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PIGMENȚI CERAMICI PE BAZĂ DE TIALIT ȘI OXID DE COBALT
CERAMIC PIGMENTS BASED ON TIALITE AND COBALT OXIDE

MARIA PREDA[1], ILEANA RĂU[1], ALINA CORNELIA BACIU[2], CRISTIAN COVACIU[2], ALINA MELINESCU[1 *]

[1] *University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Romania*

[2] *IPEC S.A. Alba Iulia, Alexandru Ioan Cuza 33-38 Street, Alba Iulia, 510193 – Romania*

Tialite (Al_2TiO_5) is a known compound for its excellent mechanical properties and it is used in many fields. However, it should be noted that this compound has a very good chemical stability against silicate melts, so lately it has been used for obtaining ceramic pigments. In this paper, three samples were synthesized in the ternary pseudosystem $MgAl_2O_4$-$CoAl_2O_4$-Al_2TiO_5, which were heat treated at temperatures between 1200 and 1450°C. The mineralogical composition of the samples was determined by X-ray diffraction. The pigments obtained were introduced into the matte glaze in a proportion of 2%. The chromatic characterization both pigments and the coloured glaze was realised by the CIELab method.

Tialitul (Al_2TiO_5) este un compus cunoscut în special pentru proprietățile sale mecanice foarte bune și este utilizat în foarte multe domenii. Totuși trebuie remarcat că, acest compus are o stabilitate chimică foarte bună față de topiturile silicatice, de aceea în ultimul timp se constată și folosirea lui pentru obținerea de pigmenți ceramici. În această lucrare s-au sintetizat trei probe în pseudosistemul ternar $MgAl_2O_4$-$CoAl_2O_4$-Al_2TiO_5, care au fost tratate termic la temperaturi cuprinse între 1200 și 1450°C. Compoziția mineralogică a probelor a fost determinată prin difracție de raze X. Pigmenții obținuți s-au introdus într-o glazură mată în proporție de 2%. Caracterizarea cromatică atât a pigmenților cât și a glazurii colorate s-a realizat prin metoda CIELab.

Keywords: *aluminium titanate, pigment, DRX, CIELab*

1.Introduction

Ceramic pigments are coloured oxide substances that can be dispersed in silicate melts such as glazes. In the application field, ceramic pigments must fulfill several specific conditions, namely to be stable when introduced by dispersion in silicate glazes, to have high coloring power, to be thermodynamically stable against to other pigments introduced into the glaze and to the combustion atmosphere from furnace. Binary or ternary compounds or its solid solutions containing chromophore elements can be used as pigments. The most used chromophore elements in ceramic pigments technology are the ions of transition metals or lanthanides, which have 3d and 4f levels respectively, incompletely occupied with electrons. Solid solutions has better chemical stability in glazes and wider possibilities to diversify the color palette [1]. In order to obtain pigments, compounds with different types of structures are used, such as spinel [2-7], willemit [8,9], sphen [10], malait [11], olivine [12]. Pigments can be obtained in several ways, ie by controlling the valence of the chromophore ion, achieving a certain coordination polyhedron or creating point defects [1,13]. When heating pigments, the liquid phase must be avoided, as this can lead to indefinite colors.

Another way to diversify colours is to create the new types of pigments that has more attractive shades than those traditionally used in ceramic technology and to withstand more aggressive conditions. Thus, there are attempts to synthesize and use pigments with a pseudobrookite structure based on compounds such as tialite (Al_2TiO_5), karrooite ($MgTi_2O_5$), ferropseudobrookite ($FeTi_2O_5$) and its solid solutions [14-17]. They are composes of high chemical stability against silicate melts and are stable at high temperatures.

However, they are thermodynamically unstable at low temperatures, when its dissociate into component oxides or intermediate compounds, which is why use stabilizers. Cobalt, chromium, manganese, vanadium, iron ions used as chromophores, were introduced in such structures.

In this paper, the synthesis and behavior in glaze of pigments obtained on the basis of tialite and cobalt ions are studied.

2. Experimental

Three samples were synthesized whose mineralogical composition and the respective theoretical oxide is given in Table 1.

The theoretical amount of tialite in synthesized pigments varies between 60 and 80%. Along with this major component, magnesium spinel and cobalt aluminate can be formed in proportions of 10-20%. The magnesium spinel solubilizes in the structure of thialite and stabilize it at lower temperatures [18],

* Autor corespondent/*Corresponding author*,
E-mail: alina.melinescu@gmail.com

Table 1

The mineralogical and oxide compositions of synthesized samples
Compoziția oxidică și mineralogică a probelor sintetizate

Sample no.	Theorethical mineralogic composition, %weight			Oxide composition, %weight			
	Al_2TiO_5	$MgAl_2O_4$	$CoAl_2O_4$	MgO	CoO	Al_2O_3	TiO_2
1	80	10	10	2.83	4.23	57.79	35.15
2	70	20	10	5.66	4.25	59.37	30.74
3	60	20	20	5.66	8.47	59.52	26.35

and $CoAl_2O_4$ is a chromophore component that also has a spinel structure and forms solid solutions with magnesium spinel. TiO_2, Al_2O_3, $MgCO_3$ and $Co(NO_3)_2 \cdot 6H_2O$ were used for the synthesis, and the homogenization was realised by the heterogeneous method. Thus, the dry raw materials were mechanically mixed until the color was homogenized. Then, the mixture was heated in an oven to 100°C when the cobalt nitrate melted in its own crystallization water and the liquid diffused into the solid phases. After complete removal of water, the mixture was again mechanically homogenized. By uniaxially pressing, the discs were obtained and were heat treated at temperatures between 1200 and 1450°C, with a two-hour at maximum temperature. The phase composition of the heat-treated samples were determined by X-ray diffraction using the Shimadzu 6100 difractometer.

The obtained pigments were introduced, in a proportion of 2%, in the matt glaze from IPEC Alba Iulia in order to establish their behavior in such an environment. The pigments were homogenized by wet route with glaze in a ball mill, after that its were pulverised on the support by casting. After drying the samples were thermally treated at 1196°C with a 6 hours burning cycle. The color parameters for both pigments and colored glaze was determined with the Thermo Scientific Evolution 220 UV-Vis spectrophotometer device. The color difference was calculated according to CIELab parameters using the relation $E = [(L)^2 + (a)^2 + (b)^2]1/2$.

3. Experimental results

3.1. Mineralogical composition

The heat-treated samples at different temperatures were examined by X-ray diffraction, in order to establish the mineralogical compounds (Figures 1-3 and Table 2).

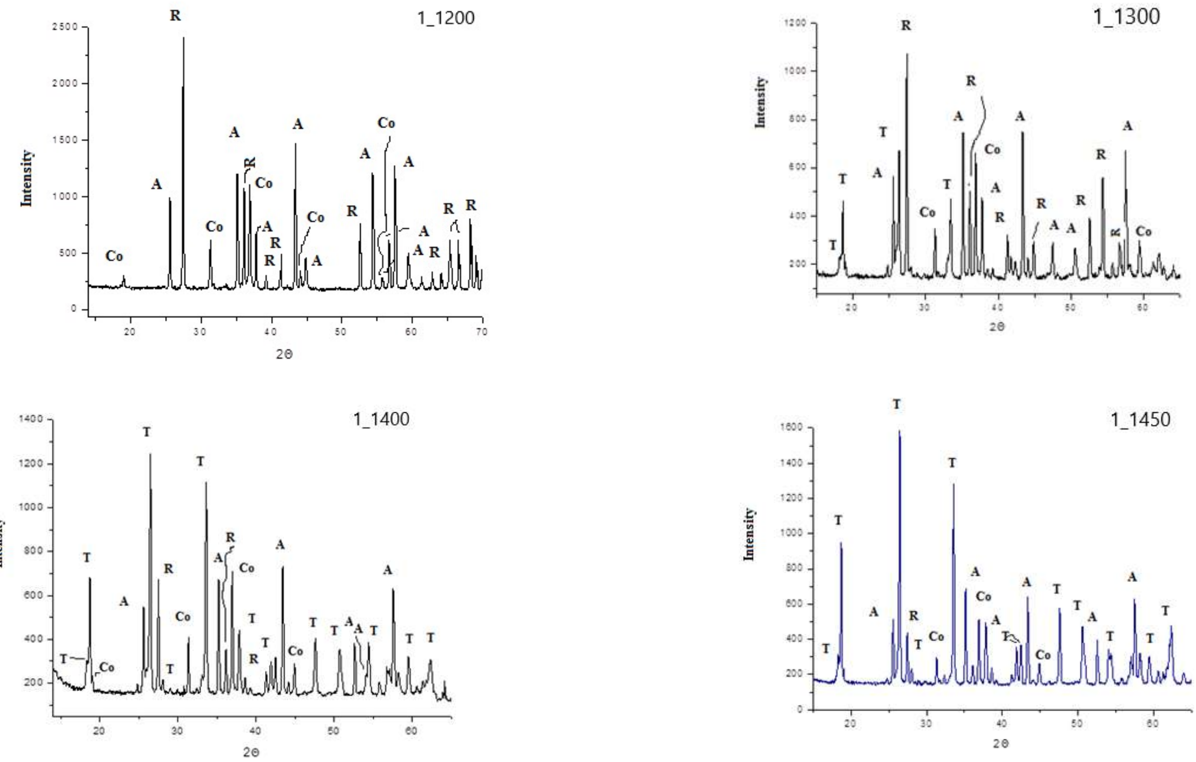

Fig. 1 - X-ray patterns of sample 1 depending on the combustion temperature; T- tialite; A - corundum; R-rutile; Co-ss ($MgAl_2O_4$-$CoAl_2O_4$)
Difractogramele probei 1 în funcție de temperatura de ardere; T – tialit; A - corindon; R – rutil; Co-ss ($MgAl_2O_4$-$CoAl_2O_4$)

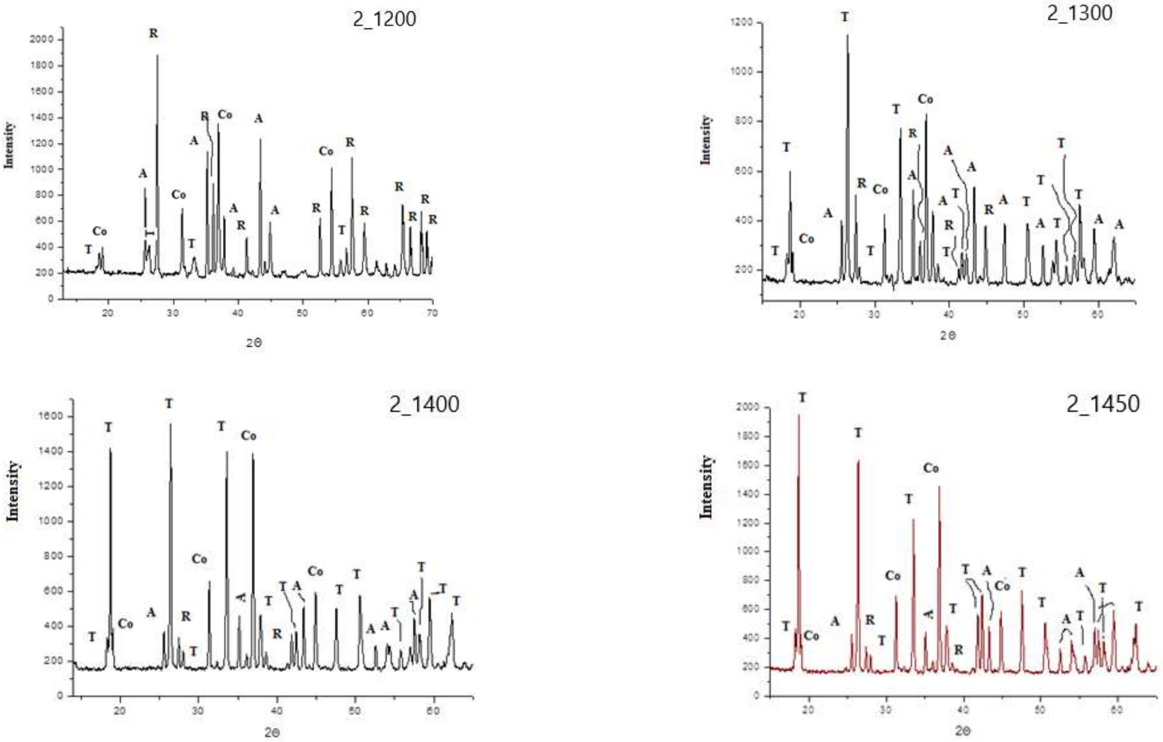

Fig. 2 - X-ray patterns of sample 2 depending on the combustion temperature; T-tialite; A-corundum; R-rutile; Co-ss ($MgAl_2O_4$-$CoAl_2O_4$)
Difractogramele probei 2 în funcție de temperatura de ardere; T – tialit; A - corindon; R – rutil; Co-ss ($MgAl_2O_4$-$CoAl_2O_4$).

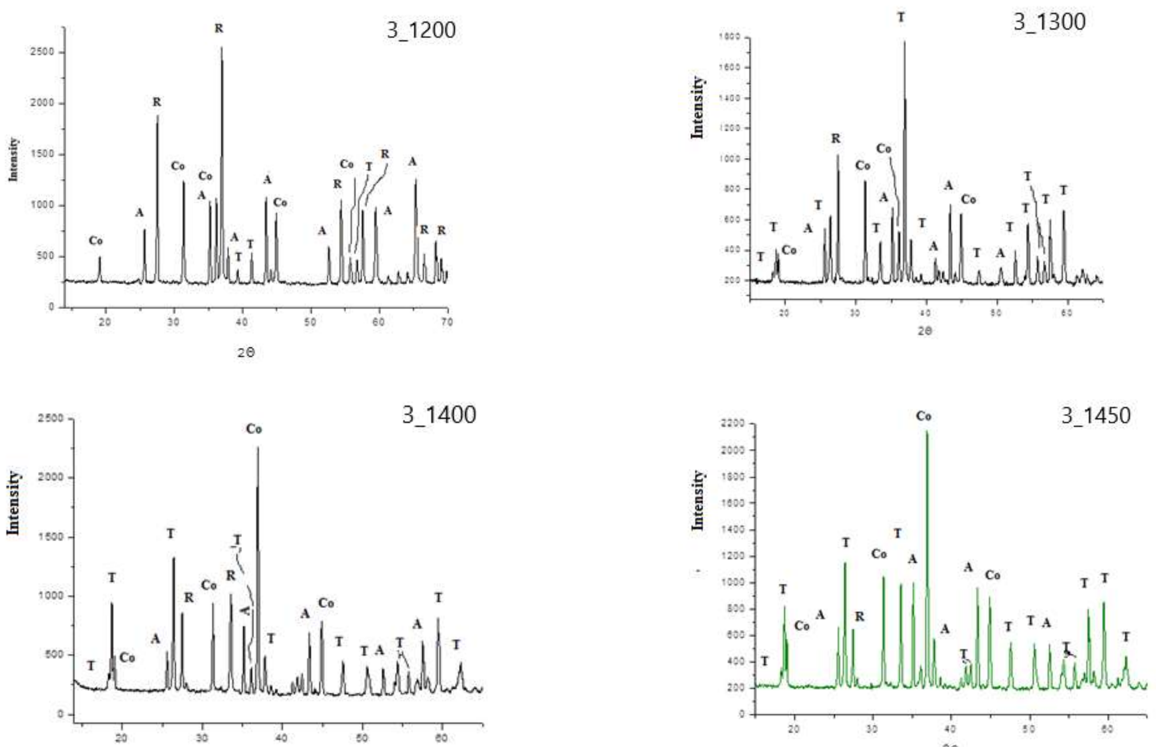

Fig. 3 - X-ray patterns of sample 3 depending on the combustion temperature; T-tialite; A-corundum; R-rutile; Co-ss ($MgAl_2O_4$-$CoAl_2O_4$)
Difractogramele probei 3 în funcție de temperatura de ardere; T – tialit; A - corindon; R – rutil; Co-ss ($MgAl_2O_4$-$CoAl_2O_4$)

Table 2

The mineralogical composition of the synthesized samples by X-ray diffraction
Compoziția mineralogică a probelor sintetizate determinată prin difracție RX

Sample	T, °C	Mineralogical composition			
		rutile	corundum	ss (MA-CoA)	tialite
1	1200	+++	++	+	-
	1300	+++	++	+	+
	1400	+	+	+	+++
	1450	+	+	+	+++
2	1200	+++	++	+	traces
	1300	+	+	++	+++
	1400	+	+	+++	+++
	1450	traces	+	+++	+++
3	1200	+++	+	++	traces
	1300	++	+	++	+++
	1400	+	+	+++	++
	1450	traces	+	+++	++

Table 3

Chromatic characteristics of pigments synthesized and heat treated at 1400°C
Parametri de culoare ale pigmenților sintetizați și tratați termic la 1400°C

Test number	L	a	b	c	x	y	H
1	60.67	4.21	14.43	15.03	0.3581	0.3627	73.74
2	63.22	9.43	21.13	23.14	0.3836	0.3719	65 ,94
3	57.65	7.84	12.80	15.01	0.3634	0.3553	58.52

where
L-brightness ; a- position of the sample on the red-green axis; b- position of the samples on the yellow-blue color
c-color purity ; x, y- colorimetric functions; H-shade angle

Thus, it is found for the first sample that at the temperature of 1200°C was first identified the spinel solid solution besides rutile and corundum. Tialite, the main mineralogical constituent was identified from 1300°C, and at temperatures of 1400 and 1450°C, this is the predominant mineralogic phase. Regarding sample 2, the thialite was identified even from 1200°C, but with very weak diffraction lines and at higher temperatures it becomes the predominant phase besides the solid spinel solution, a similar behavior being found in sample 3.

The orange color of the samples can be explained by the fact that the solid spinel solution penetrates the network of tialite, situation in which the cobalt ion can replace the aluminum ion in octahedral coordination [14].

Also, cobalt aluminate has the tendency to form an inverse spinel structure, i.e. the cobalt ion can be partially located in octahedral coordination in the solid spinel solution [12,19]. By the occupied octahedral position the Co^{2+} ion can develop a color similar to olivine structure.

3.2. Colorimetric analysis of synthesized samples

3.2.1.Colorimetric analysis of pigments

The three synthesized samples treated heat at 1400°C were analyzed colorimetrically and the results are presented in Table 3.

The data presented in the table show that the brightness of the pigments on a black-and-white line is between 63.22 and 57.65. Sample 2, although it has the same CoO content as sample 1, has a higher brightness due to the formation of the solid solution with $MgAl_2O_4$, the latter being in a

	Na_2O 0.1812	
	K_2O 0.0184	
CaO 0.5906	Al_2O_3 0.4581	SiO_2 2.8636
MgO 0.1327	Fe_2O_3 0.0048	TiO_2 0.0076
	BaO 0.0771	

Fig. 4 - The Seger molar formula of the used glaze / *Formula molară Seger a glazurii folosite*.

Table 4

The chromatic characteristics of the colored glaze with the synthesized pigments
Parametri de culoare ai glazurii colorate cu pigmenții sintetizați

Pigment no. / firing temperature (°C)	L	a	b
1/1400	80.65	-0.81	15.53
1/1450	80.69	-0.67	15.32
2/1400	80.76	-0.72	14.78
2/1450	80.29	-0.70	13.51
3/1400	79.81	-1.67	13.60
3/1450	79.67	-2.03	13.62

higher proportion. Sample 3 has the lowest brightness due to the higher proportion of $CoAl_2O_4$.

Examination of the values for *a* and *b* parameters shows that both have positive values, which shows that the three pigments are located in the red-orange-yellow area.

The value *c* shows the purity of the color, i.e. the radial distance from the gray point, denoted by zero to the pure color denoted by 100, in the spatial colorimetric diagram. The low values obtained show that the obtained pigments are far from the pure color. In the same spatial color chart, the shade is represented by the angular distance around the black-and-white vertical axis, measured from red counterclockwise. The obtained values for the synthesized pigments confirm the orange color of the samples defined above.

3.2.2.Introduction of pigments in the glaze

The three heat-treated pigments at 1400 and 1450°C, were introduced, in proportion of 2%, in the matte glaze from IPEC Alba Iulia whose molar formula Seger, calculated starting from the oxide composition [20], which is given in Figure 4.

The chromatic characteristics of the colored glazes with the obtained pigments are given in Table 4.

It was observed that the three pigments are compatible with the matte glaze in which they were immersed, without creating defects of reaction with the glaze or with the support on which it was applied. The chromatic characteristics of the colored glazes are given in Table 4. It is observed that all the samples have negative values for *b* parameter, which shows a transition of the color from orange to yellow-green. This can be explained by the fact that when the Co^{2+} ion from the solid spinel solution is introduced into the glaze, it can partially move in tetrahedral coordination and change color.

A mixture of 1% pigment 3 with 0.5% vanadium-based blue pigment and 0.5% praseodium yellow pigment was also made, which was introduced into the same glaze. It was observed that the synthesized pigment is thermodynamically compatible with these two pigments and the green color of the glaze was intensified. The color characteristics of this mixture are L = 80.14; a = -2.43 and b = 13.93.

3.2.3. The difference of color

The difference of color was analyzed according to the different working conditions, the results being given in Table 5 (a-c).

Thus in the synthesis of pigments it is observed that by increasing the temperature from 1400 to 1450°C, the color difference is small (Table 5a), which shows that the pigment thermally treated at 1400°C can be used with good results. When analyzing the 3 pigments, heat treated at 1400°C (Table 5b) there are differences due to the content of colored compound and magnesium spinel that act as a diluent. When the pigments are introduced into the glaze, the differences from one pigment to another are small, even in the case of the mixture used.

Table 5a

a) Colour difference for the pigments synthesized according to the firing temperature

a) Diferențe de culoare pentru pigmenții sintetizați în funcție de temperatura de ardere

Pigment	Temperature	Color difference
1	1400- 1450	1.49
2	1400-1450	1.96
3	1400-1450	3.72

Table 5b

b) Colour difference from one pigment to another at constant temperature

b) Diferența culoare de la un pigment la altul la temperatură constantă

Pigments	Temperature	Color difference
1-2	1400	8.88
2-3	1400	10.14
1-3	1400	5.01

Table 5c

c) Colour difference between pigment and matte colored glaze with same pigment

c) Diferența de culoare între pigment și glazura mată colorată cu același pigment

Pigment	Burning conditions	Color difference
1	1196, 6 hours	20.35
2	1196, 6 hours	20.63
3	1196, 6 hours	22.79
3-1% + 0.5% vanadium blue + 0.5% praseodium yellow	1196, 6 hours	23.17

4.Conclusions

From the studies performed on samples located in the ternary pseudosystem $MgAl_2O_4$-$CoAl_2O_4$-Al_2TiO_5, it is found that the formation of tialite begins at a temperature of 1200-1300°C, depending on the amount of spinel compound.

The chemical reactions lead to the formation of equilibrium phases tialite and solid solution of spinels, but next to them, regarding the heating temperature, there are traces of corundum and rutile, but these being white cannot influence the color. Through colorimetric studies of the pigments resulting at 1400 and 1450°C, it was found that the orange color is obtained, but when introduced into the glaze it change to the yellow-green. The obtained pigments are thermodynamically stable compared to other common pigments and can be used together with them to diversify colors. The synthesis of these pigments is interesting because they have a low cobalt oxide content compared to other cobalt-based pigments.

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