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A Novel Synthesis For Spinel Color Ceramic Materials Using Simple And Cheap Routes At Low Temperature.

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ABSTRACT

Nanocrystalline $Ni_xMg_{1-x}Al_2O_4$ spinel ($x=0.1, 0.3, 0.5, 0.7$ and 1) inorganic pigment were synthesized via low-temperature combustion route employing L-alanine as a novel environmentally benign fuel and novel fuel. After annealing the combustion synthesis powders at $500, 700, 900$ and 1100 °C for 1 h were studied. The obtained powder were characterized by means X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), diffraction thermal analysis (DTA), CIE $L^* a^* b^*$ color measurement and scanning electron microscope (SEM). XRD patterns shows that all calcite powder have single- phase $Ni_xMg_{1-x}Al_2O_4$ cubic spinel structure. All samples had blue and blue green shades, denoting the inclusion of Ni^{2+} in the spinel structure in tetrahedral configuration. The colorimetric data the formation of blue pigments for $x > 0$ to highly negative values of (b^*), and the blue green color was produced for ($x=0.7$ and 1). SEM image showed nanoparticles with less than 40 nm crystallite size and flakes-like appearance of all synthesis powders.

Keywords: ceramic; pigments; nano powder; combustion; L-alanine

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INTRODUCTION

Spinel is one of the most interesting crystalline structures in the development of stable and chemically inert pigments, containing ions at different oxidation states in both tetrahedral and octahedral sites. Moreover, there are several ways of arranging cations at these sites (normal and inverse spinel) [1].

The developments in the combustion synthesis with special emphasis on the preparation of catalysts by solid state and solution combustion were discussed [2, 3]. Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of nanosize materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). Depending on the type of the precursors, as well as on conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes. This process not only yields nanosize oxide materials but also allows uniform (homogeneous) doping of trace amounts of rare-earth impurity ions in a single step. [4]

It is well recognized that the fuel is an important component for the preparation of oxides by SCS. Urea and glycine are the most popular and attractive fuels for producing highly uniform, complex oxide ceramic powders with precisely controlled stoichiometry. The glycine nitrate process (GNP) has been billed as 'environmentally compatible'. But the recent study by Pine et al. has shown CO and NO_x as the products of incomplete combustion in GNP. Hence for GNP technique to be used on an industrial scale, the potential for producing and emitting hazardous nitrogen oxides and CO must be addressed seriously [5].

It is important to note that researchers are focusing their efforts towards the up scaling of SCS and also finding new applications of combustion synthesized nanosize powders [6-8]. In this work nanocrystalline Ni_xMg_{1-x}Al₂O₄ spinel pigment has been synthesized via low-temperature combustion route employing L-alanine as a novel environmentally benign fuel.

EXPERIMENTAL

Raw materials

Analytical-grade Ni(NO₃)₂·6H₂O in BDH Company, Al(NO₃)₃·9H₂O in Fluka Company, Mg(NO₃)₂·6H₂O in BDH Company, L-alanine in Lab. Rasayan were used as starting materials. The experimental compositions are listed in Table 1. An aqueous solution containing Mg (II), Al (III) and Ni (II) metal ion salts and fuel was heated at 60 °C under continuous stirring. After one hour, the temperature was raised to 80 °C. The mixture was stirred for two hours until high viscous and gel was formed.

Synthesis of Ni_xMg_{1-x}Al₂O₄ nano pigments

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 resulting clear solutions were rapidly heated to 200 °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 CO₂, H₂O and N₂. 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. The blue green powder were finally fired by using muffle furnace at 500, 700 °C, 900 °C, 1100 °C, respectively, and the Ni²⁺, Mg²⁺, Al³⁺ nanopowders with light blue green color were obtained.

Table 1: The Batches Composition of Ni_xMg_{1-x}Al₂O₄ Pigment Spinel

Batches	Ni(NO ₃) ₂ ·6H ₂ O	Mg(NO ₃) ₂ ·6H ₂ O	Al(NO ₃) ₃ ·9H ₂ O	C ₃ H ₇ NO ₂
Batch 1	2.13	16.89	54.91	26.07
Batch 2	6.35	13.07	54.64	25.94
Batch 3	10.54	9.29	54.37	25.81
Batch 4	16.73	3.69	53.96	25.62
Batch 5	20.81	---	53.70	25.49

Instruments

X-ray diffraction (XRD) analysis was performed using an automated (Philips type: PW1840) diffractometer equipment with Cu K α 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 .

Differential thermal analysis (DTA) was run with a coupled (SETARAM TG/DTA 92) DTA-TGA instrument. The batch was heated with rate of 5 C/min at ambient atmosphere pressure and temperature, up to 1000 $^{\circ}$ C.

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'Éclairage (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 DISSOCIATION

XRD analysis of the fired samples

The analyses of the XRD patterns of samples N1-N5 shows complete identification of peaks position. This identification peaks is directly proportional to substitution of Mg^{+2} by Ni^{+2} in Fig 1. $\text{Ni}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ samples prepared by solution combustion synthesis, exhibit different blue green tones color shades. The calcinated powders begin to form the spinel crystalline only at 900 $^{\circ}$ C. The phase composition of samples N1-N5 corroborated with their blue green color tones indicates that the formation of spinel solid solution has reached completion.

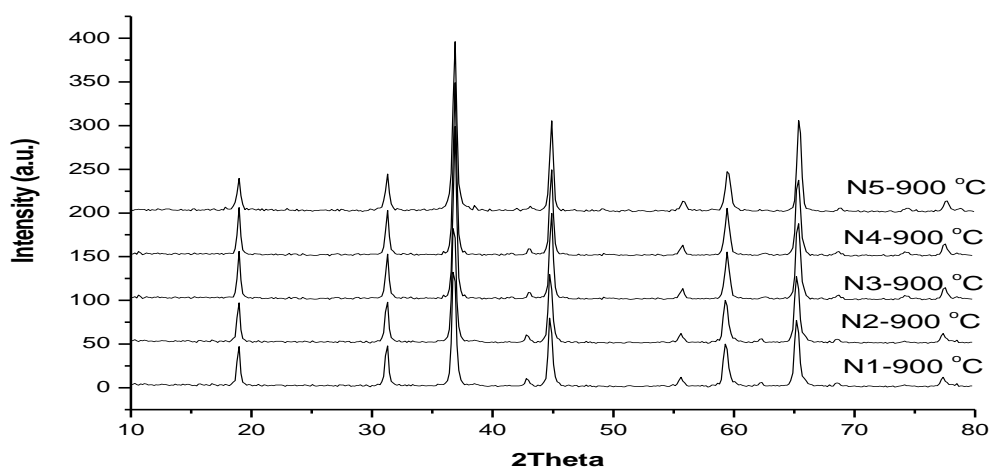


Figure 1: X-ray diffraction pattern of the pigment sample (N1-N5) at 900 $^{\circ}$ C

L-alanine which is reported as a fuel for $\text{Mg}(\text{NO}_3)_2$ [9], suggested as a suitable fuel for $\text{Al}(\text{NO}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$ in the preparation of nickel aluminate spinel-type nanopowders bright blue green 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.

Infrared Spectra of samples

Heating the parent sample (Formulas 1 and 2) at four temperatures degrees 500, 700, 900 and 1100 °C for 1hrs., leads to appearance of growing bands in the oxides (NiO, MgO and Al₂O₃) region. The weak-to-medium bands at around 1100-400 cm⁻¹ is attributed to the stretching vibration motions of ν (M–O) [10-20]. FT-IR spectra (Fig. 2) of N1 to N5 were recorded at different temperatures of (500, 700, 900 and 1100 °C). For the *in situ* FT-IR measurements; a sample of the N1 to N5 calcined at 900 °C. The spectrum as shown in (Fig. 2) has no absorption peaks detected concerning of alanine starting materials. By comparing the standard spectra of NiO, MgO and Al₂O₃, the absorption peaks of Ni_xMg_{1-x} Al₂O₄ powder are indexed as shown in Fig. 2. Those peaks are detected at 700, 650, 620, 510, 450 and 410 cm⁻¹. However, the absorption peaks of the Ni_xMg_{1-x} Al₂O₄ before thermal treatment are weak and broadened, showing a character of non-perfect crystallization which is consistent with the XRD result. After thermal treatment, the re-crystallization was finished and its spectrum is very similar to that of the powder Ni_xMg_{1-x} Al₂O₄.

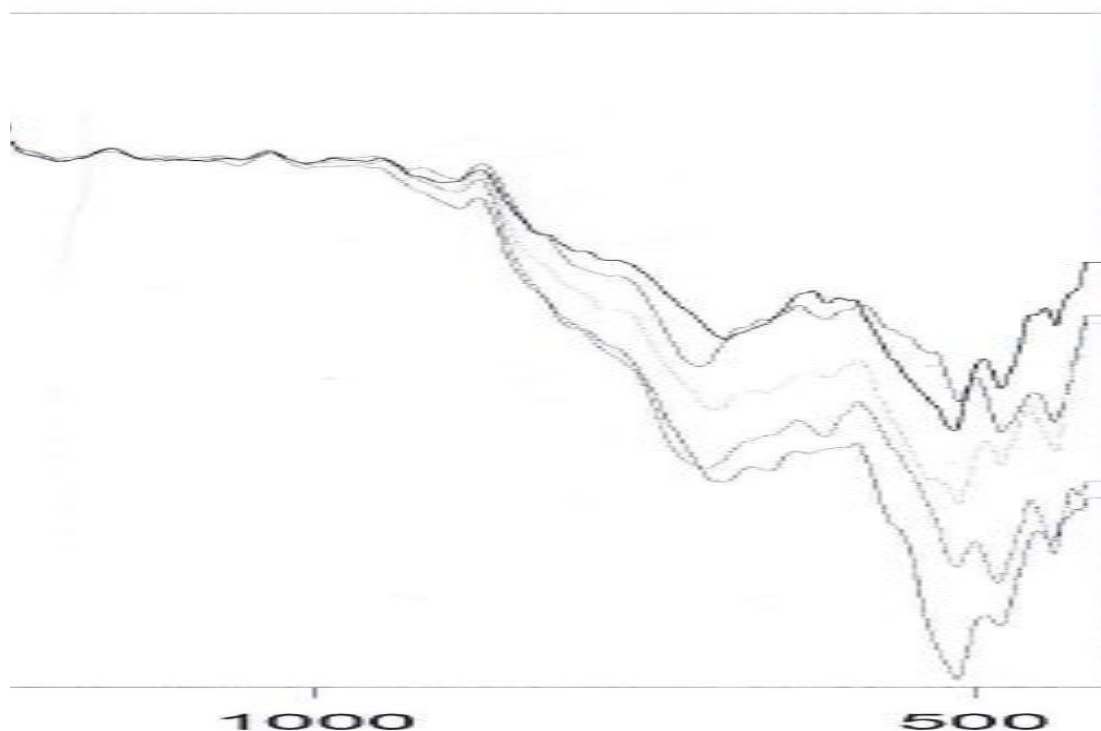


Figure 2: IR spectrum for the prepared spinel calcined at 900 °C.

Thermal analysis

The thermal gravimetric analysis for 0.1 to 1 mol of Ni ion system using L-alanine gave several steps, as shown in the DTA curve for ash materials. The DTA shows two endothermic steps at 400, 550,650°C and one exothermic peak at 900,950 °C.

Colored Measurements

The samples N1 to N5 are blue green colored because minimize L* a * b* parameters among all samples, included the ceramic optimized samples. Sample N5 have high percent of Ni and result in dark blue green pigment (Figure 3). On the other hand sample N1 gives the best pale blue green colored sample minimizing Ni presence substituted by Mg in the spinel composition (Figure 3).

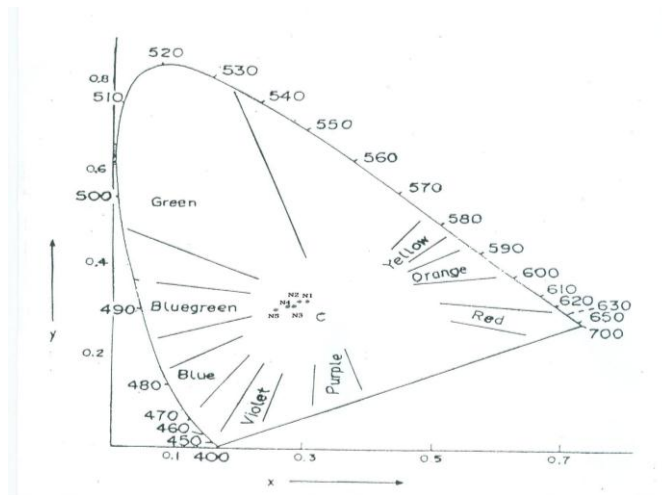


Figure 3: CIE chromaticity diagram of samples N1-N5 pigment

Scanning Electron Microscope

SEM characterization of the powder revealed a homogeneous microstructure and a similar morphology of the N1 and N5 pigment, consisting of particles agglomerates see in Fig (4-5). The decrease of the agglomeration degree from sample N1 to N5 may be related to the evolution of combustion reactions. The studies of micrographs of the calcites powders have revealed that crystallization of the powder begins above 500 °C and at 1100 °C the spinel crystallizes completely with an average crystalline size of the order 0.8- 2.0 μm. Figure (4-5) shows a micrograph for a Ni_xMg_{1-x} Al₂O₄ powder heat treated at 900 C and Figure (4-5) at 900 C. The mean particle size ranges from 0.8 to 1.0 μm are formed. This pigment displays a grain morphology consisting of perfect tetrahedral characteristic of spinel.

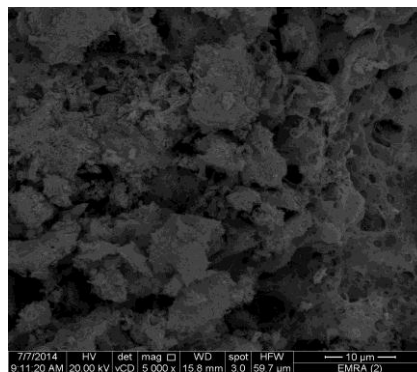


Figure 4: SEM micrographs of pale blue green pigments N1 at 900 °C

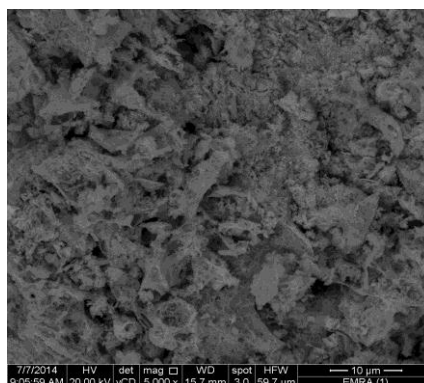


Figure 5: SEM micrographs of blue green pigments N5 at 900 °C

CONCLUSION

In summary, this study represents one of the methods to prepare color spinel structure as combustion reaction

- This paper has been the study of the mode of decomposition of coordinated L-alanine in presence of Magnesium (II)/cobalt (II) and aluminum (III) complex systems in dry grinding at room and high temperatures.
- The calcinated powders begin to form the spinel crystalline only at 900°C
- The infrared spectra of both parent adducts of L-alanine with Mg(II)/Ni(II) and Al(III), they indicated that oxygen-to-metal bonds are present in these adducts
- The thermal degradation of the Mg (II)/Ni (II) and Al (III) systems ignited previously at ~ 400 °C take place in tow degradation stages.
- The average crystallite diameter was about 30 nm. Some peaks attributed to Ni²⁺ were found because of its height amount

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