STRUCTURE AND PROPERTIES OF $Co_xZn_{1-x}Al_2O_4$ NANOPIGMENTS FABRICATED BY GEL COMBUSTION METHOD

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Cobalt aluminate ($CoAl_2O_4$) is a double oxide with a normal spinel structure which has been widely used in ceramic industry, but because of cobalt cost and its environmental problems, many researches were conducted to reduce cobalt in this spinel. Using $Co_xZn_{1-x}Al_2O_4$ instead of $CoAl_2O_4$ reduce production costs minimize the environmental damages, but its optical and physical properties have been changed by reduction of Co content. In this research, $Co_xZn_{1-x}Al_2O_4$ (x = 0; 0.25; 0.5; 0.75 and 1) ceramic pigments were synthesized by gel combustion method via glycine as a fuel and their reaction parameters, phase Structure, morphology and color were studied by XRD, TG/DTA, FTIR, CIELAB Colorimetric and FESEM respectively. Thermal analysis results showed an exothermic peak with about 80 % weight loss which was related to spinel formation at about 200°C. XRD results revealed that structure of pigments were spinel and they have average crystallite size below 64 nanometer in (311), (220) and (440) directions. The colorimetric results showed that color of pigments were changed from dark blue to light blue and this behavior was related to the Co/Zn ratio also their lightness and chroma were increased by increasing calcination temperature.

INTRODUCTION

Spinels encompass a large group of compounds with the common formula $A^{2+}B^{3+}O_4$, which have two cations in their composition: one cation with oxidation degree 2+ and the other cation with oxidation degree 3+ (A and B denote these cations). Spinels are high-melting and have high mechanical strength and chemical resistance [1]. Many years ago, application of the spinels as ceramic nanopigments has been explored, owing to their high mechanical resistance, high thermal stability, low temperature sinterability and the easy incorporation of chromophore ions the spinel lattice, allowing for different types of doping and fabrication of ceramic pigments with different colors [2]. Spinel-type pigments are commonly used in decorating porcelain and other ceramic products, as a consequence of their high thermal resistance. If the bivalent metal is either cobalt or zinc and magnesium partly replacing cobalt and the trivalent ion is aluminum, then the resulting pigments form a blue-sky-blue color range [3]. Most of the ceramic dyeing materials possess the spinel structure. These materials must produce a uniform effect on the ceramic and should not react either with the ceramic itself or glassy coating [4]. $CoAl_2O_4$ is a double oxide with a normal spinel structure. It is well known as Thenard's blue for its impressive optical property and widely used in the ceramics, glass, paint, industry, and color TV tubes as contrast-enhancing luminescent pigment [5]. But cobalt is scarce and expensive, and many studies have been performed to reduce cobalt without change spinel properties. $CoZnAl_2O_4$ system is the most important candidate which was used for reduction of cobalt and minimizing of production cost as well as environmental damages [6, 7].

In recent years, much work has been on the fabrication of $CoZnAl_2O_4$ nano particles and optimization of their optical properties, a variety of techniques such as combustion, pechini, sol-gel, micro-emulsion, co-precipitation, hydrothermal and polymeric precursor methods were proposed to fabrication of this spinel and although they have showed some successes but also revealed many disadvantages in processing method and samples properties [6, 8].

Gel combustion synthesis is a versatile, simple and rapid process and because of this, has emerged as an important technique for the synthesis of advanced ceramics, catalysts and nanomaterials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, citric acid and hydrazides). The main disadvantages of this method is its large

number of parameters which must be optimized to get good products [9]. At this study, $Co_xZn_{1-x}Al_2O_4$ (x = 0; 0.25; 0.5; 0.75 and 1) blue nano pigments have been synthesized by gel combustion method by using glycine as a fuel and effect of composition as well as calcination temperature on the phase structure, morphology and optical properties on these nano powders were studied.

EXPERIMENTAL

In this work, laboratory grade $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ (all from Scharlau company) were used as oxidants and glycine (from Scharlau company) was used as fuel.

Amount of raw materials was calculated based on the following stoichiometric reaction:

$$xCo(NO_3)_2 \cdot 6H_2O + (1\text{-}x)Zn(NO_3)_2 \cdot 6H_2O + 2Al(NO_3)_3 \cdot 9H_2O + 4.44C_2H_5NO_2 \rightarrow Co_xZn_{1-x}Al_2O_4 + 8.88CO_2 + 6.22N_2 + 35.1H_2O \quad (1)$$

Raw materials were mixed on magnetic-heater stirrer and aqueous clear, purple color solution was prepared. After adjusting pH of solution by ammonia (all experiments were performed at pH = 3 - 4), the solution was heated until clear high viscosity gel was formed and ignited spontaneously. Ignition was conducted exothermically between an organic fuel and nitrate salts and gel was converted to gray spongy ashes. The ashes were calcined in 900°C furnace for 1 hour and blue pigments were fabricated.

In order to find reaction characteristics, TGA/DTA thermal analysis (Perkin/Elmer, Pyris Diamond) were performed on unreacted gels in the oxygen atmosphere with 10°C·min^{-1} heating rate Chemical bonds of the samples were examined by FTIR (Perkin-Elmer, RX1)in the 4000-400cm^{-1} range. The phase structure of samples were studied by XRD (philips-x'pert PW3040/60), with scan range of 5° to 90°and step size of 0.02°. All XRD results were compared with 74-1136, 82-2252 and 76-0070 ICDD files which are related to ZnAl2O4, CoAl2O4 and Zn0.9Co0.1Al2O4 phases respectively. The crystallite size (D) of the powders was calculated by Debye–Scherrer's formula from X-ray diffraction curves of the samples:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (2)$$

where β is the broadening of the diffraction line measured at half maximum intensity (radians) and λ = 1.5406 Å, the wave length of Cu-Kα and θ is the Bragg's angle. The color of them was characterized by colorimetry (spectrophotometer x-rite SP64) with CELAB method. Based on this method five factors of L, a*, b*, c* and h° are measured and plotted in some curves. Flow chart of sample preparation and characterization was shown in Figure 1.

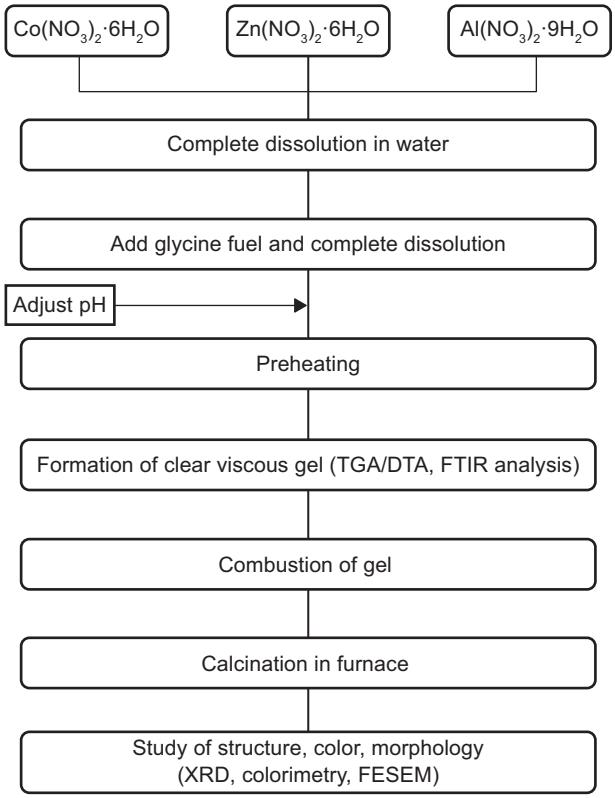


Figure 1. Schematic flowchart for synthesis and characterization of $Co_xZn_{1-x}Al_2O_4$.

RESULTS AND DISCUSSION

Figure 2 shows the TGA/DTA curves of the gel precursors from mixed oxidant and fuel before combustion. At 200°C a large amount of weight loss was revealed in TGA curve and an exothermic peak was observed in DTA curve which indicated that reaction was initiated. Before weight loss, a gradual decline occurred that would be attributed to water vapor or absorbed gases removal. Crystallization onset temperature was initiated at about 400°C without any weight loss and a small peak

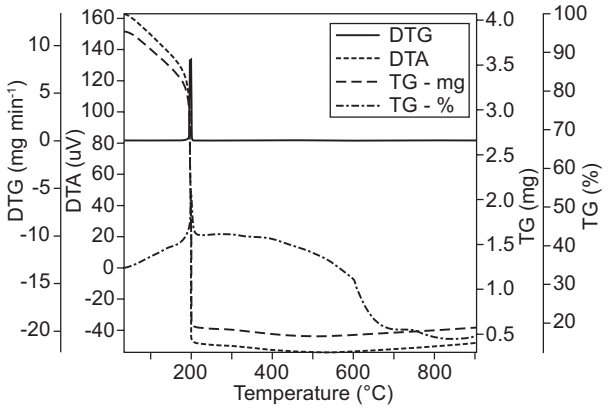


Figure 2. TGA/DTA curves of the gel precursor $Co_{0.5}Zn_{0.5}Al_2O_4$ sample.

is observed at 700°C also which may be related to phase transformation. From thermal analysis of De Souza et al. [6] for samples which were fabricated by using ethylene glycol and citric acid as fuels, it can be seen that the decomposition of the samples occurred in two steps. The first step is the removal of absorbed water and gases, and the second step is related to the combustion reaction. This behavior also reveals in our results.

Figure 3 depicts the XRD patterns of the $Co_xZn_{1-x}Al_2O_4$ samples that heat treated at 900°C. Diffraction from (220), (311), (400), (331), (422), (511), (440), (620) and (533) planes of $Co_xZn_{1-x}Al_2O_4$ were identified and marked in the Figure 3. On the other hand, spinel phase seems to be pure and patterns did not show the presence of any crystalline secondary phases. Our results are as same as previous studies for fabrication of these spinels [2, 6].

Figure 4 shows the XRD patterns for the $Co_{0.5}Zn_{0.5}Al_2O_4$ sample have been heat treated at different temperature (600, 700, 800, 900 and 1000°C). From this figure it was revealed that spinel structure pigment were formed at 600°C but crystallized well after thermal treatment at 800°C. By increasing heat treatment temperature, the peak intensities raise, but the position of the peaks and their relative intensities remain unchanged. The XRD patterns of $Co_{0.5}Zn_{0.5}Al_2O_4$ that heat treated at different temperatures was studied by De Souza et al. [6] previously and our founding on spinel formation and crystallization are same as their results.

Average crystallite size of (311), (220) and (440) planes of the $Co_{0.5}Zn_{0.5}Al_2O_4$ samples that were heat treated at different temperatures was calculated by Equation 1 and shown in Table 1. It can be seen that with increasing temperature from 600°C to 1000°C, the crystallite size grows from 21.47 nm to 70.47 nm. Effect of calcined temperature on the crystallite size was not found in pervious works.

Table 1. Crystallite size $Co_{0.5}Zn_{0.5}Al_2O_4$ sample heat treated at different temperature.

Temperature (°C)	600	700	800	900	1000
Average crystallite size (nm)	21.47	38.24	44.70	57.56	70.47

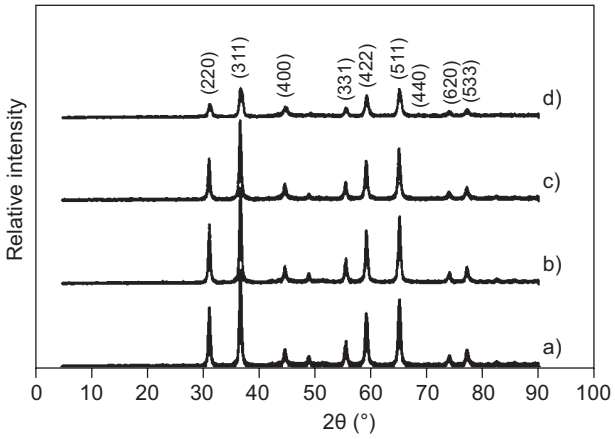


Figure 3. XRD patterns of the following powder samples, heat treated at 900°C: a) $ZnAl_2O_4$, b) $Co_{0.5}Zn_{0.5}Al_2O_4$, c) $Co_{0.75}Zn_{0.25}Al_2O_4$ and d) $CoAl_2O_4$.

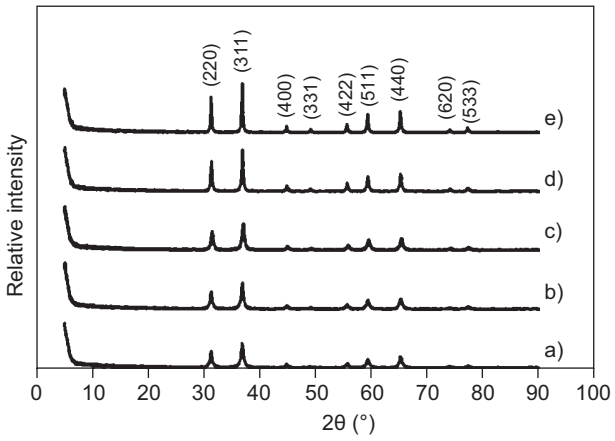


Figure 4. XRD patterns of $Co_{0.5}Zn_{0.5}Al_2O_4$ heat treated at different temperatures: a) 600°C, b) 700°C, c) 800°C, d) 900°C and e) 1000°C.

Figure 5 shows the FTIR patterns of $Co_{0.5}Zn_{0.5}Al_2O_4$ samples which were treated at different conditions. Figure 6a shows the FTIR pattern of the gel precursor sample before combustion, Figure 6b shows the FTIR pattern of the powder sample after combustion and before calcination and Figure 6c shows the FTIR pattern of the powder sample after calcination at the 900°C.

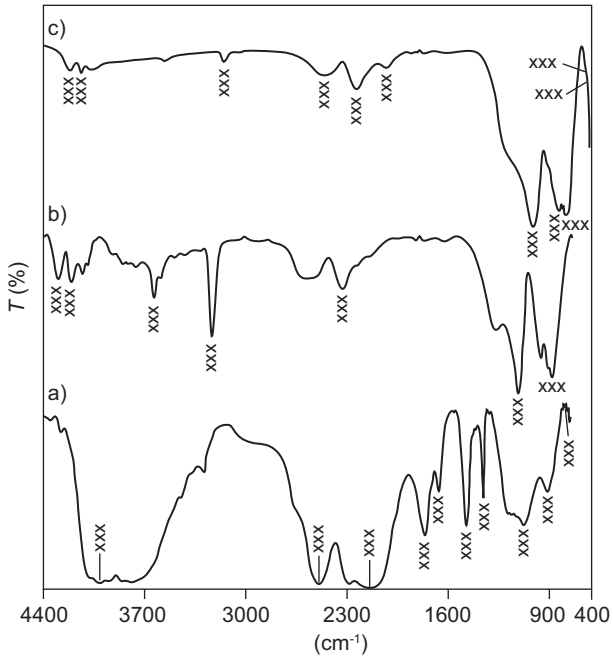


Figure 5. FTIR spectrum of the $Co_{0.5}Zn_{0.5}Al_2O_4$ sample: a) FTIR spectrum of the sample before combustion, b) FTIR spectrum of the sample after combustion and before calcination and c) FTIR spectrum of the sample after calcination at the 900°C.

At the pre-combustion (gel precursor) samples, presence of the water is observable by 1383.89 and 1637.89 cm^{-1} peaks. Visinescu et al.[11] studied gel precursor $Co_{0.4}Zn_{0.6}Al_2O_4$ sample by FTIR and found the water peak in the 1632 cm^{-1} which was as same as our result. FTIR peaks of combusted (Figure 6b) and combusted and calcinated (Figure 6c) samples revealed that peaks related to free water were omitted and some new peaks at 420 - 670 cm^{-1} appears is the samples which would be attributed to aluminum-oxygen and metal-aluminum-oxygen bonds. Also some weak absorbed moisture by KBr still presents in the samples. In previous studies [6], IR spectra of $Co_xZn_{1-x}Al_2O_4$ system that heat treated at 900°C and spectral vibrations corresponding to the spinel structure are identified at about 650, 550, 540, 520, 500 and 490 cm^{-1} which are similar to our findings.

Colorimetry was done on samples with different stoichiometric values and heat treated at 900°C. The results were arranged by CIELAB standard and were shown in Table 2. The CIELAB colorimetric coordinates allows good qualitative and quantitative characterization of the pigment colors. In this table *L* is lightness which indicates how light or dark a color is. It moves from white (at the top) to black (at the bottom). a* value describes the red/green dimension of a color. If a* value moving to positive the red color increases and if it moves to negative the green color raises in the pigment. b* shows the yellow/blue dimension of a color. If b* value moves to positive, the yellow color increases and it moves to negative, the blue the color increases in the pigment. c* is chroma which shows the colors saturation (strong or weakness of color). If c* is closer to the center of the color circle, the color become more neutral but if goes closer to the edge of the circle, the color become more saturated. h° is the hue angle which refers to the name of the color (red vs. blue) and identifies its position on the color wheel. Most hues have the greatest possible saturation at the mid-point of the lightness axis.

From Table 2 It can be seen that by increasing of Cobalt content in $Co_xZn_{1-x}Al_2O_4$ system, lightness (L*) of sample decreases but hue (h°) and chroma(c*) increases. The maximum lightness belongs to the white sample ($ZnAl_2O_4$) which is a cobalt-free sample but the maximum of chroma fit in $Co_{0.5}Zn_{0.5}Al_2O_4$ samples. On the other hand, cobalt is the main source of the blue color in the ceramic pigments. According to CIELAB standard, more negative amount of the b* and higher value of the c* are measure of the best blue color. In the present study the best blue color was achieved from $Co_{0.5}Zn_{0.5}Al_2O_4$ sample with b* = -38.28 and c* = 39.02 which has higher c* than other samples also. $CoAl_2O_4$ sample with b* = -16.34 due to the greater amount of cobalt and the absence of the Zn has the darkest blue color. For comparison, at previous studies, by increasing of the Co content, lightness (L*) is reduced also and best blue color was found in $Co_{0.5}Zn_{0.5}Al_2O_4$ sample but b* of this samples (b* = -36.24) was smaller than our result [6].

Figure 6 shows the colorimetry results samples that heat treated at 900°C on the CIELAB color space. From this figure it's obvious that negative values on the b* axis indicates blue color. Going towards more negative values from b* axis, blue color is brighter which belongs to $Co_{0.5}Zn_{0.5}Al_2O_4$ pigments.

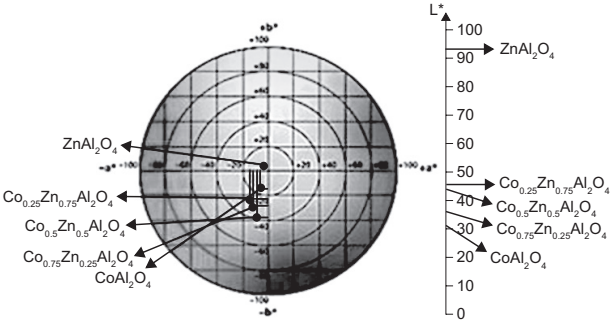


Figure 6. Colorimetric results of the samples heat treated at 900°C on the CIELAB color space.

Colorimetric results of the $Co_{0.5}Zn_{0.5}Al_2O_4$ sample that heats treated at different temperatures are collected in Table 3 and also plotted based on CIELAB color space (Figure 7). From this table it's apparent that by increasing heat treatment temperature, lightness (L*) has been increased but a* and b* values have been decreased. At 600°C and 700°C, negative values of a* which is related to green color is higher than the b^*. It means that color of these samples are closer to green, but by increasing calination temperature negative values of b* and positive values of c* were increased. This behavior was started from 800°C, was increased at 900°C and leads to change dark green to light blue in calcinated samples. Also c* is tinting strength of color and increasing of it means that

Table 2. Colorimetric results of the samples heat treated at 900°C.

sample	L*	a*	b*	c*	h°
$ZnAl_2O_4$	93.92	-1.76	1.86	2.56	133.39
$Co_{0.25}Zn_{0.75}Al_2O_4$	46.8	-12.69	-20.42	24.04	238.14
$Co_{0.5}Zn_{0.5}Al_2O_4$	45.59	-7.54	-38.28	39.02	258.85
$Co_{0.75}Zn_{0.25}Al_2O_4$	36.46	-8.26	-22.96	24.4	250.21

Table 3. Colorimetric results of $Co_{0.5}Zn_{0.5}Al_2O_4$ heat treated at different temperatures.

Temp. (°C)	a*L	a*	b*	c*	h°
600	39.94	-4.735	-2.164	7.074	197.812
700	40.715	-5.389	-4.297	8.547	210.178
800	43.358	-6.75	-18.533	20.495	244.726
900	45.59	-7.54	-38.28	39.02	258.85

less pigment was needed for reach ideal color. Incresing of lightness and decreasing b* of $Co_{0.5}Zn_{0.5}Al_2O_4$ samples by increasing calcination temperature are similar to previous researches. [6]

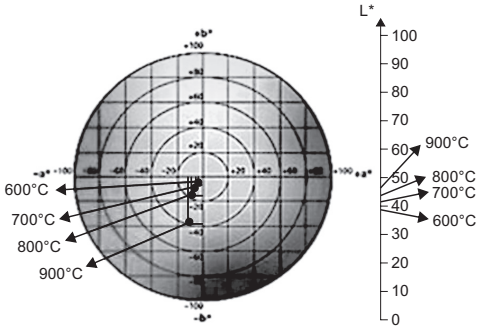
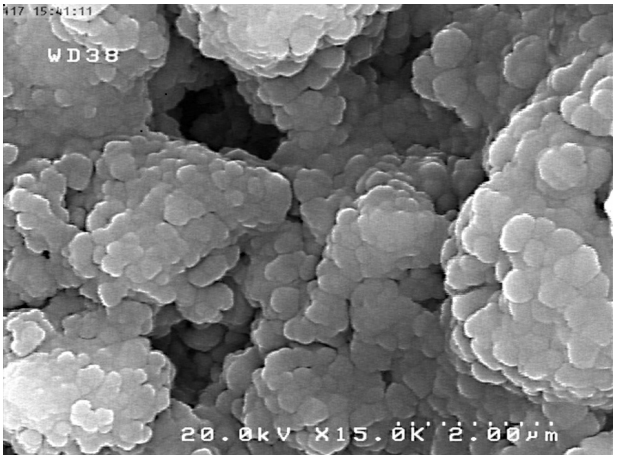
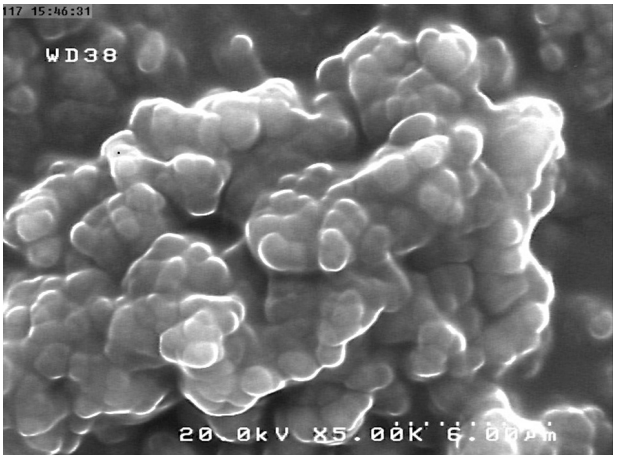


Figure 7. Colorimetric results of $Co_{0.5}Zn_{0.5}Al_2O_4$ heat treated at different temperatures on the CIELAB color space.

Morphology of $Co_{0.5}Zn_{0.5}Al_2O_4$ samples which were calcinated at different temperatures was studied by FESEM and results were shown in Figure 8 and 9. Images of Figure 8 show that nano particles are sticking together and agglomerated. Nano pigments having a small particle size, high surface energy and as a result they tend to agglomeration. On the other hand, agglomerated structure was loose then it would be separated easily by grinding. Figure 9 shows agglomerated structures of samples were calcinated at 900°C after grinding in planetary mill for 15 minutes. Results reveal that agglomerated particles were separated and particle size of nano powders were about 85nm.



a)



b)

Figure 8. FESEM images of $Co_{0.5}Zn_{0.5}Al_2O_4$ sample heat treated at different temperatures: a) 600°C, b) 900°C.

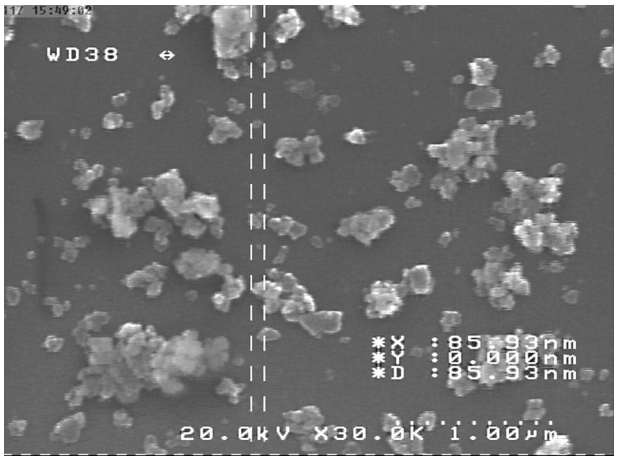


Figure 9. Sample was calcinated at 900°C after grinding in planetary mill for 15 minutes.

CONCLUSION

1. In this study $Co_xZn_{1-x}Al_2O_4$ system with different Co/Zn ratios (x = 0; 0.25; 0.5; 0.75 and 1) was synthesized by gel combustion method and results revealed that it's possible to reach the pure blue color spinel by decreasing amount of cobalt.
2. Thermal analysis curves exposed that decomposition of the samples were occurred in three stages. Before 200°C absorbed water and gases was removed, at 200°C reaction was took place and less than 600°C crystallization was initiated.
3. The color of nanoparticle spinels were changed from white to dark blue based on the Co/Zn ratio and calcination temperature. Best blue color was found in $Co_{0.5}Zn_{0.5}Al_2O_4$ sample which was calcinated at 900°C.

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