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Synthesis of Wurtzite Nano-crystalline ZnO-CoO Pigment by High Energy Milling

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ABSTRACT

$Zn_{0.9}Co_{0.1}O$ ceramic pigments were synthesized using simple high energy milling method. Zinc and cobalt oxides were used as starting materials. Products were investigated using simultaneous thermal analysis and fourier transformation infrared. Pigments were characterized using X-ray diffraction, diffuse reflectance and Scanning Electron Microscopy. The results showed the effect of calcination temperature on Co solubility and crystallite size. Nano-crystalline $Zn_{0.9}Co_{0.1}O$ pure solid solution synthesized at different temperatures consist of 300-500 nm semispherical particles. Crystallite size of $Zn_{0.9}Co_{0.1}O$ calcinated at $1000^{\circ}C$ was about 100 nm. A broad reflectance band around 540 nm (green region) for all powders indicating the appearance of deep green pigment was observed. Furthermore, elevation of calcination temperature caused the increase of color saturation. Prog. Color Colorants Coat. 2(2009), 45-51.

1. Introduction

High energy milling is one of the most common methods for processing nanocrystalline and amorphous solid materials. This method is employed in mineral processing [1], activation of silicates [2], and low temperature, solvent free preparation of inorganic compounds [3]

It provided new possibilities to produce material with benefit characteristic compared to those which prepared by conventional methods such as low temperature and controllable process to scale up [4].

ZnO based oxide have already been used for a wide range of applications such as electronic devices [5], ceramic pigments [6] and optical materials [7].

Cobalt doped ZnO, among variety of applications, has been attracted due to intense green color, and it can be used as medium pigment [6]. However, Lavat *et. al.* showed good blue pigments for ceramic industry,

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obtained by solid state reaction of cobalt low concentration with ZnO [8].

ZnO-Co nanoparticles have ferromagnetic properties, in which Co successfully incorporates into wurtzite lattice at the Zn site [9-10]. Nevertheless, ZnO-Co is a good green ceramic pigment. In previous works, it demonstrated an effective anticorrosive property and might be considered as a substitution for green-colored pigments based on the chromium (III) toxic pigment [11]. This pigment can be synthesis via different methods, such as: solid state reaction [6, 8], wet chemical [10] and combustion [12-13] methods. But easiest method for industrial applications is solid state reaction [8].

Damonte *et. al.* used the mechanical alloying, via high energy ball milling method, for cobalt incorporation into the wurtzite structure. However, they did not focus on the crystallite-particle size and color properties of the obtained ZnO-Co pigment [14].

In this paper the preparation of nano-crystalline $Zn_{0.9}Co_{0.1}O$ by high energy ball milling at different calcination temperature has been investigated. The effect of the calcination temperature on the entrance of the Co into the wurtzite structure and on the color of the pigments is being studied.

The products have been characterized by X-ray diffraction (XRD) apparatus, thermal analysis and scanning electron microscopy (SEM) and colorimetric methods.

2. Experimental

2.1. Materials & samples preparation

Solid solution of ZnO-CoO was prepared using analytical grade of ZnO (99.9% Merck) and cobalt oxide pure Co_3O_4 (99.9% Merck) 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 mins. After milling the slurry was dried in an oven at 110 ºC for 2 hrs, in order to remove residual water. Then powders were calcinated in a chamber furnace at different temperatures with a heating rate of 10 ºC/min.

2.2. Methods

A D-500 (Siemens, Karlsruhe, Germany) diffractometer was used for XRD analysis. The XRD patterns of the samples were analyzed by using Cu-Kα radiation. Morphology analysis of the particles was performed using Leo (Cambridge, UK) Scanning Electron Microscope (SEM) The powders were characterized by thermal analysis, where they. were heated with 10 ºC/min heating rate up to 1100 ºC, in air atmosphere. Simultaneous thermal analysis (STA) was performed using a PL-STA-1640 (Polymer Laboratories, Stanton Redcraft, UK) instrument at a heating rate of 10 ºC/min in an air atmosphere.

Ultraviolet 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 determination of the diffuse reflectance of the obtained powders as 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.

3. Results and discussion

Considering the aim of this work to achieve a complete solid solution of ZnO-CoO, Ahmed *et. al.* [11] showed that pure ZnO-CoO solid solution was completely formed, when 0-20% CoO was added. As the presence of Co is not detectable in XRD pattern for the amounts less than 5%, a 10% of Co have been chosen to make sure that a complete solid solution is formed. Hereafter, the sought product is symbolized by $Zn_{0.9}Co_{0.1}O$.

The X-ray diffraction patterns for the specimens with $Zn_{0.9}Co_{0.1}O$, prepared at constant rate milling and calcinated at 800-1100ºC, are shown in Figure 1. The main phase can be contributed to the wurtzite (ZnO) structure. The Figure reveals Co_3O_4 decomposition along with gradual replacement of zinc by cobalt in wurtzite structure. The diffracted X-ray peaks of the products prepared at different calcination temperatures demonstrate that the mechanical milling is a facile method to complete the reaction between ZnO and Co_3O_4 and to achieve the pure wurtzite solid solution.

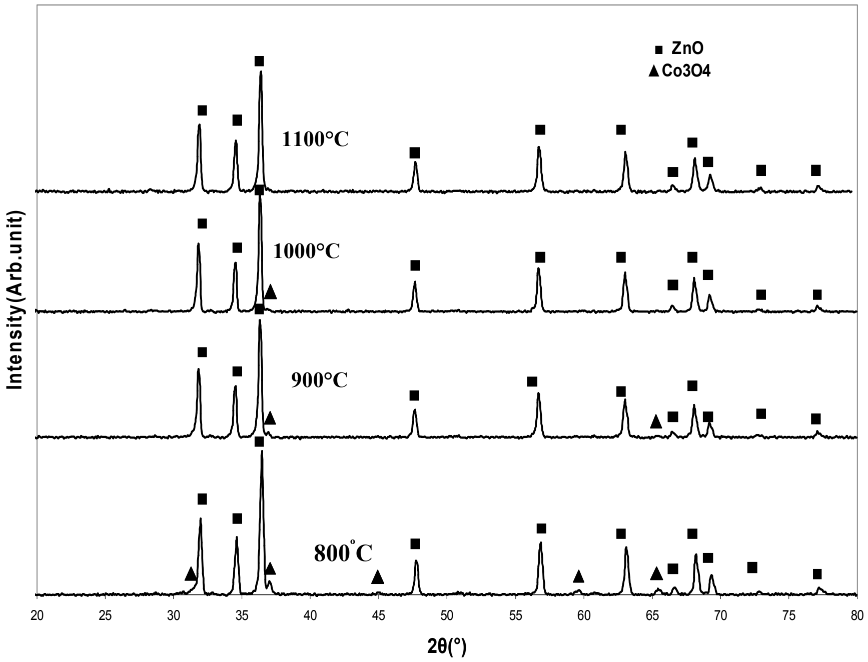

Figure 1: XRD pattern of the specimens with $Zn_{0.9}Co_{0.1}O$ calcinated at different temperatures

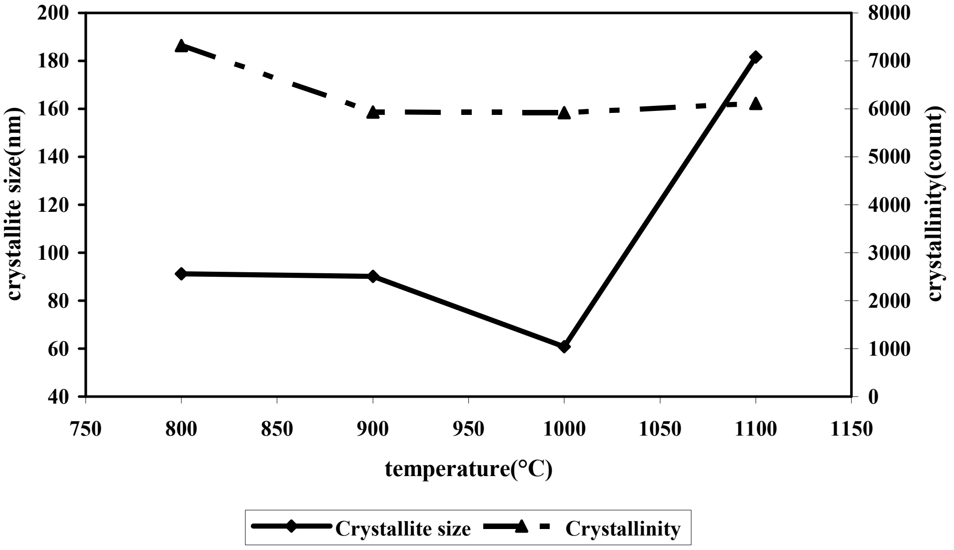

Figure 2: Crystallite size and crystallinity of the specimens with $Zn_{0.9}Co_{0.1}O$ calcinated at different temperatures

The average crystallite size which is determined by Scherer formula and crystallinity content of wurtzite (101) peak (2θ=36°) are shown in Figure 2. A decrease of average crystallite size with increasing calcination temperature (800-1000°C) is observed. Moreover, the width of peak (101) (2θ=36°), referring to wurtzite, increases with increasing calcination temperature (800-1000°C), indicating the inclusion of Co in wurtzite structure. Deka *et. al.* have reported the decrease of wurtzite crystallite size due to the influx of Mn into ZnO structure [9]. However, the broadening of peaks can be related to the distortion of the host lattice, which is presumably due to the strain induced by the occupation of Zn ion sites by Co ions, or to the presence of the cobalt precipitates or clusters [15]. The increase of crystallite size at 1100°C is ascribed to the crystal growth after completion of the solid solution.

The SEM photographs are illustrated in Figure 3. It shows that the average particle size of the sample calcinated at 800°C is about 300 nm whereas it increases to about 500 nm at 1100°C. Moreover, the morphology of particles has been changed from cubic to semi-spherical, which can be explained by particle growth at higher temperatures.

Figure 4 shows the STA thermogram of the $Zn_{0.9}Co_{0.1}O$ specimen. The weight loss of the sample at 900°C and the endothermic peak of DTA curve stem from decomposition of Co_3O_4 and release of O_2. The weight loss in the range of 100-300°C and about 900°C is due to gradual elimination of physical and structural water, and Co_3O_4 decomposition respectively. Decomposition reaction of Co_3O_4 is as follow:

$$Co_3O_4 \rightarrow 3CoO + 1/2O_2 \qquad (1)$$

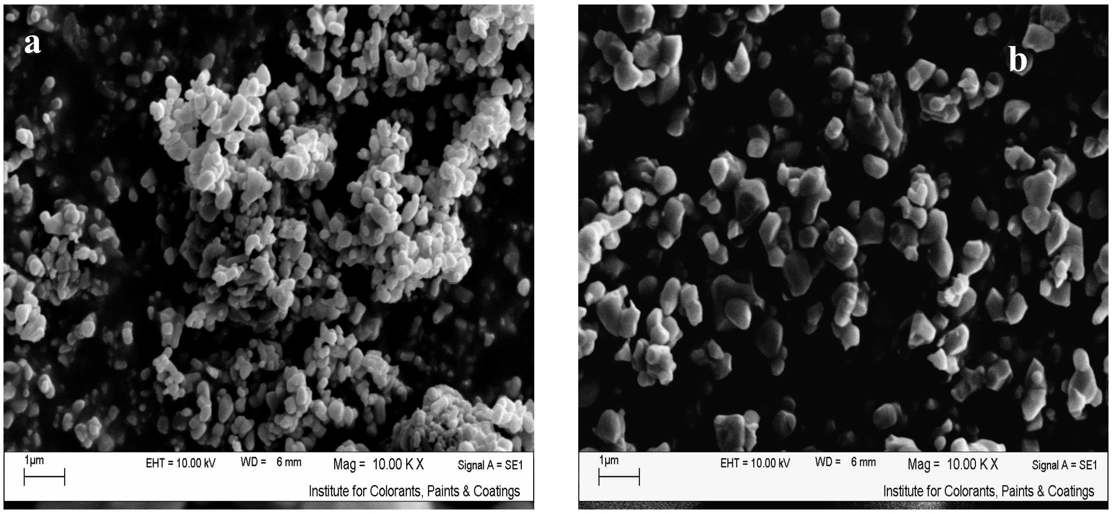

Figure 3: SEM images of specimens with $Zn_{0.9}Co_{0.1}O$ calcinated (a) at 800°C (b) at 1100°C

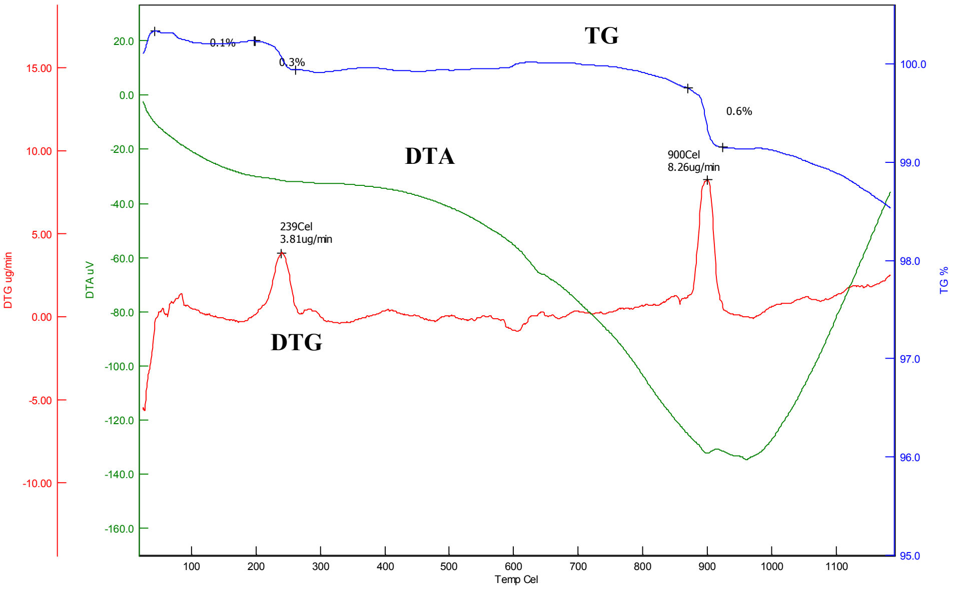

Figure 4: STA analysis of the specimen $Zn_{0.9}Co_{0.1}O$.

The chemical and structural changes that take place during milling can be monitored by the spectroscopic analysis. Figure 5 shows the FT-IR spectra of the obtained powders before and after the calcination at 900°C in the range of 450-4000 cm^{-1}. The characteristic bands at around 3400, and 670 cm^{-1} corresponding to the O-H group, disappear after calcination. In the IR curves of the calcinated powder, a broad intense band at 450-540 cm^{-1} can be observed. The strong broad band centered at 440cm^{-1} assigned to asymmetric stretching mode of the tetrahedral ZnO_4 group present in the wurtzite ZnO structure [8].

The color properties of $Zn_{0.9}Co_{0.1}O$ have been investigated by using the CIELAB coordinates and spectral reflectance. Figure 6 shows the diffuse reflectance spectra of the synthesized pigments. According to Figure.6, a broad reflection band around 540nm (green region) can be observed. Table 1 shows the result of the colorimetric coordinates L*, a*, b*.

The results show that calcination temperature could affect the color properties of the samples. Table 1 shows that calcination at 1000-1100°C has caused the formation of deep green pigment which is due to the complete inclusion of Co in ZnO structure. Sulcova and Trojan have shown that $Zn_{0.9}Co_{0.1}O$ has very good green hue ($L^*=51.26$, $a^*=-16.41$, $b^*=7.7$) which could be compatible with $Zn_{0.9}Co_{0.1}O$ calcinated at around 1000-1100°C ($L^*\approx53.9$, $a^*= -28.261$, $b^*=11.625$) [6]. However, the best method for comparison of similar pigments is the evaluation of pigment's chroma 'C^*' and hue angle 'h'. C^* and h can be calculated by the following equations [16]:

$$C_{ab}^* = \{(a^*)^2 + (b^*)^2\}^{1/2} \qquad (2)$$

$$h_{ab} = \tan^{-1}(b^*/a^*) \qquad (3)$$

Table 2 presents a comparison of the color parameters L*, C^* and h for high energy milled samples calcinated at different temperatures with those of reference [6]. Results indicate that three out of four samples have larger C^* than that of reference [6]'s sample which could be the consequence of a better solid solution formation using high energy milling.

Table 1: CIELAB coordination of $Zn_{0.9}Co_{0.1}O$ calcinated at different temperatures.

Calcinations temperature(°C)	L^*	a^*	b^*
800	57.123	-2.554	-1.300
900	59.006	-26.369	11.076
1000	53.965	-29.286	12.598
1100	53.924	-28.261	11.625

Table 2: Comparison of L*, C* and h for reference [6]'s sample and high energy milled samples calcinated at different temperatures.

Calcinations temperature(°C)	L^*	C^*	h
800	57.123	2.865	206.978
900	59.006	28.601	157.216
1000	53.965	31.881	156.724
1100	53.924	30.559	157.641
reference [6]'s sample	51.26	18.127	154.863

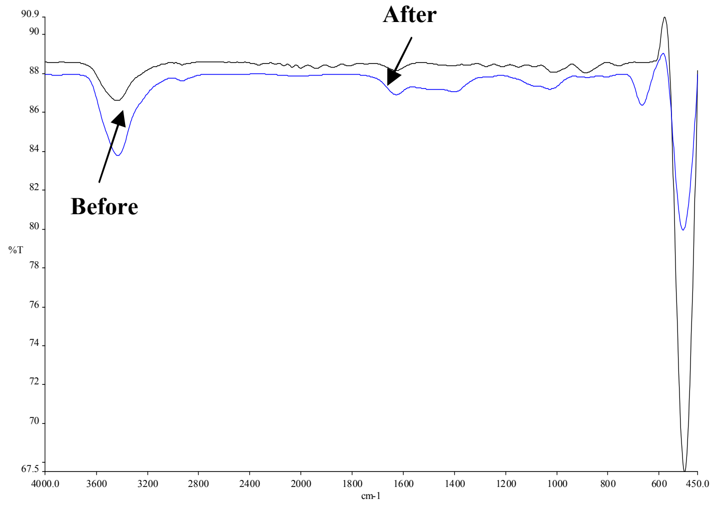

Figure 5. FT-IR spectra of the specimen before and after calcination at 900 °C.

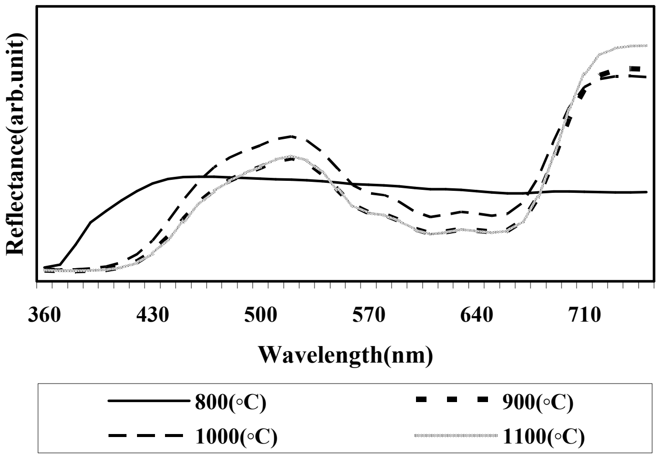

Figure 6: Reflectance spectra of $Zn_{0.9}Co_{0.1}O$ calcinated at different temperatures.

4. Conclusions

Nano-crystalline $Zn_{0.9}Co_{0.1}O$ samples were synthesized by simple high energy milling method. The results showed that Co was completely situated in the wurtzite structure at 1000°C as confirmed by X-ray diffraction and STA. Other results showed the formation of 300-500 nm semi-spherical particles of $Zn_{0.9}Co_{0.1}O$ solid solution with 100 nm average crystallite size. The color properties of the products investigated by using the CIELAB coordinates and the spectral reflectance showed a broad reflection band around 540nm which could be related to the green region. The results showed that calcination temperature could affect the color properties of the samples.

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