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## Nano $Mg_{1-x}Ni_xAl_2O_4$ spinel pigments for advanced applications



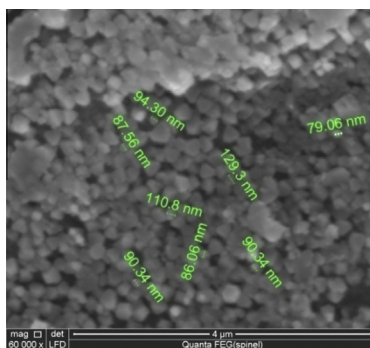
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### HIGHLIGHTS

- Nano  $Mg_{1-x}Ni_xAl_2O_4$  spinel pigments were synthesized via polymeric combustion technique upon heat treatment at 210 °C.
- $NiMgAl_2O_4$  spinel beside  $MgNiO$  phases were crystallized with particle sizes of 9–21 nm at 600 °C and 52–180 nm at 1200 °C.
- All samples exhibited green to pale green colors due to inclusion of  $Ni^{2+}$  inside spinel structure.
- The prepared pigment was suitable to convert commercial and opaque glazes to color product.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Nano  $Mg_{1-x}Ni_xAl_2O_4$  spinel pigments were synthesized via polymeric combustion technique upon heat treatment at 210 °C. Citric acid in the presence of ethylene glycol polymer, with mass ratio of 60:40, was successfully used as a host network for the synthesis process. The obtained spinel was calcined at different temperatures; 300–1200 °C and investigated by thermal analysis (TG-DTG/DTA), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). UV-Vis and diffuse reflectance spectroscopy (DRS) using CIE-Lab/parameters methods have been used for color measurements. The addition of colored pigment on different types of glazes was studied. The results revealed that  $NiMgAl_2O_4$  spinel beside  $MgNiO$  phases were crystallized with particle sizes of 9–21 nm at 600 °C and 52–180 nm at 1200 °C. All prepared samples exhibited green to pale green colors due to the inclusion of  $Ni^{2+}$  inside the spinel structure. The pale green color intensity increased with increasing calcination temperature. The prepared pigment was suitable to convert commercial and opaque glazes to color product to be used in different applications.

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### Introduction

Spinel-type oxide materials have attracted a great deal of attention from scientists and industry leaders because of their relevant magnetic, refractory and semiconducting properties [1–5]. The spinel structure is featuring the general formula  $AB_2O_4$ . It displays 64 tetrahedral sites and 32 octahedral sites, of which only

8 tetrahedral sites and 16 octahedral sites are occupied by the cations  $A^{2+}$  and  $B^{3+}$ , respectively. There are two ideal types of these structures; the first one is the normal spinel, in which the tetrahedral sites are occupied by  $A^{2+}$  cation and the octahedral sites by  $B^{3+}$  cation. The second ideal type is the inverse spinel, in which all tetrahedral sites are occupied by  $B^{3+}$  cation, while an equal number of  $A^{2+}$  and  $B^{3+}$  cations share the octahedral sites [6,7]. Besides these ideal structures, spinel can display a partially inverted structure, moreover, with the presence of a tetrahedral-dependent cation. In this case, the occupancy of tetrahedral and octahedral cations shifts toward a random distribution with increasing temperature [8].

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Color is an optical property that takes to countless applications. For ceramic tiles, pigments give a stable coloration to the glaze through a simple mechanical dispersion. The final color of each pigment is due to the addition of a chromophore ion (usually transition metals) into an inert matrix, or this ion may be part of the own matrix, as in the case of ferrites [9].

Recently, a new application of the spinels as ceramic pigments has been explored owing to their high mechanical resistance, high thermal stability, low temperature sinterability and the easy incorporation of chromophore ions into the spinel lattice, allowing for different types of doping, thus producing ceramic pigments with different colors [10].

Ceramic pigments have been synthesized by several solution techniques, such as co-precipitation [11], hydrothermal [12,13], sol-gel [14], alkoxide hydrolysis [15,16], the Pechini method [17,18] and the low combustion method [19–21]. The properties of the final powder depend on the preparation method and the calcination temperature as well as time.

In terms of crystalline structure, magnesium aluminate is the origin (normal) spinel,  $MgAl_2O_4$  [22], in which  $Mg^{2+}$  ions fill the tetrahedral sites and  $Al^{3+}$  ions occupy the octahedral positions in the cubic closed packing of  $O^{2-}$  anions. On the other hand, the cation arrangement in nickel aluminate is typical for a partially inverse spinel,  $(Ni_{1-z}Al_z)[Ni_zAl_{2-z}]O_4$ , in which  $Ni^{2+}$  and  $Al^{3+}$  ions are randomly located in both tetrahedral and octahedral positions, respectively. At ambient temperature and pressure, the inversion parameter  $z$  of  $NiAl_2O_4$  is around 0.8 ( $z$  stands for the site occupancy factor of  $Al^{3+}$  on tetrahedral sites) and it decreases as the temperature increases [23,24].

Despite the well known structure and applications of  $MgAl_2O_4$  and  $NiAl_2O_4$ , little attention has been paid to the investigation of  $MgAl_2O_4$ – $NiAl_2O_4$  solid solutions in terms of synthesis and characterization. Several authors [25,26] have investigated the distribution of  $Ni^{2+}$  ions among octahedral and tetrahedral sites in  $NiAl_2O_4$ – $MgAl_2O_4$  spinel solid solutions. Most of the  $NiAl_2O_4$ – $MgAl_2O_4$  solid solutions were prepared by solid state method which requires elevated temperature and long soaking time. For instance, the formation of  $Mg_{1-x}Ni_xAl_2O_4$  solid solutions starting from the corresponding metal oxides demands a heat treatment of at least 2 h at 1200 °C [22,27].

The present paper reports an innovative study concerning the preparation of  $MgNiAl_2O_4$  spinel-containing material for pigment applications using a polymeric precursor's method, which has been developed by Pechini. This method consists of formation of a polymeric net starting from a polyhydroxy alcohol and an alpha-hydroxy carboxylic acid, with metallic cations homogeneously distributed throughout the matrix. After synthesis, physical and optical behaviors are studied, verifying its stability as pigment under industrial conditions.

## Materials and experimental procedures

### Materials

The starting materials used in this work were nickel chloride hydrated  $NiCl_2 \cdot 6H_2O$  (Aldrich), magnesium nitrate hydrated  $Mg(NO_3)_2 \cdot 6H_2O$  (Fluka Chemika), and  $AlCl_3 \cdot 6H_2O$  (Arabian Medical & Scientific Lab. Sup. Co.). Ethylene glycol and citric acid were supplied by Merk-Schuchardt, Moviol, and Aldrich.

### Preparation and characterization methods

#### Resin preparation using polymeric precursors

The polymeric precursor solution was prepared using the Pechini method, which has been used to synthesize poly-cationic

powders. The process is based on metallic citrate polymerization using ethylene glycol. A hydrocarboxylic acid, such as citric acid, was used in an aqueous solution to chelate cations. The addition of a polyalcohol, such as ethylene glycol, leads to formation of an organic ester. Polymerization, promoted by heating, results in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix. The citric acid was added into water with constant agitation at 60–70 °C. Then, the polymeric net former;  $AlCl_3 \cdot 6H_2O$  (12.11 g),  $Mg(NO_3)_2 \cdot 6H_2O$  (12.85 g) and  $NiCl_2 \cdot 6H_2O$  (11.92 g) were added separately with continuous stirring. After mixing the salts with complete dissolution, ethylene glycol was added into the solution. The proportion of citric acid/ethylene glycol was 60:40 mass%. To promote the reaction, the temperature was increased up to 110–210 °C. At the end of the reaction, a polymeric gel (resin) was obtained.

### Powder preparation

The obtained resin was viscous with dark green color. Its heat treatment at 300 °C for 1 h (primary calcination) led to partial decomposition forming an expanded resin. It constituted of a semi-carbonized material having dark honey color with aspect similar to foam. The resultant material was de-agglomerated in a porcelain mortar and allowed to pass through 100-mesh sieve. The thermal decomposition of organic precursors and the formed crystalline phases were evaluated by thermal analysis and IR spectroscopy. After the primary calcination, the powders were calcined at temperatures varying from 600 to 1200 °C for 1 h with a heating rate of 10 °C/min followed by grinding up to 100-mesh. The obtained powders showed different grades of green color and exposed to the required characterization.

### Characterization of the prepared materials

Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) were carried out using a Setaram Labsy TM TG-DTA16 system. Fourier transform infrared spectroscopy equipment [FT-IR, MB154S, Bomem] was used to determine the main bonds in the polymer and the effect of polymer on the spectra of spinel structure. X-ray diffraction analysis (XRD) was used to investigate the respective phases of the prepared materials calcined at 600, 800, 1000 and 1200 °C utilizing Bruker D8 equipment with  $Cu K\alpha$  radiation and scanning rate of 1 degree per minute in the range

**Table 1**  
The composition of the applied opaque glaze.

Raw materials	wt.%
Feldspar	18.76
Zircon	9.02
Dolomite	0.46
Kaolinitic quartz sand	19.46
Limestone	8.96
Potassium carbonate	5.35
Penta-Borax	19.28
Boric acid	6.64
Zinc oxide	8.31
Alumina	0.1
Calcium fluoride	3.67

**Table 2**  
The chemical analysis of the commercial borosilicate glaze.

Oxides	wt.%
$SiO_2$	80
$Na_2O$	4
$Al_2O_3$	2–3
$B_2O_3$	13

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