

## Microwave-assisted gel combustion synthesis of ZnO-Co nano-pigments

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ZnO-Co ceramic pigments have been prepared by microwave-assisted gel combustion of zinc-nitrate-nitrate cobalt-citric acid precursors calcined at 700 to 1000 °C. The Combustion process has been investigated using thermal analysis and Fourier transformation infrared spectroscopy. X-ray diffraction, diffuse reflectance and scanning-transition electron microscopy was used to characterize the pigments. Results were compared with a solid state reaction. It was demonstrated that powders synthesis by combustion caused 200 °C reduction in the calcination temperature compared with the solid state reaction. The results demonstrated that the microwave-assisted combustion reaction was very simple and rapid to prepare 27-37.2 nm nano-crystalline pigments. Colorimetric results also indicated a broad reflectance band around 540 nm (green region) for all samples. It was deduced that the fuel-rich sample has more chromaticity and has a deeper green color.

**Keywords:** Microwave-assisted-gel combustion, ZnO-Co nano-crystalline, Pigment.

### Introduction

ZnO based oxides have a variety of applications in electronic devices [1], ceramic pigments [2] and as optical materials [3]. ZnO doped with cobalt has attracted much attention in various applications, due to its intense green color. In this way, the green-colored oxides of the ZnO-Co system, with a low Co content, have been demonstrated to be similar in color properties with Cr (III) green pigments [2].

Previous studies have demonstrated that parameters such as crystallite size and particle morphology could influence pigment characteristics. Accordingly, the color properties of pigments may also be influenced. Cavalcante *et al.* investigated the color performance of ceramic nano-pigments [4]. They demonstrated that in spite of acquiring saturated shades by micro-pigments, more intense colors are achievable in nano-pigments with very small particle sizes.

The conventional methods for preparing ceramic oxide pigments are based on the initial mixing of the starting materials to achieve a homogeneous oxide and further calcination to obtain the desired crystalline phase and color. For these methods, the properties of the synthesized powder such as particle size and distribution are poor and they are costly and time consuming. Between conventional methods high energy ball milling (called the solid state reaction) is the easiest method for industrial applications [5]. Damonte *et al.* used the mechanical alloying, via high energy ball

milling method, for cobalt incorporation into the Wurtzite structure [6].

In order to improve the properties of ceramic pigments, numerous synthesis techniques such as sol-gel [7], precipitation [8] and combustion synthesis [9] have been used to prepare fine pigments. Among them, the solution combustion method is one of the most interesting synthesis routes for production of homogenous nano-crystalline single and multi-component oxides. The ability to achieve high purity single and multiphase complex oxide powders is the great advantage of this technique for preparing oxide materials. Generally, a solution combustion process is based on an exothermic reaction of metal nitrates with fuel at low temperatures. Numerous studies have been made to prepare ceramic oxide materials by employing solution combustion synthesis [10-13]. In the case of ceramic pigments, other authors have reported the synthesis of zirconia [14], cobalt [15],  $Y_2BaCuO_5$  [16] and spinel based pigments [17] via the combustion synthesis method. In this case, Sulcova and Trojan [2] have reported the synthesis of a ZnO-Co pigment. They reported that an intense green hue can be obtained by  $Zn_{0.9}Co_{0.1}O$  compared to other compositions of ZnO-Co. Up to now, there is little information on the preparation and characterization of this ceramic pigment [18, 19].

Recently a novel technique called 'microwave-assisted combustion synthesis' has been used to synthesize oxide materials [20]. Microwave heating can be more advantageous than conventional heating because of short processing time and volumetric heating [21].

In the present study, microwave-assisted gel combustion was used for the synthesis of ZnO-Co pigments. The pro-

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properties of specimens obtained by this method are compared with solid state reaction samples in which a complete solid solution of ZnO-Co can be achieved by using 0-20% of  $\text{Co}_3\text{O}_4$  [14]. Because Co is not detectable in XRD patterns for amounts less than 5%, 10% of Co was chosen to ensure single-phase formation of solid solutions.

## Experimental

### Solution combustion

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck) as an oxidant and citric acid as a fuel and complexing agent were of analytical grade. At first, stoichiometric amounts of the desired metal nitrates and citric acid were calculated based on propellant chemistry. According to propellant chemistry [22], the elements Zn, Co, C and H are considered as a reducing agent with the corresponding valences +2, +2, +4. Oxygen is considered as an oxidizing agent with a valence -2 and the nitrogen's valence is considered zero because of its inertness. After adding metal nitrates and citric acid to deionized water, the solution obtained was heated up to 80-90 °C until the excess water was removed and a highly viscous precursor gel was gained. The beaker was transferred into a microwave oven (Samsung, Korea, 900 W, 2.45 GHz frequency) to complete the combustion reaction. It is noteworthy to mention that all experiments were performed at maximum microwave power for 50 seconds. In order to study the effect of fuel/oxidizer ratio (F/O) on powder properties, different citrate/nitrate ratios (0.27, 0.56, and 0.84) were used.

### Solid state reaction

For comparison, nano-crystalline  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  was also prepared via a solid state reaction. For this purpose, analytical grade ZnO and  $\text{Co}_3\text{O}_4$  (99.9%, Merck) were used as starting materials. All samples were wet milled in a planetary mono mill pulverisette 6 (Fritsch, Germany) with zirconium dioxide grinding bowls (volume of 500 ml) and grinding balls (20 balls, 20 mm diameter) at 300 rpm in air for 120 minutes. After milling the slurry was dried in an oven at 110 °C to remove residual water. Then, the powders were calcined in a chamber furnace at different temperatures varying from 800 to 1100 °C.

### Characterization techniques

A D-500 (Siemens, Karlsruhe, Germany) Diffractometer was used for the XRD analysis. Simultaneous thermal analysis (STA) was performed using a PL-STA-1640 (Polymer Laboratories, Stanton Redcraft, UK) instrument at a heating rate of 10 K.min<sup>-1</sup> in an air atmosphere. For this analysis, the precursor gel was first dehydrated at 80 °C for 24 h. Morphological analysis was performed using a LEO 1455VP (Oxford, UK) scanning electron microscope and transmission electron microscope (TEM).

The IR spectra of the dried gel and calcined powder were taken by FT-IR (Spectrum one, FT-IR spectrometer, Perkin Elmer). UV radiation spectroscopy in the visible-

ultraviolet light region was conducted with a 7000 A spectrometer (Gretag Macbeth) in the range between 350 and 750 nm for the determination of diffuse reflectance of the pigments.  $L^*a^*b^*$  color parameters of the heat-treated powders were measured using the standard lighting D65, according to the CIE- $L^*a^*b^*$  colorimetric method recommended by the CIE.

## Results and Discussion

### Solution combustion

According to propellant chemistry, the stoichiometric combustion of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  can be written as equation 1:

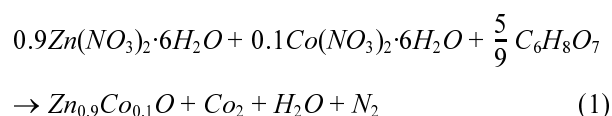
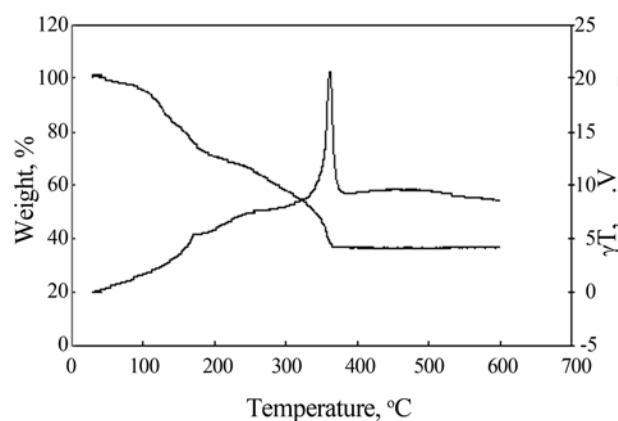


Fig. 1 shows the result of STA for stoichiometric precursor. Referring to the STA plot, a continuous weight loss can be observed up to 380 °C after which there is approximately no change in the TGA curve. The major weight loss up to 150 °C can be attributed to removal of water and the exothermic peak of DTA around 170 °C can be related to the decomposition reaction of complexes and auto-combustion reaction between the nitrate and citric acid. The significant weight loss from 250-360 °C is due to oxidation of carbonate residues. Subsequently, the weak exothermic peak is related to a combustion reaction. A low value of heat combustion creates large amounts of residual reactants and carbonaceous matters that are further oxidized around 360 °C [23]. Nair *et al.* [10] have reported the same results for a fuel-rich composition in the case of La (Ca)  $\text{CrO}_3$ .

Chemical and structural changes that take place during combustion can be monitored by a spectroscopic analysis. Fig. 2 shows the IR spectra of the dried gel and calcined powder at 900 °C in the range of 450-4000 cm<sup>-1</sup> for a stoichiometric ratio. The dried gel showed the characteristic bands around 3400, 1600 and 1380 cm<sup>-1</sup> corresponding



**Fig. 1.** STA result of precursor material for solution combustion of Co-ZnO.

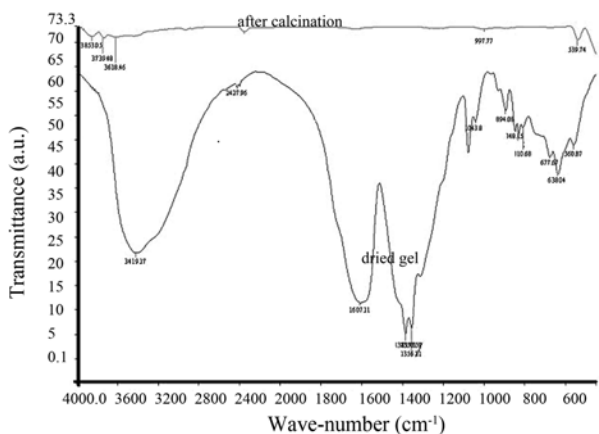


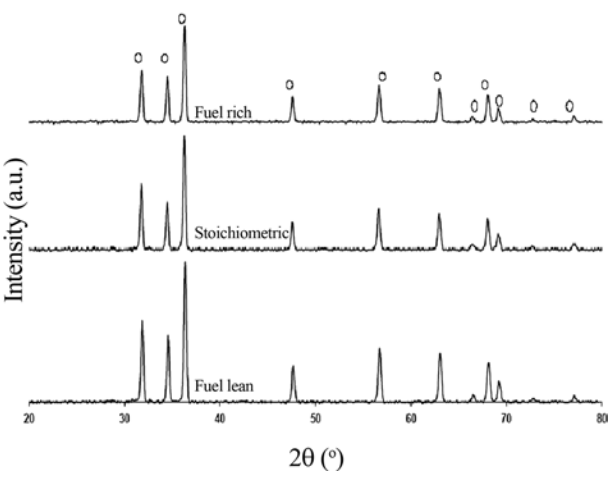
Fig. 2. FT-IR spectra of dried gel and calcined powder at 900 °C.

to the O-H group, carboxyl group and  $\text{NO}_3^-$  ion, respectively. In the IR curves of the calcined powder, a broad intense band at  $450\text{--}540\text{ cm}^{-1}$  can be observed. The broad band around  $440\text{ cm}^{-1}$  is due to the asymmetric stretching mode of the tetrahedral  $\text{ZnO}_4$  group present in the Wurtzite ZnO structure [24]. So, the band that disappeared at  $1380\text{ cm}^{-1}$  and the appearance of a band at  $440\text{ cm}^{-1}$  of the calcined powder are explained by the formation of the ZnO phase.

Generally, the fuel/oxidizer ratio is the most important controlling parameter in a combustion reaction [25]. The vigorousness of the combustion process is strongly influenced by the initial citrate/nitrate (c/n) molar ratio. In our case, the c/n initial ratio is a function of the fuel content in the precursor mixture, since we altered the fuel addition. In general, the intensity of the combustion reactions (i.e. the consumption of nitrates and fuel, as well as formation of the target oxides) increases as the initial c/n molar ratio reaches the stoichiometric values. Table 1 represents the influence of the citrate/nitrate ratio (c/n) on the combustion reaction time, final product color and crystallite size. Fig. 3 shows the effect of fuel richness and leanness on XRD patterns of Co doped ZnO. Referring to Fig. 3 and Table 1, the combustion intensity diminishes with an increase in the c/n ratio, as evidenced by: (1) a decrease in the peak intensity of the as-synthesized powders with an increase in the c/n ratio (Fig. 3) which can be attributed to a decrease of the flame temperature with an increase in the c/n ratio; (2) the amount of non-reacted materials in the as-synthesized products increases with the c/n ratio as could be identified from the color of products (Table 1). For a c/n ratio of 0.56, the presence

Table 1. Characteristics of pigment derived by combustion method

Citrate-nitrate ratio(c/n)	As synthesis color product	Crystallite size after calcinations at 900 °C (nm)
0.27	green	37.2
0.56	Light pink	27
0.84	pink	29.7



Actually, no phase can be distinguished for the as-synthesized powder before calcination and the products obtained with citric acid as fuel are generally amorphous. However, moderate heat generated by the citrate-nitrate reaction may be one of the reasons for such an observation. Hwang and Wu [26] showed that various fuels create different released energies via a combustion process, which simultaneously affect the structural properties of the combustion products. Glycine fuel unlike citric acid contains amine groups, which react with the oxides of nitrogen from the decomposed nitrates and increase the released energy of combustion. Therefore, citric acid is not an effective fuel [28]. According to Fig. 4, it seems that by increasing the calcination temperature, the decomposition of  $\text{Co}_3\text{O}_4$  occurred and cobalt atoms entered into the ZnO crystal structure.

### Solid state reaction

XRD patterns of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  by a solid state reaction and calcined at 900 and 1000 °C were investigated and the results are compared with the combustion results in Fig. 5. It seems that cobalt atoms enter into the ZnO lattice and peak broadening at a higher temperature can be due to the distortion of the host lattice, which is most probably due either to strain induced by the occupation of Zn ion sites by Co ions, or the presence of Co precipitates or cluster [2]. From Fig. 5 it seems that powder synthesis by combustion caused a 200 °C reduction in the calcination temperature compared with the solid state reaction. The decrease of the calcination temperature and entrance of cobalt into the ZnO lattice at lower temperatures is an advantage of the combustion reaction. Also the main  $\text{Co}_3\text{O}_4$  peak at 37° disappears at a lower calcination temperature (900 °C) and ZnO peaks are broad in combustion samples which is due to the complete entrance of cobalt into ZnO structure.

### Microstructures of synthesized samples

Fig. 6 shows SEM images of ZnO-Co prepared by

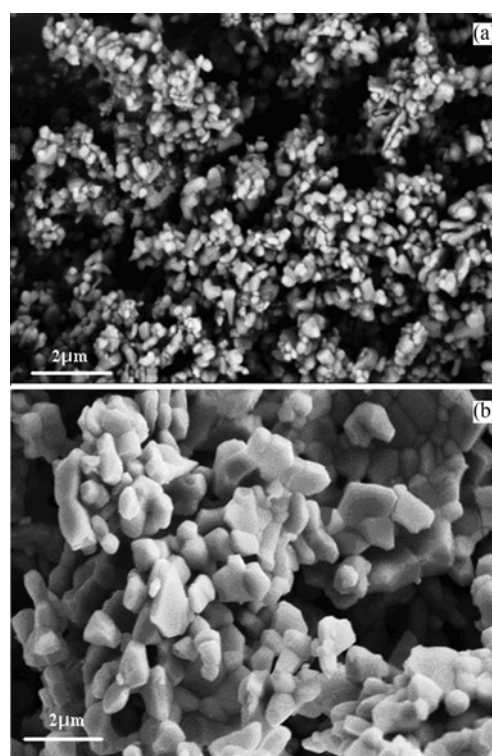


Fig. 6. SEM images of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  powder derived by a) solid state reaction calcined at 1100 °C b) combustion synthesis calcined at 900 °C.

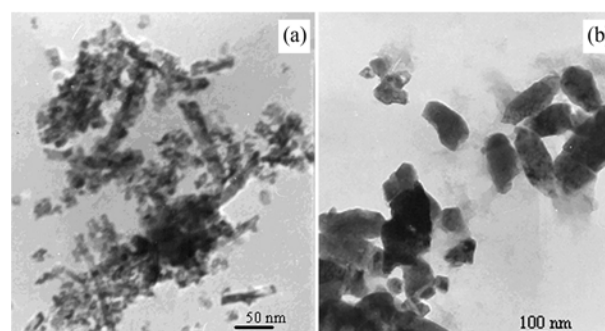


Fig. 7. The photos by TEM of the samples prepared by combustion method, a) before calcination and b) after calcination.

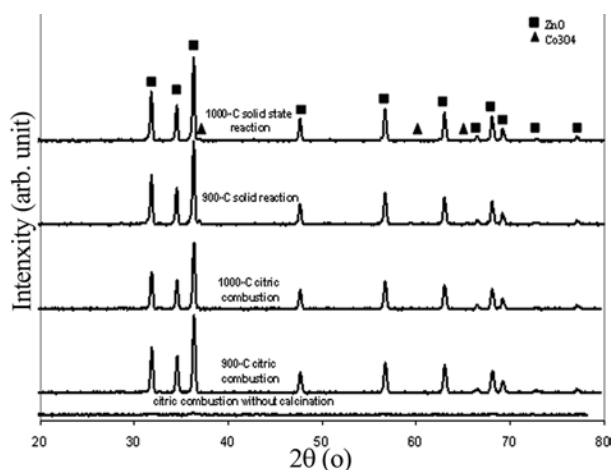


Fig. 5. XRD patterns of  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  prepared by solid state reaction in comparison with combustion as a function of calcination temperature.

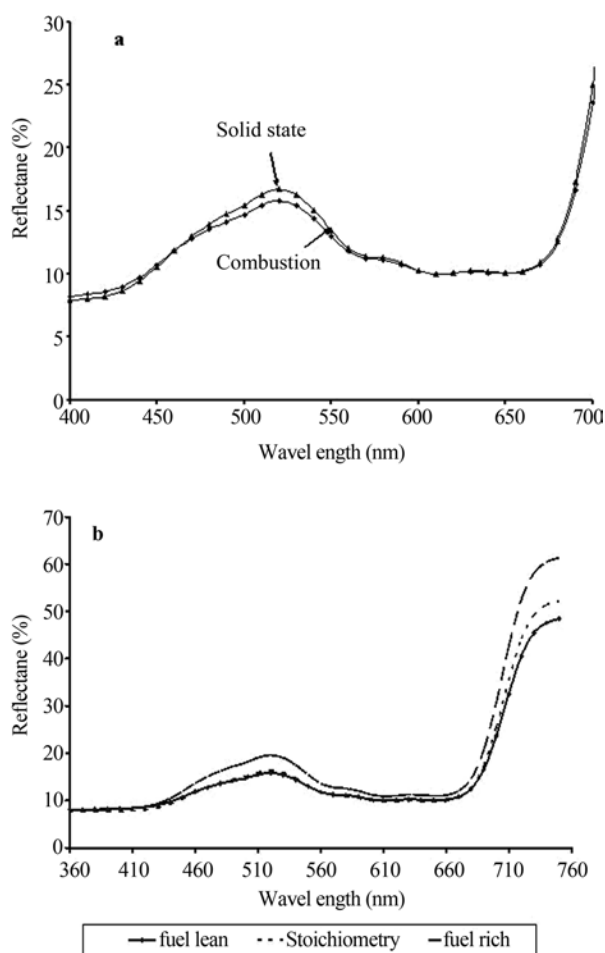
solid state reaction (Fig. 6(a), calcined at 1100 °C) and combustion synthesis (Fig. 6(b), calcined at 900 °C). The particles can be obviously seen to be agglomerated and partially sintered irrespective of the preparation method. However, powders obtained by the combustion method have higher activity, which results in partially sintered particles and grain growth during calcination.

In the case of the combustion method, the effect of the calcination step on the particle size and morphology of ZnO-Co particles was investigated by TEM and the results are shown on Figs. 7(a-b). Small rod-like nanoparticles are observed in Fig. 7(a). As mentioned above, the lower released energy of citric acid combustion than fuels contain his amine groups decrease the particle size of ZnO nanoparticles. Furthermore, citric acid is a more effective complexing agent in producing a fine powder [27]. Yang *et al.*

[29] revealed that citric acid and zinc ions form two chelate rings. Consequently, the spatial volume of growing units is expanded. When the combustion reaction starts the growth units would tend to face-land onto the growing interface and face-landing units on axis energetically. Therefore, rod like ZnO particles consist via the combustion reaction of citric acid and zinc nitrate that intensely grow during the calcination process (Fig. 7(b)). The rod-like particles in Fig. 7(b) are mainly due to the calcination process and the growth of the particle size arises from more sinterability of the particles by combustion synthesis [30]. This tendency is due to an increase of surface area and surface energy, which is the driving force for sintering.

### Color properties

In order to study the color properties of ZnO-Co pigments, the effect of the synthesis method and fuel content on the color properties have been investigated. Fig. 8(a) shows a comparison between the diffuse reflectance spectra of synthesized pigments with the combustion and solid state methods. From Fig. 8(a) a broad reflectance band around 540 nm (the green region) can be observed. However, the



**Fig. 8.** Reflectance spectra of Zn<sub>0.9</sub>Co<sub>0.1</sub>O a) comparison between solid state reaction and combustion b) combustion synthesis as a function of fuel content.

**Table 2.** Colorimetric data of Co : ZnO powders prepared by combustion (calcined at 900 °C) and solid state reaction (calcined at 1100 °C)

Sample name	L*	a*	b*	C*	h°
Fuel lean	40.22	-24.9	10.5	27.02	157.13
Stoichiometric	48.03	-27.65	11.38	29.90	157.63
Fuel rich	51.62	-27.3	11.07	29.45	157.08
Solid state reaction	53.92	-28.26	11.63	30.95	157.64

peak of solid state sample is seen to be more intense which can be related to the higher temperature of calcination.

In the case of combustion samples, from Fig. 8(b) it is observed that the peak intensity is bigger for a fuel rich sample meaning a lighter green color.

To describe the color properties, the CIEL\*a\*b\* and the CIEL\*c\*h° color spaces are applied. For the color space of CIEL\*a\*b\*, L\* is the lightness axis, b\* shows the color varying from blue to yellow and a\* represents the color varying from green to red [31]. In a polar coordinate system, i.e. CIEL\*c\*h°, c\* indicates the chroma axes with a minimum value equal to zero for an achromatic shade and h° is the hue angle varying from 0 to 360.

Table 2 shows the colorimetric coordinates (L\*, a\*, b\*, C\*, h°) for fuel lean, stoichiometric and fuel rich samples in comparison with the solid state sample. The calculated hue angle values around 157 confirmed a similar green shade with the lightness ranging from 40 to 54 corresponding to a dull green shade to a bright green shade.

According to Fig. 8 and Table 2, the pigment prepared by a combustion reaction (with a fuel rich ratio) indicates more green color due to the larger amount of a\* compared to the solid state reaction. Furthermore, depending on the fuel content, different color properties are obtainable. From the C\* values, it is concluded that the fuel rich sample has more chromaticity and has a deeper green color. However, the hue angle of the samples is similar showing that the color sample is similar in the green region.

### Conclusions

Nano-crystalline Zn<sub>0.9</sub>Co<sub>0.1</sub>O ceramic pigment was synthesized using combustion synthesis under microwave irradiation. Results showed that combustion reaction occurred more vigorously in the fuel-lean region. The crystallite size changed in the range of 27-37.2 nm depending on the amount of fuel content. In comparison with the solid state method, combustion synthesis requires a lower calcination temperature to enter Co into the ZnO lattice by about 200 °C. Finally, it was deduced that the powder synthesized by the solid state reaction showed a more intense color than the pigment by the combustion method. However, pigments obtained from combustion synthesis seemed to have the technological potential to be used as a high temperature green pigment due to the low production costs and fast heating method using microwave irradiation.

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