STUDIA UBB CHEMIA, LXI, 3, Tom I, 2016 (p. 263-273)
(RECOMMENDED CITATION)

Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of her 65th anniversary

INFLUENCE OF THE THERMAL TREATMENT ON THE COLOUR OF RO·Al_2O_3 (R=Co, Ni) TYPE SPINEL PIGMENTS PREPARED BY A MODIFIED SOL – GEL METHOD

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ABSTRACT. This paper presents the results obtained through the synthesis of spinel - structured, ceramic pigment nanopowders ($CoAl_2O_4$ si $NiAl_2O_4$), using a modified sol – gel method. This study focuses on the influence of the thermal treatment, applied during gel calcination, on the properties of the obtained powders. The behavior of the dried gels during calcination was studied by differential thermal analysis. The formation of the spinel structure after the thermal treatment, was analyzed using X-ray diffraction. The colour of the powders was characterized by UV–VIS spectroscopy, determining the absorption spectra. Additionally, the trichromatic coordinates were determined, and the corresponding pigment positions were fixed on the chromaticity diagram.

Keywords: *ceramic pigment nanopowders, cobalt spinels, nickel spinels, sol–gel method, sucrose, pectin.*

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INTRODUCTION

Oxide materials with a spinel structure are employed in a large number of fields due to their refractory, magnetic, semiconductor, and optical properties [1]. Spinel structured oxides are one of the most important classes of pigments, primarily due to their high thermal and chemical stability and their capacity to “host” different cations, which leads to a great variety of colours and colour shades [2, 3].

Synthetic blue pigments are widely used in the ceramics industry as colouring agents for glazes or porcelain stoneware. The traditional source of blue colour in a ceramic pigment, remains the divalent cobalt ion (Co^{2+}) in the tetrahedral coordination site - Co_2SiO_4 (olivine), $(Co,Zn)_2SiO_4$ (willemite) and $CoAl_2O_4$ (cobalt spinel). However, recent publications have focused on the elaboration of aluminate spinels for cyan pigments (one primary colour in the subtractive system) with Ni^{2+} as a chromophore ion [4].

The development of the blue colour, specific to the Co^{2+} and Ni^{2+} chromophores, tetra-coordinated in spinel structures, relies on their inclusion into the “host” crystalline lattice, in a uniform distribution. This raises the necessity for a better homogeneity of the raw materials, as well as a high synthesis temperature to ensure the proper arranging of the crystalline network. In the case of the classical method, based on a mechanical mixture of salts or oxides, reaching a good homogenization proves difficult. Another problem with this approach would be the high temperatures needed in order to obtain the desired colour (over 1200 °C) [5]. Due to these difficulties, unconventional synthesis methods were developed. These methods, such as co–precipitation, hydrothermal synthesis, microemulsion and sol–gel method, utilize advanced homogeneous precursors. The sol–gel method is commonly used in the synthesis of oxide nanomaterials, its advantages consisting of mixing the raw materials at a molecular level, low temperature processing, and a better control over the obtained nanomaterials [6, 7].

The sol–gel method entails the reaction of the precursors in the solution, with the purpose of creating the nanometric units, “sols”, which, further assemble to form a three – dimensional lattice, “gel”. The liquid phase of the gel fills the open pores of the structure. The structure of the gel is uniform, as both the constituent particles and pores are nanometric in scale. This homogeneity ensures an evenness of the materials properties [6].

In the present paper, for the synthesis of the $CoAl_2O_4$ and $NiAl_2O_4$ spinels, a modified sol – gel method was applied, using metal nitrates as well as sucrose and pectin as organic precursors. This modified method was successfully utilized in the synthesis of other oxide compounds as nanometric powders [8-10]. Sucrose and pectin are inexpensive materials, as well as nontoxic, making their use instead of other organic components, beneficial.

RESULTS AND DISCUSSIONS

Differential thermal analysis

The diagrams for the two gels are presented in figures 1 and 2. The thermal analysis for the cobalt gel indicates an endothermic process up to 150°C, with a mass loss of approximately 15%, represented by the loss of residual water present in the pores. Between 150 and 548 °C, two exothermic processes, with an important mass loss, can be seen. This is due to the calcination of the organic compounds with a formation of volatile components. The first exothermic process, present between 150 – 443 °C, is more intense, having a mass loss of 60.30%. The second one, seen between 443 – 548 °C, has a loss of only 9.06%. At temperatures higher than 548 °C, the mass loss is insignificant (1.18%).

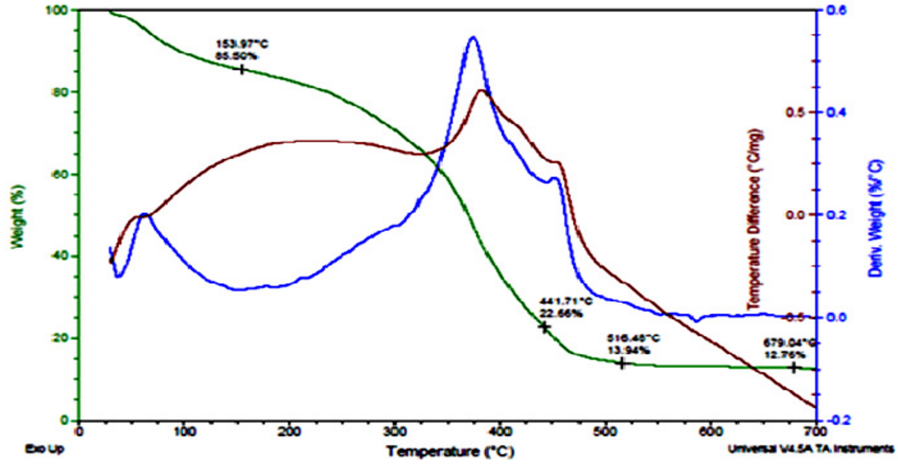

Figure 1. TG – DTG – DTA diagram for the $CoAl_2O_4$ gel

The thermal behaviour of the $NiAl_2O_4$ gel is similar to that of $CoAl_2O_4$. The residual water is eliminated in two steps, up until 144 °C, and the oxidation of the organic compounds takes place between 144 – 520 °C. It manifests with two exothermic processes, one less intense, at 144 – 190 °C, and the second one, more so, at 190 – 520 °C. The mass loss due to the calcination of the organic precursors consists of 77.76%. Prior to 700 °C, a small mass loss of 1.03% is attributed to the volatile compounds formed and remained inside the materials pores. According to the thermal analysis, the oxidation and elimination of the organic compounds takes place up until a temperature of 550 °C. The thermal treatment on the dried gels was performed at 600 – 1000 °C, with a 30 minutes plateau at maximum temperature.

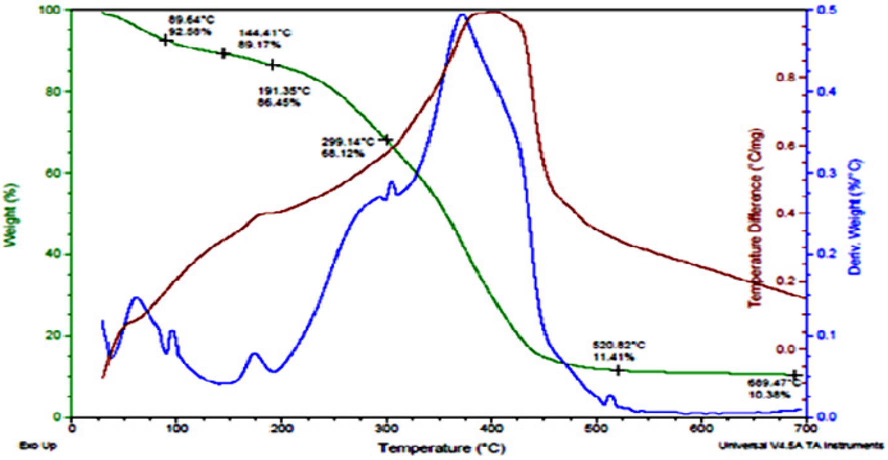

Figure 2. The TG – DTG – DTA diagram for the $NiAl_2O_4$ gel

X – ray diffraction analysis

X – ray diffraction analysis performed on samples thermally treated at 600, 700, 800 and 1000 °C respectively, are illustrated in figures 3 and 4. The $CoAl_2O_4$ patterns indicate that all samples are well crystalized, with the spinel structure already evidenced for samples thermally treated at a 600 °C temperature. At higher temperatures, the crystallinity of $CoAl_2O_3$ is increased. Conversely, the $NiAl_2O_4$ pattern shows a lower crystallization temperature of the spinel phase. The patterns for the samples thermally treated at lower temperatures, 600 and 700°C, respectively, illustrate only three of the specific reflexes of the spinel structure. This indicates a week index of crystallization, the amorphous phase being predominant. No other crystalline phases are evidenced. In the case of the powder obtained at 800 °C, (figure 5) there are two spectral lines barely visible that tend to intensify with a longer thermal treatment time. The consolidation of the crystalline structure of $NiAl_2O_4$ can be seen on the 1000 °C diffraction pattern that shows a high crystallinity index. According to the results presented in [11] the arrangement of the $NiAl_2O_4$ structure, begins at 900°C. An increase of the spinel structure lattice parameter with the increase of the thermal treatment temperature can be noted for both $CoAl_2O_4$ and $NiAl_2O_4$ samples, as presented in table 1.

The sizes of the CoAl2O4 crystallites, calculated using the Debye-Scherrer formula, are in the range of 28–39 nm (table 1). The NiAl2O4 crystallite sizes are smaller than those of CoAl2O4. The nanometric crystallite sizes represent an important factor in the case of pigments, an increase the coloration capacity being dependent on the specific surface.

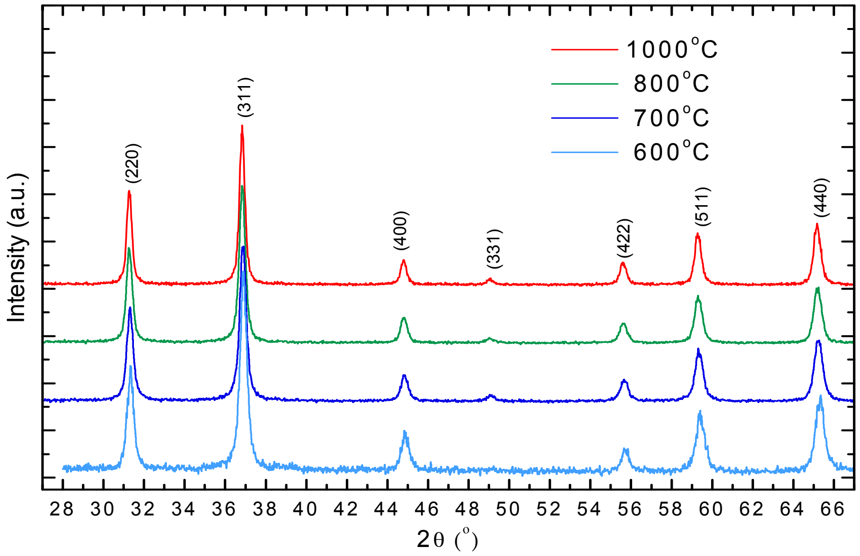

Figure 3. The X-ray diffraction pattern for $CoAl_2O_4$ thermally treated for 30 minutes at 600, 700, 800 and 1000 °C

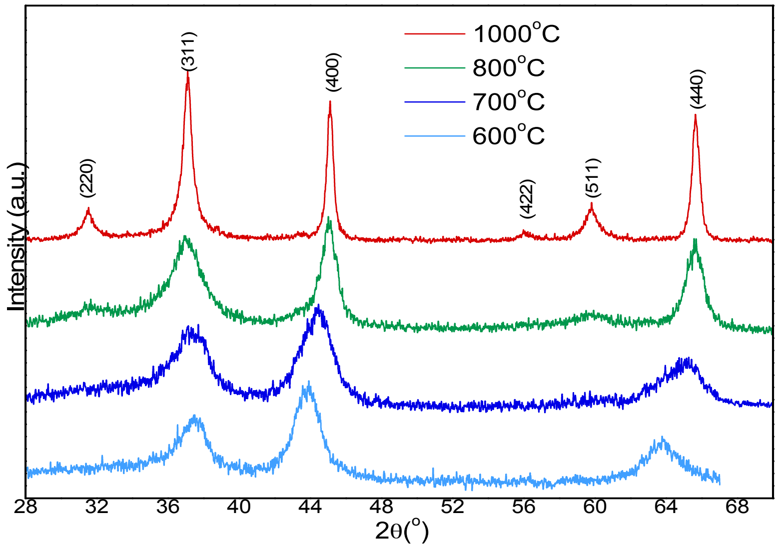

Figure 4. The X-ray diffraction pattern for $NiAl_2O_4$ thermally treated for 30 minutes at 600, 700, 800 and 1000 °C

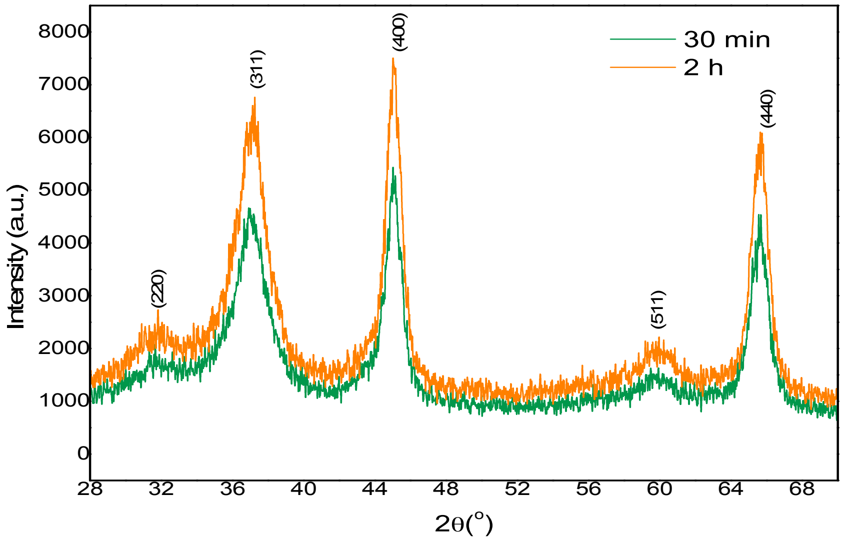

Figure 5. The X-ray diffraction pattern for $NiAl_2O_4$ thermally treated for 30 minute and 2 hours at 800 °C

Table1. XRD values for the structural lattice parameter and the crystalline particles diameter, correlated to the calcination time

Thermal treatment temperature °C	**a (Å)**		**D (nm)**	
	$CoAl_2O_4$	**$NiAl_2O_4$**	**$CoAl_2O_4$**	**$NiAl_2O_4$**
600°C	8.081		28±1	
700°C	8.092		30±1	
800°C	8.098	8.033	33±1	9±1
1000°C	8.102	8.044	39±1	23±1

Colour characterization of the obtained pigments

The pigment colour is in the blue range for $CoAl_2O_4$ and cyan for $NiAl_2O_4$, being strongly influenced by calcination temperatures.

The absorption spectra for $CoAl_2O_4$ and $NiAl_2O_4$ are shown in figure 6 and 7, respectively.

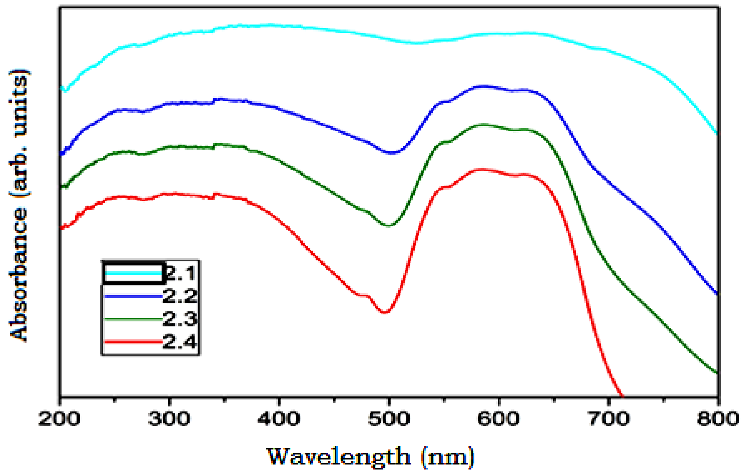

Figure 6. The absorption spectra of $CoAl_2O_4$ powders, obtained by calcination, for 30 min at : 2.1 – 600 °C, 2.2 – 700 °C, 2.3 – 800 °C, 2.4 – 1000 °C

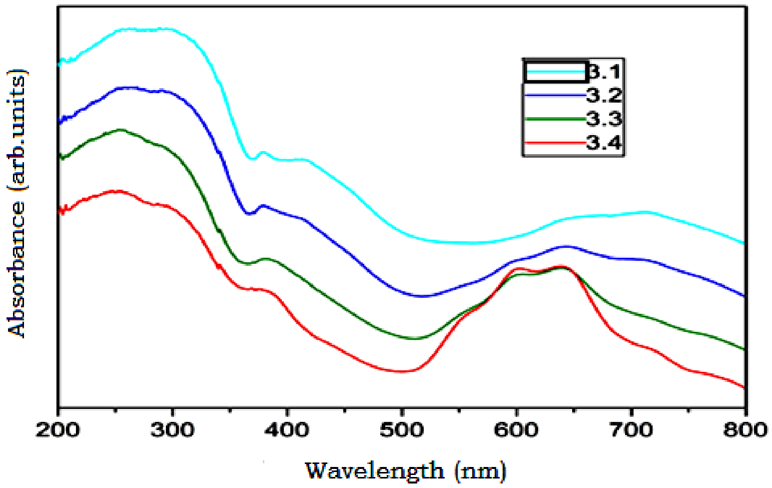

Figure 7. The absorption spectra of $NiAl_2O_4$ powders, obtained by calcination, for 30 min at : 3.1 – 600 °C, 3.2 – 700 °C, 3.3 – 800 °C, 3.4 – 1000 °C

In the case of $CoAl_2O_4$ thermally treated at 600°C, the colour is dark green, almost black and has a tendency of becoming blue with a raise in temperature. The blue colour observed at 700 °C becomes clearer, and more luminous at 800 and 1000 °C. This is accordingly to the UV – VIS absorption spectra, that, at 600 °C, shows high intensity absorption almost on the entirety of the visible spectrum. In the case of the powders thermally treated at 700, 800 and 1000 °C, the spectra shows an absorption broadband at 500 – 700 nm, with maximums at 580 and 640 nm, that accordingly to literature data [1,2,4, 5,12] can be attributed to the $^4A2(F)\rightarrow{}^4T_1(P)$ transition of Co^{2+} (d^4) in Td configuration. The rise in temperature leads to a narrowing of the absorbtion broadband, which indicates a high purity of colour.

The colour of $NiAl_2O_4$ powders varies among yellowish green for the 600 °C sample, bluish green for the 700, 800 °C one, and cyan blue for the 1000 °C sample. The absorption spectra for the powders calcined at 800 and 1000 °C show well contoured absorption bands with maximums at 370, 600, 640 nm, a characteristic of tetracoordinated Ni2+. According to literature data [1,11,13,14], the absorption bands at 600 – 640 nm, correspond to the 3T1(F) →3T1(P) transition, a feature specific to Ni^{2+} tetracoordinated. The bands from 710 and 760 nm correspond to the 3A2g(F) →3T1g(F) transition, attributed to Ni^{2+} octahedrally coordinated, and the 370, 430 nm maximums correspond to the transfer in charge [11]. The experimental spectra do not show significant values for the absorbance at wavelenghts greater than 700 nm, so it can be concluded that the amount of Ni^{2+} octahedrally coordinated is verry small.

The determination of the tricromatic coordinates and the location of the representative points on the cromicity diagram confirms that the obtained colours belong in the blue domain in the case of $CoAl_2O_4$ and the cyan one, in the case of $NiAl_2O_4$ (figure 8).

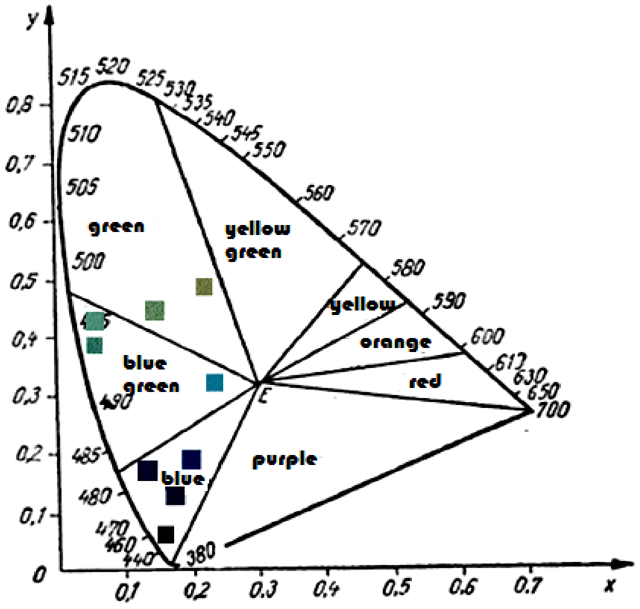

Figure 8. The Cromicity diagram. The fixed positions for the $CoAl_2O_4$ and $NiAl_2O_4$ pigments calcined between 600 – 1000 °C

CONCLUSIONS

The modified sol – gel method, utilizing sucrose and pectin as organic precursors, leads to the formation of powders with crystallite dimensions under 50 nm, when applied to $CoAl_2O_4$ and $NiAl_2O_4$ spinels. Sucrose and pectin are inexpensive and nontoxic both in terms of an economical, as well as an environmental point of view.

After XRD analysis on powders obtained by gel calcination at temperatures ranging between 600 – 1000 °C, it is found that the structure of $CoAl_2O_4$ spinel arranges itself easily. The diffraction pattern indicates a consolidated crystalline structure even at a lower temperature as 600 °C. The crystalline structure of $NiAl_2O_4$ arranges itself with more difficulty, at 600 °C the amorphous phase being predominant. The ordering of the crystalline structure begins at 800 °C.

The crystallite dimensions, determined with the Debye – Scherrer formula, indicate values in the range of 9 – 39 nm. These values rise with the rise in temperature, from about 28 nm for $CoAl_2O_4$ fired at 600 °C to about 39 nm for $CoAl_2O_4$ fired at 1000 °C. Comparatively, the crystallite dimension for $NiAl_2O_4$ is approximately 9 nm for the 800 °C sample and about 23 nm for the 1000 °C one. The differences shown are due to the differences in the ordering of the crystalline structure for the two pigments

The colour of the powder is characteristic for the two spinel structures: blue in the case of $CoAl_2O_4$ and cyan for $NiAl_2O_4$. The UV – VIS absorption spectra shown specific maximums in conformity to the literature data. The colour of the powders is dependent on the calcination temperature – for $CoAl_2O_4$ there can be observed a dark green, almost black colour for the 600 °C sample, dark blue for the 700 °C one, colour that becomes more luminous at higher temperature calcination. The colour for $NiAl_2O_4$ varies from a yellowish green, obtained at 600 °C to a bluish green at 700 - 800 °C and finally cyan, for the sample fired at 1000 °C.

EXPERIMENTAL SECTION

The sol – gel process is based on the formation of a solution that contains metal salts or alkoxides, followed by the conversion of the gel, by hydrolysis and condensation, into the oxide gel lattice. The hydrolysis is accomplished under a strict control of the temperature, pH, concentration, water/ alcohol ratio. By controlled drying and calcination, the gel becomes an oxide [2,6].This mechanism, and the role played by sucrose and pectin in the formation of the oxide structures, is discussed in more detail in reference [8,9,10].The addition of sucrose, and pectin, to the solution of the metal cations, forms a polymer matrix in which the Co^{2+} and Al^{3+} respectively Ni^{2+} and $Al^{3+.}$cations are distributed through the polymeric network structure. Sucrose, which is always in excess, acts as a strong chelating agent and as a pattern material. The sucrose solution contains NO^{3-} ions that help hydrolyze the sucrose molecule into glucose and fructose, and afterwards, oxidize it to gluconic acid, or polyhydroxyl acid. Gluconic acid contains carboxylic acid groups and hydroxyl groups which can participate in the complexation of metal ions and may form branched polymer with pectin. Pectin chains form long layers and sucrose molecules may bind between these layers. In the present process, metallic ions are bound by the sucrose molecule and the resulting complex molecule is trapped between pectin layers. During calcination this polymeric metal ion complex is decomposed into CO_2 and H_2O and a large amount of heat is generated preventing agglomeration by ensuring that the mixture remains porous [9].

For obtaining $CoAl_2O_4$ and $NiAl_2O_4$ spinels, $Co(NO_3)_2{*}2H_2O$, $Al(NO_3)_3{*}9H_2O$ and $Ni(NO_3)_2{*}6H_2O$ were used. The salts were dissolved in water, to obtain concentrated solutions. The solutions were stirred in with the sucrose for 1 hour (with a 2:1 molar ratio for sucrose: oxides), at 40 – 45 °C and with a pH corrected to 1 – 1.5. After stirring, the mixture is left in a repose state, at 60 °C, for 24 h, to ensure the formation of the gel lattice, with the elimination of the water present in the pores and the final formation of a porous structure. The thermal treatment of the dried gels was done in an electric furnace, in porcelain crucibles. The furnace temperature had an increase rate of 300°C/h, with an isothermal plateau of 30 minutes, at 600, 700, 800, 1000 °C. At 800 °C an additional thermal treatment for 2 hours was realized.

The behavior of the gels during heating was studied with a Differential Thermal Analysis, done with a TA Instruments SQD 600 analyzer, on an interval of 30 – 700 °C, and a heating rate of 10°C/min, in alumina crucibles and a dynamic air atmosphere.

The structural characterization was carried out at room temperature by powder X-ray diffraction using a Bruker D8 Advance AXS diffractometer with Cu Kα radiation. The crystallite-sizes were calculated using the Debye – Scherrer formula:

$$D = \frac{\mathrm{k}\lambda}{\beta \cos\theta} \qquad [1],$$

where β is the peak full width at half maximum (in radians) at the observed peak angle θ, k is the crystallite shape factor (was considered 0.94) and λ is the X-ray wavelength.

The characterization of the pigment colour was realized by measuring the absorption in UV - VIS and by determining the trichromatic coordinates (X, Y, Z), with an MOM colorimeter.The UV-visible absorption spectra were recorded with a Jasco V-650 spectrophotometer (Japan) equipped with an ISV-722 Integrating Sphere, in the range 200-800 nm with a scan rate of 400 nm/min.

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