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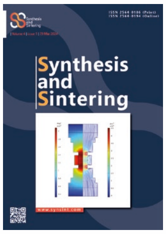
Synthesis and Sintering

ISSN 2564-0186 (Print), **ISSN** 2564-0194 (Online)



Review article

Synthesis and doping of high-temperature resistant spinel nano pigments: A review

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ABSTRACT

Spinel nano-pigments are high-performance super small particles, combining the stable properties of the spinel structures with the high activity of Nanomaterials. While entrapment of highly toxic yet beautiful chromophores in the spinel structure diminishes the toxicity and improves the thermal resistance, a high surface area provided by the nano-scale pigments results in a uniform bright coating with a sufficiently high color strength and enhanced light transmission. Although the spinel nano pigments are promising for the coating and ceramic industries, the applications are limited, mostly due to the required high sintering temperature. Various synthesis processes have been tried for these pigments with the sol-gel method being the most frequent one. Many elements have been considered as dopants for these spinel systems to enhance, change, or improve the optical and physical properties. This comprehensive review aims to summarize the work done in this field, covering almost 20 years of research dedicated to the synthesis and doping of spinel nano pigments.

KEYWORDS

Spinel
Nano pigments
Doping
Synthesis
High-temperature resistant

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1. Introduction

Pigment comes from the Latin word, pigmentum. Ceramic pigments are defined as insoluble inorganic coloring particles, mostly used in molten glasses (glazes) for decorations, which require high chemical and thermal stabilities [1, 2]. In addition to aesthetic purposes, inorganic pigments also increase corrosion resistance and surface hardness [3]. High tinting strength is a crucial factor for the pigments, as seen in the fine particles with high specific surface areas [4]. Optical properties of pigments including light scattering, reflection, and absorption are governed by the refraction index, wavelength, particle size, and morphology. Reducing the pigment particle size to the nano-scale brings new size-dependent optical properties with the most dramatic changes in the color at 0.1–10 nm [5]. Nano-sized ceramic pigments (1–100 nm) with high specific surface areas, as a characteristic property of Nanomaterials, can cover the surface more efficiently and could be more homogenously dispersed in the binders and glazes [6]. Being smaller than the visible light wavelength, nano pigments can also contribute to the production of transparent coatings with enhanced UV shielding for many purposes, including cosmetic sunscreens [7]. Potentially, nano pigments can have a massive market, but some problems like unwanted agglomeration have delayed the expansion of applications.

Mixed metal oxides are a category of inorganic pigments, defined as the solid solutions of oxides with various crystalline structures including hematite, rutile, normal and inverse spinels, etc. The spinel materials have a general formula (AB_2O_4: A^{2+}, B^{3+}, O^{2-}) and take their name after the spinel material, $MgAl_2O_4$. Spinel pigments have not shown any acute toxicity in the investigations. These compounds are chemically inert without any harmful bioactive materials and are considered nontoxic substances. Because the toxic heavy metals are fixed within a compact structure and are not available for any external

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Received 23 November 2023; Received in revised form 10 February 2024; Accepted 14 February 2024.

https://doi.org/10.53063/synsint.2024.41191

reactions [8]. In a spinel, the oxygen ions form a close-packed cubic structure with 32 octahedral and 64 tetrahedral sites but only one-fourth of them are occupied with tri- and di-valent cations, respectively. As said, in a normal spinel, the tetrahedrals are occupied with divalent cations and the octahedrals with the trivalent ones. But in a reverse spinel, the divalent ions go to the octahedrals, and the trivalent ions are seen in both sites [9]. Many factors can determine the occupancy of cations in a spinel structure, including the preparation method, the heat-treatment parameters, the crystal field effect, the ionic concentration, coordination, and oxidation states [10]. Low-temperature sinterability, high mechanical strength, and high thermal and chemical stabilities have made the spinel materials suitable for pigment applications. Furthermore, the incorporation of new chromophores in the spinel structure (doping) is a straightforward process, providing the possibility of obtaining a wide new range of colors [11].

Various synthesis methods have been applied to obtain nano spinel pigments, including the Pechini method [12–14], Self-propagating high-temperature synthesis (SHS) [15–23], co-precipitation [24–27], polyacrylamide gel method [28–33], sol-gel [34–59], hydrothermal [60–72], the flame spray pyrolysis [73, 74], and the microwave combustion [75]. As in this approach, controlling the size and obtaining a pure spinel phase is mandatory, the selected synthesis method must satisfy these requirements. So, the synthesis and heat treatment parameters must be precisely adjusted. In this review, some groups of spinel pigments are introduced. Then, various synthesis methods, reported for the spinel nano pigments, are discussed. Finally, the effects of various dopants on the coloring behavior of the spinel nano pigments are reviewed.

2. Classifications of spinel pigments

Inorganic pigments constitute two major components: matrix and chromophore. The matrix which is usually a simple oxide (Al_2O_3, TiO_2, etc.) plays an important role in the formation of a crystalline structure. Optical, morphological, chemical, and physical properties of the pigments determine their quality. The mentioned properties, themselves, are affected by the purity, crystal structure, and chemical composition. The chromophore ion, mostly a transition metal, is the main coloring component that is emplaced within the matrix, capable of producing various shades of colors. Spinel pigments are a group of inorganic pigments with the formula of AB_2O_4 which can have normal, fully or partially inverse spinel structures. These pigments are known for high staining capacity, high abrasion resistance, high chemical/thermal stability, high opacity, and uniformly small particles [76]. In addition to the crystal structure, spinels can be classified based on the matrix type: aluminates (Al), chromites (Cr), ferrites (Fe), vanadites (V), manganites (Mn), cobaltates (Co), and gallites (Ga) [80]. The first three major groups include the most cited spinel pigments in the literature, which are introduced in Table 1 and the following subsections.

2.1. Aluminates

Aluminate pigments are a major group of spinel pigments with a colorless alumina matrix. Cobalt aluminate with cobalt oxide as its colorant is the most applied aluminate-based pigment in the literature [10, 15, 22, 31–33, 36, 47, 49, 56–58, 60–62, 65, 69, 72, 76]. Obtained from a mixture of cobalt (II) and aluminum oxides in a normal spinel structure, cobalt aluminate ($CoAl_2O_4$) is a thermally/chemically stable pigment, able to preserve its color even in aggressive harsh environments. The major drawback of this pigment is its poor UV absorption, compared to the other high-performance pigments. $CoAl_2O_4$ is considered the most durable commercial blue pigment [85]. The oxidation states and coordinations of cobalt in the $CoAl_2O_4$ determine the pigment color. If the cobalt chromophores are fully emplaced in the tetrahedral sites of the spinel, the pigment color will be blue. However, the cobalt residence in the octahedrals results in a green hue [15].

Table 1. Some examples of spinel pigments with their chemical formula, spinel structure type, and color (obtained from the literature survey).

Pigment group	Composition	Chemical formula	Spinel structure	Color	Ref.
Aluminates	Cobalt aluminate	$CoAl_2O_4$	Normal/ inverse	Blue/greenish blue	[15, 21, 22, 31, 32, 34, 36, 47, 49, 54, 56, 60, 61]
	Copper aluminate	$CuAl_2O_4$	Inverse	Brown	[10, 37]
	Nickel aluminate	$NiAl_2O_4$	Partially inverse	Cyan	[77]
	Iron aluminate	$FeAl_2O_4$	Normal	Red-brown	[76]
	Manganese aluminate	$MnAl_2O_4$	Normal	Brown	[76]
Chromites	Cobalt chromite	$CoCr_2O_4$	Normal	Dark green, bluish green	[46, 48, 55, 74]
	Nickel chromite	$NiCr_2O_4$	Inverse	Black	[78]
	Copper chromite	$CuCr_2O_4$	Normal	Deep black	[18]
	Iron chromite	$FeCr_2O_4$	Normal	Brown-black	[79]
	Magnesium chromite	$MgCr_2O_4$	Normal	Black	[80]
Ferrites	Nickel ferrite	$NiFe_2O_4$	Inverse	Dark brown	[81]
	Zinc ferrite	$ZnFe_2O_4$	Normal	Yellow-brown/orange-brown	[81]
	Cobalt ferrite	$CoFe_2O_4$	Inverse	Black	[24]
	Manganese ferrite	$MnFe_2O_4$	Normal	Brown to black	[82]
	Magnesium ferrite	$MgFe_2O_4$	Inverse	Yellow-orange	[83, 84]

2.2. Chromites

Chromites are another group of spinel pigments with a green chromium (III) oxide matrix. Although these pigments are mostly seen in black or brown colors, only a few of them are green or green-blue. Some examples of the MCr_2O_4 pigments include cobalt, iron, and copper chromites with dark green, brown-black, and black colors, respectively [85]. It is worth mentioning that producing pigments with chromium (III) in their structures is also beneficial for health and environmental issues. In the free form, Cr(III) is easily oxidized into Cr (IV), which is a highly toxic carcinogen material for all living organisms, even in very low concentrations. So preserving chromium (III), the least toxic form of the element, in the compact spinel structure to avoid its oxidation is a safe preventive method [86].

Among the chromite pigments, nickel chromite ($NiCr_2O_4$) is a unique black ceramic pigment with a normal spinel structure, known for its high refractoriness and unique color stability in ceramic glazes. Nickel chromite has the lowest diffuse reflection coefficient (DRC), making it a good black pigment for aerospace and nuclear-related coating systems [78].

2.3. Ferrites

Ferrites constitute an iron (III) oxide-based matrix and a transition oxide colorant. Zinc, magnesium, zinc-chromium, and cobalt ferrites are some examples of this group with yellow-brown, red-brown, brown, and black colors, respectively [85]. The ferrite pigments are seen in both normal and inverse modes of the spinel structure. For example, nickel ferrite is an inverse spinel, because nickel ions prefer the octahedral site. But zinc ferrite has a normal spinel structure because zinc is located in the tetrahedrals [87]. In addition to being beautiful brown and black pigments, spinel ferrite nanoparticles have remarkable electric and magnetic properties [66].

3. Synthesis of spinel nano pigments

A system must be chosen to synthesize pure spinel pigments, where the spinel crystal has the highest formation rate. Also, the synthesis temperature must be selected carefully, as the low temperatures will not bring sufficient color brightness due to the incomplete spinel formation and a too-high temperature makes the cobalt-bearing pigments unstable [88]. Various synthesis methods have been applied to obtain nano spinel pigments. Among them, the wet chemical-based methods, especially the sol-gel process, are the most frequently reported ones. The mentioned methods provide precise control over the size and the chemical composition, critically necessary to obtain pure small-sized spinel particles. Some of the mostly applied synthesis methods for the spinel nano pigments are described in the following subsections.

3.1. Pechini method

The Pechini process is based on chelating the cations with a hydroxycarboxylic acid. The first recommended chelating agent was citric acid. Later, ethylenediaminetetraacetate (EDTA) was suggested as a better cross-linker. Because it could easily build a gel network with almost every metal. After the elimination of organic matter, nanoparticles are obtained. There are two fundamental reactions involved in the Pechini process: (a) chelation between citric acid and cations, and (b) polyesterification of the residual hydroxycarboxylic acid with glycol in a mild acidic solution [89].

Yongvanich et al. [12] used the Pechini process to obtain zinc-aluminum-chromium-oxide spinel nano pigments. After the dissolution of metallic salts in water, citric acid and polyethylene glycol were added as the chelating and gelation agents, respectively. The organic matter was removed by firing at 350 °C for three hours. The main calcination temperatures were 600, 800, 1000, and 1200 °C. The spinel amount in the sample sintered at 600 °C was lower than the results obtained from a solid-state method. The particle size ranged between 100–200 nm. The pigments showed a pinkish hue. Hedayati et al. [13] also selected the Pechini method to obtain spinel pigments in the cobalt-zinc-chromium-aluminum system. The obtained coatings from the synthesized pigments showed a high near-infrared solar reflectance. Bao et al. [14] also synthesized cobalt-magnesium-aluminum-iron oxide spinel pigments using a Pechini method. A single-phase composition was obtained at 900 °C. These pigments also had a high near-infrared solar reflectance, a criterion for application in cool coatings.

3.2. Self-propagating high-temperature synthesis

Self-propagating high-temperature synthesis (SHS) is a simple economical method for the fabrication of nanomaterials, benefiting from the exothermic reactions without any electrical power requirements [90]. A combination of this process with sol-gel is often used to synthesize high-purity ultra-small nanoparticles at relatively low temperatures. Spinel pigments have also been synthesized using this combined system [15–23]. Ali et al. [22] applied this method to obtain near-infrared reflecting blue cobalt aluminate nano pigments using different fuels such as glycine (G), malonic acid dihydrazide (M), and a mixture of G/M fuels. Aluminum and cobalt nitrates were dissolved on a hot plate. Then, the fuel was added to the solution. The heating was continued up to 200 °C, where the auto-combustion reaction occurred in the dried gel within a few seconds. The obtained pigments were annealed at 400–1000 °C to improve the crystallinity. The prepared cobalt aluminate spinel pigments were highly resistant to acids and bases. In another research [16], cobalt chromite pigments were synthesized by a single-step gel-combustion. 6-aminohexanoic acid was selected as the fuel. The obtained green pigments were thermally stable up to 1050 °C in a commercial frit.

3.3. Co-precipitation

In the precipitation method, various materials are often dissolved in a solution, where the product is precipitated after adding a precipitant agent. The precipitate is collected, washed, filtered, dried, and calcined at high temperatures. Controlling over particle size and composition is possible [91]. In a research study [92], the synthesized $COMgAl_2O_4$ spinel nano pigments via a coprecipitation combustion method had an average particle size of 24–35 nm. Ahmed et al. [27] used a combined co-precipitation combustion method to produce $CoMgAl_2O_4$ nano pigments. Urea was used as the fuel and the combustion temperature was 500 °C. The average particle size was in the range of 30–38 nm. Changing the calcination temperature affected the particle size and color of the product. The best blue color matching was obtained at 1200 °C. Also, Fernández-Osorio et al. [25] synthesized the ultra-small luminescent nano pigments with a particle size of about 9 nm using a coprecipitation method.

3.4. Polyacrylamide gel method

The polyacrylamide gel method is a promising approach for nanoparticle synthesis. In this method, the metallic reactants are homogenously distributed in a solvent. The polymerization reaction turns this solution into a gel network. The metal ions are trapped within the network formed by the crosslinking of the acrylamide and the methylene bis acrylamide (Fig. 1a). This gel restricts the particle growth during the heat-treatment step. A high-purity nanopowder is the final product of the process [93]. According to the literature, the polyacrylamide gel method has been successfully used for the synthesis of spinel nano pigments [28–33]. Rahimian et al. [28] reported the synthesis of the blue cobalt-zinc aluminate nano pigments with a mean particle size of 32 nm via a polyacrylamide gel method at a calcination temperature of 600 °C. Ahmadyari and Hassanzadeh-Tabrizi [30] synthesized cobalt chromite, nickel chromite, and nickel-cobalt chromite nano pigments using the polyacrylamide gel method. The obtained mean particle size was 22 nm, confirmed by the TEM. Jafari and Hassanzadeh-Tabrizi [31] obtained pure flaky cobalt aluminate nano pigments by the polyacrylamide gel method. Increasing the calcination temperature to 1000 °C resulted in the breakage of the layered structure, producing smaller flakes. Co^{2+} transitions in the tetrahedral sites of the spinel structure were the reasons for the three noticeable bands at 551, 590, and 628 nm in the UV-visible spectra.

In a comparative study, Xiong et al. [94] synthesized $ZnAl_2O_4$ nanopowder via the polyacrylamide gel and the microemulsion methods. Schemes of both methods are shown in Fig. 1a & b. Briefly, microemulsion is a stable oil-water-based immiscible mixture. Surfactant acts as a stabilizer for this system. The regular microemulsion systems for the synthesis of nanoparticles are based on water-in-oil mixtures with ultra-small micelles. The results showed that the nanoparticles obtained from the microemulsion method were finer and more uniform. $ZnAl_2O_4$ crystallite sizes were 21.7 nm and 26.3 nm, obtained from the microemulsion and polyacrylamide gel methods. According to the SEM images, the microemulsion-based and the polyacrylamide particles were in the size ranges of 10–50 nm and 30–100 nm (Fig. 1c & d).

3.5. Sol-gel

The sol-gel method is one of the most applicable approaches to obtaining nanoparticles. Many reports are found in the literature, applying aqueous or non-aqueous sol-gel for the synthesis of spinel nano pigments [34–59]. In this method, a sol is obtained from the

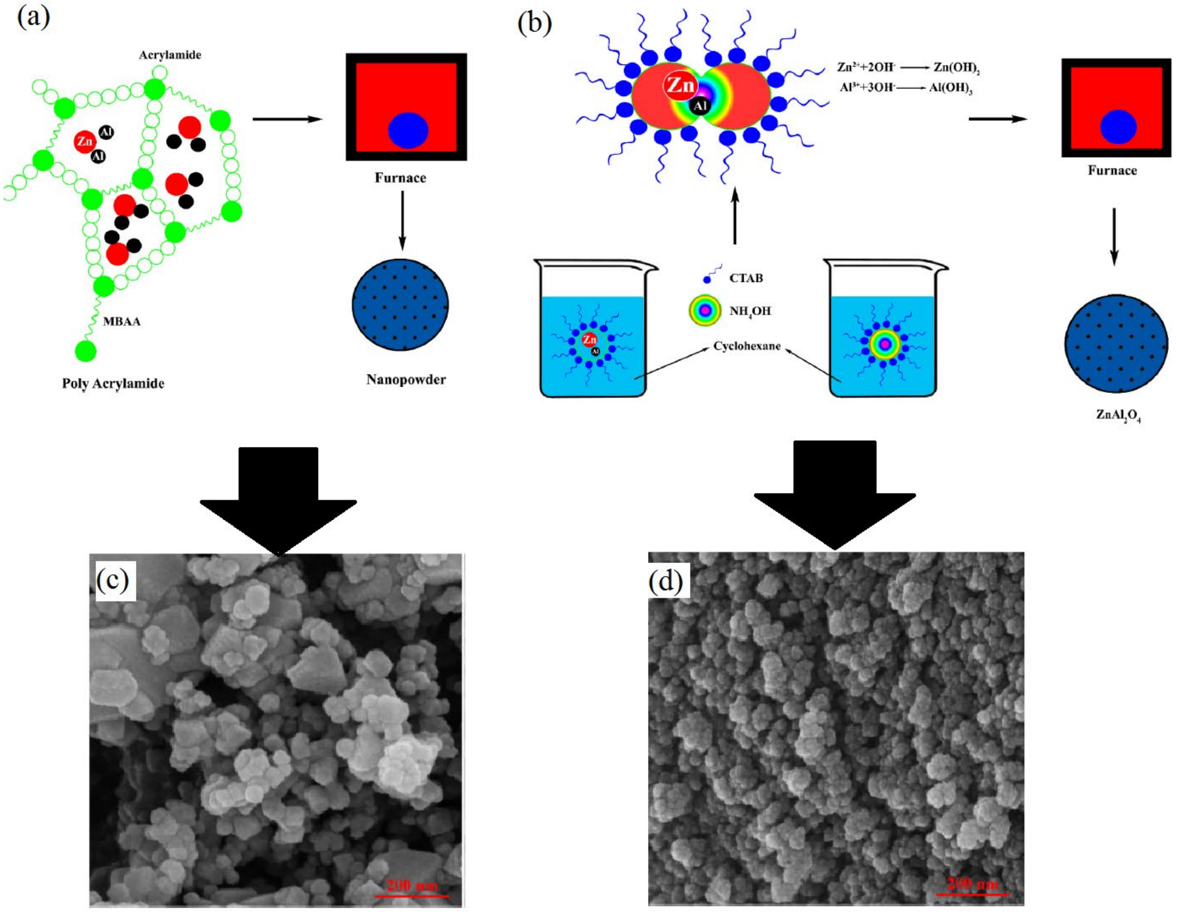

Fig. 1. a) A scheme of the polyacrylamide gel method, b) a scheme of the microemulsion method, c) the SEM image of its product: $ZnAl_2O_4$ nanoparticles, and d) the SEM image of its product: $ZnAl_2O_4$ nanoparticles. "© Reprinted from Ref. [94] with permission from Elsevier. All rights reserved".

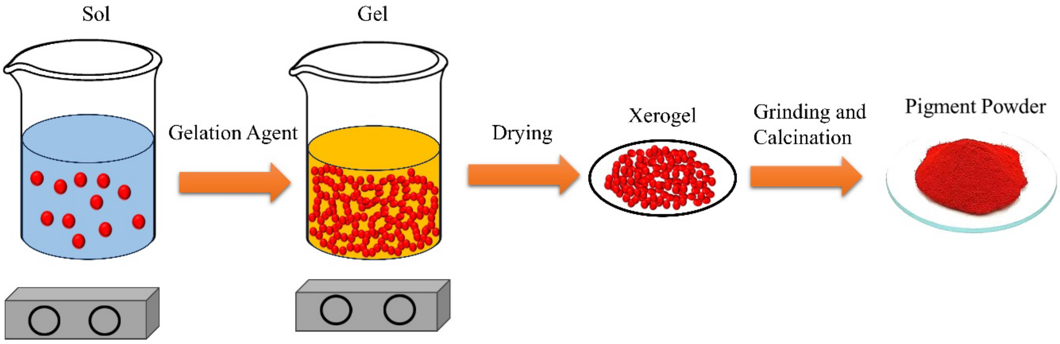

Fig. 2. General scheme of the sol-gel process for the pigment synthesis.

metallic salts which later turns into a gel through the evaporation of solvent. The obtained gel is dried and calcined according to a predefined heat-treatment program and a homogenous small-sized product is obtained (Fig. 2). Kurajica et al. [36] examined the effect of annealing temperature on the properties of cobalt aluminate nano pigments. The cobalt oxidation state changed with the temperature variations. A greenish color was seen below 700 °C due to the presence of Co^{3+}. Then a blue color was noticed, attributed to the presence of Co^{2+} above 700 °C. Salavati-Niasari et al. [37] reported the synthesis of copper aluminate nanocrystalline pigments using a modified sol-gel method. Solid intermediates were formed during the synthesis process, leading to a decreased atomic diffusion in the subsequent heat treatment. Ma et al. [39] applied a sol-gel solution combustion method to obtain $CuMn_2O_4$ nano pigments and the sample annealed at 500 °C for 1 h corresponded to the characteristic XRD patterns of the copper manganite spinel. Hcini et al. [41] prepared the nickel-manganese chromite spinel pigments using a mixture of the related metallic nitrate salts in the citric acid and distilled water as the sol. Ethylene glycol was the gelation agent. The obtained gel was collected, dried in an oven, granulated in air, calcined at 600 °C for 24 hours, ground, and the calcination process continued at 800 °C for 24 h. Abdel-Mohsen and Emira [42] prepared black $CoCuMnO_x$ spinel nano pigments with an average particle size of 10–80 nm using a sol-gel approach. The obtained pigments showed a low reflection and a high absorption in the visible light. Rani et al. [59] could synthesize the magnesium chromite nano pigments with an average particle size of 20–71 nm using an aqueous sol-gel method. In another study [43], $CoFe_2O_4$, $NiFe_2O_4$, and $ZnFe_2O_4$ nanoparticles were obtained by an aqueous sol-gel method. The nature of the transition metals affected the obtained nano ferrite particle size. Jabbar et al. [47] evaluated the effects of annealing temperature and various complexing agents, including glycine, citric acid, and polyacrylic acid on the structure and optical properties of the sol-gel derived cobalt aluminate nano pigments. Dark green powders were obtained by calcination at 500 °C for 5 h, but no spinel phase was noticed. A blue normally structured spinel nanopowder was formed at 900 °C and the polyacrylic acid was chosen as the optimum complexing agent, resulting in quasi-spherical particles with an average size of 20–40 nm. Increasing the calcination temperature led to particle growth, agglomeration, and even sintering step by step.

In a comparative study, Grazenaite et al. [48] synthesized cobalt chromite ($Co_{1-x}M_xCr_2O_4$, M = Zn, Cu, and Ni) pigments using two different aqueous methods: sol-gel and sonochemical. In the sonochemical process, the stirred solution was irradiated with ultrasound for 2.5 hours in an argon atmosphere. Then, the obtained precipitates were centrifuged, washed twice (first with water, then with acetone), and dried. Heat-treatment conditions were the same for both methods (600, 700, and 800 °C; 3 h; 10 °C/min). SEM micrographs of sol-gel and sonochemical-derived $CuCr_2O_4$ samples at various temperatures (600, 700, and 800 °C) are shown in Fig. 3. As seen, the platy agglomerates with a size range of 200–400 nm covered with fine particles were obtained using the sol-gel method at 600–700 °C (Fig. 3a & b), while fine particles are formed at 800 °C with a narrow particle size distribution (150–200 nm) (Fig. 3c). In the sonochemical process, the particle morphologies were almost identical at all temperatures (Fig. 3d–f) (composed of spherical particles). Agglomeration started at 800 °C (Fig. 3f). The authors [41] claimed that the crystallinity was higher in sol-gel samples.

3.6. Hydrothermal

The hydrothermal method is a facile way to synthesize super-small particles from homogenous solutions under high pressures and temperatures. This method is frequently reported for the synthesis of nano spinel pigments [60–72]. Because the particle size and morphology are easily controlled. Almost two decades ago, an early work [65] reported obtaining the nanosized heat-resistant cobalt aluminate pigments with a particle size of 70 nm and a maximum absorption at 600 nm. Nejati and Zabihi [66] prepared nickel ferrite nano pigments with an average particle size of 12–53 nm via a hydrothermal method and found that the crystallinity decreased when the surfactant was applied. Wang et al. [61] combined the emulsion method with the hydrothermal for the synthesis of cobalt aluminate pigments with an urchin-like morphology and investigated the effects of various amounts of pH and temperatures. Enhancing the pH amounts from 8.24 to 11.18 resulted in a decreased blue tone intensity and an enhanced greenish one. On the contrary, a black pigment was obtained at a pH of 12.30. The hydrothermal temperature also had a determining role in the particle morphology. Recently, Tanveer et al. [67] applied a sol-gel extended hydrothermal method to synthesize magnesium ferrites. In this method, the obtained gel was poured into an autoclave. After the hydrothermal process at 180 °C for 8 h, the solid product was collected, washed, and dried. Lu et al. [69] used two types of reactor: continuous and batch types, and only the former produced the spinel particles. The product of the batch reactor was a layered double hydroxide.

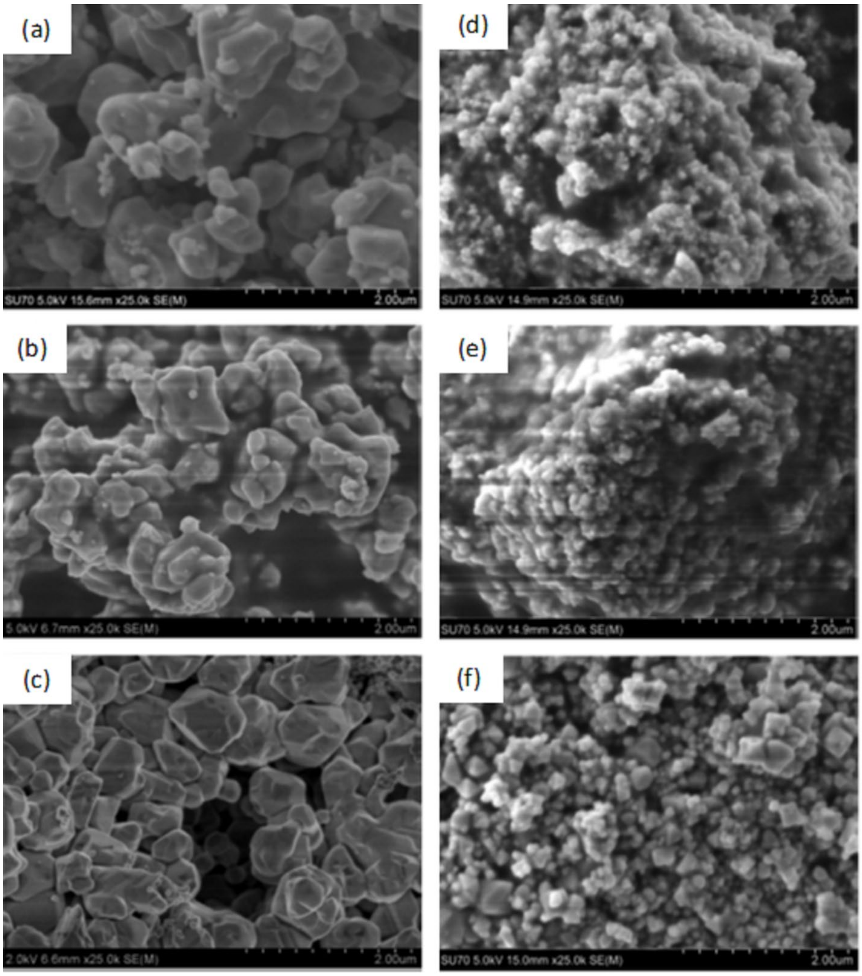

Fig. 3. SEM images of sol-gel and sonochemically-derived $CuCr_2O_4$ nano pigments at various calcination temperatures (a & d: 600 °C; b & e: 700 °C; and c & f: 800 °C). "© Reprinted from Ref. [48] with permission from Elsevier. All rights reserved".

3.7. Flame spray pyrolysis

Flame spray pyrolysis is an aerosol-based approach for the synthesis of nano-particles. This process provides precise control of the chemical composition. In this method, the prepared aerosol is ignited in a chamber using two horizontal torches (Fig. 4). Granados and Baena [74] synthesized cobalt chromite nano spinel pigments via FSP and a conventional solid-state method and compared the results. The FSP-derived pigments had a higher brightness and reflectance. In another study, Granados et al. [73] obtained zinc-cobalt aluminate nano pigments via the FSP method. The combustion of the aerosolized solutions rapidly resulted in the formation of nanoparticles with an average particle size of 26–31 nm. According to the TEM results, the morphology of the obtained nanoparticles was spherical and some faceted particles were also seen as a result of high crystallinity.

3.8. Microwave combustion

The microwave combustion method is a fast heat-treating process to obtain ultra-small nanoparticles at a lower temperature in a short duration. The high speed of this process does not allow the particle growth. Khattab et al. [75] used this process to synthesize cobalt-magnesium-aluminum oxide spinel nano pigments. The starch was used as the fuel and the chloride salts were the reactants. The calcination was performed at three different temperatures: 400, 550, and 800 °C. The obtained pigments had an average crystallite size between 35–100 nm.

A microwave-assisted sol-gel process was applied for the preparation of cobalt aluminate blue nano pigments [56]. The optimum microwave time was 15 min and an intense blue color was obtained. The final $CoAl_2O_4$ product had a quasi-spherical morphology with a mean particle size of 60 nm. A prolonged microwave time enhanced the powder crystallinity. The authors [56] claimed that the microwave heat treatment was a clean, fast, and reproducible approach that could be extended to the whole family of cobalt spinels.

4. Doping the spinel nano pigments

A partial replacement of the elemental constituents of the pigments with new chromophores of the same valence is called doping, a widely applied method to create new colors, shades, or even various novel properties in the product. Incorporation of new chromophores in the spinel structure (doping) is a straightforward process, providing the possibility of obtaining a wide new range of colors [11]. Numerous

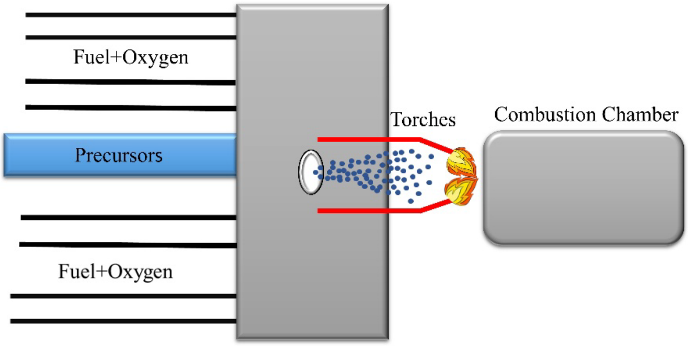

Fig. 4. A scheme of the flame spray pyrolysis method.

new coloring systems have been obtained using this method. Some examples are included in the following.

Chromium is frequently used in the doping systems. In a study [12], a partial replacement of aluminum with chromium in the octahedral sites of $ZnAl_2O_4$ created a pink color. Zhang et al. [57] investigated the co-additions of Cr^{3+}, Zn^{2+}, and Sm^{3+} to the cobalt aluminate and observed a change in the ion occupancies in the structure, resulting in a yellow-green color instead of green-blue. High amounts of chromium led to an absorption peak at 420 nm, attributed to the presence of chromium in the octahedrals. Sm also tended to occupy the octahedrals due to their big radius. Zn dopant substituted Co ions in the tetrahedrals and reduced the blue reflection. Shang-Pan et al. [64] doped chromium in the zinc aluminate. The band gap of the doped sample became smaller and a red shift was seen. Also, the photoluminescence intensity decreased with an increased amount of chromium. Chromium only occupied the tetrahedral sites.

Cobalt is another famous dopant. Ahmed et al. [92] doped minor amounts of cobalt in the magnesium aluminate and obtained the bluest color at 1100 °C. Although cobalt enriched the blue color, Khattab et al. [75] suggested a low concentration of Co^{2+} due to economic and

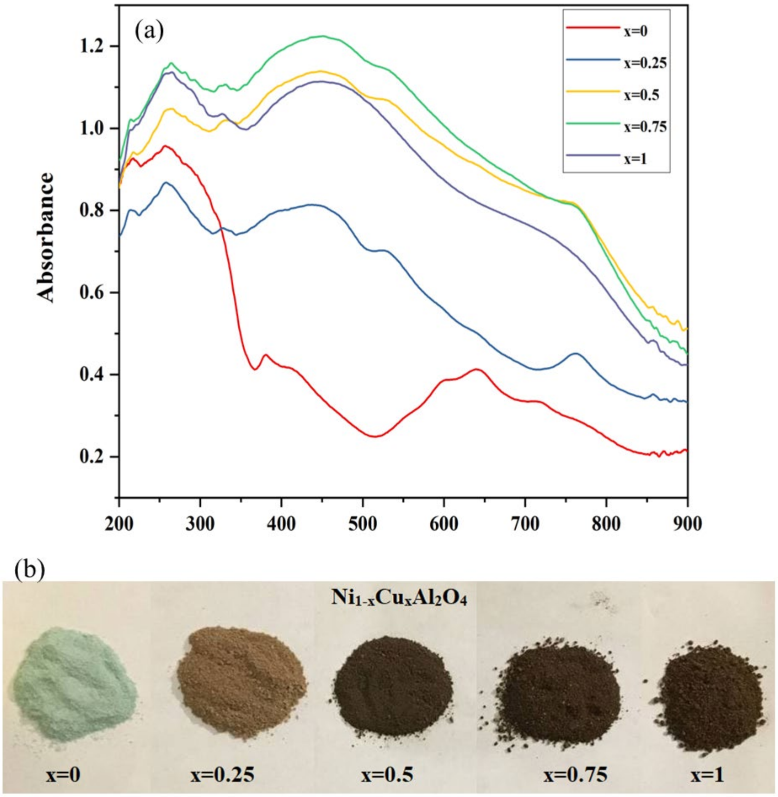

Fig. 5. a) UV-Vis spectra and b) photographs of $Ni_{1-x}Cu_xAl_2O_4$ "© Reprinted from Ref. [77] with permission from Elsevier. All rights reserved".

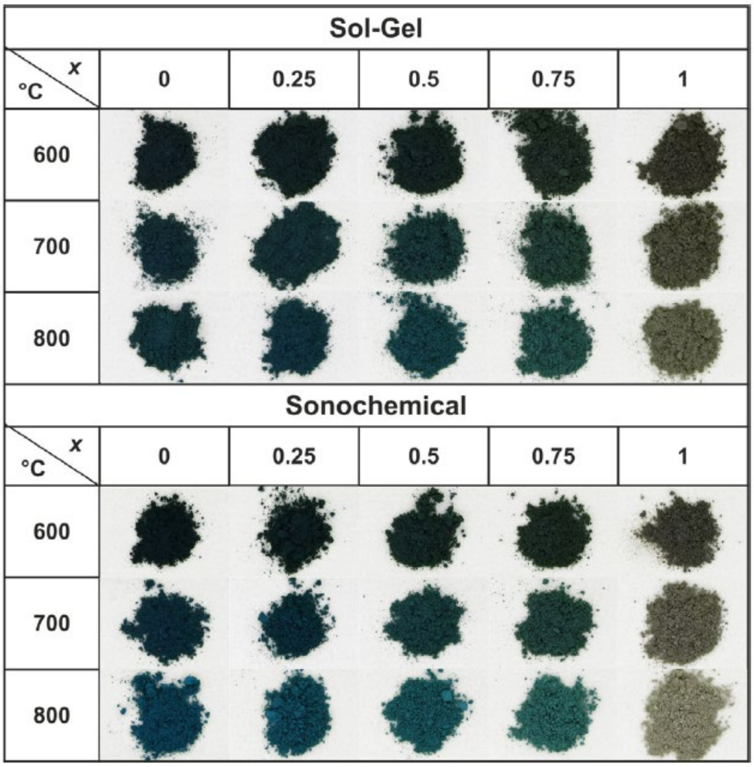

Fig. 6. Photographs of Zn-doped cobalt chromite pigments synthesized using sol-gel and sonochemical methods with various amounts of dopants and calcination temperatures. "© Reprinted from Ref. [48] with permission from Elsevier. All rights reserved".

environmental issues. Surprisingly, Fernández-Osorio et al. [26] observed a pink color in the cobalt-doped zinc aluminum with an average particle size of 10 nm. This different color was related to the incorporation of cobalt in the octahedral sites instead of the common tetrahedrals.

Nickel is widely used as a dopant in the spinel systems. Ahmadiyari and Hassanzadeh [30] doped nickel in the cobalt chromite pigments and investigated the effects of nickel incorporation on the optical properties, morphology, and crystal structure. Nickel in the cobalt chromite structure increased the brightness, the greenness, and the yellowness. It also decreased the particle size. Migrations of cobalt, nickel, and chromium elements between the octahedral and tetrahedral sites were also confirmed. Lu et al. [44] synthesized the $Zn_{1-x}Ni_xAl_2O_4$ pigments (x=0, 0.025, 0.05, 0.075, and 0.1) by a sol-gel method. Nickel ions were located in the tetrahedral sites. Increasing the Ni amount decreased the photoluminescence property. Saeed et al. [50] added various amounts of nickel to cobalt chromite. Equal amounts of cobalt and nickel produced a black color, but a higher Ni content gave greenish hues.

Copper is another common dopant in the spinel systems. Tan et al. [15] doped copper in the cobalt aluminate blue pigments. Increasing the amount of dopant resulted in a decreased blue intensity. But $Cu_{0.1}Co_{0.9}Al_2O_4$, synthesized at 700 °C was similar to the pure cobalt aluminate. Hassanzadeh-Tabrizi et al. [77] doped various amounts of copper in the structure of nickel aluminate nano pigments. The UV-Vis spectra and the photographs of the obtained pigments are shown in Fig. 5a & b. As seen, the absorption regions were at 230–430 nm and 590–670 nm, corresponding to the charge transfer between metal-oxygen and the tetrahedrally-coordinated nickel ion ($^3T1(F) \rightarrow {}^3T1$), respectively. The blue-green (cyan) color in the nickel aluminate is attributed to this tetrahedrally-coordinated ion. The addition of copper led to more absorption regions (430–580 nm) due to the simultaneous presence of copper and nickel ions in both tetrahedral and octahedral sites, resulting in various brown colors.

Grazenaite et al. [48] doped Zn, Cu, and Ni ions in the cobalt chromite, synthesized using sol-gel and sonochemical methods. Copper induced a black color, while nickel resulted in more greenish hues. The higher Zn-containing samples indicated a yellowish green. Images of Zn-doped pigments are shown in Fig. 6 with the most evident color changes. Gradual substitution of zinc ions in the spinel structure increased the lightness (L*) and b* values, resulting in an intensified yellow shade. Up to x=0.75 zinc additions, green colors were seen in the samples, but after that the blue shade disappeared and the colors became more yellowish. It was also proved that the dopant type (octahedral cation in this case) also had a determining role in the size and shape of the pigment particles. So, the copper (previously shown in Fig. 3), cobalt (ultrafine spherical nanoparticles), nickel (highly agglomerated), and zinc (microporous) doped cobalt chromites had various particle morphologies. Nickel-doped chromite was mostly heterogeneous, while zinc-doped chromite had a single phase.

5. Discussions

Synthesis of spinel nano pigments has some challenges, especially regarding the heat-treatment temperature. In a regular solid-state (ceramic) method, a mixture of carbonates, nitrates, or oxides is ground and calcined at a high temperature for a prolonged time to prepare spinel pigments [91]. Besides, solid-state methods are not suitable for the synthesis of nanoparticles, due to the unwanted grain growth and agglomeration at high temperatures [95]. The purity and homogeneity of the obtained product are yet questioned. The spinel powders obtained from the chemical methods are often purer, more homogenous, and more uniform with a narrower particle size distribution [96]. The products are a result of chemical reactions between metal nitrates, chlorides, etc. Co-precipitation is a chemical economic low-temperature synthesis method, also suffering from the agglomeration of particles during precipitation. Combining two synthesis methods to benefit from the advantages of both is a new strategy. For example, a combined co-precipitation combustion method would avoid the agglomeration problem during calcination, by obtaining fluffy fine particles from the fuel auto-combustion process at around 400 °C [27]. The microemulsion method is an efficient synthesis method, able to control the particle geometry, size, and morphology by the micelle composition [96]. This method can also be combined with other synthesis methods to obtain more magnificent morphologies and finer particle sizes. Wang et al. [61] used a combined hydrothermal-microemulsion-precipitation method for the synthesis of cobalt aluminate nano pigments with an urchin-like morphology. The new combined method did not have the shortcomings of a hydrothermal method such as low yield, high temperature, and prolonged duration requirements, resulting in an undesirably lighter color in the pigments and severe wear of the equipment. It also did not suffer from the unwanted carbon residue or uncontrollable morphology of the products in the combustion method, nor did it need the multiple washing processes in the precipitation process, wasting tonnes of pure water. Sol-gel and polyacrylamide gel methods with moderate calcination temperatures also have a unique control on morphology, purity, and microstructures but agglomeration is seen in some cases. A sol-gel extended hydrothermal method [67] or a microwave-assisted sol-gel process [56] can result in ultrafine spinel particles at lower temperatures in shorter durations. In conclusion, the combined synthesis methods are the optimum alternatives for the conventional ones and a step forward for the mass production of spinel nano pigments.

Doping is a widely applied method to expand the spectra of the pigment colors. Minor doping of metallic ions in the spinel structures significantly affects the optical and physical properties. The dopant occupancy is a determining factor in the resultant color. For example, the substitution of cobalt ions in the octahedral sites would induce a pink color instead of the regular blue (in the tetrahedrals) [26]. Doping can also affect the particle size and morphology [53]. Endless options for creating new spinels are available through doping and many new beautiful spinel pigments are expected in the future.

6. Concluding remarks

Spinel nanoparticles are considered high-performance pigments, due to their extraordinary thermal/chemical stability, magnificent color performance, facile synthesis, and doping. The small size of the particles brings a higher coverage and more intense colors as a result of an enhanced specific surface area and activity. The compact structure of spinels keeps the toxic yet beautiful chromophores inside, resulting in an enhanced color intensity and stability with less harmful effects on human health and the environment. Many methods have been used to synthesize spinel nano pigments with the sol-gel method being the most frequently reported one. The combined synthesis processes have also been successfully applied for spinel nano pigment synthesis, a step forward toward more industrialization. The occupation of metallic ions in the tetrahedral or octahedral sites has a determining effect on the resulting color. The dopants, that can change the original ionic coordination, represent the most significant effects on the observed hue and other optical properties.

CRediT authorship contribution statement

Rayehe Tavakolipour: Conceptualization, Writing - Original Draft, Project administration, Investigation, Supervision, Validation.
Reza Pournajaf: Writing – review & editing, Investigation, Resources.
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Data availability

The data underlying this article will be shared on a reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

Funding and acknowledgment

This research received no external funding. The authors have no acknowledgments to declare.

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