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Synthesis and characterization of Fe^{3+} doped $Co_{0.5}Mg_{0.5}Al_2O_4$ inorganic pigments with high near-infrared reflectance

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ABSTRACT

In this work, a series of near-infrared reflective inorganic pigments with a general formula $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were successfully prepared by Pechini-type sol–gel method. Comprehensive analyses were carried out to characterize the developed pigment powders including thermogravimetry and differential scanning calorimetry, X-ray diffraction, field emission scanning electron microscopy, ultraviolet–visible near infrared diffuse reflectance spectroscopy, and CIE-$L^*a^*b^*$ 1976 color scales. The results demonstrated that the single-phase $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ was synthesized at an optimum temperature of 900 °C. The resulting calcined powders have a well-developed cubic spinel structure. The substitution of Fe^{3+} for Al^{3+} in $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ changes the color from blue to black and the band gap shifts from 4.40 eV to 3.50 eV. And Fe doped pigments possess high near-infrared solar reflectance (>43%) in the range of 780–2500 nm. Therefore, these $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ powders have great potential in serving as cool pigments for building coatings.

1. Introduction

Solar radiation consists of ~5% UV radiation, 43% visible radiation and 52% near-infrared radiation (NIR; ~780–2500 nm). Solar energy is absorbed by buildings and paved surfaces, which leads to temperature rise of urban structures. These surfaces thereby warm up the surrounding, causing measurable ambient temperature rise [1,2]. This phenomenon, termed "urban heat island" (UHI), has been urging a drastic increase in the demand for energy, especially-energy consumed by central air conditioning systems in large buildings for cooling. One of the most effective methods to alleviate Heat Island Effect involves developing near-infrared reflective (NIR) pigments [3,4]. Induced by energy conservation, these pigments and the materials related have been gaining increased attention from researchers over the years. Particularly, one of these materials, the spinel-type oxide have been widely studied as attributed to the potential in electrochemical, catalytic and pigment applications [5–7]. The spinel-type oxides are generally formulated as $A^{2+}B_2^{3+}O_4$, in which the anions arranged in a cubic close-packed lattice that is classified as cubic. In addition, the A and B cations can occupy up to all the octahedral and tetrahedral sites in this lattice. Notably, there are two ideal structures of significance: normal spinel structure and inverse spinel structure [8]. For example, $CoAl_2O_4$ is one of the best known members of cobalt spinel-type oxides possessing various uses in ceramic, glass, paint industries; e.g., contrast-enhancing luminescent $CoAl_2O_4$ pigments for television tubes to produce Thenard's blue color [9].

One of the common methods for manufacturing pigment powder involves a solid-state reaction in which the oxides are mechanically ground at high calcination temperatures above 1200 °C for a considerable amount of time. Though the mentioned process is relatively uncostly, undesired byproducts can be produced due to lack of homogeneity indicated by larger and uneven grains in the final product as a result of the weak control [10–12]. Recently, scientists have proposed various novel wet-chemical synthetic routes that would alleviate this problem, which include sol–gel method (polymer precursor method) [13,14], low temperature combustion technique [15,16], polymer pyrolysis method [17,18], co-precipitation reaction [19,20], emulsion precipitation [21], and hydrothermal crystallization [22].

In this work, $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ pigment was synthesized using Pechini-type sol–gel method. Over the years, other kinds of compound powders, such as $LaFe_{1-x}Al_xO_3$ yellow pigment powder [2], $Zn_{1-x}Mg_xFe_2O_4$ [23], and $Co_xZn_{1-x}Al_2O_4$ [24], have also been synthesized using sol–gel method. This method has many great advantages as compared to others; e.g., lower energy-consumption, relatively low temperatures of synthesis, good stoichiometric and morphological control. Most importantly, these pigment powders exhibit higher homogeneity and stronger chemical activity.

$CoAl_2O_4$ is one of the commercially important materials which has super properties and extensively used as a pigment. But cobalt is scarce and expensive, thus increasing the production costs of cobalt-based pigments. Therefore, in the present work, Mg^{2+} for Co^{2+} ion substitution in the $CoAl_2O_4$ was done. On the other hand, spinel-type materials

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have attracted more attention from researchers. Due to their capabilities of accommodating different cations, they display various colors and tonalities [25]. Doping of Fe^{3+} for Al^{3+} in $Co_{0.5}Mg_{0.5}Al_2O_4$ changes the color properties of pigments. Therefore, in this paper, a series of NIR reflectance inorganic pigments with the formula $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ was used as a cool pigment. $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ samples were synthesized through a sol–gel route within a defined calcination temperature range. The crystal structure, NIR reflective chromatic properties, thermal and chemical stability were investigated.

2. Experimental

2.1. Materials and methodology

Pure and substituted $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) powders were synthesized using Pechini-type sol–gel method. The reagents used were cobalt nitrate ($Co(NO_3)_2\cdot 6H_2O$), magnesium nitrate ($Mg(NO_3)_2\cdot 6H_2O$), aluminum nitrate ($Al(NO_3)_3\cdot 9H_2O$), ferric nitrate ($Fe(NO_3)_3\cdot 9H_2O$), citric acid (CA) and ethylene glycol (EG). The CA/metal molar ratio was 3:1, while the CA/EG mass ratio was 3:2. Initially, citric acid was dissolved in distilled water under constant stirring at a temperature of 80 °C. Later, cobalt nitrate, magnesium nitrate, aluminum nitrate or ferric nitrate was added in stoichiometric proportion to the acid solution. After being kept at around 80 °C for 1 h, ethylene glycol was then added. The beaker was kept in an oven at 120 °C until a viscous gel was obtained. Then the gel undertook a preliminary heat treatment for 2 h at a temperature of 350 °C in an air atmosphere. Following the heat treatment, gas liberation during the combustion led to a partial degradation of the organic structure and its expansion. Finally, a fragile and black material, the powder precursor, is thus formed. Next the powder precursor was deagglomerated and underwent the final heat treatment at the desired temperature (600–1000 °C) for 6 h to eliminate the remaining organic material. All reagents used in this study were of analytical grade.

2.2. Characterization techniques

Thermal analysis of the powder precursor and synthesized pigments were characterized by thermogravimetry and differential scanning calorimetry (TG/DSC1, Mettler Toledo, Switzerland) under air in a temperature range of 50–900 °C at a heating rate of 20 °C/min. Tests were performed with approximately 10 mg of the sample contained in aluminum crucibles. Tabular α-Al_2O_3 was used as reference weight losses.

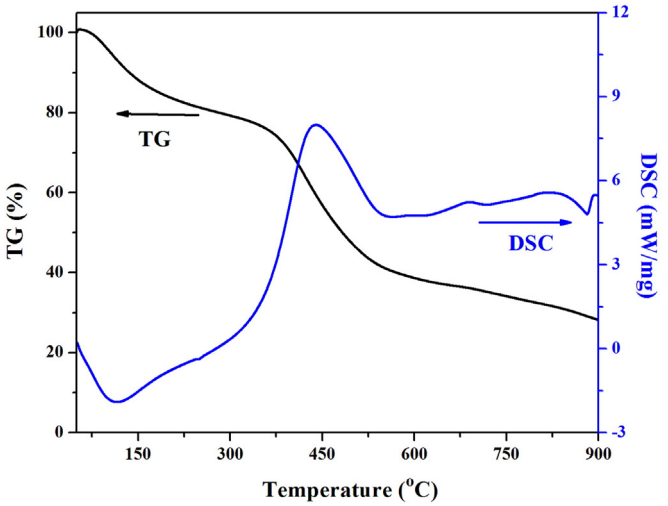

Fig. 1. TG/DSC analysis of $Co_{0.5}Mg_{0.5}Al_2O_4$ pigment precursors.

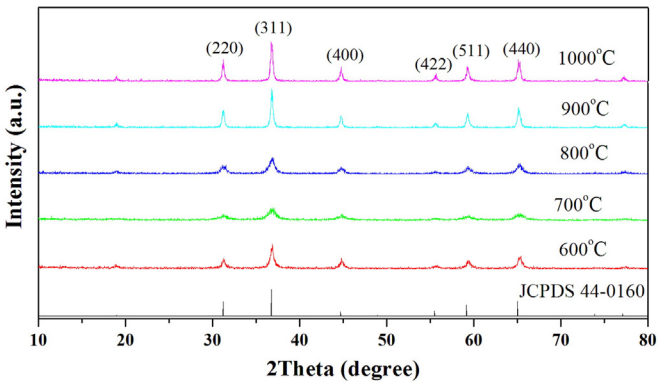

Fig. 2. The XRD patterns of $Co_{0.5}Mg_{0.5}Al_2O_4$ calcined at different temperatures.

The crystalline nature and phase purity of the synthesized samples were determined using a Rigaku Ultima IVX-RAY diffractometer employing Ni-filtered Cu Kα radiation (λ = 0.15406 nm), which was operated with voltage and current settings of 40 kV and 40 mA, respectively. Data were collected by step scanning over a 2θ range from 10 to 80°, with a step size of 0.02° and 5 s counting time at each step.

The morphologies of the pigment samples were obtained by field emission scanning electron microscopy (FESEM, S-4800, Japan). The samples used for SEM characterization were dispersed in absolute ethanol and ultrasonicated before preparation.

The diffuse reflectance of the pigment powders were measured using a UV–vis-NIR spectrophotometer (Lambda 950, Perkin Elmer, America) with integrating sphere, where poly-tetrafluoroethylene (PTFE) was used as the white standard. The reflection spectra were scanned in a range of 300–2500 nm with a 5 nm interval. The spectral

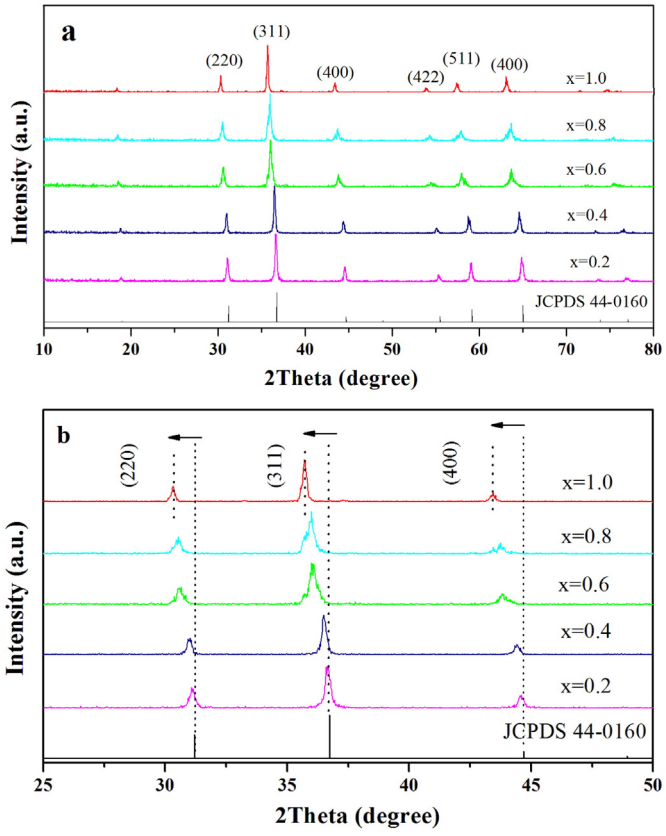

Fig. 3. (a) XRD patterns of $Co_{0.5}Mg_{0.5}Al_{2-x}Fe_xO_4$ pigments and (b) shift of the Bragg reflections (220), (311) and (400) for the different studied compositions.