Evaluation of green and blue cobalt aluminate spinels synthesised using the combustion method

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Abstract

$CoAl_2O_4$ is known as Thenard's blue and is widely used in ceramic, glass, paint industry and for colour TV tubes. $CoAl_2O_4$ falls into the category of normal spinel with aluminium in octahedral sites and cobalt in tetrahedral ones. The most common method for preparing $CoAl_2O_4$ is through a solid-state reaction of the mechanically mixed parent oxides followed by calcinations at ~1300 °C for a long period of time as well as extended grinding. Although this process is relatively inexpensive, it may allow non-homogeneity, larger and uneven grains and poor control of stoichiometry. Recently oxide spinels have been synthesised using several wet-chemical techniques such as sol–gel, emulsion precipitation, hydrothermal crystallization, coprecipitation, etc. Regardless the available solution chemistry routes, the combustion technique is an inexpensive method that allows the preparation of highly purified, nano-sized crystalline powders at lower calcination temperatures during the significantly shorter time. The fuel type, pH, the amount of fuel to nitrates and the calcination temperature, etc. strongly affect the characteristics of nano powders synthesized by this production method. Li et al. found that the molar ratio of fuel (citric acid, CA) to nitrates in the redox mixture have a significant influence on the characteristics of the as-synthesized $CoAl_2O_4$ crystallites. Wang et al. reported that the as-prepared metal organic precursors with different Co and Al contents display different thermal behaviour, crystal development, powder morphology and specific surface area. Effect of calcination temperature on the colour behaviour of cobalt-aluminate spinel synthesized by combustion method has not yet been considered.

In this investigation, cobalt-aluminate spinel was synthesized by combustion method. In order to study the colour behaviour of powder after heat treatment, UV-Vis., elemental analysis, FT-IR, XRD, DTA and Raman spectroscopy, were used. TEM was applied to estimate the crystal size and observe the morphology and agglomeration state of the pigments. The results showed that the inverse spinel phase presented in the as-synthesized powders was transformed to the normal spinel phase as temperature was increased. In particular the normal nano crystalline spinel can be successfully produced by combustion technique and successive calcination at 800 °C. This phase behaviour was also correlated to a colour change from the green of the inverse spinel structure to the characteristic blue colour produced at higher temperatures. Calcination at 1000 °C is the optimized heat treatment to obtain a pigment with the highest colorant efficiency. The obtained results can be useful in industrial practice

Keywords; powders-chemical preparation, spinel, combustion, calcination, colour

Experimental

Analytical grade $Co(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and glycine (Gl) were used as starting materials. A mixed solution of metal nitrates was prepared by dissolving $Co(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ in de-ionized water with a Co/Al molar ratio of 1:2. To this solution, an appropriate amount of glycine was added to adjust the Gl/NO_3^- molar ratio (R) to 0.56. Subsequently, ammonia was added to fix the solution's pH to 7.

The mixed solution was heated on a hot plate kept at a steady temperature of 110 °C. As the water evaporated, the solution formed a dense liquid, then a viscous gel. The viscous precursor was then heated rapidly in a pre-heated furnace kept at 500 °C. During the smouldering type combustion, which lasted for more than 7 minutes, the material underwent foaming followed by decomposition generating a large volume of gases, and then spontaneous ignition and smouldering combustion with massive swelling, producing foamy and voluminous ashes. The voluminous and foamy combustion ashes were easily crushed to form powders. The crushed powders were further calcined at 600, 800, 1000 °C for 1 h to observe their thermal behaviour. The powder calcined at 600, 800 and 1000 °C had green, dark blue and bright blue colour respectively.

Colour measurements on calcined powders was determined by UV–Vis spectroscopy (model Lambda 19, Perkin Elmer) using the CIE Lab method in order to obtain a* and b* values. The diffuse reflectance (R) spectra were used to calculate Kubelka–Munk absorption function (F(R)) by Eq. 1.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = F(R) \qquad (1)$$

where R is the fractional reflectance, K is the absorption coefficient and S is the scattering coefficient at each wavelength of light in the visible region (400-700 nm).

Results and discussion

As reported, powders calcined at 600 °C had green colour whereas powders calcined at temperatures higher than 800 °C had a blue colour. The CIElab colorimetric coordinates allowed the characterization of the pigment colours. The results show that increasing the calcination temperature strongly decreases the b^* coordinate and slightly increases a^* values.

The curves of Kubelka-Munk absorption function of powders calcined at 800 and 1000 °C show three absorption peaks in the visible region at around 537, 580 and 633 nm due to spin-allowed transitions of Co^{2+} ions in tetrahedral coordination which gives rise to the blue colour, whereas the curve of green powder calcined at 600 °C does not show these peaks.

The results of elemental analysis show that the amounts of carbon and nitrogen after calcination step at different temperatures are very low and approximately the same, allowing us to suppose that the colour difference between the powders is not related to the carbon or nitrogen content.

Corresponding to the SSA data, measured using the BET method, green powder calcined at 600 °C has the largest SSA whereas blue powder has the lowest SSA. This could be related to the temperature increases, suggesting particle grain growth.

The XRD patterns of the powders calcined at different temperatures show that there is no clear difference in the peak position between the XRD patterns of green and blue powders. It also indicates that higher calcination temperatures promote an increase in crystallite size. This result is confirmed by the average particle sizes calculated with Scherrer's equation and is in agreement with the results obtained for SSA.

The results of the Rietveld-RIR experiments show that the proportion of the crystalline phase increases with temperature, although the powders obtained thus have very high crystalline phase content.

SEM images of powders calcined at 600, 800 and 1000 °C shows that the spinel samples are always agglomerated regardless of the calcination temperature.

According to the transmission electron micrographs of powders calcined at 800 and 1000 °C, most of the particles calcined at 800 and 1000 °C have sizes lower than 30 and 75 nm respectively. The powders calcined at 1000 °C present a higher aggregation in agreement with the data calculated using Scherrer's equation.

Green and blue powders have different FT-IR spectra. By comparing these spectra, it can be concluded that normal spinel is formed after calcination at 800 °C due to the two characteristic bands (assigned to Al-O stretching vibrations) at around 550, and 640, with a shoulder at around 590 cm^{-1}, which are attributed to the vibrational bands of normal spinel $Co^{2+}Al_2O_4$ whereas the band around 661cm^{-1} observed in the spectrum of green powder indicates that normal spinel is not formed at 600 °C. Based on FT-IR spectra the difference between green and blue coloured powders is related to a different crystal structure. Moreover, the results show that by increasing temperature from 800 to 1000 °C, bands around 547 and 640 cm^{-1} become stronger corresponding to a colour change from dark to bright blue. This behaviour could suggest the structure change from inverse to normal spinel is not complete after calcination at 800 °C.

The Raman spectra of green and blue powders calcined at 600 and 1000 °C also show a variation in the structure of green and blue powder. Normal spinel can be distinguished from inverse spinel by these spectra. In fact, blue powder has a Raman band at 380 cm^{-1} that is not present in green powder. High intensity Raman bands are observed in blue.

Conclusion

This work shows that the colour of $CoAl_2O_4$ nanopowders produced by solution-based combustion synthesis is strongly related to the temperature of the successive calcination step. Various characterisation methods were used in order to identify the possible cause. Results of elemental analysis and X-ray quantitative analysis indicate that the colour differences are not related to the carbon content and proportion of crystalline phase of powders. The XPS data are very similar because the powders share the same spinel cubic structure. FT-IR and Raman spectroscopies allowed us to distinguish between the structure of green and blue powders. In particular, the Raman results show that the green powder is characterised by an inverse spinel structure whereas a normal spinel $CoAl_2O_4$ (blue powder) is produced at higher temperatures

EVALUATION OF GREEN AND BLUE NANO COBALT ALUMINATE SPINELS SYNTHESISED BY COMBUSTION METHOD

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ABSTRACT

In this investigation, cobalt-aluminate spinel was synthesized by combustion method. In order to study the color behavior of powder after heat treatment, UV-Vis., elemental analysis, FT-IR, XRD, DTA and Raman spectroscopy, were used. TEM was applied to estimate the size of the pigments. The results showed that the inverse spinel phase presented in the as-synthesized powders was transformed to the normal spinel phase as temperature was increased. This phase behavior was also correlated to a color change from the green of the inverse spinel structure to the characteristic blue color produced at higher temperatures. Calcination at 1000 °C is the optimized heat treatment to obtain a pigment with the highest colorant efficiency.

Keywords: Cobalt spinel; Color; Combustion; Calcination temperature; Nano crystal.

1- INTRODUCTION

Spinels are generally formulated as $A^{2+}B_2^{3+}O_4$. There are two ideal spinel structures: Normal an inverse structures which are slightly different due to the presence of transition metals in the crystal field [1]. $CoAl_2O_4$ is the best known member of cobalt spinels and is widely used in ceramic, glass, paint industry to produce Thenard's blue color [2]. $CoAl_2O_4$ is classified into the category of normal spinel in which aluminium and cobalt locate in octahedral and tetrahedral sites respectively [3]. Regardless the available solution chemistry routes, the combustion technique is an inexpensive method that allows the preparation of highly purified, nano-sized crystalline powders at lower calcination temperatures during the significantly shorter time [4]. Some researches have been performed to produce nano $CoAl_2O_4$ by combustion method but the effect of calcination temperature on the color behavior of cobalt-aluminate spinel synthesized by combustion method has not yet been considered.

2- EXPERIMENTAL

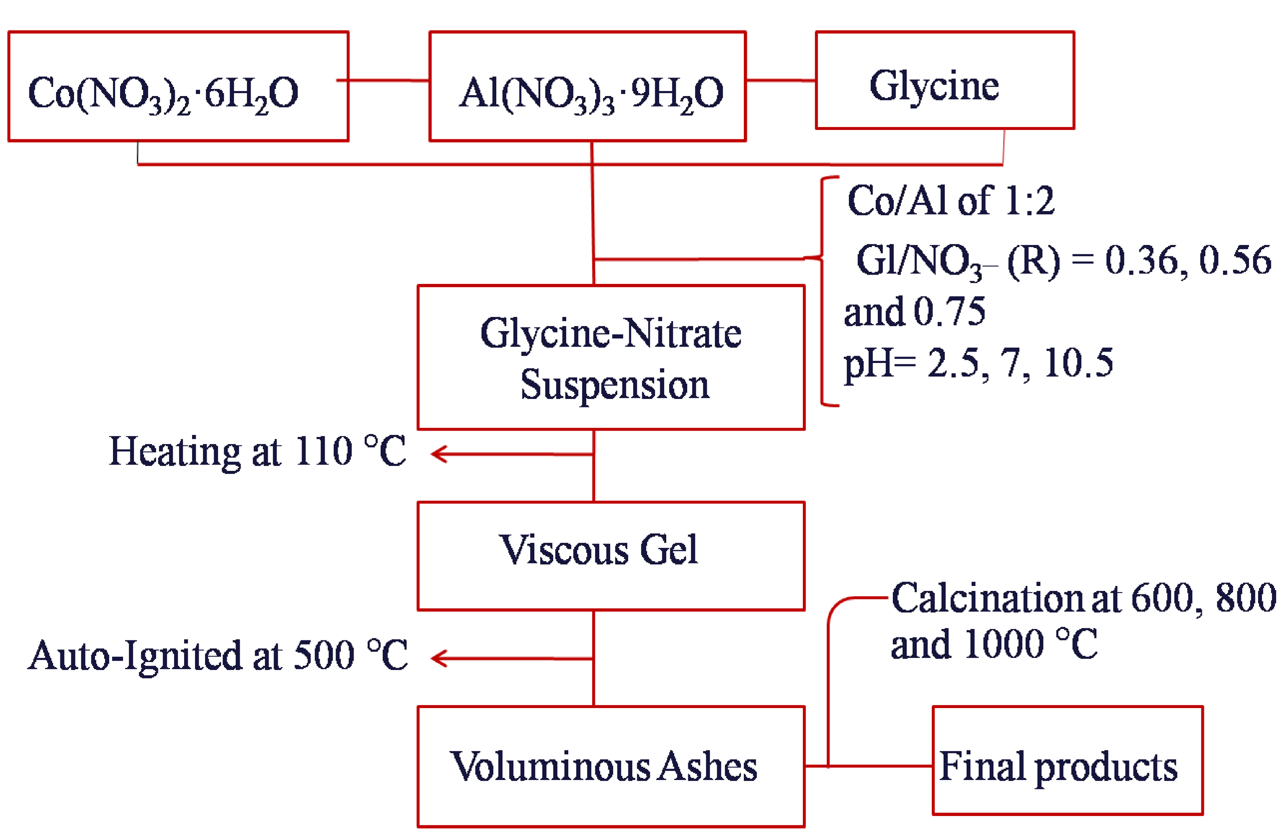

Fig. 1. A general flowchart of the combustion process for the synthesis of cobalt-aluminates

3- RESULTS AND DISCUSSION

Table 1: The colorant behaviour of powders as function of calcination temperature, carbon and nitrogen percentage

Temperature (°C)	L^*	a^*	b^*	C (wt.%)	N (wt.%)
600	39.4	-3.45	-1.5	0.53	
800	41.0	-1.64	-7.3	0.40	0.14
1000	41.4	-1.09	-10.1	0.30	

Table 2: Proportion of crystalline and amorphous phase of samples

Temperature (°C)	Crystalline phase (wt %)	Amorphous phase (wt %)
600	77.8	22.2
800	88.0	12.0
1000	98.2	1.8

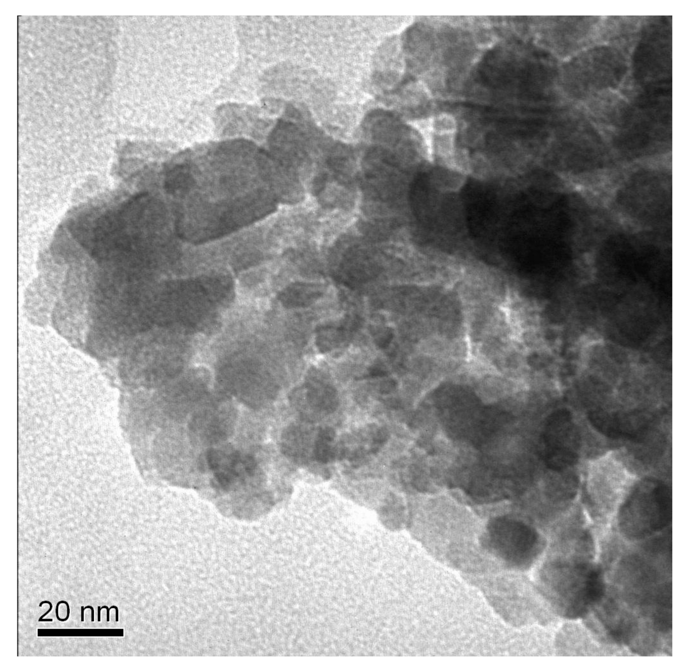

Fig. 3. The TEM of powders calcined at 800 °C

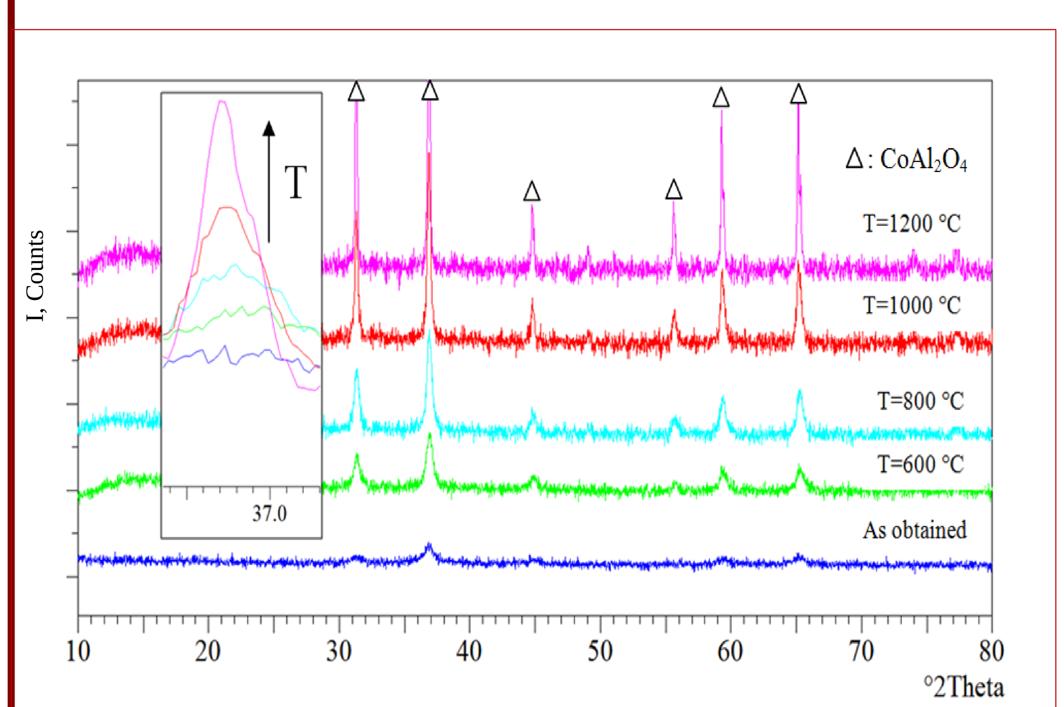

Fig. 2. The XRD patterns of calcined powders

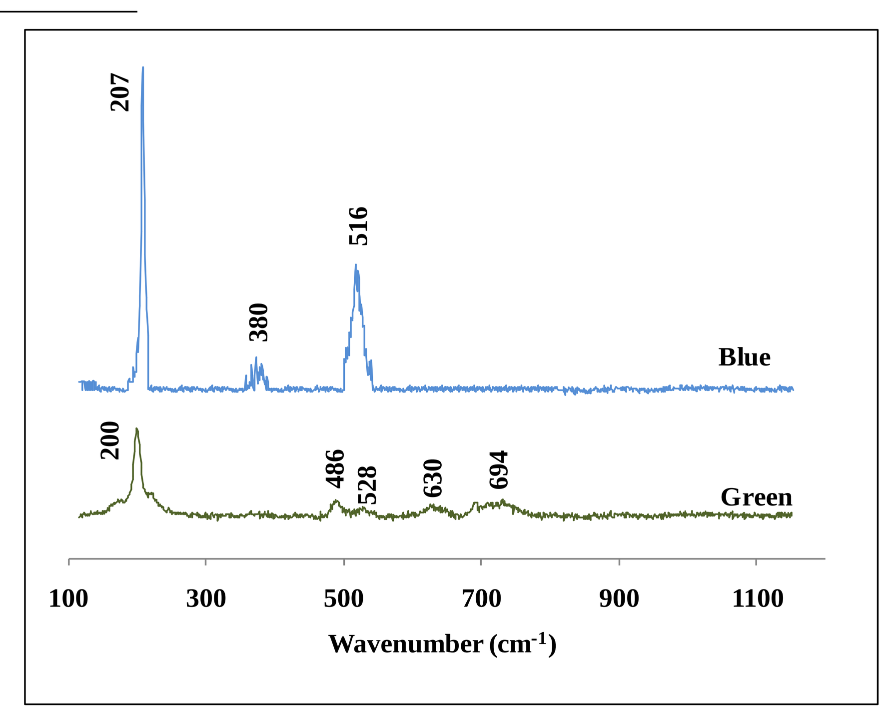

Fig. 4. The Raman spectra of green and blue powders

4- CONCLUSIONS

1- The nano particles of $CoAl_2O_4$ spinel was successfully produced by combustion technique.
2- The color measurement results indicated that the color of cobalt-aluminate spinel is strongly related to the successive calcination temperature.
3- The crystallinity and the crystal size of the pigment were significantly increases by heat treatment and directly influence the color behavior of powder.
3-Raman and FT-IR spectroscopies allow to define that the green powder is characterized by an inverse spinel structure whereas a normal spinel, $CoAl_2O_4$, is obtained at higher temperatures.

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