ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis of Nano-Ceramic Compound Using Amino Acids as A Self-Combustion Fuel.

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ABSTRACT

Gel-combustion synthesis is an important procedure to saving time and energy with low cost. This process involves an intimate mixing of suitable green fuel like Lysine and glutamate with metal nitrates in an aqueous solution and a self- sustained and exothermic redox reaction between fuel and oxidizers (i.e. nitrates). Nano crystal ceramics pigment Cu_xMg_{1-x} Al_2O_4 ($0.1 \leq x \geq 1$) were prepared by the solution combustion technique. The powders have been prepared by using a low temperature combustion reaction of the corresponding metal nitrates with Lysine and Glutamine as a fuel at 350 ˚C in a hotplate. The resulted samples were characterized by X- ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Diffuse reflectance spectroscopy (DRS) using CIE – L a b parameter methods have been used for color measurements. The results show that the Cu_xMg_{1-x} Al_2O_4 samples are the crystalline phase with a particle size of 10-20 nm in the temperature range 500 - 1100˚C.

Keywords: Nono-ceramic, combustion, amino acids.

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INTRODUCTION

Generally, combustion based method is an easy and convenient method for the preparation of a variety of advanced ceramics, catalysts and nanomaterials. Through the combustion-based method, it is possible to produce the monophasic nanopowders with homogeneous structure at lower temperatures with shorter reaction times [1-4]. Moreover, solution based methods have been reported for the preparation of copper aluminate nanoparticles that include polymeric precursor method [5], combustion [6] and sol–gel method [7]. Another versatile solution-based technique, i.e. the gel-combustion synthesis, is a time-and energy-saving, and cost-effective strategy [8- 10]. This process involves an intimate mixing of suitable fuel (i.e. glycine, urea or citric acid) and metal nitrates in an aqueous solution, and a self- sustained and exothermic redox reaction between fuel and oxidizers (i.e. nitrates).The nature and amount of the fuel chosen, and the pH of the precursor solution are important factors in inhibiting selective precipitation and/or phase separation during the evaporation of solvents, which may in turn depend on the powder characteristics [9]. Such types of zwitterionic character can effectively complex various metal ions, which aids in preventing them from precipitating selectively and thus keeps the compositional homogeneity among the constituents [11]. Furthermore, Glutamine and Lysine can also serve as a fuel in the combustion reaction, being oxidized by nitrates. Namely, metal nitrates coupled with Glutamine and Lysine as complexing agent is highly promising in synthesis of a variety of amorphous and nanocrystalline oxides [12-14].

Among the various inorganic solids, spinel – type mixed oxides (AB_2O_4) are well known for their excellent catalytic action. These oxides are non-toxic, in expensive and very stable materials with strong resistance to acids and alkalis. They possess high melting point and relatively high surface area in the range10–100 m2/g. Mixed metal oxides have long been a topic of interest, because of their application as magnetic materials, pigments, catalysts and refractory materials. Aluminates spinels have high thermal stability, high mechanical resistance, hydrophobicity and low surface acidity [15, 16]. Several studies have suggested that metal oxide nanostructures may function as active species in various organic reactions. Some reports [17] have revealed that the supported metal nano- structures have attractive catalytic performances for the oxidation of alcohols. The experimental enthalpies of combustion for a large number of amino acids have been reported by different researchers, such those obtained by Tsuzuki et al. [18,19], Hutchens et al. [20], Kamaguchi et al. [21], Sabbah et al. [22,23] and very recently by Yang et al. [24-34].

EXPERIMENTAL

Chemical materials

Analytical-grade $Cu(NO_3)_2$, $Al(NO_3)_3.9H_2O$, Mg $(NO_3)_2.6H_2O$, Lysine and Glutamine were used as starting materials. The experimental compositions are listed in Table 1.

Table 1: The Batches Composition of Cu_xMg_{1-x} Al_2O_4 Spinel

Batches	$Cu(NO_3)$	$Mg(NO_3)_3.9H2O$	$Al(NO_3)_3.9.H2O$	Lysine	Aspartic
G1	18.8	230.8	750.3	---	665.6
G2	93.8	128.2	750.3	---	665.6
G3	187.6	---	750.3	---	665.6
L1	18.8	230.8	750.3	731.0	---
L2	93.8	128.2	750.3	731.0	---
L3	187.6	---	750.3	731.0	---

Nano ceramics pigment Cu_xMg_{1-x} Al_2O_4 ($0.1 \leq x \geq 1$) were prepared using the solution combustion technique. The amount of Lysine and Glutamine were according to the following chemical reaction formula and equaled to that of di-valence metal ions. The general procedure followed in the case of combustion synthesis consists in the preparation of aqueous solution containing the starting materials mixed under the right proportion (Table 1). The starting raw materials were dissolved in 40 ml of distilled water. The aqueous solution containing metal ion salts and fuel was heating at 60 ˚C under continuous stirring. After one hour, the temperature was raised to 80 ˚C. The resulting clear solutions were rapidly heating to 350 ˚C in a heating on hot plate. Metal nitrate/ fuel were used in all samples and it was assumed that combustion reaction by produced are CO_2, H_2O and N_2. After the water had evaporated, an exothermic self-sustaining combustion reaction occurred, which lasted for about 60 s. the precipitate initially started to swell producing a foaming precursor, this foaming consisted of very light and homogeneous flakes of a very small particle size. The pale brown and blue green powder were finally fired by using muffle furnace at 500˚C, 700 ˚C ,900 ˚C 1100 ˚C , respectively, and the Cu^{2+} , Mg^{2+} : Al^{3+} nano- powders with light blue green and pale brown color were obtained.

Instruments

X-ray diffraction (XRD) analysis was performed using an automated (Philips type: PW1840) diffractometer equipment with Cu Kα radiation source and at a step size angle of 0.02 θ, scan rate of 2 θ in 2 h unit, and a scan range from 10 θ to 60 θ.

The infrared spectra of the reactants and the resulting samples were recorded in KBr discs on a Bruker IFS 113V FT–IR spectrometer, in the wave number range (4000–200 cm–1). Morphology of the samples was determined by SEM. The samples were previously coated with gold. The samples were studied with a Philips®30 Analytical Scanning Electron Microscope. Particle images were obtained with a secondary electron detector.The CIE *L***a***b** colorimetric method, recommended by the Commission Internationale de l’Eclairage (CIE) was followed. In this method, *L** is lightness axis: black (0) – white (100), *b** is the blue (−), yellow (+), *a** is the green (−) – red (+) axis

RESULTS AND DISCUSSION

The X-rays diffraction for cupper ion as doping for $MgAl_2O_4$ system using L-glutamine ($C_5H_{10}N_2O_3$) and L-Lysine ($C_6H_{14}N_2O_2$) as fuel is investigated as powders at different calcinations temperatures. Fig. (1-2) shows the XRD patterns of the samples (G and L) fired at 900 ˚C for 1 h, respectively. The Figure (1) the x-ray patterns it is clear that the intensity of the bands is increasing with calcined temperatures. With the increase of the temperature above 900˚C, in tensities of the peaks same high at 1100 ˚C are observed. The color pale blue green spinel was obtained for sample fired at 900 ˚C in sample (G1 and L1). The calcinated powders will start to form the crystalline at 700˚C in sample (G1, G2, G3, L1, L2 and L3) and the intensity of the peaks increase by increase temperature at 900˚C and 1100˚C. The samples G2to G3 and L2 to L3 were the color formed as brown yellow spinel. The XRD patterns of samples (G-L) shows complete identification of peaks position. This identification peaks is directly proportional to substitution of Mg^{+2} by Cu^{+2} in Figure (1-2). Cu_xMg_{1-x} Al_2O_4 samples prepared by solution combustion synthesis, exhibit different pale blue green tones color shades in sample (G1, L1). But, the brown yellow tones color intensifies from batches G2 to G3and L2 to L3, as the substitution degree of Mg^{+2} by Cu^{+2} increases. XRD patterns revealed that Cu_xMg_{1-x} Al_2O_4 solid solution is the only crystalline phase contained in batches G to L see in (Fig. 1-2).

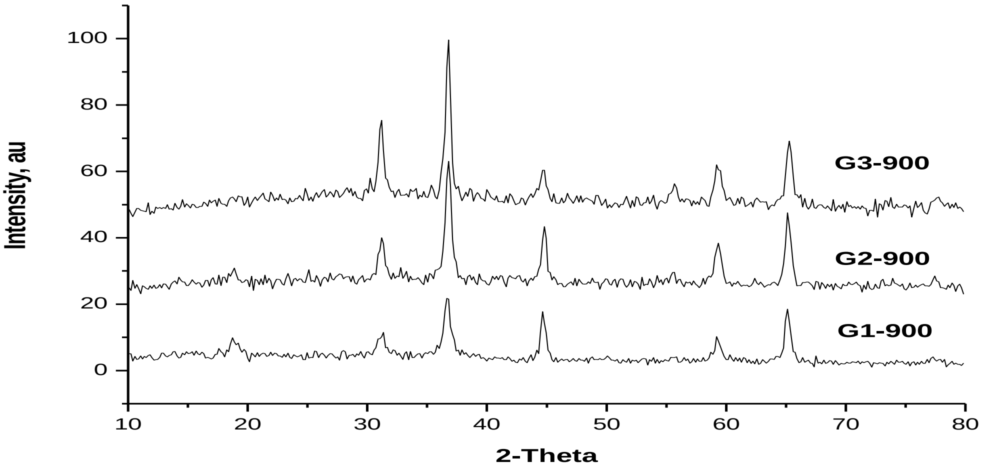

Fig.1: X-ray diffraction pattern of the pigment sample (G) at 900˚C

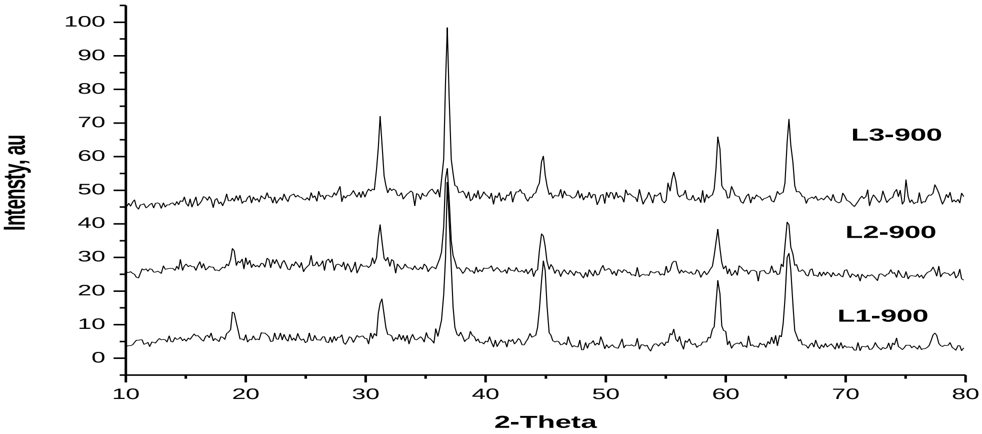

Fig.2: X-ray diffraction pattern of the pigment sample (L) at 900˚C

Generally, fuel mixtures applying in combustion method must be selected based on metal nitrate/fuel compatibility, which is experimentally determined. Glutamine ($C_5H_{10}N_2O_3$) and L-Lysine ($C_6H_{14}N_2O_2$) are the commonly used chelating ligands that contains aliphatic amine group. It possesses strong complexing ability for Cu and Al metal-ions, and therefore was chosen as the complexing agent. In this work Glutamine and L-Lysine which is reported as a fuel for Mg $(NO_3)_2$ [35], suggested as a suitable fuel for Al $(NO_3)_3$ and Cu $(NO_3)_2$ in the preparation of copper aluminate spinel –type nanopowders bright blue green and brown yellow color in low temperatures. Increasing temperature treatment increase the crystalline size of powders, so preparation of single phase spinel nano particles at lower temperatures makes this method technically simple and cost effective[36]. The crystalline diameters were calculated on each diffraction peak for the sample fired at 900 ˚C and the average crystallite diameter was about 30 nm.

The heating sample at four temperatures degrees 500, 700, 900 and 1100 ^oC for 1hrs, leads to appearance of growing bands in the oxides (CuO, MgO and Al_2O_3) region were studies. The weak-to-medium bands at around 1100-400 cm^{-1} is attributed to the stretching vibration motions of ν (M–O) [37, 38]. FT-IR spectra in Figure (3-4) the samples (G1 to G3) and (L1to L3) were recorded at different temperatures of 500, 700, 900 and 1100 ^oC. The spectrum as shown in Figure (3-4) has no absorption peaks detected concerning of Glutamine and L-Lysine starting materials. By comparing the standard spectra of CuO, MgO and Al_2O_3, the absorption peaks of Cu_xMg_{1-x} Al_2O_4 powder are indexed as shown in Figure (3-4). Those peaks are detected at 700, 650, 620, 510, 450 and 410 cm^{-1}. However, the absorption peaks of the Cu_xMg_{1-x} Al_2O_4 before thermal treatment are weak and broadened, showing a character of non-perfect crystallization which is consistent with the XRD result. The metal ions distributed in two different environments in spinel at 730 and 521cm^{-1} is attributed to the presence of tetrahedral (Td) and octahedral (Oh) coordinated M–O bonds, respectively, and the phase formation can be very well assigned from the appearance of two broad bands.

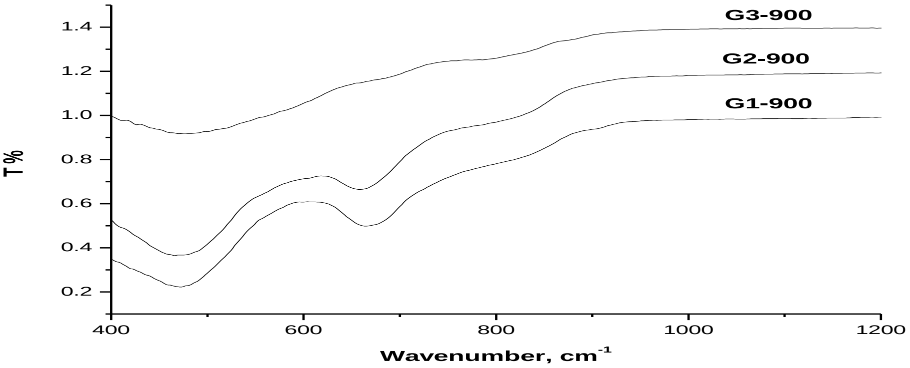

Fig.3: IR spectra for the spinel calcined at 900 ^oC for G1, G2 and G3.

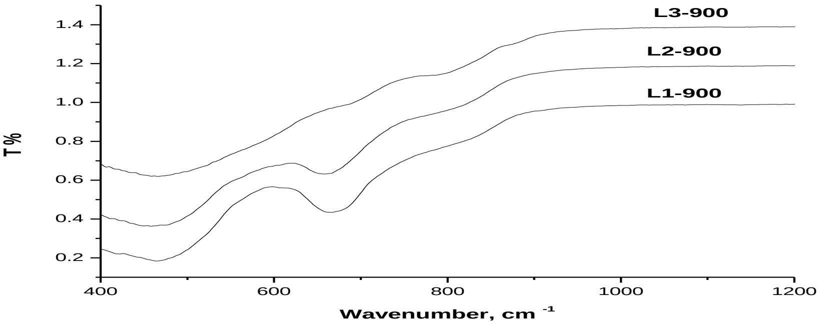

Fig.4: IR spectra for the spinel calcined at 900 °C for L1, L2 and L3.

The broad absorption bands for copper aluminate indicated the nature of the spinel for all the compositions. The M–O stretching frequencies in the range of 500–920 cm^{-1} are associated with the vibrations of Al–O and M–O–Al bonds for both the samples. The two broad bands's observed at 720 and 521cm^{-1} are characteristic of copper aluminate spinels [36, 39]. These bands correspond to the AlO6 groups, which build up the copper aluminate spinels and indict the formation of copper aluminate spinels. The IR spectra in the (4000-400 cm^{-1}) region have provided information regarding the coordination mode in the Glutamine and L-Lysine complexes and were analyzed by comparison with data for the free Glutamine and L-Lysine ligand. The most relevant bands and proposed assignments for all the complexes were discussed. In the FT-IR spectra, extensive coupling occurs for several vibrations, making qualitative deductions about the environment around metal ions difficult. The region 1700-500 cm^{-1} the assignments of the observed bands are accomplished by a comparison of the spectrum of each chelate with that of the Glutamine and L-Lysine free ligand. For the metal chelates, the NH_2 deformation vibrations appear instead of NH_3^+ deformation vibrations of the ligand. The ν (COO^-) antisymmetric stretching vibrations of the benzene ring and the δ (NH_2) vibrations to some extent, the ν (COO^-) antisymmetric stretching are observed at the same frequencies and symmetric stretching vibrations are at the same region frequencies (with varying in the intensity of bands) than those of the ligand in the Zwitterion feature. The OH in plane and out of plane deformation vibrations has no detected frequencies. From 500 to 400 cm^{-1}, absorption bands which cannot be observed in the ligand or appear with shifted in frequencies or the intensities were defected dependently on the complexation. The absorption bands appear at 432 cm^{-1} for M-O vibration, respectively. They are assigned to the metal-nitrogen stretching vibration by comparison of the chelate spectra with the ligand spectrum and referring to the metal chelate amino acids [40-44]. No other impurity phase is detected by FT-IR spectra, and is in good agreement with the result so btained by XRD. Thus, from XRD and FT-IR studies, it is confirmed that copper aluminate phase is not formed when the plant extract is not used. Hence, we have carried out other studies with the samples prepared by using the plant extract.

The CIE L* a* b* chromatic coordinates of powder samples and optimum parameters obtained in the optimization of ceramics samples are shown in Table (2). The samples G1 to G3 are blue green and brown yellow colored because minimize L* a * b* parameters among all samples. Sample G3 have high percent of Cu and result in brown pigment. On the other hand sample G1 gives the best pale blue green colored sample at minimizing Cu presence substituted by Mg in the spinel composition. Sample G2 to G3 are located in the brown yellow region see in Figure (5).The blue green proportion (-b) can be observed in sample G1and increase of the brown proportion (a*) can be observed in samples G2 to G5prepared by combustion synthesis. In order words, as the amount of Cu^{2+}, which occupies tetrahedral site in $Cu_xMg_{1-x}Al_2O_4$, increases the brown hue of the sample intensifies.

Table 2: CIE L* a* b* parameter and tristimulus values of color samples

samples	L*	a*	b*	X	y
G1	87.44	-0.06	-0.11	0.31	0.32
G2	38.10	3.30	6.00	0.34	0.35
G3	33.50	3.50	7.7	0.35	0.36
L1	84.21	-0.01	0.19	0.31	0.33
L2	40.20	3.25	5.8	0.34	0.35
L3	35.21	3.42	7.6	0.35	0.35

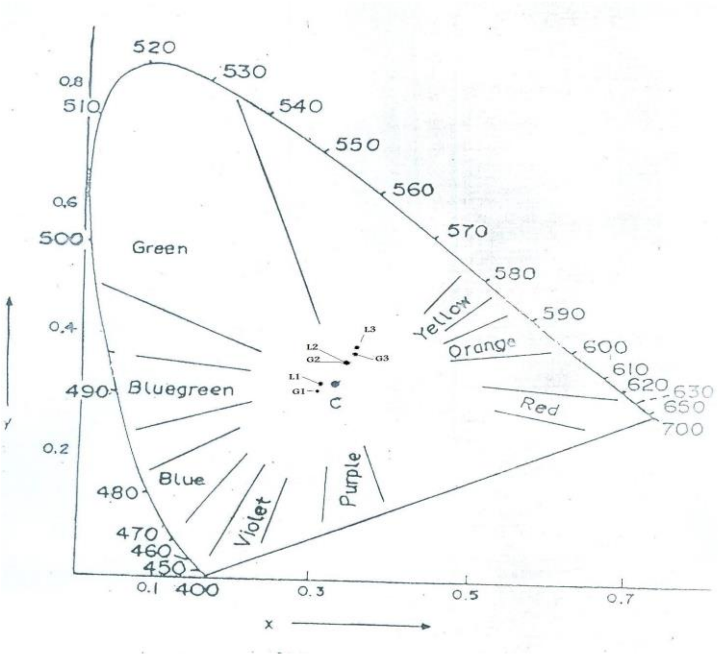

Fig. 5: CIE chromaticity diagram of sample G and L

The evolution of(L*) parameter as a function of Cu^{+2} by Mg^{+2} substitution Table 2 shows a progressive decrease as the amount of Cu^{+2} increases. The color degradation may be related to the large specific surface area and small crystalline size of $Cu_xMg_{1-x}Al_2O_4$ pigment prepared by solution combustion synthesis.

SEM characterization of the powder revealed a homogeneous microstructure and a similar morphology of the G and L pigment samples, consisting of particles agglomerates see in Fig (6-9). The decrease of the agglomeration degree from sample G1 to G3 may be related to the evolution of combustion reactions.

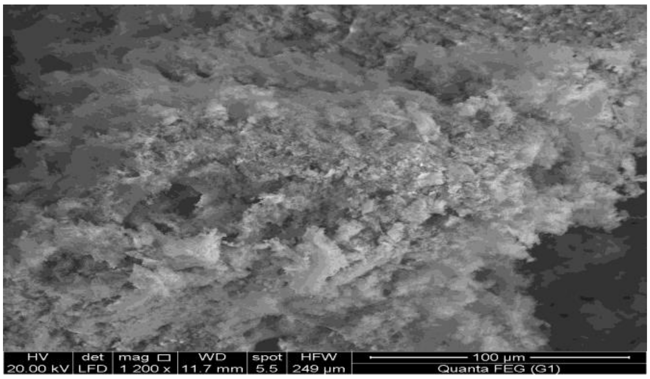

Fig.6: SEM micrographs of pale blue green pigments G1 at 900 ˚C

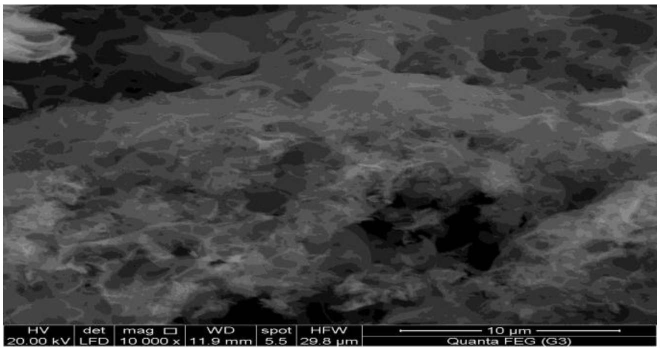

Fig.7: SEM micrographs of pale brown yellow pigments G3 at 900 ˚C

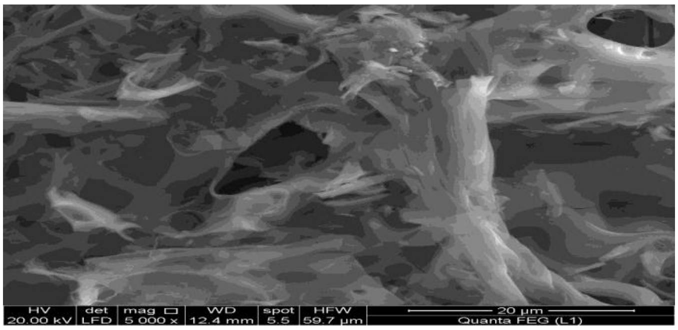

Fig.8: SEM micrographs of blue green pigments L1 at 900 ˚C

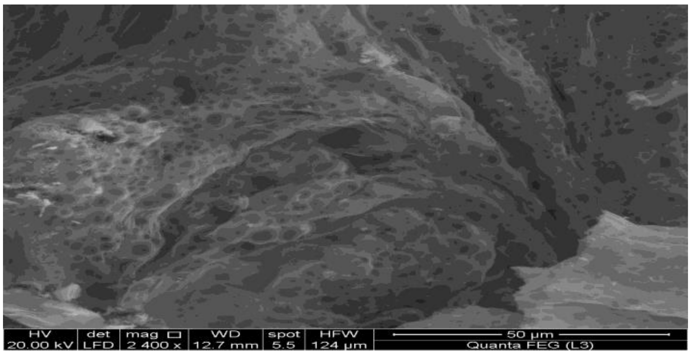

Fig.9: SEM micrographs of brown yellow pigments L3 at 900 ˚C

The studies of micrographs of the calcites powders have revealed that crystallization of the powder begins above 700 ˚C and at 1100 ˚C the spinel crystallizes completely with an average crystalline size of the order less than 20µm. Figure (6-9) shows a micrograph for a Cu_xMg_{1-x} Al_2O_4 powder heat treated at 900 ˚C. The mean particle size ranges less than 20 µm are formed. This pigment displays a grain morphology consisting of perfect tetrahedral characteristic of spinel

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