CHAPTER (I)

1. Introduction

1.1. General Introduction

Inorganic pigments find important in industry due to their applications in color of plastics, polymers, paints, glasses, ceramics tableware, sanitary ware, tiles and surface decoration of different classes of pottery [(1)], have traditionally been based on transition metal compounds or heavy metals. Transition metal ions or rare earth ions doped oxide pigments form a group of ceramic pigments. Ceramic pigments are inorganic products of metal oxides or compounds capable of forming metal oxides. Ceramic pigments are white or colored crystalline materials.The oxidation state, coordination of dopants, the synthesis route, doping metals(chromophorous ions) and matrix decide the nature of color of ceramic pigments that attributed to partly filled d or f block elements [(2)]. The synthesis route affects particle size distribution, and resistance to acids, alkalis [(3)]. The final color of each pigment is due to the addition of a chromophore ion (usually transition metals) into an inert matrix. The host can be a single oxide (e.g. SnO_2, TiO_2) or a mixed oxide (e.g. $ZrSiO_4$, $MgAl_2O_4$). Typical examples of the chromophores are transition metal ions (Fe, Cr, Mn, Ni, Co, Cu, V, etc.) and rare earth elements (Ce, Pr, Nd) **[(5)]**. The normal spinel structure $R^1O.R^2{}_2O_3$, is formed by association of a trivalent oxide (acid character) R^2 that present on octahedral sites and with a bivalent oxide (alkaline character) R^1 that present on tetrahedral sites **[(4)]**. In inverse spinels, the R^1ions and half the R^2 ions are on octahedral sites; the other half of the R^2 are on tetrahedral sties, $R^2(R^1R^2)O_4$. The mixture of these

substances that has been obtained by reactions in solutions or solid-state reactions or even by milling undergoes a proper thermal treatment. They must show high thermal, chemical stability and chemical resistance at high temperatures and must be inert to the chemical action of the molten glaze with their low toxicity.

2. The classification of ceramic pigment [6]:

2.1. Idiochromatic (self-colored) pigment.

The first type of pigment (idiochromatic pigment) are those in which transition metal ions are an essential part of structure and contribute to the nature of the ligand filed, for example such as Cr_2O_3 (green color), $CoAl_2O_4$ (blue color) and other.

2.2. Allochromatic (external colored) pigment.

The second type pigment (allochromatic pigment) has external effect for appearance color and this type can be sub- divided into two types:

2.2.1. Substitution type pigment.

In substitution pigment, the transition or lanthanide metal ions are present in the ligand filed of the host lattice and for example, the pink color of Cr^{3+}/Al_2O_3 as result of the present trace amount of chromium in the octahedral sites of lattice.

2.2.2. Inclusion type pigment.

In inclusion pigment are in which colored oxides are present in inert hosts and can be considered as solid solution type emulsion, for example Fe^{3+}:$ZrSiO_4$ red pigment as result to the entrapment of Fe^{3+} ion within zircon crystal.

3. Chemical Survey on ceramic pigment:

The synthesis [7] of a new white binary compounds zinc(II)-calcium(II) cyclotetraphosphates can be obtained. The synthesis is based on a thermal procedure making use of the reversible transformation of cyclotetraphosphates to higher linear phosphates. With respect to the proposed application of these products as special inorganic pigments the following properties have been determined: density, thermal stability and anticorrosion activity. Melting temperatures and densities decrease with increasing calcium content (the respective intervals are 810-730°C and 3.50-3.05 $g.cm^{-3}$).The binary Zn(II)-Ca(I1) cyclotetraphosphates $Zn_{2-x}Ca_XP_40_{12}$ exhibit very good anticorrosion-inhibition properties; their maximum value is obviously reached at a Zn/Ca molar ratio in the region of 1.67.

The synthesis [8] of a white precipitate is yielded on heating a solution of $Y(NO_3)_2$ equivalent to 8 wt.% Y_2O_3 , Al $(NO_3)_3$ equivalent to 7wt.% Al_2O_3 and molar ratio of 1:1.9378 for Y_2O_3 to Al_2O_3 and citric acid in isopropanol with a citrate–nitrate molar ratio of 0.098 to 60°C. The dried precipitate is then combusted at 200°C and produces a solid product ash. X-ray powder diffraction patterns of the ash and its calcined forms show that the ash is amorphous and remains amorphous up to 600°C. The ash starts crystallizing to form a $Y_3Al_5O_{12}$ (YAG) phase at 800°C and completely transforms into YAG below 900°C. A certain amount of $Y_4Al_2O_9$ (YAM) phase co-exists with the YAG phase between 850°C and 900°C. Finally at 900°C, only the YAG phase exists. The formation temperature of YAG phase is significantly low, compared to solid state reaction routes of

constituent oxides. The information can be useful for the processing of Y_2O_3: Al_2O_3 sintering additives for non-oxide ceramics such as silicon nitride by a citrate–nitrate combustion route.

The combustion synthesis technique can be used to successfully produce [9] pure white and doped colored crystalline ZnO varistor powders, with good compositional control. The combustion synthesis route enables synthesis at low temperature by using stoichiometric mixtures of the relevant water soluble metal nitrates as cation precursors and urea as fuel. The mixtures were ignited at 500°C resulting in a dry, very fine powder. The products obtained are characterized by XRD, SEM, TEM and show high specific surface area, have very small particle sizes and are crystalline.

The combustion synthesis technique can be used to produce nano-crystalline white alumina powder [10] by using citric acid as fuel and ammonia was investigated by varying the pH of the precursor solution, which played an important role in controlling the morphology of the synthesized powder. The flaky morphology obtained at pH = 2 could be modified to fine desegregated particulate form by varying the pH of the solution to 10. The sluggish decomposition rate at low pH (2, 4, and 6) was found to be responsible for the generation of flaky powders, whereas the rapid decomposition at high pH = 10 yielded the fine desegregated powders. The as-prepared powders were amorphous in nature, which yielded the nano-crystalline alumina powder after calcinations at elevated temperatures.

The combustion synthesis [11] is an efficient, quick and straight forward method for the preparation of dry, loose and white γ-$LiAlO_2$ powders without further calcinations. The fuel type and the ratio of fuel to nitrates dramatically influenced the phase formation of the final products. By contrast with citric acid, glycine and alanine, urea, carbohydrazide and 3-methyl-pyrozole-5-one were efficient fuels to react with the mixed nitrates, the mixture of nitrate and fuel could be ignited at 450°C and result pure γ-$LiAlO_2$.When the ratio of fuel to nitrates was stoichiometric or 200% stoichiometric, the final products were mainly attributed to γ-LiAlO2, but much less (50% stoi.) or much more (300% stoi.) fuel was not reacted completely with the nitrates to result γ-$LiAlO_2$. The γ-$LiAlO_2$ phase could be obtained until the calcinations temperature reached1000°C by a solid state reaction, which means that combustion synthesis is more efficient, quick and economic method for the preparation of γ-$LiAlO_2$ than conventional solid state reaction method.

The combustion synthesis technique is using glycine as fuel and aluminum nitrate as an oxidizer is able to produce white alumina [12] powders. Thermodynamic modeling of the combustion reaction shows that as the fuel-to-oxidant ratio increases, the amount of gases produced and adiabatic flame temperatures also increases. X-ray diffractions showed the amorphous structure for as-synthesized powder and presence of well-crystallized α-Al_2O_3 after calcinations at 1100°C during soaking time of 1 h. Characterization of product by large specific surface area (15 m^2/g) that be measured by BET method that produced by 0.51 glycine-to-nitrate ratio.

The synthesis of a new Magnesium aluminate ($MgAl_2O_4$) white spinel[13] powder can be prepared by nitrate citrate auto-ignition route taking different ratios of nitrate and citrate solution. The 'as prepared' black ash was calcined at different temperatures in the range 650–1250°C for 9 h. Phase evolution of calcined powder samples as studied by X-ray diffraction indicates the presence of disorder at lower calcination temperatures, which transforms to an ordered structure at higher calcination temperatures. Finally, Raman spectroscopy confirms the order–disorder phase transition in spinel sample. A disorder–order phase transition was found in $MgAl_2O_4$ spinel due to combined effect chemical composition and the associated exothermicity of the reaction. So, the disordering is chemically induced. The phase transition was probably due to formation of an intermediate phase having different, but related structure. With increase in citrate content in the precursors the spinel gets increasingly order. This effect can be related to higher exothermicity of the reaction. However, the degree of disorder is dependent on the nitrate–citrate ratio.

A new black-color ceramic pigment has been developed on the basis of the $CoO–Fe_2O_3$ ($CoFe_2O_4$) [14] system under a decreased temperature of synthesis (1000 – 1200°C). The optimum temperature range of the spinel-forming reaction in the specified oxide system is determined. When the obtained pigment is introduced into raw glaze for sanitary ceramics in milling, the resulting glaze coatings have intense and stable black color within a sufficiently wide interval of firing temperatures.

The synthesis of light or dark beige, brown and black ceramic powders[15] $Co_xZn_{7-x}Sb_2O_{12}$ (x=0–7) were prepared by using the polymeric precursor method. Pigments were evaluated using colorimetry, X-ray diffraction, UV–vis. and infrared spectroscopy. The optical band gap values vary with the Co^{2+} substitution. These results suggest that the concomitant presence of Co^{2+} and Zn^{2+} in the spinel lattice leads to the rupture of the Ve´gard law, as well as other properties of the studied system, such as unit cell volume. The Co-richer samples display a higher absorbance than the Co-lean samples. The high absorption of the $Co_7Sb_2O_{12}$ sample at most of the visible region makes this compound a candidate for a black pigment. It was shown that color depends on the site where the chromophore ion is located, in agreement with the ligand field theory. Colorimetric data were related to XRD and infrared spectroscopy results, in order to evaluate the influence of cation coordination in the resultant color. For the spinels $Co_xZn_{7-x}Sb_2O_{12}$ (x = 0–7), the presence of both Co^{2+} and Zn^{2+} ions causes a higher distortion of unit cell, increasing the number of intermediate states within the band gap, rendering the pigments darker. At this point, a deviation of Vegard law was observed. When $x < 4$, Co^{2+} occupies octahedral sites, leading to a yellow color. When $x > 4$, Co^{2+} also occupies tetrahedral sites, increasing the blue reflectance and leading to a green color.

Nickel-iron black ceramic pigments of $(Fe_{0.8}Mg_{0.2})(Fe_{0.2}Ni_{0.8}Cr)O_4$ and $(Fe_{0.8}Mg_{0.1}Zn_{0.1})(Fe_{0.2}Ni_{0.8}Cr)O_4$[16] compositions have been prepared by non conventional methods such as co-precipitation, microemulsion and polymeric gel routes (alkoxides hydrolysis-condensation), and compared with ceramic samples prepared by the solid state reaction from oxide

precursors. The mineralizing effect of a 2NaCl:NaF flux agent has been also analyzed. Both non conventional methods and mineralizer presence increase the reactivity of the samples. The highest reactivity and the best black color are obtained in the polymeric gel sample prepared from alkoxides; co-precipitated and microemulsion fired pigments are partially solubilised by glazes due to the small particle size exhibited, leading to brown colors.

Black ceramic pigments [17] were prepared from industrial wastes as raw materials, namely, Cr/Ni-rich sludge generated from Cr/Ni plating and Fe-rich galvanizing sludge generated during steel wiredrawing. The pigment was based on the chrome-iron-nickel black spinel $(Ni,Fe)(Fe,Cr)_2O_4$ catalogued as 13-50-9 in the DCMA classification and prepared by the common solid-state reaction method, under optimal formulation and processing conditions. The characterized synthesized pigments were tested in typical ceramic glazes and ceramic bodies. Optimal color development was achieved when the spinel compound with the three elements Fe, Ni and Cr was the major phase formed. This situation was obtained for mixtures in which the amount of Cr/Ni-rich sludge varied between 50 and 75%. The coloring properties were similar to those imparted by a commercial black pigment.

The ceramic brown pigment $BaFe_2O_4$ [18] can be synthesized by the polymeric precursor method, which presents iron as the chromophore ion, and barium as net modifier. After calcination at different temperatures, characterizations were done by X-ray diffraction, infrared spectroscopy, surface area by BET, scanning electron microscopy, UV–vis spectroscopy

and colorimetric analysis, using CIE-Lab system. The soft chemical synthesis method leads to a high crystallinity material after calcination at 700°C with single phase, while usual methods require higher temperatures (above 850°C) or lead to secondary phases. Diffuse reflectance and chromatic coordinate's results indicate that carbonate presence as well as sintering among particles change the color, leading to its variation as a function of the heat treatment of the pigment precursor. Differences between UV–vis spectra of $BaFe_2O_4$ and other ferrites are probably due to the iron ligand field—while the former presents iron in tetrahedral sites, the latter present iron in octahedral and tetrahedral sites. The pigment presents a suitable technological behavior without reactions between glaze and pigment, indicating that powders are chemically and thermally inert up to 1000°C.

Pseudobrookite pigments [19] were synthesized by the conventional ceramic route, calcining at 1300°C four mixtures, with a Fe_2O_3:TiO_2 ratio ranging from 47:53 to 40:60. Brown pigments were characterized by XRPD, DRS and coloring performance in several ceramic matrices. Titania in moderate excess of the Fe_2TiO_5 stoichiometry, necessary to minimize the occurrence of unreacted precursors, induced lattice parameters smaller than ideal pseudobrookite, in agreement with the different radii of Fe^{3+} and Ti^{4+} ions. These pigments exhibit a peculiar, intensely brown coloration originated by several light absorptions in the visible spectrum due to both d^5 electronic transitions and a magnetically-coupled paired transition between iron ions in adjacent lattice sites. A doubling of the $^6A_1/^4T_1$ and $^4T_2$ bands is related to the occurrence of Fe^{3+} in both octahedral sites of pseudobrookite.

Besides, distinct metal-oxygen distances imply different energy absorptions in good accordance with the crystal field theory, despite the strongly covalent character of the Fe-O bonding. Although an entropy-stabilized phase, pseudobrookite persists dispersed in glazes and glassy coatings even after fast firing at 1200^{o}C, so being suitable as ceramic pigment.

The phase transformations and coloring mechanisms [20] that occur during the ceramic processing of titania slag were investigated using XRFEDS, XRD, DRS and laboratory-scale application in glazed and unglazed tiles. The slag transforms to pseudobrookite, undergoing a drastic color change during firing as a consequence of thermal oxidation with Fe^{2+} to Fe^{3+} and Ti^{3+} to Ti^{4+} reactions. The intense b color imparted by titania slag is stable at both low (up to 1050^{O}C) and high (around 1200^{O}C) temperatures and is suitable for porcelain stoneware tiles. Its coloring mechanism is due to changes in valences of transition metals hosted in the crystalline (ilmenite and TiO_2 polymorphs in the sample under investigation) and amorphous phases. During ceramic firing, the crystalline and amorphous phases in the slag undergo thermal oxidation with (re)crystallization of pseudobrookite. Absorbing most of the green to violet light, these bands provoke a color virage to reddish brown. An additional optical band in the red region, likely due to $Fe^{2+/}Fe^{3+}$ IVCT, is responsible of the dark shade. The decrease of color performance is connected with a progressive decomposition of pseudobrookite as the temperature increases. Decomposition is accelerated in aggressive media, such as Ca- and Zn-rich glazes used at intermediate temperatures (1100-1150^{O}C) in the production of wall tiles.

$V_xTi_{1-x}O_2$ ($0 \leq x \leq 0.20$) rutile solid solutions with potential usefulness as gray ceramic pigments [21] have been synthesized from alkoxides. Gels built from hydrolysis-condensation of V(IV) oxyacetilacetonate and Ti(IV) isopropoxide mixture (polymeric gel). These solid solutions are stable at high temperature (1200–1400◦C) and into glazes. The coloration of the glazes together with the thermal stability of these rutile solid solutions indicates their potential usefulness as gray ceramic pigments. The results obtained are compared with those obtained from V_2O_5 and TiO_2 (anatase) mixtures (ceramic method).From alkoxides, noticeable change in coloration is obtained on glazes, when $x < 0.10$.Nodesirable brown materials are obtained from oxide mixtures when $x < 0.10$ but only bluish gray colorations are obtained from gels.

The studied [22] of a new blue-violet doping zirconium silicate a pigment and is suitable for ceramics. Its color is due to particles of condensed cobalt phosphates incorporated as the so-called inclusions in zirconium silicate microcrystals. A combination of disodium hexafluorosilicate and lithium hydroxide with cryolite has been used as the mineralizer in the pigment synthesis. The chromophore is cobalt dihydrogen phosphate or the corresponding mixture of cobalt (II) oxide and phosphoric acid, which are calcined to give intensely colored particles of the condensed cobalt phosphate. The effects of the chromophore and of the individual components of the mineralizer on the color hue of the pigment have been evaluated and their optimum amount in the starting mixture estimated. The calcinations temperatures found and the yields of products correspond to other zirconium silicate pigments. The pigment exhibits high thermal and

chemical stability and can be applied to all types of ceramic glazes including those requiring high temperatures, i.e. glazing temperatures of 1300°C. When used in the amount of 3-7% (w/w) it effectively imparts the same blue-violet hue to these glazes. The colored glazes are smooth, glossy and without any surface unevenness.

The synthesis [23] of a new zirconium silicate pigment having an interesting green-blue hue can be prepared and its color is based on the perturbation principle: vanadium ions, together with molybdenum ions, are incorporated into the zirconium silicate structure. A combination of disodium hexafluorosilicate, lithium hydroxide and sodium chloride proved useful as the mineralizer for the pigment synthesis. Further ingredients include molybdenum trioxide, which is a component of the mineralizer: in addition there is another important factor, which helps the chromophore to obtain the required greenish-blue hue. The effect of the V_2O_5, content in the starting mixture on the color of the pigment has been evaluated, and also the effect of MoO_3. The temperature conditions of the pigment synthesis have been established. The products have been evaluated from the standpoint of their structure, degree of conversion, color hue, and ability to dye ceramic glazes. The green-blue zirconium silicate pigment is best prepared by the procedure suggested in this communication from the starting mixture that containing (%, w/w): 51 ZrO_2, 23.8 SiO_2, 5.35 Na_2SiF_6, 2.95 LiOH, H_2O, 1.5 NaCl, 9.5MoO_3, and 5.9 V_2O_5. The calcinations temperature and time are advantageously 675-700°C and 0.5-l h, respectively. After an extraction with diluted HCl, the colorless calcinate is submitted to short (about 10min) bisque firing at about 1450°C to produce an intense green-blue pigment. The

pigment exhibits high thermal and chemical stability and can be applied to all types of ceramic glazes including the high-temperature ones (with glazing temperatures of 1300°C). When used in an amount of 3-10 % (w/w) it effectively imparts the same green-blue hue to these glazes. The colored glazes are smooth, glossy, and without any surface unevenness.

The preparation [24] of a new zirconium silicate (zircon) pigments of blue-green color can be obtained from the mineral, zircon, as the starting raw material. As a first step this material was decomposed with a waste mixture of hydroxides, NaOH-KOH. In the second step the pigments were synthesized with the application of a mixture of CrOOH and $PbCrO_4$ as the chromophore. The optimum conditions for the synthesis of pigments have been estimated and the properties of the product (color hues and their applicability to ceramic glazes) have been evaluated. The pigments are characterized by intensive color, high thermal stability and can be applied to all kinds of ceramic glazes.

The preparation [25] of fine particles of green yttrium–barium–copper–oxide pigments Y_2BaCuO_5 studied by using two different synthesis methods. The process of combustion of mixed nitrates and urea needs a maximal temperature of 900°C and provides samples formed by aggregates of homogeneous small particles with a size of about 0.3 mm. However, the ceramic method requires 1050°C as synthesis temperature, and yields rather higher particle sizes. Diffuse reflectance spectra reveal that the samples obtained using the former method present a higher brilliancy, so they have been selected to be tested as green pigment in ceramics with good results.

The green Y_2BaCuO_5 oxide obtained using the combustion method presents appropriate particle sizes and optical properties to be suitable for being used as pigment in ceramics. Inorganic green pigments are based in chromium compounds suspected of having carcinogenic effects, or in copper oxide which decomposes above 900C. Containing a rather lower copper concentration, Y_2BaCuO_5 produces the same shades and a more homogeneous coloration than the green pigment CuO.

The synthesis of a new green pigment [26] based on a $Cr_{2-x}Al_xO_3$ solid solution, using a standard ceramic industry composition with and without different mineralisers and using raw materials industrial grade reagents. The resulting products were compared with a pigment made using chemically pure (CP grade) to establish the most appropriate reagents for achieving minimum Cr(VI) segregation during the pigment washing stage, and comparable chromatic qualities to those of a standard industrial pigment. Chromium sesquioxide was used as Cr(III) precursor instead of a Cr(VI) compound, and the chromium content was also optimized. The X-ray photoelectron spectroscopy (XPS) results indicated that a solid solution only forms when CP grade reagents are used. This is consistent with the scanning electron microscopy (SEM) and X-ray diffraction (XRD) data obtained in the study. Smaller Cr(VI) and B contents were found in the washing liquids when CP grade reagents were used, but the resulting chromatic quality was slightly lower than that of a standard pigment made and used in the ceramic industry. Using H_3BO_3 as a mineralizer enables synthesizing a green pigment with Cr_2O_3 as chromium precursor and avoiding the use of Cr(VI) compounds. Resulting pigment chromatic co-ordinates are better than to

those of a STD pigment, with lower Cr(VI) contents in the washing waters than the sample without a mineralizer. The use of industrial grade reagents improves pigment chromatic co-ordinates, but their use in pigment production has a greater environmental impact compared with that of a sample prepared under the same conditions using reagents of greater purity. The study has enabled producing a more environmentally friendly green pigment, with good chromatic quality, in which the chromium content has been reduced.

Synthesis [27] of the deep green spinel pigment $Co_{0.46}Zn_{0.55}(Ti_{0.064}Cr_{0.91})_2O_4$ by a novel two-step method of preparation have been investigated. Inorganic pigments are almost always prepared by a solid state reaction. It is classical ceramic method which used oxides, hydroxides or carbonates as precursors. The reaction is performed at temperature higher than 1300°C and an agent of mineralization is usually present. The presented novel method of preparation decreases the calcining temperature necessary for reaching of bright and clear hue of the pigments prepared. Main attention was focused on the influence of two types of titanium raw materials on the temperature region of the spinel structure formation and on the color properties of the pigments. The mixture of precursors with TiO_2 gives a one-phase system when calcining at 1100°C but the color properties are more interesting at 1150°C. Thermal stability of this pigment is limited by temperature 1300°C. This temperature is connected with partial oxidation of Cr(III) to Cr(VI). Thermal analysis provided the first information about the temperature region of the pigment formation and determined the thermal stability of pigment.

Preparation of a cobalt blue pigment based on the systems $CoZnSiO_3$[28] by a sol-gel method has been studied. Sol-gel preparations were compared with conventional ceramic solid state synthesis. The samples were heat-treated within the temperature range of 200-1200 ^{o} C and analyzed by X-ray diffraction and infrared spectroscopy. It was established that the application of the sol-gel method lowered the synthesis temperature of the pigments.

The ceramic blue pigment $CoAl_2O_4$ nanocrystals can be synthesized [29] by a polymerized complex technique. Cobalt nitrate, aluminum nitrate, citric acid, and ethylene glycol were used as precursor materials. The formation of pure crystallized $CoAl_2O_4$ nanocrystals occurred when the precursor was heat-treated at 350°C in air for 2 h. We propose a model for formation $CoAl_2O_4$ from the polymeric precursor. The model contains a series of steps such as the transformation of the precursor to amorphous cobalt aluminate, three-dimensional nucleation and growth, and solid-state reaction pure cobalt aluminate ($CoAl_2O_4$) nanocrystals have been synthesized by heat-treating the polymeric precursors in air at 350 to 1000°C for 2 h. XRD measurements revealed no traces of impurities. Microstructure evolution during the heat treatments was investigated using high-resolution transmission electron microscopy (HRTEM).

The synthesis of a new Thermal treatment and the addition of V_2O_5 [30] and of different mineralizing agents (NaF, NaCl and borax) have been optimized in terms of blue color yield (L*a*b*) and of environmental

considerations (atmospheric emissions and vanadium leachates). The formation of different reaction intermediates depending on mineralizing agent (ZrV_2O_7 for no mineralizer, $NaVO_3$ and/or sodium-vanadium bronzes for added sodium halides, and a borosilicate vitreous phase for added borax) proves be important for the pigment synthesis, leading to different zircon yields and to different color performance in the fired pigments. The composition $(ZrSiO_4)(V_2O_5)_{0.19}\,(NaF)_{0.05}(NaCl)_{0.10}$ has been found to be the optimal environmentally (firing loss=5.8%, vanadium leached=284 ppm and b^*=-16.4), though the non-mineralized composition (with 0.19 mol of V_2O_5 per zircon formula weight) also performs well.

The preparation ceramic glaze blue pigments [31] (The SnO_2:xSb) obtained by synthesis methods was compared. The fired pigments and enameled samples were characterized by XRD, UV-vis-NIR spectroscopy, CIE-L*a*b* color-measurements, and SEM. The pigments obtained by the Penchini method presented a better solubility in the molten glazes than the pigments obtained by the mechanical mixture of the oxide precursors (OM). The pigments obtained by the Penchini method also developed more blue intensive color hue than the pigments obtained by the mechanical mixture of the oxide method. The temperature needed to obtain a monophase structure for the pigment system was 800°C by the Penchini method and 1000°C by OM. As for the powders obtained by the Penchini method, both the crystallite size and the particle size increased with temperature. On the other hand, as for the powders obtained by OM, the crystallite size was approximately constant and the particle size increased with temperature,

although at a smaller rate than in the case of Penchini method. So does the particle size, which directly depends on the preparation method used.

$CoAl_2O_4$ blue pigment powder was obtained from a mixture of Co and Al oxalates [32] at a ratio of 1:8 (Co:Al). The material was calcinated at different temperatures, established from TG data, and characterized using FTIR spectroscopy, X-ray diffraction, BET surface area, and thermal analysis. The dyeing characteristics of $CoAl_2O_4$ were established by coating ceramic substrates with different concentrations of the powder. The calcining temperature affects the color of the pigments on glassy ceramic coatings. The best results were obtained calcining the spinel $CoAl_2O_4$ phase at 1000 or 1200^oC. Different temperatures also resulted in the formation of crystalline phases but with unsatisfactory coloring effects on ceramic tiles.

The preparation of the Co-doped alumina powders [33] by using of the polymeric precursor method is obtained ceramic blue pigments. The effect of different contents of Co^{2+} on phase transition γ to α-Al_2O_3 and appearing of $CoAl_2O_4$ spinel were studied by means of X-ray diffraction. A partial phase diagram of the system $CoAl_2O_4$ was proposed from these data by means of determination of the percentages of these phases according to the calcining temperature. Critical particle size to phase transition was determined by means of calculations of crystallite size and determination of superficial area through the BET method. UV–vis spectroscopy of the samples allows comparing the band shift with the phase transition that show Co^{2+} in tetrahedral sites in γ-Al_2O_3 and octahedral sites appears with the phase transition to α-Al_2O_3 + $CoAl_2O_4$. Besides, a study of thermal stability and

intensity of the blue coloration of the synthesized powders with the presence of cobalt in relation to the calcining temperature was accomplished and compared to the phase transition. The results show that the higher blue color intensity was obtained for the powders with Co-doped γ-Al_2O_3 closest of phase transition to α-Al_2O_3 + $CoAl_2O_4$. The wavelength position of the band with maximum intensity was plotted against the calcining temperature demonstrating that there is a relationship between the phase transition and the spectroscopic bands shift.

The inorganic ceramic Fe_2O_3/SiO_2 red pigment [34] synthesized by inclusion of hematite in a fumed silica matrix using solid state reaction. The occlusion of hematite occurs by calcination at 1150–1200°C for 2–4 h. Better results were obtained by using fumed silica having surface area ranging from 300 to 400 m^2/g. A continuos change in color was measured by comparing L*a*b* values of the calcined samples and more information were obtained by the Kubelka-Munk absorption function. Because its chemical and thermal stability, the obtained heteromorphic pigment may be considered a suitable red pigment for ceramic manufacturing by fast firing cycles. Very easily occluded small crystalline particles of formed hematite after calcination in the temperature range 900-1300°C, crystals of hematite occluded in an amorphous silica matrix were prepared and calcination temperatures in air no more than 1200°C to prevent the Fe^{3+} to Fe^{2+} reduction.

The preparation of praseodymium-doped ceria red pigments, $Ce_{1-x}Pr_xO_{2-\delta}$, (x=0– 0.5) studied [35] by the thermal decomposition of the redox

compound $Ce_{1-x}Pr_x$ $(N_2H_3COO)_3.3H_2O$ as well as by the combustion of aqueous solutions containing cerous nitrate, praseodymium nitrate and oxalyl dihydrazide (ODH) /ammonium acetate. Formation of the pigment has been confirmed by its characteristic red color and reflectance spectra which shows the reflection edge ≈690 nm corresponding to charge transfer from the ligand orbitals to the localized 4f of Pr^{4+}.The preparation of fine particle $Ce_{1-x}Pr_xO_{2-\delta}$ red pigments by the thermal decomposition of precursors gives nanosize oxides with particle sizes in the range of 3–7 nm. Whereas the combustion of the redox mixtures with ODH yield pigments gives particle sizes in the range of 30–40 nm. The use of ammonium acetate as fuel controls the combustion reaction and yields particles in the range of 7–12 nm.

The solid solution $(Ce_{1-y}\ Nd_y)_{10}\ S_{14+x}\ O_{1-x}$ $(0\leq y\leq 0.70)$ $(0\leq x\leq 1)$ were prepared [36] to produce different shades of red pigment. The microstructure investigated using SEM and TEM. The scanning electron micrographs (SEM) show small particle size (around 100 nm). The samples have been characterized by transmission electron microscopy (TEM) and associated techniques. The observed variation in the powder X-ray diffraction refined unit cell parameters is due to the variable oxygen content. Color parameters of samples studied by using reflectance spectra show a strong absorption band under 600 nm for all the samples, and over this wavelength the reflection band intensity increases with the Nd^{3+} content up to y= 0.30. The band intensity decreases with higher contents of Nd^{3+}.

The synthesis of a new colored orange red [37] oxides in the Bi_2O_3–RE_2O_3 system that can be prepared by the solid state reaction of mixed

oxides $(Bi_2O_3)_{1-x}(RE_2O_3)_x$, where RE: Y or Ce with nominal compositions: x= 0.2 and 0.5 for Y and x = 0.3 and 0.5 for Ce. The products formed were characterized by the X-ray powder diffraction, scanning electron microscopy, energy dispersive spectrometer analysis and by reflectance spectral data. All the synthesized pigment samples are found to be having color coordinates, low a* and high b* and exhibit the color from pale yellow to orange red. Reflectance spectra of the samples show high reflectance percentage in the 600–800 nm range. Because of the homogeneity of the phase formed and the intense coloration, the Y doped pigments have been found to be superior to Ce doped pigments, as possible ecological inorganic pigments. It is also clear that with the increase of the rare earth concentration, the intensity of the color increases and lightness L decreases moderately. These pigments are heat and chemical resistant and can be used even in high temperature glazes and represent potential alternate inorganic pigments from the environmental point of view.

The red ceramic pigments $CaFe_2O_4$ [38] are prepared by using the polymeric precursors method. The characterization was accomplished using thermal analysis, X-ray diffraction (XRD), nitrogen adsorption, scanning electronic microscopy (SEM) and diffuse reflectance. It observed successions exothermic reactions, adequate in events of thermal decomposition of the organic material, reach your stability in 700°C. The material became completely crystalline at 800°C. Between 700 and 1100°C, the color was stabilized, showing an absorption band in the region of 650 to 750 nm, characteristic of the red color. The Penchini method leads to a material with high degree of homogeneity at molecular level, as well as finer

powders presenting thus higher surface areas. The color of the pigment depends on the oxidation state of the chromophore ion. Monophasic powders are obtained at temperatures a slow as 800°C and a completely defined color is observed at 900°C.

Polymeric precursor method was using for synthesis [39] of both pure and praseodymia-doped ceria. Their red pigments use as for overlaying coating of dental ceramic restorations. These pigments were characterized by thermogravimetric and differential thermal analyses, X-ray diffraction, X-ray fluorescence, scanning electron microscopy, while UV-Vis spectroscopy was used to determinate the reflectance curves of both pure and praseodymia-doped ceria. The referred pigments were added to feldspathic-glass frits in order to simulated the overlaying ceramic coatings on ceramic dental restorations. It was found to be a fluorescent coating by using the synthesized pure ceria but, a coating displaying a shade comparable to those of some commercial opaque layers when using praseodymia-doped ceria pigments with the lowest praseodymia content. Colorimetric coordinate measurements were carried out and used to plot the reflectance curves in the visible range for all types of the considered overlaying coatings. The increment in the praseodymia content provided a substantial change in reflectance characteristics of the synthesized pigments, once 1 mol% of Pr in the ceria conducted to a red-like pigment, with the reflectance restricted to the range of 600-700 nm, while the pure ceria presented intense reflectance in all range of the visible spectrum. The increase of praseodymia content in the pigment also provided an increase in the values of a* and decrease of L*,

characteristic of the increase of red shade, both in the pure pigments and in the pigment containing ceramic coatings.

Novel inorganic brick red pigments [40] of general formula $TiCe_{1-x}Pr_xO_4$ (x ranges from 0 to 0.7) were synthesized using a solid-state route with the aim of preparing environmentally friendly red pigments. Characterization using X-ray powder diffraction, UV-Vis spectroscopy and color measurement revealed the formation of pigments with colors ranging from white to brick red. The color of the pigments arises from the introduction an additional electronic energy level in the forbidden band of the unpaired 4f electron of the praseodymium ion. The red ceramic pigments were found to be interesting alternatives to existing inorganic red pigments for the coloration of plastics. It is suggested that the coloring mechanism is based on the shift of charge transfer band of CeO_2 to higher wavelengths, introducing an additional electronic level by doping praseodymium. The developed pigments are found to be thermally and chemically stable and also do not contain toxic metals. Thus, the present pigments may find potential alternative to the classical toxic inorganic red pigments for coloring plastics and paints.

The morphology and the dimensions of the hematite particle influenced the shade of the red pigments [41] obtained; both fine (<30 nm in length) spherical and long (>250 nm in length) acicular shapes gave poor red shades. The morphology of the hematite particles depends on the precipitant used; ammonia provided spherical, whereas NaOH produced acicular hematite particles. The dimensions of the hematite particles depended on the

mineralisers used; while the silica structure did not influence pigment shade, the use of mineralisers promotes tridymite structure crystallization.

The cubic Ca–ZrO_2 structure has been used as host for preparing a yellow ceramic [٤٢] stain using praseodymium as dopant. Samples with $Ca_xPr0.1Zr_{0.9-x}O_2$ (X=0.14, 0.17, 0.2) compositions have been prepared by the ceramic method and by several gel processing techniques: the colloidal method, the gelatine method, the citrate method and a polymeric route. Fired samples have been evaluated as ceramic pigments following enameling with the powders in ceramic glazes. The results show that a yellow ceramic pigment is obtained in all samples without significative differences among the different methods and compositions. This yellow ceramic pigment has been identified as a Pr–(Ca–ZrO_2) solid solution. The pigment produces a soft yellow color in ceramic glazes. The yellow color is slightly modified by the Ca content: a* (yellow) increases but also b* (red) and L*.The pigment is associated to a Pr–Ca–cubic zirconia solid solution as indicated by lattice parameters, XRD and SEM-EDX analysis.

The structure-microstructure and color parameters of the $Mg_{1-x}Yb_{(2/3)x}\square_{(1/3)x}S$ ($0 \leq x \leq 0.45$) (□ cation vacancy) [43] were investigated. The samples present exclusively the NaCl-type average structure up to x = 0.35, when a phase with spinel-type structure is observed. Its composition, measured with X-ray energy dispersive spectroscopy (XEDS), corresponds to an intermediate phase between the NaCl-type (MgS) and the normal spinel ($MgYb_2S_4$) structures. The selected area electron diffraction patterns (SAEDPs) show diffuse scattering attributed to short-range order (SRO) in

the cation sublattice. Extended defects (x = 0.30, 0.35 and 0.45) have been observed both in the SAEDPs and in the corresponding high resolution transmission electron microscopy (HRTEM) images. The samples yellow color variation was characterized with reflectance spectra in the visible region. This system has possible applications as inorganic pigments in plastics and paints due to its high color quality.

The synthesis of the a light reddish-yellow[44] ceramic pigment with an $MgFe_2O_4$ spinel structure that obtained by the polymeric precursor method at low temperatures, followed by a heat treatment in order to obtain the final oxide. The powders were calcined between 500 and 1100°C, and characterized by thermal analysis, X-ray diffraction, nitrogen adsorption, scanning electronic microscopy and diffuse reflectance. The pigment is single phase, with a cubic system. A low temperature synthesis was possible, with a crystalline material after heat treatment at 800°C. The colors obtained varied, according to the crystallization of the $MgFe_2O_4$.The pigment presented thermal stability, being single phase. Alight reddish-yellow hue, characterized by a reflectance in the 600–650 nm range was obtained. Colors varied with heat treatment temperature, due to ordering of the crystalline structure.

The synthesis [45] of a new inorganic brilliant yellow color pigments based on amorphous cerium tungstate, $Ce_{1-x}M_xW_2O_8$ (M=Zr or Ti, $0 \leq x \leq 0.6$) can be synthesized by a simple co-precipitation method and their color properties were characterized from the viewpoint of possible ecological inorganic pigments. The $Ce_{1-x}M_xW_2O_8$ materials absorb the visible and the

ultraviolet light under 500 nm efficiently, which is originated in the O(2p)–Ce (4f) and the O(2p)–W(5d) double charge transfer transitions, and, as a result, the pigments can show a brilliant yellow color. The optical absorption edge wavelength of these pigments depends on $Ce_{1-x}M_xW_2O_8$ materials absorb the visible and the ultraviolet light under 500 nm efficiently, which is originated in the O(2p)–Ce (4f) and the O(2p)–W(5d) double charge transfer transitions, and, as a result, the pigments can show a brilliant yellow color. The optical absorption edge wavelength of these pigments depends on the Zr^{4+} or Ti^{4+} content, and the effective yellow hue was observed at x = 0.2 for both pigments. The color properties of the present pigments suggest that they used as coloring agents for paints and inks. Furthermore, they are inert and safe and do not produce side effects in the human body because they are composed of non-toxic and safe elements.

Zinc titanate, Zn_2TiO_4, can be used as yellow ceramic pigment [46], due to its stability up to approximately 1550°C. These ceramic pigments obtain using the polymeric precursor method, based on zinc titanate spinel (Zn_2TiO_4), containing 5 mol% of iron. The synthesis was carried out with pH values of 1, 7 and 10, in order to verify the influence of the chelation upon the obtained color. The characterization of the samples was performed by thermogravimetric analyses TG/DTG and DTA, X-ray diffraction and colorimetry. The crystallite size decreases with the increase of pH. The segregation of zinc oxide or titanium oxide was observed, according to the pH of the polymeric resin. The pH of the synthesis changed the color of pigment due to the iron ligand field. From the X-ray diffraction results it was verified that the Undoped Zn_2TiO_4 spinels are single phase compounds.

Samples synthesized at pH = 1 presented higher a* and b* values, indicating that the change in the pH of the solution also changes iron ligand field and/or the oxidation state.

$Ce_{1-x}Zr_xBi_yO_{2-y/2}$ solid solutions were synthesized [47] as new inorganic yellow pigments and their color properties have been investigated as possible ecological materials. Although the optical absorption edge of the $Ce_{1-x}Zr_xBi_yO_{2-y/2}$ pigments depends on their composition, all samples absorb the ultraviolet and the visible light under 500 nm efficiently. As a result, the pigments show a brilliant yellow color, and the most effective yellow hue was obtained at x = 0.37 and y = 0.20. The importance of the presence of Bi^{3+} in the CeO_2–ZrO_2 lattice has been elucidated by comparing the color of $Ce_{0.43}Zr_{0.37}Bi_{0.20}O_{1.9}$ with that of $Ce_{0.43}Zr_{0.37}La_{0.20}O_{1.9}$ Characterization of the $Ce_{1-x}Zr_xBi_yO_{2-y/2}$ solid solutions suggests that they have a potential to be alternative yellow colorants for paints, inks, plastics, and ceramics. Since they are composed of non-toxic and safe elements, they would be inert and safe and exhibit no side effects in the human body.

Doped-rutile has been traditionally used in ceramic yellow pigments [48] for its intense optical properties. We compare the classical ceramic (solid-state) synthesis of $Ti_{1-2x}Nb_xNi_xO_{2-x/2}$ system with the sol–gel methodology, which allows a reduction of the anatase–rutile transformation temperature. The composition was optimized in order to obtain a unique rutile phase with the minimum amount of pollutant Ni2+and enhanced chromatic coordinates. Incorporation of the doping ions in the rutile structure was corroborated by XRD. The species responsible for the color mechanism were studied by

different techniques. UV–Vis spectroscopy showed the characteristic features of Ni^{2+} ions, whose existence was corroborated by EPR and magnetic measurements. From these results, (Ni, Nb) doped-TiO_2 powder samples can be now shaped as thin films, monoliths, etc. by using sol–gel methodology without modifying their properties. This study introduces new possibilities of colored TiO_2-based solid solutions in new combined advanced applications (coloring agent and photocatalyst, etc.).

In this work the screening results of the scientific activity conducted on the possibility to use rice husk ash as silica precursor for ceramic yellow pigments [49] are synthesized. Ceramic pigments were synthesized by solid-state reactions and the color developed in a suitable ceramic glaze was investigated comparison with the color developed by the pigments prepared from pure SiO_2.The using of silica precursor for the development of praseodymium doped zircon yellow pigment. The characterization carried out corroborates the thermal and chemical stability of the synthesized powders and allow us to determine the optimal synthesis conditions for the formation of the Pr–$ZrSiO_4$ solid solution. The obtained pigments are stable and develop an intense yellow color that is very similar to the color developed by the pigments obtained starting from pure quartz.

A new ceramic yellow pigment [50] with the cordierite high temperature structure was synthesized by sol–gel processing. A small region of a solid solution phase was detected containing <5 wt-% vanadium pentoxide, (V_2O_5). The crystallization behavior and thermal stability of the pigment was studied. Unit cell parameters, crystallite size, and the phase constitution of

calcined powders were determined by X-ray diffraction. The xerogel powders were studied by thermal analysis and infrared spectroscopy. The compositions of fired samples were obtained by inductively coupled plasma analysis and the L *a*b* color parameters were measured.

The synthesis of new inorganic Cyclo-tetraphosphates of type $Zn_{2-x}Ni_xP_4O_{12}$ yellow or yellow-green pigments[51] has been investigated, with the goal of preparing heat stable, anticorrosive and environmentally friendly special pigments. The synthesis of the title pigments is based on temperature calcination of the starting materials, and the optimum reaction conditions for this process have been assessed. The pigments have been evaluated from the standpoint of their structure, color hue and ability to dye ceramic glazes. New binary condensed phosphates were synthesized based on results of thermal analyses.

New tungstate-based ceramic pigments, displaying $Zn_xNi_{1-x}WO_4$ stoichiometry, were obtained at low temperature using a polymeric precursor method [*2]. The powder precursors were milled in an attritor mill in an alcoholic medium and heat treated for 12 h, yielding homogeneous and crystalline powder pigments. Characterization (TG/DTA, XRD, IR and colorimetry) showed that mass loss increased with increasing Zn contents. Despite the presence of secondary phases and impurities, the wolframite phase was present in all samples. IR analysis revealed bands related to Me-O and $[WO_6]_6$ group stretching was observed. The intensity of the yellow color of the pigments increased with increasing amount of nickel. The colorimetric data showed increased brightness with increasing zinc content. As the Ni

content increased, higher b* values were recorded, while the a* value remained small, giving rise to stronger yellow colored pigments. The absorption spectra of the $Zn_xNi_{1-x}WO_4$ pigments separated into discrete absorption Gaussian bands, showing absorption bands centered in the range of 2.71-2.78 eV, due to [NiO_6] transitions. An absorption band due to [WO_6] was observed between 3.43 and 3.48 eV. Thus, the maximum absorption of such band takes place in the blue region, from 458 to 446 nm, and the pigment color perceived corresponds to yellow, the complementary color of blue, as pointed out in the colorimetric results.

The preparation of Mn-doped alumina pink pigments [53] in the absence of fluxes through the pyrolysis of liquid aerosols procedure from aluminum (III) nitrate and manganese (II) nitrate aqueous solutions is reported and compared with the traditional ceramic procedure. It was found that the pyrolysis method requires a lower temperature (900°C) for the development of the corundum phase and the pink color than that required by the traditional procedure (1300°C) yielding a more intense color, as a consequence of the incorporation of a higher amount of Mn in solid solution to the alumina lattice. In addition, the use of the pyrolysis procedure allows the preparation of pigments grains with uniform shape and controlled and reproducible size distribution, not requiring grinding.

The synthesis of new colorants based [54] on CeO_2 has been investigated, the focus of which was the preparation of pigments for coloring ceramic glazes. The synthesis of these colorants involved high-temperature calcinations of the oxides and determination of the optimum conditions for

their synthesis. The pigments were evaluated in terms of their structure, color and ability to color ceramic glazes. The $Ce_{0.95-y}Pr_{0.05}Sm_yO_{2-y/2}$ pigments with fluorite structures are heat and chemical resistant and can be used even in high temperature glazes for sanitary ceramics. These pigments have very good hiding power and intense colors in glazes. Increasing the Sm content produces pigments having pink-orange (5–35 mol% Sm), yellow-orange (45–55 mol.%) to light yellow hues (85 mol.% Sm) in middle-temperature transparent leadless glazes.

Chromium-doped malayaite ceramic pink pigments, $CaSnSiO_5$:Cr were obtained [55] 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 color 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 color 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. 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.

Layered double hydroxides with the hydrotalcite-like structures, containing Mg^{2+} and Al^{3+}, doped with Cr^{3+} and Y^{3+}, have been prepared by precipitation at constant pH. The weight percentages of Cr^{3+} and Y^{3+} were 1, 2, or 3%, and 0.5 or 1%, respectively. Single phases were obtained in all cases, whose crystallinity decreased as the content in Cr and Y was increased. The pink ceramic pigments[56] have been characterized by element chemical analysis, powder X-ray diffraction, thermal analyses (differential, thermogravimetric and programmed reduction), FT-IR and UV-Vis spectroscopies; the specific surface areas have been determined from nitrogen adsorption isotherms at 196^{O}C. Upon calcination at 1200^{O}C for 5 h in air all solids display a mixed structure (spinel and rock salt for MgO); these solids have also been characterized by these techniques and their chromatic coordinates (CIE-L*a*b*) have been determined. Incorporation of Cr in the structure of the spinel obtained upon calcination of the LDH precursor gives rise to development of a pink color, characteristic of the ruby structure, and a decrease of lightness.

The using Fe_2O_3 as ceramic pigment [57] due to excellent colorimetric characteristics combined with thermal stability. The introduction of La^{3+} to Fe_2O_3 yields the precipitation of the perovskyte structure ($LaFeO_3$) with corresponding differences in the color of the resulting pigment. The compound was synthesized from polymeric precursors and characterized by thermal and colorimetric analyses, infrared and UV-visible spectroscopy, and X-ray diffraction. The characteristic light brown color of Fe_2O_3 changed to orange with the addition of La^{3+}. As the calcinations temperature increased

from 900 °C to 1100°C the pigment darkened as a result of the reduction of Fe^{3+}/Fe^{2+} with corresponding change of the colorimetric coordinates from L*, a*, b*=49.003, 10.541, 12.609 to L*, a*, b*=31.279, 6.096, 6.877.Adding La^{3+} to Fe_2O_3 changed the color of the pigment due to the formation of $LaFeO_3$ with perovskyte structure at 900 °C. The hue of the resulting color (orange**)** can be adjusted by adjusting the calcinations temperature. The pigment darkened by increasing the calcinations temperature from 900 to 1100°C possibly due to the reduction of Fe^{3+} to Fe^{2+}.

The oxidation state and the localization of the chromium ions in the ceramic matrix of Cr-doped cassiterite (SnO_2) and Cr-doped malayaite ($CaSnSiO_5$) violet pigments have been investigated [58] through the use of X-ray absorption near-edge (XANES), extended X-ray absorption fine structure (EXAFS), optical absorption and electron spin resonance (ESR) spectroscopies as well as by measurements of the unit cell parameters and the magnetic susceptibility of the pigments. Three types of chromium species are present in the Cr-doped cassiterite pigments, Cr(III) oxide clusters, which represent the majority phase, a very small amount of CrO_2 nanoparticles and Cr(IV) dissolved in the cassiterite lattice (≈5% of the total Cr amount), which must be responsible for the violet pigment color. In the case of Cr-doped malayaite, most chromium cations are in the tetravalent state and form a solid solution with the malayaite lattice by mainly substituting for the sixfold coordinated Sn(IV) cations in isolated octahedral positions, although a very small amount is also present substituting for tetrahedral Si(IV).

Karrooite, $MgTi_2O_5$, is a promising ceramic pigment [٥٩] due to its high refractoriness and refractive indices, as well as its ability to host transition metal ions in two crystallographically distinct octahedral sites. The coloring performance was investigated combining X-ray powder diffraction with UV–Vis–NIR spectroscopy on karrooite doped with V, Cr, Mn, Fe, Co or Ni (M) according to the formula $Mg_{1-x}Ti_{2-x}M_{2x}O_5$, with x = 0.02 and 0.05. Transition metals solubility in the karrooite lattice is not complete and a second phase is always present (geikielite or rutile). Structural data proved that incorporation of different chromophore ions into the karrooite structure affects unit cell parameters, bond length distances and angles, site occupancies and therefore cation order–disorder. Optical spectra exhibit broad absorbance bands of Co(II), Cr(IV), Fe(III), Mn(II), Mn(III), Ni(II), V(IV) with distinct contributions by cations in the M1 and M2 sites. Karrooite pigments have colors ranging from orange to brown-tan (Cr, Fe, Mn, V) to green (Co) and yellow (Ni) that are stable in low-temperature ($<1050^{O}C$) ceramic glazes and glassy coatings.

The transition metal ions (cobalt, manganese and nickel)-doped ZnO-based ceramic pigments can be prepared [60] by combustion synthesis. The combustion synthesized ceramic pigments have been characterized by powder XRD and diffuse reflectance spectra. The solution combustion process has been successfully extended to prepare various shades of new class of ceramic pigments. The exothermicity of the redox reaction between metal nitrate/hydrazide provides the heat required for the synthesis of ceramic pigments and the low temperature initiated, self-propagating gas producing combustion process yields voluminous products. All the samples

are crystalline in nature. Cobalt, manganese and nickel are present at Zn^{2+} site as Co^{2+} (bright green), Mn^{2+} (orange) and Ni^{2+} (pale yellow), respectively. Simultaneous doping of two or three colorants engenders new shades of colures. The solution combustion process is simple, fast and energetically attractive. It has all the advantages of wet chemical methods like homogeneity, purity and molecular level doping of transition metal ions (or colorants) in the oxide matrix.

Nanocrystalline metal aluminates MAl_2O_4 , M= Mn, Cu and Zn have been prepared by the combustion of aqueous solutions [61] containing corresponding metal acetate, aluminium nitrate, ammonium nitrate and different fuels, e.g., urea/ carbohydrazide/ oxalyldihydrazide/ hexamethylenetetramine/ glycine. The spinels obtained are nanosize (10–80 nm) oxides with surface area varying from 40 to 180 m /g depending upon the fuel used. The products have been characterized by powder XRD and Al MAS NMR spectroscopy. The particulate and morphological properties have been investigated using TEM and SEM techniques. Both $ZnAl_2O_4$ and $CuAl_2O_4$, prepared with carbohydrazide and glycine fuels are porous.

While the enormous increase in kinetics during the synthesis and sintering of complex ceramics in a microwave field is now well established, there are less examples where synthesis and sintering to high density have been demonstrated in one single step. In this communication, we report the simultaneous synthesis and sintering of $NiAl_2O_4$ from NiO +Al_2O_3 powder [62] mixture in just 15 min in a 2.45-GHz microwave field. The ‘‘anisothermal reaction’’ condition that was achieved in a microwave field

appears to be responsible for the observed enhancement in the reaction kinetics of $NiAl_2O_4$ formation.

The synthesis [63] of a new binary manganese(II)-calcium(II) tetrametaphosphates compounds of type $Mn_{2-x}Ca_xP_40_{12}$, where $0 \leq x \leq 1$ as special inorganic anticorrosion pigments. The synthesis is based on a thermal procedure making use of the reversible transformation of tetrametaphosphates to higher linear phosphates. Temperatures and heats of formation of these products have been determined (i.e. formation by thermal recrystallization from higher linear phosphates) together with the yields using this procedure, which increase with increasing x (the calcium content). The structure of the binary Tetrametaphosphates belongs to the monoclinic system (over the whole range of x); the structural parameters determined usually increase with increasing calcium content. The melting temperatures and densities decrease with decreasing calcium content (the respective intervals are 950-843°C and 3.15-2.88 $g.cm^{-3}$). The binary manganese (II)-calcium (II) Tetrametaphosphates $Mn_{2-x}Ca_xP_40_{12}$ exhibit very good anticorrosion-inhibition properties; their maximum value is obviously reached in the product of Mn/Ca molar ratio near l.67.

The thermal stable emulsion and co- precipitation method system is prepared by using metals nitrates and surfactants that add to water-oil system (W/O) [64]. Within the emulsion system, there are small numbers of atoms per droplet. It is necessary that exchange of reactive species takes places between droplets in order to form a stable precipitation (nucleus). Therefore, the nucleation and growth in emulsion produces small particles (nano-particles)

comprised to the homogeneous solution that producing large particles. This method is using of multi-surfactants as effective in forming stable emulsion and controlling droplet size. Also, it is useful for preparing nano-scale particles such MAl_2O_4 spinel using cyclohexane or n-heptane as oil phase mixed with T-orgital surfactants and octan-1-ol as co-surfactant [65]. The solid product obtained after decantation of organic phase was dried and transformation to nano-crystalline spinels after calcinations and the disadvantage of this method for the cost of starting materials.

Hydrothermal method is a process that used for single or heterogeneous phase reaction in aqueous solution that contains metals salts, alkoxides, hydroxides and organic solvent at elevated temperature and pressure to crystallize anhydrous ceramic directly form solution [66]. This synthesis offers a low temperature, direct route to oxide powders with a narrow size distribution avoiding the calcination step, low cost for instrumentation, energy, and precursors (stating material). This method has been used for synthesis of the nano-crystalline oxide powder such as cobalt aluminate $CoAl_2O_4$ as blue pigment, zinc aluminate $ZnAl_2O_4$ as white pigment[67].

The sol-gel process is the most widely used developed one among various synthetic powder preparation methods [68]. The method has advantages that the formation gel with a high degree of homogeneous and reduces the using of atomic diffusion during the solid state calcination to preparing multi-component oxides. Metals alkoxides is using as starting material which be liquid or volatile solids that easily purification. The

problem in this method the relative high costs of metal alkoxides and the release of large amount of alcohol during calcinations step requires special safety consideration. In this method, a solution of metal salts or alkoxides is formed first, followed by conversion into network gel after hydrolysis and condensation. Dry and calcination of this gel yields an oxide product. The stability and particle size of fine product depend on controlling temperature, pH, concentration, time, add water and alcohol. This method is using for preparation $CoAl_2O_4$ [69] as blue pigment.

Penchini method (citrate-gel) metal ion stabilized by an organic network in precursor solution, the fine oxide powders are obtained after a heating process [70]. They have the ability of preparing multi-component composition with good homogeneous and control of stoichiometry. This method depends on the poly-chelates between the C=O ligands of citric acid (CA) and metal ions and then the polyesterification occurs on heating with a polyfunctional alcohol such as ethylene glycol ($C_2H_6O_2$).The chelating in this process takes place during the evaporation of the precursor solution containing metallic salts and citric acid (CA). During heating produces a viscous, resin, and a rigid transparent, glassy gel. Mixture of different metal ions becomes immobilized in an early stage of the rigid formation network. Different oxides compositions produce during subsequent calcinations. Fine powder Sr_2CeO_4 [71] was synthesized using citrate gel method.

In recent years, Low temperature combustion synthesis (CS), also called self-propagating high temperature synthesis (SHS), is initially

developed in Russia by Merzhanov and has been successfully used to speed up the synthesis of complex oxide materials such as spinel and high temperature superconductors [72-74]. This method is characterized by its simpler process, a significant saving in time and energy consumption over the traditional methods. It also has been demonstrated that combustion synthesis of oxides can produce metastable phases. The low temperature combustion synthesis (LCS) method is based on mixed metal nitrates with organic fuel in small amount of water and than combustion of an aqueous solution on desired temperature (may be on heat plate) that giving a voluminous and dehydration which is followed by a sudden self-combustion and the evolution of large amounts of gases and formation of fluffy product with large surface area. The low temperature combustion synthesis (LCS) method depends on the reaction between oxidizing metal salts such as metal nitrates and combustion (reductant) agent (fuel), such as citric acid, urea, glycine, pyrozlone and other material that may be used as starting materials. As result of the controlling the molar ratio between metal salts and fuel, molar ratio between metal salts, and calcinations temperature, the homogeneous crystalline powder are appeared with a nano-scale particles size. This method characterized by time- saving and energy-efficient route for the synthesis of ultra fine powder.$BaTiO_3$ and $LiMnO_4$ [75] were synthesized using this method.

The combustion synthesis technique begins with the mixture of reactants that oxidize easily (such as nitrates) and a suitable organic fuel (such as urea $CO(NH_2)_2$) that acts as a reducing agent [76]. The mixture is brought to boil until it ignites and a self-sustaining and rather fast

combustion reaction takes off, resulting in a dry, usually crystalline and unagglomerated, fine oxide powder. While redox reactions such as this are exothermic in nature and often lead to explosion if not controlled, the combustion of metal nitrate–urea mixtures usually occurs as a self-propagating and non-explosive exothermic reaction. The large amount of gases formed can result in the appearance of a flame, which can reach temperatures up of 1000°C.The calcinations at different temperatures, the precursors decomposed into metal oxides upon heating to or above the phase transformation temperature. A constant external heat supply is necessary in this case, to maintain the system at the high temperature required accomplishing the synthesis of the corresponding phase. In combustion synthesis, the heat energy released from the exothermic reaction between the nitrates and the fuel, which is usually ignited at a temperature much lower than the actual phase formation temperature, can rapidly heat the system to a high temperature and sustain it long enough, even in the absence of an external heat source, for the synthesis to occur. The basis of the combustion synthesis technique comes from the thermo chemical concepts used in the field of propellants and explosives. The need for a clear indication of the effective constitution of a fuel-oxidizer mixture led Jain et al.[77] to devise a simple method of calculating the oxidizing to reducing character of the mixture. The method consists on establishing a simple valency balance, irrespective of whether the elements are present in the oxidizer or in the fuel components of the mixture, to calculate the stoichiometric composition of the redox mixture which corresponds to the release of the maximum energy for the reaction. The assumed valencies are those presented by the elements in the usual products of the combustion reaction, which are CO_2, H_2O and

N_2. Therefore, the elements carbon and hydrogen are considered as reducing elements with the corresponding valencies, oxygen is considered an oxidizing element with the valency (2-), and nitrogen is considered as having a valency of zero. The extrapolation of this concept to the combustion synthesis of ceramic oxides means that metals like zinc and Aluminum, Magnesium, Cobalt, Nickel, Manganese, (or any other metals) should also be considered as reducing elements with the valencies in the corresponding oxides.

Urea (U), 3-methyl-pyrozole-5-one (3MP5O) and various other fuels such as (citric acid, carbohydrazide, glycine and alanine) [78] have been used in the combustion synthesis of a variety of single and mixed ceramic oxides, all of them containing nitrogen but differing in 'reducing power' and the amount of gases they generate, which obviously affects the characteristics of the reaction products. The reaction is not isothermal and larger amounts of gases dissipate more heat, there by preventing the oxides from sintering and since the temperature reached isn't so high. The coincident sintering effect in the higher temperature reactions may result in a loss of sub-micron features of the powders. The first fuel, urea has the lowest reducing power (total valencies +6) and produces the smallest volume of gas (4 mol/mol of urea). For most purposes, it is the most convenient fuel to use: it is readily available commercially, cheap and generates the highest temperature, although fuel-rich mixtures might produce prematurely sintered particle agglomerates. The fuel, 3MP5O has the large reducing power (total valencies +20)and produces the large volume of gas (8 mol/mol of 3MP5O) [79].As oxidizers, metal nitrates are the preferred salts because they also contain nitrogen, are water soluble (a good homogenization can be achieved in the solution) and a few

hundred degrees are usually enough to melt them. Hydrate salts are even more favored in this respect, although the water molecules do not affect the total valencies of the nitrate and are, therefore, irrelevant for the chemistry of the combustion. The total valencies in all divalent metal nitrates (e.g. $Mg(NO_3)_2 .6H_2O$) add up to (-10) and the total valencies in all trivalent metal nitrates(e.g. $Al(NO_3)_3.9H_2O$) add up to (-15).

Aim of Work

1. The synthesis of a new ceramic pigment $Co_xMg_{1-x}Al_2O_4$ and $Ni_yMg_{1-y}Al_2O_4$ based on combustion synthesis (CS) method as result of important in industry due to their applications in color of plastics, polymers, paints, glasses, ceramics surface decoration of different fields.

2. The preparation of ceramic pigment powders by combustion synthesis (CS) method using different fuels: Urea (U), 3-methyl-pyrozole-5-one (3MP5O), oxalyl dihydrazide (ODH) and N, N-bis-(3-amino-propyl) oxalamide (3APOA).

3. The spectral characterization of ceramic pigments is studied by Infrared spectroscopy (IR), UV-visible spectroscopy and Diffuse reflectance spectroscopy (DRS) using CIE- L*a*b* parameters method for color measurements.

4. The chemical structure and phase formation of these pigments are characterized using different techniques (Thermogravimetric, Differential thermal and differential thermogravimetric analysis), X-ray diffractions (XRD) and Transmission electron microscopy (TEM).

5. The application of pigment powder of $CoxMg_{1-x}Al_2O_4$ and $Ni_yMg_{1-y}Al_2O_4$ systems on glaze with different calcinations times.

6. The effect of acids and bases on the pigment powder and on the color glaze.