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Dedicated to Professor Liviu Literat, at his 80th anniversary

SYNTHESIS AND CHARACTERIZATION OF SOME THERMORESISTANT PIGMENTS BASED ON THE $Al^{3+} \rightarrow Cr^{3+}$ SUBSTITUTION

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ABSTRACT. The paper presents the obtained results in the synthesis of some thermoresistant pink pigments with different structures, such as: corundum ($Al_{2-x}Cr_xO_3$), spinel ($ZnAl_{2-x}Cr_xO_4$, $MgAl_{2-x}Cr_xO_4$) and perovskite ($LaAl_{1-x}Cr_xO_3$). An unconventional synthesis method has been used in order to increase the substitution of Al^{3+} with Cr^{3+}. The method used is based on the thermal decomposition of organic complex combinations containing as ligand the glyoxylate dianion, ($C_2H_2O_4^{2-}$). The evolution of the crystalline phases with temperature has been investigated by XRD. The colorimetric characterization of the obtained pigments has been studied by diffuse reflectance spectrophotometry.

Keywords: *thermoresistant pink pigments, chromophore chromium (*Cr^{3+}, Cr^{4+}*), mineralizers.*

INTRODUCTION

$Al^{3+} \rightarrow Cr^{3+}$ substitution in the crystalline networks of some oxide compounds leads to a wide range of pigments with colors varying from pink → red → purple → chestnut red. These pigments develop a special interest due to their color and difficulty to achieve constant nuances in a number as large as possible of vitreous compositions to be colored.

The α-Al_2O_3 - α-Cr_2O_3 continuous isomorphy represents the basis of the $Al^{3+} \rightarrow Cr^{3+}$ substitution [1].

In the crystalline structure of the two oxides, as well as in the solid solutions, they form, Al^{3+} and Cr^{3+} cations octahedrally coordinated. α-Cr_2O_3 is green, whilst α-$Al_{2-x}Cr_xO_3$ solid solutions are pink for $x \leq 0.10$. This major color difference is assigned to the compression of the Cr^{3+} cations in the

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electrostatic field of the anions, when Cr^{3+} cations take the place of Al^{3+} cations (with smaller ionic radius). The corresponding absorption bands in the VIS electronic spectrum move towards lower wavelengths and the color consequently changes from green (α-Cr_2O_3) to pink (α-$Al_{2-x}Cr_xO_3$) [2].

The development of the pink color requires the uniform (statistical) inclusion of Cr^{3+} cations in the $Al_{2-x}Cr_xO_3$ network and thus, the initial raw materials mixture has to be as homogenous as possible. Nevertheless, the synthesis temperature has to ensure the structuring of the solid solution crystalline network.

In the case of the classical (ceramic) method based on the thermal treatment of some Al_2O_3 and Cr_2O_3 mechanical mixtures, the temperatures required for the formation of the pink solid solutions are very high, often above 1300ºC. When the mixture is melting (which is the case of the ruby single crystals fabrication), the homogeneity is achieved in the melt and the specific color is ruby-red. Still, this requires temperatures above 2100ºC, which are not to be take into account in the case of thermoresistant pigments synthesis. A much more interesting and promising direction is represented by the unconventional methods. They start from highly homogenous precursors mixtures, usually at ionic scale.

It is possible to obtain pink pigments not only by using $Al^{3+} \rightarrow Cr^{3+}$ substitution in the Al_2O_3-Cr_2O_3 system, but also in more complex systems, which provide appropriate host - crystalline networks for Cr^{3+}. Among these, the most interesting crystalline network is that of spinel, in the ZnO-Al_2O_3-Cr_2O_3 system [3]. Recently, the perovskite structure [4, 5] in the Ln_2O_3-Al_2O_3-Cr_2O_3 system (Ln= Y, La, Nd, Dy, Gd) and also the cordierite structure $2MgO\cdot(2-x)Al_2O_3\cdot xCr_2O_3\cdot SiO_2$ [6-8] have developed practical interest.

The aim of the paper is to highlight the particularity and the advantages offered by one of the unconventional methods currently used in the synthesis of the thermoresistant pigments based on the $Al^{3+} \rightarrow Cr^{3+}$ substitution in various structures: corundum, spinel and perovskite. The effect of the mineralizer's addition has also been studied.

RESULTS AND DISCUSSION

The unconventional method chosen to obtain the studied pigments is based on the annealing of the organic complex combinations formed during ethylene glycol oxidation by the desired metal nitrates.

The results mentioned in literature [9-11], as well as some of our own previous results [12-18], have proven the possibility to obtain oxide compounds by annealing these complex combinations at temperatures at least 200 - 300ºC lower than in the case of the classical method based on the annealing of mechanical mixtures of oxides and/or salts.

The method is based on the 1,2-ethanediol to glyoxylate dianion oxidation reaction by the nitrate anion, according to the reaction:

$$C_2H_4(OH)_2 + 2NO_3^- \rightarrow C_2H_2O_4^{2-} + 2NO + 2H_2O \quad (1)$$

One or more metallic nitrates can be used in the oxidation reaction, depending on the designed product. For example, in order to obtain $ZnO \cdot Al_2O_3$ spinel, 1,2 - ethanediol is being oxidized by a mixture of $Al(NO_3)_3$ and $Zn(NO_3)_2$ in the molar ratio 2:1. It has been established [19] that in this particular case the following reactions take place:

$$Al(NO_3)_3 + H_2O \rightarrow Al(OH)(NO_3)_2 + HNO_3 \quad (2)$$

$$6C_2H_4(OH)_2 + 4\,Al(OH)(NO_3)_2 + 2Zn(NO_3)_2 \xrightarrow{xH_2O} \rightarrow Al_4Zn_2(OH)_4(C_2H_2O_4)_6 \cdot xH_2O + 12NO + 12H_2O \quad (3)$$

$$NO(g) + 1/2O_2(g) \rightarrow NO_2(g) \quad (4)$$

During the reaction HNO_3 and NO_2 evolve and the complex combination separates as a solid product. This decomposes during the annealing and an oxide powder forms, together with CO_2 and H_2O. At the beginning the resulting powder is amorphous, but an increase in the temperature leads to the formation of the designed oxide compound (reaction 5):

$$Al_4Zn_2(OH)_4(C_2H_2O_4)_6 + 6O_2 \xrightarrow{t>250^\circ C} 2(ZnO \cdot Al_2O_3) + 12CO_2 + 8H_2O \quad (5)$$

In the case of other metal nitrates, it may be possible that the oxidation reaction of 1,2 - ethanediol takes place differently, with the formation of carboxylates. Still, the intimate mixtures of the precursors preserve the advantage of the high initial homogeneity of the reaction mixtures and thus, enhance the reactions of the designed products, which take place at temperatures 200 or 300ºC lower than in the case of the traditional method.

In order to enhance the chromophore binding in the host-crystalline network, two of the common mineralizers have been used (CaF_2 and LiF), as well as the recently mentioned in the literature Li_2O. The latter is proven to develop a very good effect on the obtaining of mauve pigments with cassiterite structure [20] and pink pigments with tin sphene structure [21].

In Table 1 there are presented the studied compositions.

The observations made on annealed samples at different temperatures, as well as on the color of the rinsing water, phase analysis and diffuse reflectance spectra are shown as follows.

Trichromatic coordinates (L*a*b*) of some of the obtained samples are presented in Table 2. The three coordinates of CIELAB represent the lightness of the color (***L**** = 0 yields black and ***L**** = 100 indicates diffuse white; specular white may be higher), its position between red/magenta and

green (***a****, negative values indicate green, while positive values indicate magenta) and its position between yellow and blue (***b****, negative values indicate blue and positive values indicate yellow).

Table 1. Studied compositions

Sample number	Molar ratio						Mineralizer (1%)	Crystalline network
	$Al(NO_3)_3$	$Cr(NO_3)_3$	$Zn(NO_3)_2$	$Mg(NO_3)_2$	$La(NO_3)$	Ethylene glycol		
0.	-	2	-	-	-	3	-	Corundum - eskolaite
1.1.	1.90	0.10	-	-	-	2	-	Corundum
1.2.	1.90	0.10	-	-	-	2	CaF_2	Corundum
1.3.	1.90	0.10	-	-	-	2	Li_2O	Corundum
1.4.	1.90	0.10	-	-	-	2	LiF	Corundum
1.5.	1.80	0.20	-	-	-	2	-	Corundum
1.6.	1.80	0.20	-	-	-	2	CaF_2	Corundum
1.7.	1.80	0.20	-	-	-	2	Li_2O	Corundum
1.8.	1.80	0.20	-	-	-	2	LiF	Corundum
2.1.	1.90	0.10	1	-	-	3	-	Spinel
2.2.	1.90	0.10	1	-	-	3	CaF_2	Spinel
2.3.	1.90	0.10	1	-	-	3	Li_2O	Spinel
2.4.	1.90	0.10	1	-	-	3	LiF	Spinel
3.1.	1.90	0.10	-	1	-	3	-	Spinel
3.2.	1.90	0.10	-	1	-	3	CaF_2	Spinel
3.3.	1.90	0.10	-	1	-	3	Li_2O	Spinel
3.4.	1.90	0.10	-	1	-	3	LiF	Spinel
4.1.	0.95	0.05	-	-	1	2.5	-	Perovskite
4.2.	0.95	0.05	-	-	1	2.5	CaF_2	Perovskite
4.3.	0.95	0.05	-	-	1	2.5	Li_2O	Perovskite
4.4.	0.95	0.05	-	-	1	2.5	LiF	Perovskite

a) Pigments with corundum structure $Al_{2-x}Cr_xO_3$

All the samples within the series 1 (1.1 ÷ 1.8) are amorphous after annealing at 500ºC. At 900ºC δ-Al_2O_3 is present in the XRD pattern and after annealing at 1000ºC α-Al_2O_3 is present as single phase.

The color of the samples within the series 1 varies much, depending on the composition and annealing temperature.

The free chromium as soluble Cr^{6+} (aluminium chromate), assessed by the color of the rinsing water varies with the annealing temperature and the mineralizer used. Since the objective was to reach an advanced chromium binding degree in the crystalline network of corundum, we considered the quantitative assessment of free chromium was not necessary. The purpose was to find the working conditions to allow the development of an

intense color by the homogenous inclusion of the chromophore Cr^{3+} in the host crystalline network. From this point of view, the color of the samples is more intense at 1100ºC than at 1000ºC, and there is no significant difference between the colors at 1200ºC compared to 1100ºC.

Table 2. CIELAB trichromatic coordinates of the samples annealed at different temperatures

Sample number	Sample	Mineralizer [wt.%]	Temperature [ºC]	L*	a*	b*
0.	Cr_2O_3	-	1100	44.4697	-14.8240	16.7534
1.5.	$Al_{1.80}Cr_{0.20}O_3$	-	1100	67.3149	2.8066	2.0216
1.6.	$Al_{1.80}Cr_{0.20}O_3$	CaF_2	1100	66.4278	4.2003	1.2662
1.7.	$Al_{1.80}Cr_{0.20}O_3$	Li_2O	1100	65.7919	3.1277	1.2063
1.8.	$Al_{1.80}Cr_{0.20}O_3$	LiF	1100	66.4393	1.9980	1.7037
2.1.	$ZnAl_{1.90}Cr_{0.10}O_4$	-	1100	79.4996	15.2079	2.3690
2.2.	$ZnAl_{1.90}Cr_{0.10}O_4$	CaF_2	1100	87.7384	9.8321	2.9288
2.3.	$ZnAl_{1.90}Cr_{0.10}O_4$	Li_2O	1100	82.4761	15.6099	2.5786
2.4.	$ZnAl_{1.90}Cr_{0.10}O_4$	LiF	1100	85.6378	11.8808	1.8574
3.1.	$MgAl_{1.90}Cr_{0.10}O_4$	-	1200	85.1272	5.8948	0.6873
3.4.	$MgAl_{1.90}Cr_{0.10}O_4$	LiF	1200	80.0045	6.8176	1.8102
4.1.	$LaAl_{0.95}Cr_{0.05}O_3$	-	1000	81.9325	7.5195	7.7448
4.2.	$LaAl_{0.95}Cr_{0.05}O_3$	CaF_2	1000	67.7153	8.9423	4.0135
4.1.	$LaAl_{0.95}Cr_{0.05}O_3$	-	1200	52.6236	13.9397	5.9973
4.2.	$LaAl_{0.95}Cr_{0.05}O_3$	CaF_2	1200	42.4616	14.8593	6.0388

Interesting differences have been noted between samples obtained with mineralizer addition:

- The samples with 1% CaF_2, which is considered in the literature as a highly efficient mineralizer, show a less intense color than in the case of the similar sample without CaF_2 content (within series 1). Accordingly, the samples with CaF_2 show higher free soluble chromium content.
- Samples with 1% Li_2O present a more intense color and lower free soluble chromium content than in the case of samples with CaF_2 or without mineralizer.
- Samples with LiF are very similar to those with Li_2O.

The negative effect of CaF_2 is assigned to the Ca^{2+} cation, with marked alkaline nature, which determines the calcium chromate ($CaCrO_4$) formation, enhancing the displacement of the $Cr^{6+} \leftrightarrow Cr^{3+}$ equilibrium towards Cr^{6+}.

The increase of the Cr^{3+} content in the series 1.5 ÷ 1.8 leads to impurifying of the pink color with green.

The explanation of the pink color in the case of the solid solutions resulted by the substitution of Al^{3+} with Cr^{3+} cations lays in the higher Cr^{3+} radius ($r_{Cr^{3+}} = 0{,}62$ Å, $r_{Al^{3+}} = 0{,}53$ Å after Shannon and Kingery cited in [22]). Thus, Cr^{3+} cations are subjected to compression, which leads to a more intense electrostatic repulsion between the load of the oxygen anions in the corners of the coordination polyhedron (octahedron) and the *3d* electrons of the chromophore, implicitly increasing the splitting parameter Δ_o. The effect of Δ_o increase is a displacement of the absorption bands corresponding to the $3d^3$ electrons transitions towards higher frequencies ($\Delta E = h\nu$), lower wavelengths respectively, with a change in color from green (α-Cr_2O_3) to pink-red (ruby, α-$Al_{2-x}Cr_xO_3$). This displacement of the absorption bands may be easily observed on the diffuse reflectance spectra presented in Figure 1.

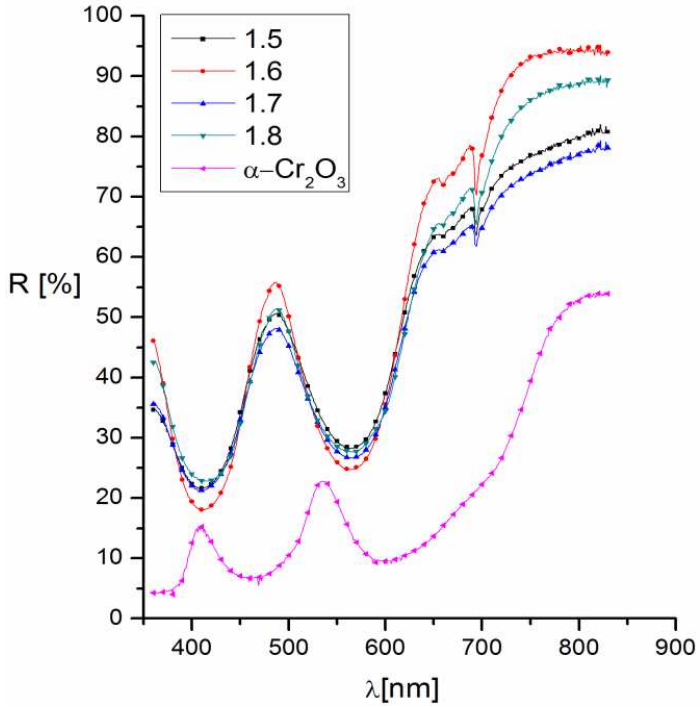

Figure 1. Diffuse reflectance spectra of samples 1.5-1.8 annealed at 1200ºC and α-Cr_2O_3.

b) Spinel structure pigments

The compositions presented in Table 1 show two groups of spinel structure pigments:

- derived from zinc spinel $ZnAl_{2-x}Cr_xO_4$, samples 2.1. ÷ 2.4;
- derived from magnesium spinel $MgAl_{2-x}Cr_xO_4$, samples 3.1 ÷ 3.4.

In both series, the effect of mineralizer addition (CaF_2, Li_2O, LiF) upon the color development has been studied.

There is very few information in literature concerning the use of magnesium spinel for thermoresistant pigments. Usually, the zinc spinel is the one used for obtaining a wide range of colors by Al^{3+}, Zn^{2+} or both cations substitution with different chromophore cations (Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, etc.). This situation is due to both experimental results and to thermodynamic calculus. Starting from the thermodynamic standard functions of each chemical compound [23] and considering the relations for the temperature dependence of the thermal effects ($\Delta_r H_T^0$) and Gibbs energy ($\Delta_r G_T^0$) [24], the thermodynamic calculations have been done. The $\Delta_r H_T^0 = f(T)$ dependence (Figure 2) calculated for zinc and magnesium spinels show that the reaction of the spinel starting from oxides as raw materials (the classical method) is more exothermal for $ZnAl_2O_4$ than for $MgAl_2O_4$. Moreover, the $\Delta_r G_T^0 = f(T)$ calculated dependence show that zinc spinel forms easier than magnesium spinel (Figure 3).

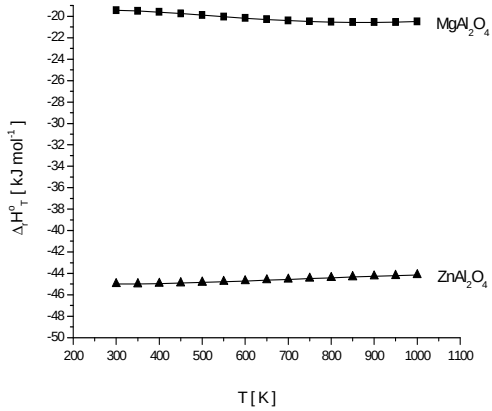

Figure 2. $\Delta_r H_T^0 = f(T)$ dependence for the reactions of zinc and magnesium spinels.

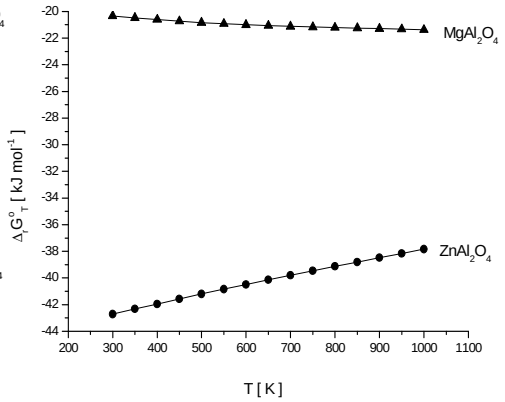

Figure 3. $\Delta_r G_T^0 = f(T)$ dependence for the reactions of zinc and magnesium spinels.

$ZnAl_2O_4$ formation by solid state reaction takes place quite easily and thus, the zinc spinel represents an accessible base for thermoresistant pigments, whilst $MgAl_2O_4$ is more difficult to obtain.

Pink pigments derived from $MgAl_2O_4$ have been obtained by the method based on annealing the complex combinations, which enhances the formation of the designed products.

The results of the XRD phase analysis in the case of the samples annealed at temperatures comprised between 500ºC and 1000ºC confirmed the easier formation of the zinc spinel (samples 2.1 ÷ 2.4). At 600ºC this is present as single phase in the XRD pattern. In the case of $MgAl_2O_4$ (samples 3.1÷ 3.4) the powder is amorphous. The spinel presents a good crystallization degree at 800ºC.

One notes that in the case of the traditional synthesis method, when starting from a mixture of $MgCO_3$ and aluminum hydroxide, the spinel is still not the single phase present at 1200ºC [25].

The diffuse reflectance spectra of the synthesized zinc and magnesium spinels are presented in Figures 4 and 5.

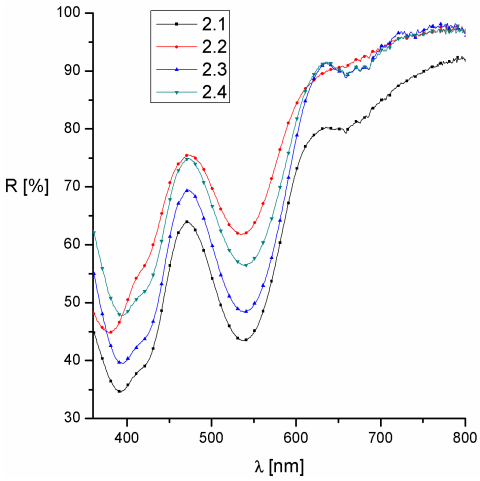

Figure 4. Diffuse reflectance spectra of samples 2.1 ÷ 2.4 annealed at 1100℃.

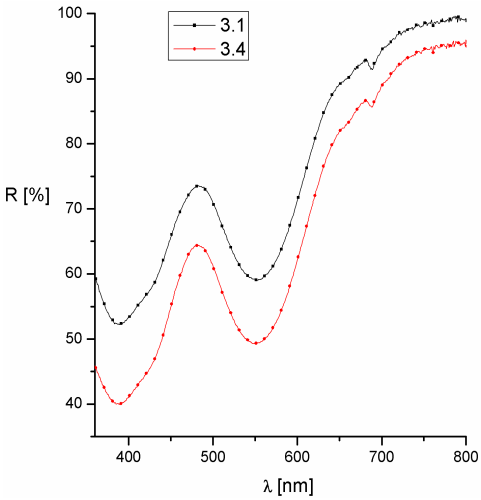

Figure 5. Diffuse reflectance spectra of samples 3.1 and 3.4 annealed at 1200℃.

From the point of view of the pink color development via the $Al^{3+} \rightarrow Cr^{3+}$ partial substitution, the observations are similar to those made in the case of the corundum solid solutions:

- the temperature required to obtain an intense pink is 1100℃. It is only in the case of the magnesium spinel, when raising the temperature up to 1200℃ leads to a color enhancement. This may be assigned to the specific $MgAl_2O_4$ formation conditions, which are more sensitive to temperature.

- the effect of mineralizers additions is similar to the 1. series – negative for CaF_2 and positive for Li_2O and LiF, with the same explanation for the negative role of Ca^{2+} ions.

c) Perovskite structure pigments

The crystalline structure of perovskite is one of the most recent used in thermoresistant pigments synthesis [26-28]. Starting from the ABO_3 stoichiometry, where A^{3+}= Y^{3+}, La^{3+}, Nd^{3+}, etc. (large radius cations) – dodecahedrally coordinated, and B^{3+}= Al^{3+} (relatively small radius cations) octahedrally coordinated, there may be obtained pink pigments by $Al^{3+} \rightarrow Cr^{3+}$ partial substitution.

The formation of the above-mentioned pigments (samples 4.1 – 4.4) via thermal decomposition of the complex combinations, as well as the influence of the mineralizers upon the color, were studied.

The diffuse reflectance spectra of the samples with no mineralizer, respectively with CaF_2 as mineralizer, at 1000 and 1200℃ there are presented in Figures 6 and 7.

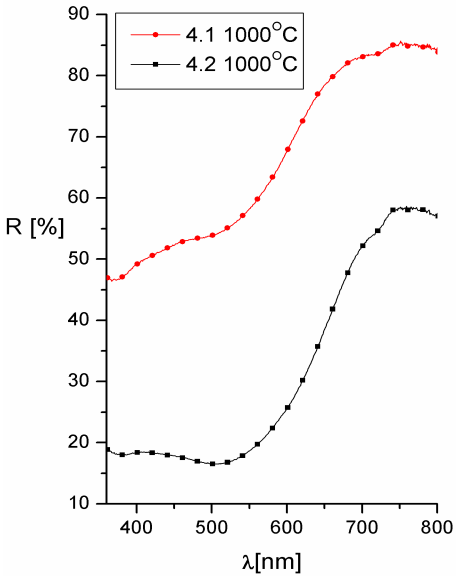

Figure 6. Diffuse reflectance spectra of samples 4.1 and 4.2 annealed at 1000℃.

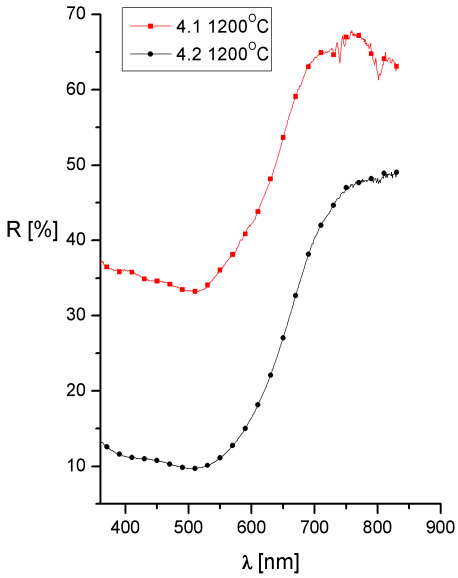

Figure 7. Diffuse reflectance spectra of samples 4.1 and 4.2 annealed at 1200℃.

These spectra are practically identical with those of the same pigments obtained by the traditional method at 1400℃ [4].

One can note the presence of the specific wide absorption band between 450 and 600nm. At both 1000 and 1200°C samples with CaF_2 show lower reflectance values, which indicate more intense colors than in the case of the samples with no mineralizer addition.

The XRD patterns presented in figure 8 show that the sample annealed at 600°C is amorphous and starting with 750°C perovskite is the single phase in the sample. The yellow color of the sample annealed at 600°C is assigned to Cr^{6+} as lanthanum chromate and the pink color at 750°C is associated with the presence of perovskite.

Regarding the oxidation number of chromium, which is substituting the octahedrally coordinated Al^{3+} cations in the perovskite network, the literature data are still controversial. Some authors [29-31] consider that chromium is trivalent. But if one takes into account the diffuse reflectance spectra of these pigments (Figures 6 and 7), which are essentially different from those of the pink pigments with corundum and spinel pigments, this hypothesis is questionable.

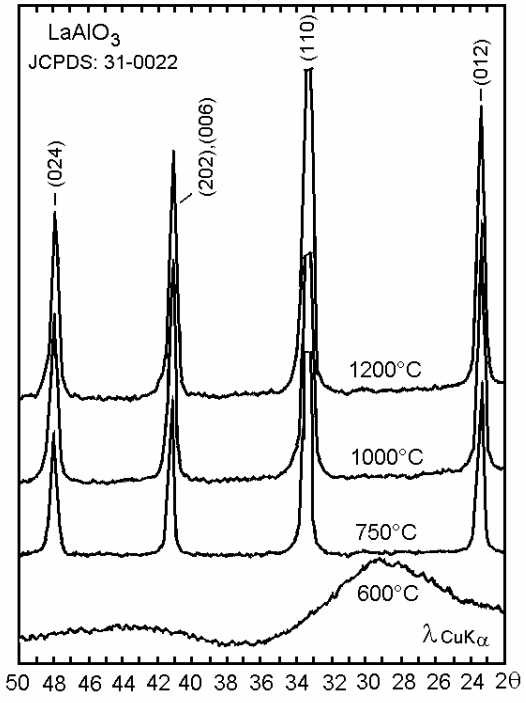

Figure 8. XRD patterns of La^{3+}, Al^{3+} and Cr^{3+} glyoxilate annealed at different temperatures.

The diffuse reflectance spectrum of pink perovskite pigments show a large absorption band between 380 and 600nm, very similar to that of the tin sphene ($CaO \cdot SnO_2 \cdot SiO_2$) pigments – in which the presence of octahedrally coordinated Cr^{4+} is already accepted, as a result of the $Sn^{4+} \rightarrow Cr^{4+}$ substitution [32-35]. Based on this analogy, one can assume the presence of Cr^{4+} as well in the pink perovskite pigments. As a matter of fact, Pavlov [34] indicates the presence of Cr^{4+} in $YAlO_3$, in which Al^{3+} is partly substituted by chromium. The overall structure is electrically neutral due to cationic vacancies generated by the substitution $4Al^{3+} \rightarrow 3Cr^{4+}$. Another possibility is the coupled substitution $(La^{3+} + Al^{3+}) \rightarrow (Ca^{2+} + Cr^{4+})$, where Ca^{2+} cations come from the used mineralizer (CaF_2) – a plausible hypothesis taking into account the marked positive influence of CaF_2 upon the color of these pigments. Unlike the case of corundum and spinel pigments, where CaF_2 has a negative effect, in the case of perovskite the $La^{3+} \rightarrow Ca^{2+}$ substitution (as A – type cations) enhances the $Al^{3+} \rightarrow Cr^{4+}$ substitution and hence, the color. $La^{3+} \rightarrow Ca^{2+}$ substitution is possible due to the close values of the ionic radius of the two cations and also to the Ca^{2+} possibility to form a perovskite network (see the case of $CaTiO_3$ – where the tetravalent B cations are octahedrally coordinated).

CONCLUSIONS

The method based on the annealing glyoxylate-like complex combinations enables the chromium (Cr^{3+}, Cr^{4+}) containing pigments formation at temperatures at least 200-300ºC lower than in the case of the classical method.

Zinc spinel ($ZnAl_2O_4$) and the pink pigments derivated from this are easier to obtain than magnesium spinel ($MgAl_2O_4$), which is in accordance with the thermodynamic data.

The method used ilustrates the possibility to obtain magnesium spinel and substitute Al^{3+} with Cr^{3+} even at 800℃, whilst in the traditional method temperatures above 1200℃ are needed.

Choosing the right mineralizers to enhance the color and reduce the soluble chromium ratio must be done according to the crystalline network type, basicity of the host-network cations, desired substitutions and final chromophore oxidation number.

CaF_2 is not recommended in the case of corundum and spinel structure pigments. The use of LiF or Li_2O leads to the desired pink pigments at temperatures between 1000 and 1100℃.

In the case of perovskite, the use of CaF_2 clearly enhances the specific color of these pigments.

EXPERIMENTAL SECTION

Organic combinations obtained by the oxidation reaction of 1,2-ethanediol with the desired metal nitrates according to the reactions (1), (2), (3), (4) and (5) were dried in a drying oven at 110℃ and annealed in porcelain crucibles at temperatures between 500℃ a nd 1200℃ in static air using an electrical (Nabertherm) furnace.

The free chromium content (soluble Cr^{6+}) after annealing the samples has been assessed by the colour of the rinsing water. After drying, the samples were subjected to colorimetric characterization by diffuse reflectance spectrophotometry – using a Varian CARY 300 spectrophotometer with integration sphere, D65 illuminant at 10 degrees observer's angle. The CIELAB trichromatic coordinates L*a*b* were established using Varian CARY WinUV Color 3.1. software. The phase composition analysis of the samples was investigated by XRD, using a DRON 3 diffractometer with CuK_α radiation.

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