1150ºC and 1190ºC show that:

- at 1150ºC and 1160ºC the studied pigments develop a proper resistance against the aggression generated from the basic glaze melt (without W, Q or ZnO addition); the purple-red

Table 4

Observations regarding the studied glazes, at different annealing temperatures
Observații asupra glazurilor studiate, pentru diferite temperaturi de ardere

Glaze index *Indicativ glazură*	The used pigment *Pigmentul folosit*	Addition /*Adaosuri* (wt%)			Observations at different firing temperatures *Observații pentru diferite temperaturi de ardere* (ºC)				
		W	Q	ZnO	1150	1160	1170	1180	1190
G.1	1a	-	-	-	●	●	●●	●●●	●●●
G.2	1a	x	-	-	●	●	●	●●	●●●
G.3	1a	-	x	-	●	●	●	●●	●●●
G.4	1b	-	-	-	●	●	●	●●	●●●
G.5	1b	x	-	-	●	●	●	●	●●
G.6	1b	-	x	-	●	●	●	●	●●
G.7	2a	-	-	-	●	●	●	●●	●●●
G.8	2a	x	-	-	●	●	●	●	●●
G.9	2a	-	x	-	●	●	●	●	●●
G.10	2a	-	-	x	●	●	●●	●●●	●●●
G.11	2b	-	-	-	●	●	●	●	●●
G.12	2b	-	-	x	●	●	●	●●	●●●
G.13	Ref.	-	-	-	●	●	●●	●●	●●●
G.14	Ref.	x	-	-	●	●	●	●●	●●
G.15	Ref.	-	x	-	●	●	●	●●	●●

● – proper bahavior, purple-red color / *comportare corespunzătoare, culoare roz-roşietică;*
●● – inappropriate bahavior, the beginning of the alteration of the pink color / *comportare necorespunzătoare, început de alterare a culorii roz;*
●●● – totally inappropriate bahavior, green color / *comportare total necorespunzătoare, culoare verzuie;*
W-wollastonite / *wollastonit;* Q- quartz / *cuarț.*

Table 5

CIELAB trichromatic coordinates of some of the studied glazes
Coordonatele tricromatice CIELAB ale unora dintre glazurile studiate

Glaze index *Indicativ glazură*	Firing temperature *Temperatura de ardere* (ºC)	CIELAB trichromatic coordinates *Coordonatele tricromatice CIELAB*		
		L*	a*	b*
G.1	1150	62.7748	27.5739	9.9634
G.2	1170	67.2303	19.6936	10.7898
G.3	1170	69.0488	17.9880	10.0643
G.4	1170	65.7263	21.0649	11.9563
G.5	1180	72.4712	18.5388	10.2881
G.7	1170	55.6892	25.4995	11.3795
G.8	1180	57.2768	24.4539	11.2584
G.13	1150	62.5948	23.4352	11.7355
G.1	1180	74.2013	-1.7314	19.8702
G.4	1190	76.5740	-4.2011	19.2473
G.10	1180	79.5296	-5.0593	21.9431
G.13	1190	91.5142	-6.4480	26.1805

color is not altered;

- at 1170ºC there are present some differences in the pigment behavior: pigment 1 (obtained at 1200ºC), glaze G.1 and Ref. – glaze G.13, suffers a beginning alteration of color. Pigment 2a obtained at 1200ºC using $K_2Cr_2O_7$ – glaze G.7, behaves properly also at 1170ºC. The pigment 1a – glazes G.2 and G.3 and Ref. – glazes G.14 and G.15 behaves properly in the glazes containing wollastonite, respectively quarts addition. Pigments obtained at 1300ºC (1b and 2b) behave properly even in the glazes without addition (G.4 and G.12);
- at 1180ºC only the pigments obtained at 1300ºC resist in the glazes with W or Q addition (glazes G.5, G.6, G.8, G.9). An exception is pigment 2b (1300ºC, $K_2Cr_2O_7$), which presents a inappropriate bahavior in the glazes without additions. ZnO addition in the glaze with pigment 2a (1300ºC) – glaze G.10, causes inappropriate behavior of the pigment at 1170ºC and in the glaze G.12 even the pigment 2b behavior becomes inappropriate at 1180ºC;
- at 1190ºC all the glazes used for the pigments testing present a alteration of the pink color, turning into green. Even at this temperature it can be noticed differences between the degree of the color alteration in accordance with pigments stability evidenced at lower temperatures (1180ºc and 1170ºC).

An objective assessment of the pigments behaviour in the studied glazes was done by the trichromatic coordinates values. CIELAB L*a*b* values are presented in Table 5 for some of the glazes, in which the studied pigments resist (remain unaltered) G.1-1150, G.2-1170, G.3-1170, G.4-1170, G.5-1180, G.7-1170, G.8-1180 and G.13 -1150) respectively some of the glazes in which pigments were dissolved by the molten glaze (G.1-1180, G.4 -1190, G.10-1180, G.13 -1190).

A good behavior of the pigments means

closer values of the glaze trichromatic coordinates to the values of the used pigments; the glazes color needs to be in the red-orange area. The appearance of the green color, as a result of the chromophore transfer from the pigment crystalline network in the glaze vitreous matrix is assessed by negative (-a*) values reflecting the green proportion.

The obtained results regarding the behavior of the studied pigments in the colouring of some ceramic glazes show that:

- increasing the temperature synthesis from 1200ºC to 1300ºC in case of pigment 1 using $(NH_4)_2Cr_2O_7$ as chormophore provider, can lead to a better behavior of the pigment in the glaze. This is explained by the better crystallization and increased of crystallites size;

- using $K_2Cr_2O_7$ as chromophore provider, in case of pigment 2, ensures a better behavior, even in the case of pigment obtained at 1200ºC. This is explained by the fondant effect of K_2O, with positive effect on the crystallization of the main phase (D=82.4 nm);

- the glaze composition influences the behavior of the same pigment: wollastonite respectively quartz addition in the basic glaze, leads to an improvement of the pigment behavior. On the contrary, the ZnO addition leads to a worse pigment behavior;

- in the reference pigment, the quartz respectively cristobalite addition, resulted from quartz partial polymorphic transformation, do not represent a quality deficiency. Using of some recipes with a small SiO_2 excess in report to malayaite stoichiometry, does not only provide positive economic effects for the pigment producer but also has positive effect on the pigment behavior in the glaze melt.

4. Conclusions

Pink pigments with malayaite structure obtained in laboratory after annealing at 1200ºC and 1300ºC present a similar behavior compared to the reference pigment in coloring of some tableware faience glazes with 1150-1160ºC firing temperature. Increasing the glaze firing temperature over 1170ºC, only the pigments with higher degree of crystallization, obtained at 1300ºC or even at 1200ºC with $K_2Cr_2O_7$, resist well at the melt aggressiveness of the generating glazes if the firing temperature of the glaze is increased over 1170ºC.

The pigment behavior during the glaze annealing can be modified taking action on the glaze composition: wollastonite, respectively quarts addition improves the pigments behavior, whilest ZnO addition does not.

Acknowledgements:
This work was partially supported by the strategic grant POSDRU/89/1.5/S/57649, Project ID 57649 (PERFORM-ERA), co-financed by the European Social Found – Investing in People, within the Sectoral Operational Programme Human Resorces Development 2007-2013.

REFERENCES

1. I. Rotsche, U. Reichel, R. Schöder, and C. Pietysch, Undersuchungen an Farbkörper auf der Basis von SnO_2 für die Keramische Industrie, Silikattechnik, 1985 (10), 316.
2. E.A. Filipova, A.I. Glebîceva, L.A. Bizir, and N.N. Kazakova, Ceramic pigments on tin-sphene basis, with zinc content, Steklo I Keramika, 1983, (7), 23.
3. E. López-Navarrete, and M. Ocaña, A simple procedure for the preparation of Cr-doped tin sphene pigments in the absence of fluxes, Journal of European Ceramic Society, 2002, **22** (3), 353.
4. R. Stefani, E. Pongo, P. Escribano, E. Cordoncillo, and J.B. Carda, Study of malayaite synthesis $CaSnSiO_5$, Key Engineering Materials, 1997, **132-136**, 277.
5. V. Harisanov, R.S. Pavlov, I.T. Marinova, V. Kozhukharov, and J.B. Carda, Influence of crystallinity on chromatic parameters of enamels coloured with malayaite pink pigments, Journal of European Ceramic Society, 2003, **23** (3), 429.
6. P. Cristea, B. Zsupun, G. Negruț, O. Martin, and I. Lazău, Procedure for obtaining pink pigments in the $CaO-SiO_2-SnO_2$ system with chrome chromophore, RSR Patent, nr.100210/1990.
7. A.R. Eppler, Ullman's Enciclopedia of Industrial Chemistry, 1986, **A5**, VCH, Verlagsgesellschaft mbH, Weinheim.
8. A.N Wichell, and H. Wichell, Opticeskie Svoistva Iskussvennîth Mineralov, Izd. "Mir" Moskva, 1997
9. I. Lazău, C. Păcurariu, Z. Ecsedi, and R. Ianoş, Unconventional methods used in the synthesis of oxide compounds, Politehnica Publishing House, Timişoara, 2006.
10. L. Tcheichvili, and A.W. Weyl, The synthesis of ceramic pigments, Glass Industry, 1963, 208.
11. C. Păcurariu, I. Lazău, and R.I. Lazău, Considerations concerning the correlation between the structure, the electronic spectra and the color of some oxide compounds, Revista de Chimie, 2000, **51** (11), 821.
12. I. Lazău, D. Cor, R.I. Lazău, C. Păcurariu, and T. Bartiş, Factors that influence the color of the compounds containing transitional ions, Chemical Bulletin Politehnica University (Timişoara), 2000, **45** (2), 219.
13. E. Navarrete Lopez, A. Caballero, V.M. Orera, F.J. Lázaro, and M. Ocaña, Oxidation state and localization of chromium ions in Cr-doped cassiterite and Cr-doped malayaite, Acta Materialia, 2003, **51** (8), 2371.
14. M.A. Heyns, and P.M. Harden, Evidence for the existence of Cr(IV) in chromium-doped malayaite Cr^{4+}:$CaSnOSiO_4$:a resonance raman study-presented in part at the IX^{th} international conference on high-temperature materials chemistry held at Pennsylvania State University, May 19971, Journal of Physics and Chemistry of Solids, 1999, **60** (2), 277.
15. S. Ishida, S. Kanaoka, I. Kato, and M. Hayashi, Chemical state of chromium in tin-sphene, J Journal of the Ceramic Society of Japan, 1986, **94** (5), 457.
16. B. Tihamér, R.I. Lazău, D. Becherescu, I. Lazău, C. Păcurariu, and O. Matea, Synthesis of some pink malayaite pigments and study of their behavior in ceramic glazes, Romanian Journal of Materials, 2007, **37** (2), 113.

****