



Synthesis and characterization of $\text{Co}_{1-x}\text{Ca}_x\text{Al}_2\text{O}_4$ composite blue nano-pigments by the polyacrylamide gel method



Nianying Zhou^a, Yun Li^a, Yin Zhang^{a, b, *}, Yan Shu^a, Shangjiu Nian^a, Weijing Cao^a, Zhenning Wu^a

^a College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China

^b Nanjing Haoqi Advanced Materials Co., Ltd., Nanjing, 211300, China

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ABSTRACT

Blue nano-pigments of $\text{Co}_{1-x}\text{Ca}_x\text{Al}_2\text{O}_4$ ($x = 0.1, 0.2, 0.4, 0.6,$ and 0.8) were synthesized by the polyacrylamide gel method. The obtained powders were characterized by XRD, SEM, colorimetry and UV-vis. The XRD patterns indicated the characteristic peaks were attributed to the CoAl_2O_4 and CaAl_2O_4 phases with a good crystallinity. The crystallite sizes decreased with the increase of calcium content. The colorimetric data revealed that the increases of blue intensity and bright component originated from the enrichment of calcium. When the content of Co was 0.2 (sample P5), the pigment showed the bluest and brightest color. The UV-vis absorption spectra in the range of 430–670 nm decreased with the increase of calcium content thus causing the pigments became brighter and bluer. Incorporation of calcium elements into the CoAl_2O_4 reduced the production costs and also minimized the damage to the environment. These facts show the potential of the obtained powders for cool coatings.

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1. Introduction

In recent years, the cobalt aluminate oxide is one of the most popular blue inorganic pigments, cobalt ions are located on tetrahedral positions within a conventional, cubic, spinel type structure [1–3]. Cobalt aluminate has attracted significant attention as a ceramic pigment from scientific research and industry owing to exhibiting a series of superior properties, such as high resistance to acids, chemical and thermal stability, color stability and high refractive index [4–9]. At present, CoAl_2O_4 pigments have been widely used in coloration of paints, enamels, glass, paper, plastics, rubber, fibers, cement, and ceramics bodies [10].

It is well known that the method of synthesis plays an important role in influencing the final desired properties of nano-pigments [11]. A variety of techniques, such as solid state reaction [12], combustion [13], sol-gel [14], micro-emulsion [15], co-precipitation [16], polyacrylamide gel method [17] and liquid-feed flame spray pyrolysis method [18], have been developed successfully obtaining cobalt aluminate oxides. Among them, the polyacrylamide gel

method provides a the mixing at a molecular level during the synthesis process, because the metal ions are dissolved in the polymeric network [19], thus making the calcination temperature lower (1000 °C) [20].

Taken into consideration that cobalt is scarce and expensive, adding suitable metal ions to partially replace the Co^{2+} ions in the spinel structure has been explored [19,21]. This method can reduce the cost of production, it can also alter and improve the materials properties. Recently, this method has been further investigated. Leila Torkian et al. [19] and I.S. Ahmed et al. [21] reported the blue intensity decreased with the increase of the Mg content in Mg^{2+} -doped cobalt. In the Zn^{2+} -doped system, the highest blue intensity was observed in medium Zn content samples [22]. They thought that the blue hue was associated with the absorption bands in the range of 530–670 nm. Ba^{2+} was added in the blue pigment to improve the optical properties by Mahsa Jafari et al. [20]. They put forward a different explanation that the blue hue was ascribed to three spin-allowed and three spin-forbidden electronic transitions of cobalt ions, and the addition of Ba^{2+} decreased the intensity of the absorption band at 450 nm and yielded a blue pigment with an improved color point.

In this work, nano-sized metal aluminates (CoAl_2O_4 and CaAl_2O_4) were synthesized by polyacrylamide gel method. It is well known that Ca^{2+} can improve the degree of color and brightness of

* Corresponding author. College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China.

E-mail address: zhang.512@njtech.edu.cn (Y. Zhang).

glaze and glass. Meanwhile, Ca^{2+} can weaken the absorption of UV-vis in a certain wavelength range and enhance the reflection properties of the crystal [23]. In addition, the dopant of calcium ions would affect mineralizing agent, which is able to effectively reduce the sintering temperature [24]. Since cobalt is widely considered to be scarce and hazardous, incorporation of non-toxic and inexpensive elements to the CoAl_2O_4 would reduce the production costs and also minimize the environmental damage [25,26]. So far little report has been focused on dealing with the use of calcium ion in pigments. Therefore, we comprehensively discussed the effect of Ca^{2+} on the structure, morphology, chromatic coordinates and optical properties of obtained powders. What's more, the relationship between the chromatic coordinates and the UV-vis absorbance spectrum was investigated.

2. Experimental procedure

2.1. Materials and preparation

In this work, samples of nano-pigment Ca^{2+} -added alumina/cobalt with the different molar ratio of aluminum, cobalt and calcium in composition were prepared by the polyacrylamide gel method. Firstly, cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were dissolved in distilled water according to the stoichiometric ratio. Then, acrylamide ($\text{C}_2\text{H}_3\text{CONH}_2$) and methylene bisacrylamide ($(\text{C}_2\text{H}_3\text{CONH}_2)_2\text{CH}_2$) were added to the above solution at a molar ratio of 22: 1 [17]. After stirring for 45 min, 10% (w/v) ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and 1% (w/v) N, N, N', N'- tetramethyl ethylene diamine ($\text{C}_6\text{H}_{16}\text{N}_2$) were added to the mixture, which initiated the polymerization reaction, followed by rapidly forming a transparent gel. The resulted gel was dried at 110°C for 3 h. Finally the formed xerogel was calcined at 1000°C for 2 h and then cool down to room temperature. The sample codes with corresponding molar ratio composition are shown in Table 1.

2.2. Characterization

XRD data were collected from the synthesized powders for phase identification by an X-ray powder diffractometer (Geigerflex, Rigaku, Japan) using $\text{CuK}\alpha$ radiation from 10° to 70° 2θ . In XRD analysis standard silicon was used as a reference to define the FWHM (full width at half maximum) values. Measured peak widths were used in Scherrer's formula to evaluate crystallite sizes. Morphology and particle size were observed by SEM (S-4800, JEOL, Tokyo, Japan) and TEM (Philips CM-10, 60 keV, Holland). The CIE- $L^*a^*b^*$ chromatic coordinates and UV-vis absorption spectra were taken by means of a SC-20 colorimeter and a Jasco-670 spectrophotometer UV-vis, respectively, using standard D65 illumination and barium sulfate as a reference.

Table 1
Corresponding molar ratio composition, crystallite size and color coordinates of synthesized samples.

Sample code	Co	Ca	Al	Crystallite size (nm)	L^*	a^*	b^*
P1	1	0	2	51.0	46.24	-3.81	-12.87
P2	0.8	0.2	2	47.8	46.49	-3.45	-13.61
P3	0.6	0.4	2	31.2	49.57	-2.08	-22.06
P4	0.4	0.6	2	28.8	57.17	-0.08	-31.95
P5	0.2	0.8	2	27.6	64.43	0.01	-34.51

3. Result and discussion

3.1. X-ray powder diffraction

Fig. 1 shows the XRD patterns of synthesized samples calcined at 1000°C for 2 h. Compared with other synthetic method [11,31], the polyacrylamide gel method can make the calcination temperature lower (1000°C). At this temperature, the characteristic peaks are correspondent with the JCPDS files 10–458 [27,28] and 23–1036, for CoAl_2O_4 and CaAl_2O_4 , respectively. This peak is characteristic for the CoAl_2O_4 phase and the related pattern was investigated in more details at $2\theta = 65^\circ$ [27]. P1 sample represents the pure cobalt aluminate, the characteristic peaks for CoAl_2O_4 spinel structure are broad with maximum at $2\theta = 31.11^\circ, 36.58^\circ, 59.12^\circ$ and 64.97° , no secondary phases were observed. With the increase of calcium content, the CaAl_2O_4 peaks were also observed in the XRD patterns of the samples P2–P5. The intensity of the CoAl_2O_4 spinel peaks decreased with increasing the concentration of calcium, which was along with gradual increasing of peaks of CaAl_2O_4 . The XRD patterns of synthesized samples suggested that they have been prepared for a composite of CoAl_2O_4 and CaAl_2O_4 systems.

The mean crystallite size (D) of the synthesized samples is estimated from the full width at half maximum (FWHM) of the strongest diffraction Bragg peak 220 of the powders using the Scherrer's formula. The mean crystallite sizes for intermediate and extreme compositions were calculated and listed in Table 1. It is shown that the calcium content influences the mean crystallite size values of the formed oxides and crystallite sizes continuously decrease from 51.0 nm (P1) to 27.6 nm (P5) with the increase of Ca content. Due to the different effective ionic radius between doping Ca^{2+} and Co^{2+} ions, the crystal lattice was distorted after doping. So $d(220)$, $d(311)$, $d(511)$ and $d(440)$ of spinel phases decreased after Ca^{2+} doping (in Fig. 1), which indicated that calcium ions entered into the structure of crystal successfully and partially replaced Co^{2+} to form CaAl_2O_4 , which caused the changes of the crystallinity and the particle size. It is almost consistent with those observed in Fig. 1. In the previous reports, Leila Torkian et al. [19] and Chunlan Liu et al. [29] reported that employing Mg^{2+} to substitute the positions of Co^{2+} and prepare MgAl_2O_4 , resulted in smaller crystallite sizes in high magnesium contents. It seems that substitution ions entered

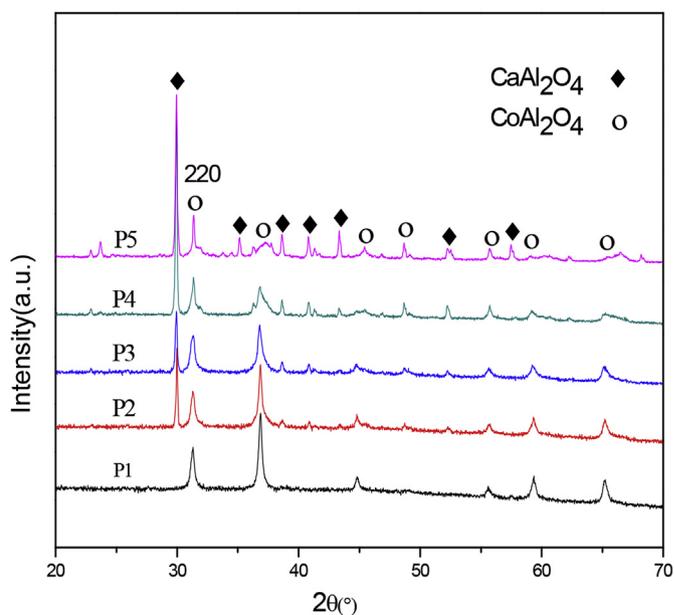


Fig. 1. X-ray diffraction patterns of synthesized samples calcined at 1000°C for 2 h.

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