

SYNTHESIS AND SPECTRA CHARACTERIZATION OF $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ NANOSIZED PIGMENTS BY GEL COMBUSTION METHOD

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Nano sized pigments with the general formula $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) were synthesized using chlorides by gel combustion method at 700, 800, 900, 1000, 1100°C. DTA/TG, XRD, UV-Vis. and SEM were used to characterize the samples. The DTA results revealed that the formation of the spinel phase occurred at 600 to 670°C. XRD results showed that all the samples, except those treated at 1000 and 1100°C, were constituted of only one phase. The ones treated at 1000 and 1100°C showed extra peaks related to Al_2O_3 . The cobalt containing samples showed a low reflection in the range of 540 to 630 nm, corresponding to the absorption of the colors yellow and orange. Therefore, the cobalt containing samples demonstrated diverse blue colors. The results also revealed that by increasing the cobalt content, the crystallite size decreased from 32 to 9 nm, while by the rise in heat treatment temperature it decreased from 17 to 26. The SEM micrographs revealed the formation of nanosized pigments, with some degree of agglomeration.

INTRODUCTION

Cobalt aluminate spinel (CoAl_2O_4), also known as Tenard's blue, is one of the most popular inorganic pigments [1], and has high thermal and chemical stability and resistance to acids, alkalis, light and various atmospheric agents, making it suitable for various industrial applications, such as ceramics, glass, plastics, paint, paper, rubber, and color TV tubes, etc. [2-5].

The spinel structure has the general formula AB_2O_4 , in which A and B are divalent and trivalent ions, respectively. In this structure the unit cell is consisted of 8 face centered cubic (FCC) formed by oxygens, with 64 tetrahedral and 32 octahedral sites, of which only 8 tetrahedral and 16 octahedral sites are occupied by the divalent and trivalent cations. There are two ideal types of this structure: the first one is the normal spinel, in which the tetrahedral sites are occupied by the divalent cations and the octahedral sites by the trivalent cations. The second ideal type is the inverse spinel, in which all the tetrahedral sites are occupied by trivalent cations, while an equal number of divalent and trivalent cations share the octahedral sites [6, 7]. In addition to these ideal structures, spinels can form in a mixed structure, in which the distribution of the cations in the tetrahedral and octahedral sites is random [8].

Using spinel structure for making pigments has the benefit of high mechanical strength, high thermal stability, low sintering temperature and the easy incorporation

of chromophore ions into the lattice, which allows for different types of dopands, thus producing ceramic pigments with different colors [6 - 11]. However, cobalt is expensive and causes serious environmental problems, therefore some researchers have incorporated Co in ZnAl_2O_4 (gahnite) to reduce the problems [12 - 16].

As far as the authors know, data on the synthesis of $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ pigment is very scarce and only a few papers have been published on the issue.

de Souza et al. [12] used a polymeric precursor method involving citric acid and ethylene-glycol to obtain cobalt(II)-aluminates containing a reduced amount of cobalt to synthesized $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0; 0.1; 0.3; 0.5; 0.7; 0.9$ and 1) with a final heat treatment at 600, 700, 800 and 900°C. They found that by increasing the Co content the lattice parameter increased from about 8.083 to 8.095 Å and the crystallite size decreased from about 21 to 39 Å for the samples heat treated at 800°C. They observed a strong absorption in the range of 570 to 630 nm, i.e. absorption of the colors yellow, orange and red. Thus, the reflectance occurs in the complementary colors, namely violet, blue and cyan, centered in blue.

Popovic et al. [13] used a sol-gel method to synthesize the pigments. They found that cobalt doping caused a nonuniform increase of unit-cell parameter and induced the inverse spinel structure.

Visinescu et al. [14] synthesized nanosized pigments of $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0, 0.1, 0.2, 0.4, 0.6, 0.8$ and 1) by a starch-based route and a final heat treatment at 800°C.

Kurajica et al. [15] synthesized $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0.04, 0.08$ and 0.12) using sol-gel method by heat treatment at temperatures up to 900°C . They observed that by heat treatment at lower temperatures a partial oxidation of Co^{2+} to Co^{3+} occurred and Co^{3+} ions were accommodated in octahedral sites causing a green color, while by heat treatment at temperatures above 700°C Co^{3+} ions reduced to Co^{2+} , which occupied tetrahedral sites accompanied by a change of color from green to blue.

Osorio et al. [16] synthesized $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0.2, 0.4, 0.6, 0.8$ and 1) pink nanosized pigments using a co-precipitation reaction following by calcination at 700°C . They believed that the particle size has a profound effect on the coordination number of Co^{2+} ions, that is, a coordination of four when in bulk size and six in when in nanosize.

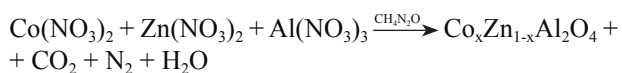
Recently, use of nanosized pigments for ink-jet printing to decorate products such as glazed tiles and porcelains has become popular [17, 18]. The advantages of this technique include no direct contact between the printer and the surface of the product to be printed, high speed of decoration and low cost.

In the present work $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1) nanosized pigments were synthesized for the first time by combustion gel method and a thorough investigation of the effect of composition and calcination temperature was conducted.

EXPERIMENTAL

Materials and Method

The raw materials ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2CO_3 , HNO_3 and HNO_3) used in this work were all of analytical grade. Aluminum, zinc and cobalt chlorides were weighted in stoichiometric ratios (total weight of about 35 g). They were added to 300 ml distilled water and stirred for complete dissolution. The pH in all the resulted pinkish solutions was equal to 3. Then 100 ml sodium carbonate was added to the solutions to reach a pH of 7. During this step the chlorides reacted to form carbonates as precipitates. The precipitates were filtered with distilled water and acetone several times and dried. The resulted powders were then dissolved in nitric acid to form nitrates. Then urea was added as fuel in 0.5 ratio to form $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ [19]:



Urea was added during magnetic stirring at 110°C to first obtain a transparent solution and then a purple gel. The gel was combusted in a furnace at 500°C for 15 min. to reach a fluffy mass which was calcined at 700, 800, 900, 1000 and 1100°C for 1h to reach the blue pigment.

Characterization

DTA/TG (Perkin Elmer, Pyris Diamond, alumina crucible, Ar atmosphere, with a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$) was used to study the reactions during heat treatment of the gels (about 1 mg). Crystalline phases formed by thermal heat treatment of the samples were identified by X-ray diffraction (XRD, X-pert Philips, CuK_α , 40 kV, 30 mA, 0.02° , 2 sec.). The average crystallite size (D) was determined by

Debye-Scherrer's formula according to the following equation (1):

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where λ is wavelength of the incident X-ray, β is half width of the diffracted peak and θ is diffracted angle.

The powders were examined by spectrophotometer (X-Rite SP64 Portable Sphere Based Spectrophotometer) to obtain reflection spectra using D65 illuminant. Scanning electron microscope (FESEM, Hitachi, S-4160) was used to observe the morphology of the samples.

RESULTS AND DISCUSSION

Figure 1 shows the DTA/TG curve of three of the prepared gels. The endothermic reaction accompanied by a weight loss of about 10 % at about 100 and 200°C is attributed to the evaporation of the moisture and chemisorbed (bound) water, respectively. The exothermic peak at about 275°C again accompanied by a weight loss of about 45 % is due to urea combustion. The endothermic peak between 600 to 670°C is believed to be a result crystalline phase formation. Apparently by increasing the cobalt content the crystallization occurs at lower temperatures. The weight loss of about 20 % coincident with that is believed to be due to the decomposition of nitrates. In the case of the gels with the composition $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ and CoAl_2O_4 , an exothermic peak starting at about 900°C is observed. Such a behavior is unprecedented in the literature and later with the support of XRD patterns was found to be owing to formation of Al_2O_3 .

Figure 2 shows the XRD patterns of the samples with different Co content calcined at 900°C . It is observed that only spinel-type phase is formed in the samples. It is observed that by increasing the cobalt content, the peaks shifted to lower angles, indicating the increase in d-spacings, whereas considering that ionic radius of 4-coordinated Co^{2+} is smaller than that of 4-coordinated Zn^{2+} the opposite was expected. Popovic et al. [13] also observed the same trend. They attributed this to the fact that a considerable level of structure inversion occurs in gahnite due to Co doping. That means that only a part of Co^{2+} substitutes for Zn^{2+} on tetrahedral sites, and the remaining Co^{2+} substitutes for Al^{3+} on octahedral sites

in the ZnAl_2O_4 lattice, causing the increase of unit-cell parameter. These results are valuable because previous publications [20] indicated that both CoAl_2O_4 and ZnAl_2O_4 have normal spinel structure. They believed that by increasing cobalt content Co^{2+} simply substitutes for Zn^{2+} , obviously disregarding the fact that this would lead to a decrease of unit-cell parameter (cation radii for tetrahedral Zn^{2+} and Co^{2+} is 0.60 and 0.58 Å, respectively). The XRD patterns also indicate that with increasing cobalt content the intensity of the peaks initially rises and then falls. No previous record of such a behavior was found in literature. This is believed to be due to the randomness of the structure as a result of forming mixed spinel structure.

Figure 3 illustrates the XRD patterns of the sample $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ heat treated at various temperatures. It shows that with the increase of heat treatment temperature up to 1000°C, the peaks intensity increased

as a result of higher crystallinity, but the position of the peaks and their relative intensities remained unchanged. On the other hand, by increasing temperature the peaks became narrower, showing the growth of crystallites.

In the sample heat treated at 1000 and 1100°C, however, Al_2O_3 phase also appears in the expense of the spinel phase. This is in consistence with the DTA results. It seems that at high temperatures the spinel phase is not stable and decomposes.

The effect of cobalt content and temperature on the crystallite size is shown in Figure 4. It is observed that by increasing the cobalt content the crystallite size decreased. This could be a result of higher lattice strain when more cobalt is introduced. Figure 4 also indicates that by increasing temperature the crystallite size increased. This was expected, since increasing temperature, increases the growth rate. de Souza et al. and Visinescu et al. [12, 14] also observed the same results.

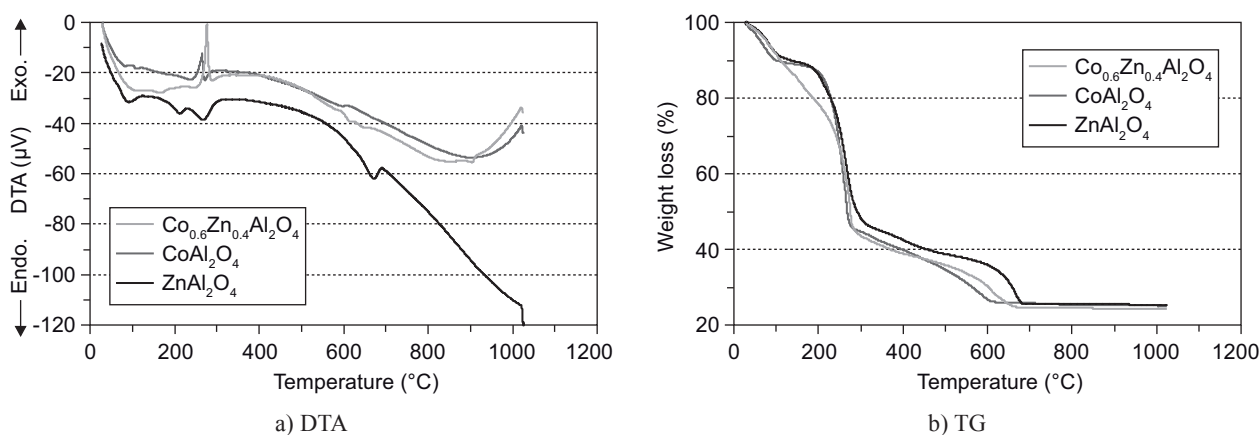


Figure 1. Thermal analysis of the dried gels

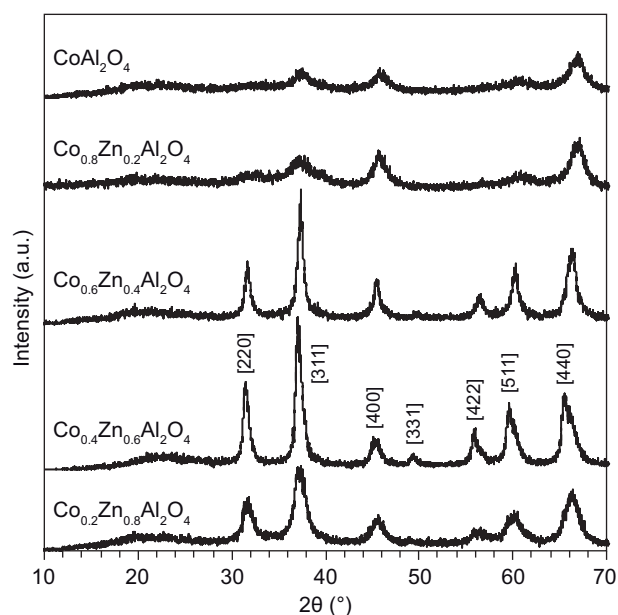


Figure 2. XRD patterns for the samples with different cobalt content heat treated at 900°C.

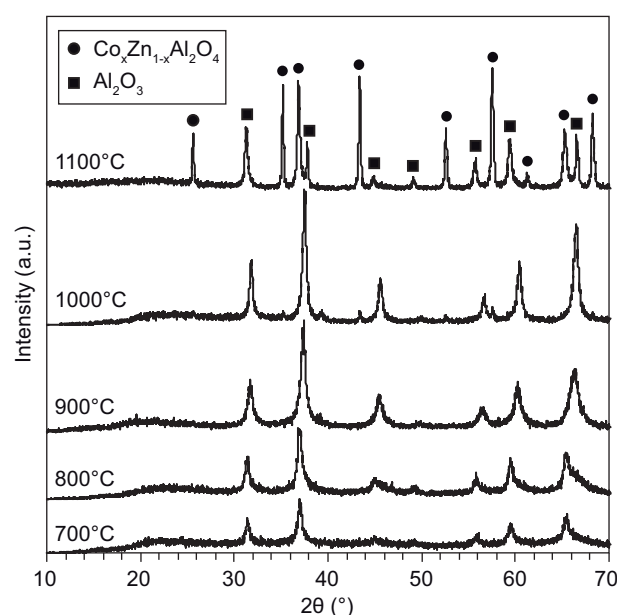


Figure 3. XRD patterns for the sample $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ heat treated at different temperatures.

Figure 5 and 6 show the effect of cobalt content and temperature, respectively, on the UV-Visible reflectance spectra of the powder samples. Since the samples without cobalt doping did not have any blue color (it was white)

no spectrum was taken from it. For all the samples a poor reflection in the range of 540 to 630 nm, corresponding to the absorption of the colors yellow and orange is observed. This is in accordance with the results obtained by de Sousa et al. [12] and Visinescu et al. [14]. It can be observed that by increasing temperature the reflection

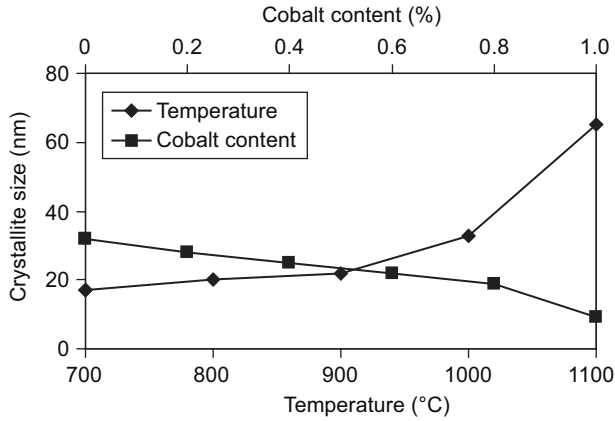


Figure 4. The effect of cobalt content and temperature on the crystallite size of the samples.

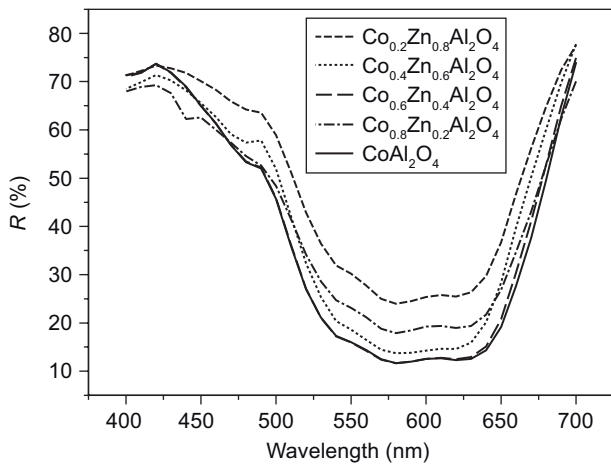


Figure 5. UV-Vis. reflectance spectra of the samples heat treated at 900°C.

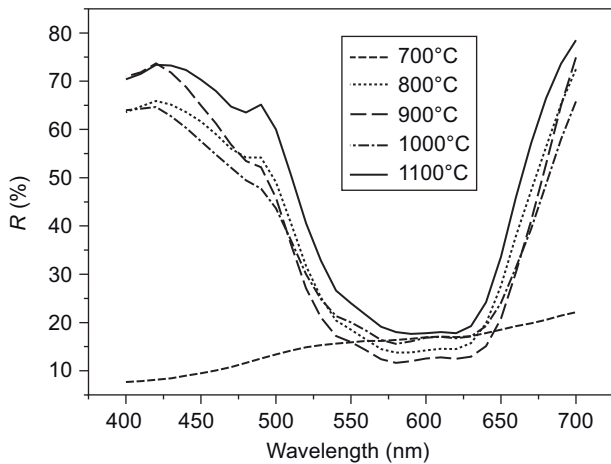
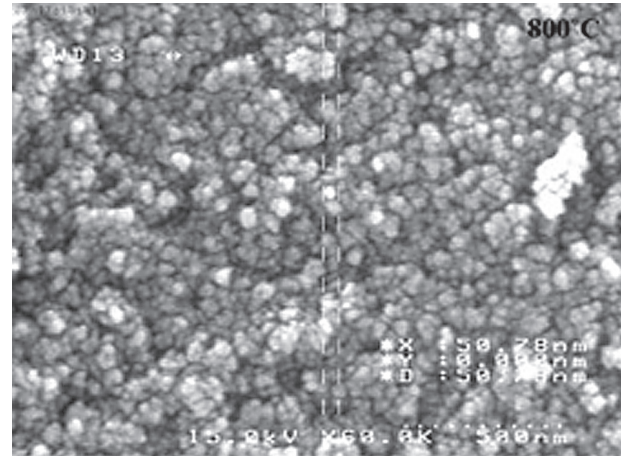
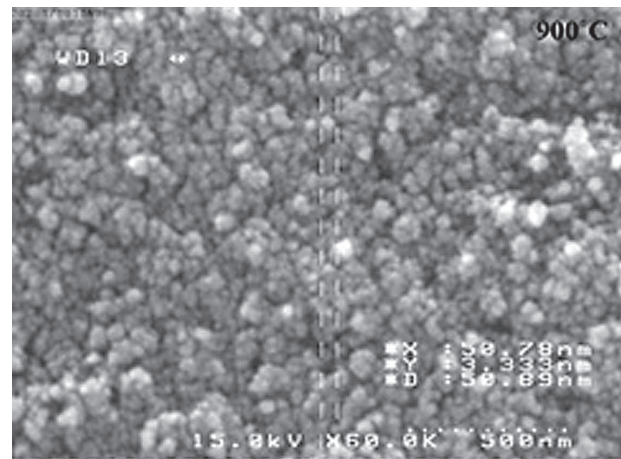


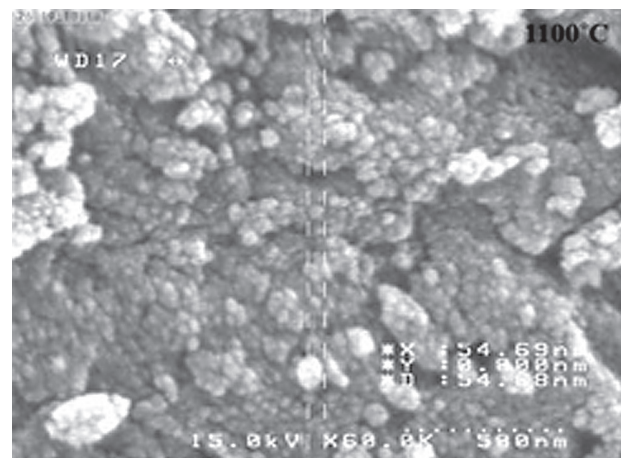
Figure 6. UV-Vis. reflectance spectra of the sample $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ at different heat treatment temperatures.



a) 800°C



b) 900°C



c) 1100°C

Figure 7. SEM micrograph of the sample $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ calcined at different temperatures ($\times 60\text{k}$).

risers indicating a brighter color. The sample treated at 700°C had a dark color, probably due to the low amount of the crystalline phase formed in this sample.

Figure 7 shows the SEM micrograph of the sample $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ calcined at different temperatures. It is obvious that due to high surface area of the samples, agglomeration has occurred, a characteristic of the fine powders. It is obvious that the particle size of the samples is less than 100 nm and therefore they are nonosized. Nanosized pigments have recently found applications for decorating glazed tiles and glasses by jet printing method.

CONCLUSIONS

Pigments with the composition $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) were synthesized using gel combustion method. The DTA results revealed that the formation of the pigment phase occurred at 600 to 670°C. XRD results showed the formation of a single phase in all the samples, except the ones treated at 1000 and 1100°C, which showed extra peaks related to Al_2O_3 . The cobalt containing samples a low reflection in the range of 540 to 630 nm, corresponding to the absorption of the colors yellow and orange was observed. The cobalt doped samples had a strong reflection in the range of 540 to 630 nm, indicating the absorption of the yellow and orange colors was observed. The results also revealed that by increasing the cobalt content, the crystallite size decreased from 32 to 9, while by the rise in heat treatment temperature it decreased from 17 to 26.

These facts proves that the system $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) can be employed to obtain ceramic blue pigments of diverse lightnesses and hues, which offer potential industrial applications.

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