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Research Article

Simple and Efficient Rout for Synthesis of Spinel Nanopigments

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Nano-sized $Co_xMg_{1-x}Al_2O_4$ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1) inorganic pigments were synthesized via combustion method using β-alanine, as a single and novel fuel, at 800°C in open furnace. The obtained powders were characterized by means of X-ray diffraction (XRD), energy dispersive X-ray (EDX) elemental analysis, diffuse reflectance spectrum (DRS), CIE $L^*a^*b^*$ color measurements, and scanning electron microscope (SEM). XRD patterns show that all calcined powders have single phase cubic spinel structure. EDX analysis revealed the composition of desired spinels. The diffuse reflectance spectra of the $Co_xMg_{1-x}Al_2O_4$ ($x > 0$) pigments confirmed the presence of tetrahedrally coordinated Co^{2+} ions in the spinel lattice. The colorimetric data pointed out the formation of blue pigments (for $x > 0$), corresponding to highly negative values of b^*, and the bluest color was produced for x = 0.8 and 1. SEM images showed nanoparticles with less than 30 nm crystallite size and flakes-like appearance of all synthesized powders.

1. Introduction

Inorganic blue pigments are widely used in industry to bring color to plastics, paints, fibers, papers, rubbers, glass, cement, glazes, ceramics, and porcelain enamels [1]. The traditional source of blue color in inorganic pigments depended on cobalt ion [2]. As cobalt is scarce and expensive, spinel type $Co_xMg_{1-x}Al_2O_4$ ($0 < x < 1$) allows for a reduction of the production costs and environmental problems [3]. Moreover owing to the high mechanical resistance, high thermal and chemical stability, and low temperature sinterability of spinel-type oxide materials, $Co_xMg_{1-x}Al_2O_4$ feels a need for qualified nanoinorganic blue pigment [4].

In recent years, a variety of techniques, such as coprecipitation [5], solid state reaction [6], hydrothermal synthesis [7], and sol-gel [8] and combustion syntheses [9], have been developed and successfully used for the preparation of pure spinel powders. The synthesis route is very important for determining the final properties of inorganic pigment such as color, particle size, and chemical and thermal stability. The liquid combustion method has the advantage of preparing crystalline powders with nanosize and high purity at low temperatures [10]. In this work nanocrystalline $Co_xMg_{1-x}Al_2O_4$ spinel pigment has been synthesized via low-temperature combustion route employing β-alanine as a novel environmentally benign fuel [11] and characterized by applying different techniques.

2. Materials and Methods

2.1. Powder Synthesis. Merck (Germany) analytical reagents were used as raw materials: cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), and β-alanine ($C_3H_7NO_2$). An aqueous solution containing Mg(II), Al(III), and Co(II) metal ion salts and fuel was heated at 60°C under continuous stirring. After 1 h, the temperature was raised to 80°C, and the mixture was stirred for several hours until a pink-reddish gel was formed. The used ratio M(II)/Al(III) {M(II) = Mg and Co} is 0.5, and M_{total}/β-alanine {M_{total} = M(II) and Al(III)}was 4 according

to the following equation:

$$(1-x)\,Mg(NO_3)_2 \cdot 6H_2O + xCo(NO_3)_2 \cdot 6H_2O + 2Al(NO_3)_3 \cdot 9H_2O + 4C_3H_7NO_2 + 5O_2 \longrightarrow Co_xMg_{1-x}Al_2O_4 + 12CO_2 + 38H_2O + 6N_2 \quad (1)$$

The blue mixed oxide has been obtained after a heat treatment of the gel precursors at T = 800°C for 1 h, with a heating rate of 30 K/min in an open furnace in air atmosphere.

2.2. Characterization Methods. X-ray diffraction patterns were recorded using a D_4-BRUKER diffractometer (Germany) by Cu Kα radiation at 20 KV and 30 mA. A Philips XLΦ-30 scanning electron microscope (SEM Tech Solutions, North Billerica, MA, USA) was used to observe the morphology of nanoparticles. The infrared spectra of the powders were taken in a Thermo Scientific Nicolate iS 10 FT-IR (USA) equipment, in the 4000–400 cm^{-1} region. The elemental analysis of the powders was performed by electron dispersive X-ray analysis (EDAX) (FEI Inspect S Eindhoven). Diffuse reflectance spectra and CIE $L^*a^*b^*$ chromatic coordinates were determined using a Varian UV-VIS spectrophotometer (Cary 300 Bio, Mulgrave, VIC, Australia) under D65 illuminant and 10° standard observer angle.

3. Result and Discussion

Figure 1 depicts the XRD patterns of the samples from the $Co_xMg_{1-x}Al_2O_4$ system heat treated at 800°C. At this temperature for all the values of x studied, the characteristic peaks of the spinel structure were noticed, according to the JCPDS files 21-1152 and 10-0458, for $MgAl_2O_4$ and $CoAl_2O_4$, respectively. The patterns did not show the presence of secondary phases. The development of the spinel phase at a relatively low temperature indicates one advantage of this synthesis route, as compared with other methods [12].

Table 1 shows the crystallite sizes of the calcined pigments $Co_xMg_{1-x}Al_2O_4$ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1) based on the XRD patterns using the Williamson-Hall method: $B{\cdot}\mathrm{Cos}(\theta) = K\lambda/D + \eta{\cdot}\mathrm{Sin}(\theta)$, where D is the crystallite size, B is the full width at half-maximum intensity (FWHM) of the diffraction line, θ is the Bragg angle, K is a dimensionless shape factor with a value close to unity and ranges from 0.8 to 1.39, λ is the X-ray wavelength (0.15418 nm), and η is related to strain. Based on the XRD data for x = 0.8, when we plotted $B{\cdot}\mathrm{Cos}(\theta)$ versus $\mathrm{Sin}(\theta)$ we got a straight line with intercept 0.00907 ($Y = 0.0004X + 0.00907$); therefore the crystallite size (D) was estimated to 17 nm. Same measurements led to calculate the crystallite sizes of other samples with different x values by applying the Williamson-Hall method (Table 1). All samples had crystallite sizes bellow 30 nm and the smallest size was obtained for x = 0.2 (6.8 nm). It seems that low level of cobalt content decreases the crystallite size of nanopigments. Experimental results evidenced that Co enrichment has different effects on crystallite sizes of Co^{2+}-doped spinels synthesized via combustion method in the presence of various fuels [13]. According to Ionas et al., β-alanine is a suitable fuel for $Mg(NO_3)_2$, while urea is preferred for $Co(NO_3)_2$. Employing mixtures of urea and β-alanine to prepare $Co_xMg_{1-x}Al_2O_4$, resulted in smaller crystallite sizes in high cobalt contents [11]. It seems that applying β-alanine as a sole fuel in our work resulted in higher combustion temperatures and larger crystallite sizes in Co-enrichment samples.

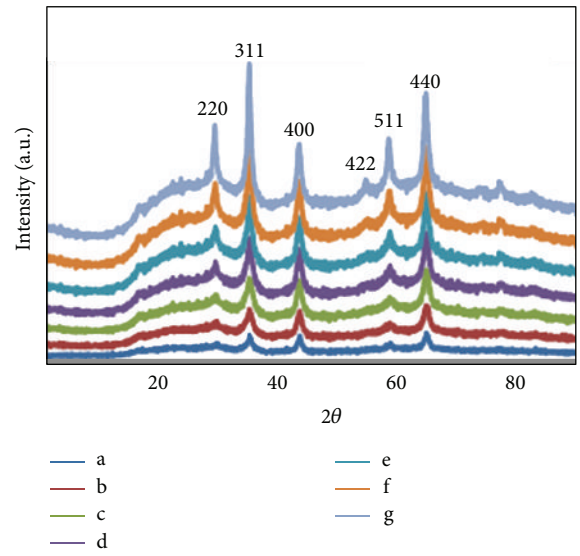


Figure 1: Powder X-ray diffraction patterns of $Co_xMg_{1-x}Al_2O_4$ {x = 0(a), 0.1(b), 0.2(c), 0.4(d), 0.6(e), 0.8(f), and 1(g)} calcinated for 1 h at 800°C.

The chromatic coordinates (L^*, a^* and b^*) are also displayed in Table 1. It can be seen that the lightness, L^*, decreases with the increase of the Co content, pointing out the formation of darker pigments. The coordinate a^* is kept negative for all the samples, indicating a slight green condition. In terms of the b^* coordinate, negative values lead to a blue color for all the samples, except for x = 0 which excludes of Co^{2+} ions, with the tendency of showing the highest blue intensity for the high level of Co content. These results confirm the visual observations (Figure 2) which indicate that the appearance of intense blue color in pigment powders occurs for x = 1 and 0.8; however as low Co^{+2} content is preferred, x = 0.1 is recommended. There are different reports about the relation between the cobalt content and observed blue colors of other spinel type pigments. According to de Souza et al. higher Co enrichment leads to darker blue pigments, but the most negative values of b^* are observed in medium cobalt content samples in the $Co_xZn_{1-x}Al_2O_4$ system [13].

The x-dependence of lattice constant which is calculated by applying the XRD data is depicted in Table 2. Accompanying the decreasing tendency shown in the theoretical values for the lattice parameters of $CoAl_2O_4$ (8.106 Å) and $MgAl_2O_4$ (8.086 Å), the experimental values of lattice parameters gradually decrease upon the Co substitution by Mg, from 8.101 Å to 8.087 Å. Such reduction in the lattice constants in agreement with the values from JCPDS files 10-0458 and 21-1152, for $CoAl_2O_4$ and $MgAl_2O_4$, respectively, confirmed

FIGURE 2: Various colors for $Co_xMg_{1-x}Al_2O_4$ {x = 1(a), 0.8(b), 0.6(c), 0.4(d), 0.2(e), 0.1(f), and 0(g)}.

the successful occupation of magnesium ion instead of cobalt ion in tetrahedral sites. Similar results have been reported by de Souza et al. [13].

Figure 3 shows the results of the electron dispersive X-ray analysis (EDAX) for $Co_{0.8}Mg_{0.2}Al_2O_4$ sample. From the elemental analysis in combination with the results obtained from EDAX, the stoichiometry of the precursor heated at 800°C for 1 h was found to be 7.87% (atom percent) of Co, 2.12% of Mg, 23.44% of Al, and 65.97% of O. This observation, corroborated with the XRD analysis result on

Table 1: Crystallite size and colorimetric analysis of the calcined samples.

Sample	Crystallite size (nm)	L^*	a^*	b^*	ΔE
$CoAl_2O_4$	27	41.5	−10.6	−30.815	52.765
$Co_{0.8}Mg_{0.2}Al_2O_4$	17	43.2	−14.5	−18.125	49.040
$Co_{0.6}Mg_{0.4}Al_2O_4$	13	45.7	−12.2	−6.171	47.72
$Co_{0.4}Mg_{0.6}Al_2O_4$	18	50.4	−12.0	−6.213	52.23
$Co_{0.2}Mg_{0.8}Al_2O_4$	7	63.7	−10.6	−10.612	65.52
$Co_{0.1}Mg_{0.9}Al_2O_4$	9	71.4	−8.1	−12.57	73
$MgAl_2O_4$	8	81.8	−0.31	2.501	81.93

Table 2: Lattice parameter of $Co_xMg_{1-x}Al_2O_4$ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1), heat treated at 800°C.

Sample	Lattice parameter/A°
$CoAl_2O_4$	8.101
$Co_{0.8}Mg_{0.2}Al_2O_4$	8.097
$Co_{0.6}Mg_{0.4}Al_2O_4$	8.096
$Co_{0.4}Mg_{0.6}Al_2O_4$	8.094
$Co_{0.2}Mg_{0.8}Al_2O_4$	8.090
$Co_{0.1}Mg_{0.9}Al_2O_4$	8.089
$MgAl_2O_4$	8.087

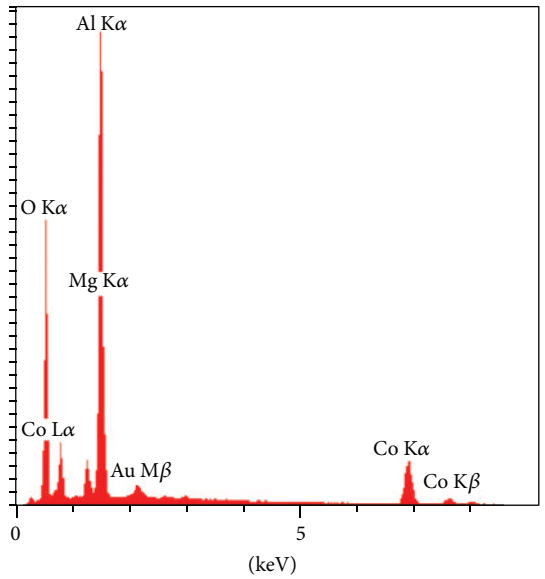


Figure 3: X-ray emission pattern of $Co_{0.8}Mg_{0.2}Al_2O_4$ powder and its elemental composition.

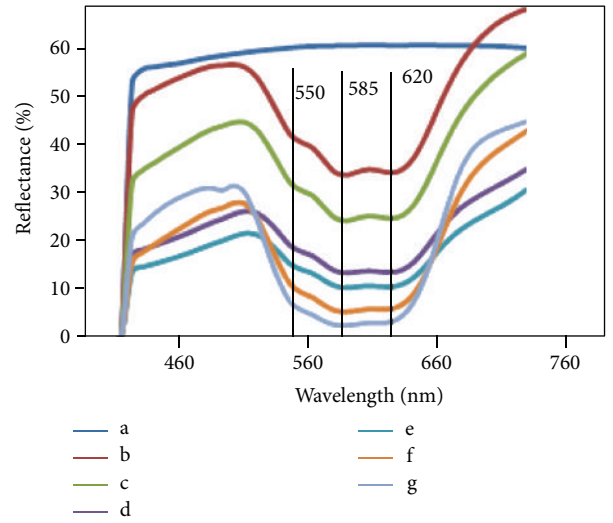


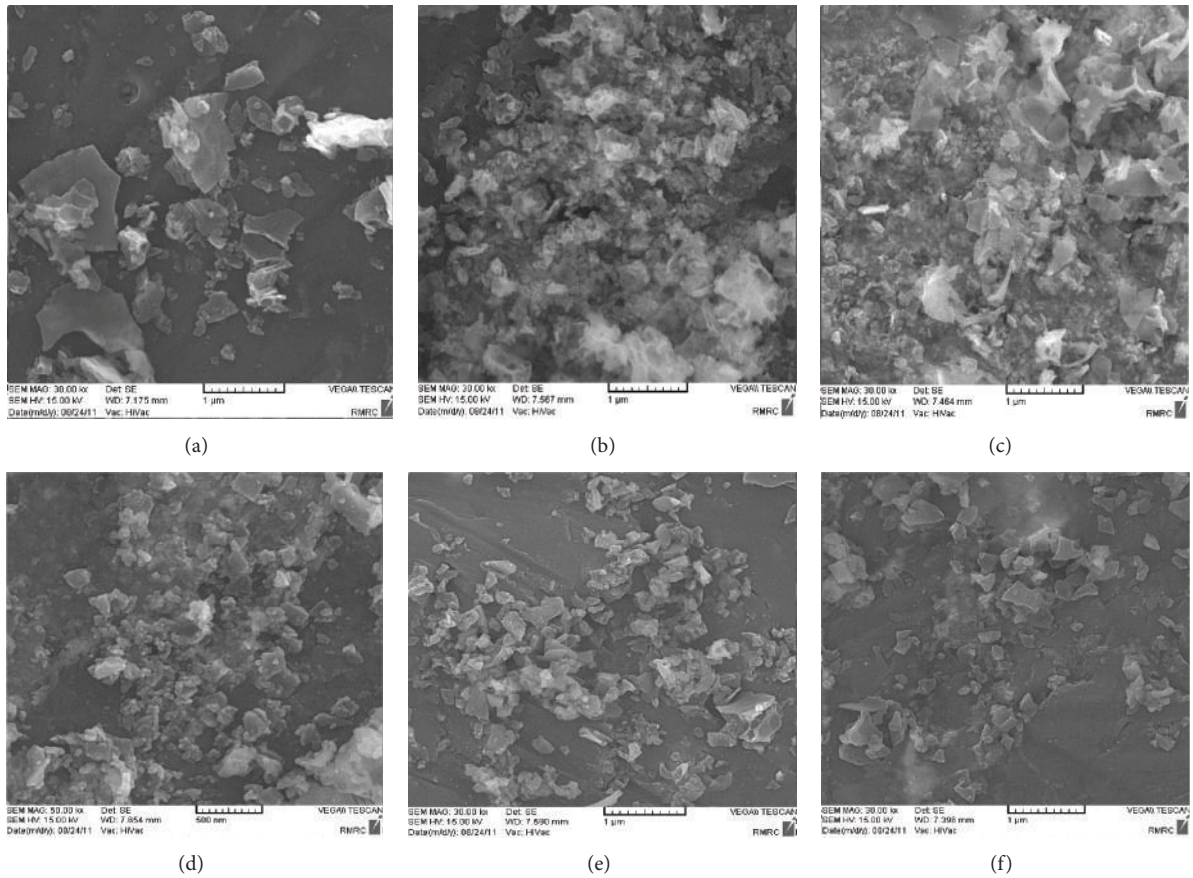
Figure 4: Diffuse reflectance spectra for the calcined powders of $Co_xMg_{1-x}Al_2O_4$ {x = 0(a), 0.1(b), 0.2(c), 0.4(d), 0.6(e), 0.8(f), and 1(g)}.

the calcined powder, indicates the formation of the designed spinel with desired chemical composition. Same results have been obtained for other values of x, too.

Diffuse reflectance spectroscopy (DRS) (Figure 4) indicates the appearance of three bands centered at approximately 550, 580, and 620 nm, which are attributed to the spin-allowed $^4A_2(F) \rightarrow {}^4T_1(P)$ transition of the Co^{2+} ions in tetrahedral sites. Same results were reported in the spectroscopic characterization of $CoAl_2O_4$ coatings by Stangar et al. [14] and Zayat and Levy [15].

SEM characterization of the powders (Figure 5) revealed a homogeneous microstructure and a similar morphology (flakes-like appearance) of all powders, similar to the reports of Ionas et al. for the preparation of $Mg_{1-x}Co_xAl_2O_4$ (x = 0.1–0.3) blue pigments by applying mixtures of fuels [11]. The decrease of the agglomeration degree for lower cobalt content (x = 0.2 and 0.1) is obvious.

In previous reports, pure and crystalline $Mg_{1-x}Co_xAl_2O_4$ powders were obtained only after annealing the as-prepared amorphous powders at high temperatures [16, 17]. Few reports on this topic show that the preparation of same ceramic pigments involves annealing at 1400°C for 3 h [4]. Even applying new methods such as sonochemical synthesis requires heating treatment at 1000°C at least for 2 hours for the formation of pure cobalt aluminate spinel phase [18]. Generally, increasing temperature treatment increases the crystallite sizes of powders [19–22]. So preparation of single phase spinel nanoparticles at lower temperatures is the advantage of our liquid combustion method and makes it technically simple and cost effective. In our previous work



(a) (b) (c)

(d) (e) (f)

Figure 5: SEM images of the calcined powders of $Co_xMg_{1-x}Al_2O_4$ {x = 1(a), 0.8(b), 0.6(c), 0.4(d), 0.2(e), and 0.1(f)}. The scale is in 1 micrometer.

applying starch instead of β-alanine resulted in the formation of black and grayish blue nanopigments for most values of x in the preparation of $Co_xMg_{1-x}Al_2O_4$ [23]. It seems that applying β-alanine improves the presence of tetrahedrally coordinated Co^{2+} ions in the spinel lattice.

4. Conclusions

Blue inorganic nanopigments $Co_xMg_{1-x}Al_2O_4$ (x = 0.1, 0.2, 0.4, 0.6, 0.8, and 1) have been prepared, via a combustion process using stoichiometric amounts of corresponding metal nitrates and β-alanine as an environmentally benign fuel. Relatively low synthesis temperature was employed, once the single and pure spinel phases were identified for all nanopigments by XRD and EDAX analyses. SEM micrographs revealed a homogenous flakes-like microstructure with a tendency to reduce the agglomeration degree for lower cobalt contents (x = 0.2 and 0.1). Appearance of bands around 550–630 nm in diffuse reflectance spectra confirmed the presence of Co^{2+} ions in tetrahedral sites of the spinel structure. CIE $L^*a^*b^*$ chromatic coordinates indicated that the blue color was obtained for all nanopigments. Although the cobalt enrichment increases the intensity of blue color, low Co^{2+} content (x = 0.1) is recommended in order to reduce the cost and environmental problems. These facts reveal that β-alanine can be employed lonely as a novel and environmentally benign fuel to prepare $Co_xMg_{1-x}Al_2O_4$ (x = 0.1, 0.2, 0.4, 0.6, 0.8, and 1) spinels in an efficient, low temperature combustion method. These spinel nanopigments with intense blue color are thermally and chemically stable and offer potential industrial applications.

Acknowledgments

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