From nano-structured polycrystalline spheres with $\text{Zn}_{1-x}\text{Co}_x\text{O}$ composition to core-shell $\text{Zn}_{1-x}\text{Co}_x\text{O}@\text{SiO}_2$ as green pigments

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Abstract:

ZnO doped with Co^{2+} , a well-known green pigment which is an alternative to the chromium based inorganic pigments, has been prepared by a polyol process and investigated in terms of crystallographic structure and UV–visible properties. Thanks to the obtaining of nanometric crystallite size from our process, the incorporation of a very high concentration of Co^{2+} in the ZnO matrix is achieved. Thus, different grades of more or less deep green pigments can be produced. Furthermore, the obtaining of spherical aggregates allows the easy preparation of $\text{ZnO}:\text{Co}@\text{SiO}_2$ core-shells, minimizing hence the problems linked to the zinc oxide high solubility into slightly acidic conditions and the metal cation's toxicity.

Keywords: *Polyol synthesis, Zinc-Cobalt oxide, Green Pigment, Core-shell*

I. Introduction

Zinc oxide doped with cobalt, $\text{ZnO}:\text{Co}$ is a well-known green pigment which is largely developed, especially as an alternative to the chromium based inorganic pigments [1-6]. Indeed, the chromium has adverse effects on environment and the chroma a^* value is often poorer than the cobalt green materials [2]. Furthermore, chromium exist in oxides with various oxidation states [7], and the change of the Cr-O valence bond with the effect of oxygen partial pressure and/or temperature makes it difficult to uniform the hue of such Cr-based pigments; it is not easy to control in the actual production. The green cobalt pigments can meet the requirements

of the color stability, lower toxicity for, as illustration, building materials. Nevertheless, to get different grades of green hues, the solubility of cobalt inside the ZnO matrix must be varied with great amplitude [2]. New synthesis process allowing the introduction of high content of cobalt inside zinc oxides must be found [8-12]. Also, the toxicity and the chemical stability of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ pigments (the oxide is quite soluble in slightly acidic aqueous solution) has to be increased. That is why, during recent past years, there are many methods for preparation of these pigments such as solid state reaction [13], hydrothermal technique [14] co-precipitation method [15], combustion synthesis [16], High Energy Ball milling processes... But at the exception of solid state reaction, those methods are easy to introduce impurities, and experimental process can be expansive and complex. The solid state route, due to the obtaining of large particle size, gets the disadvantage to lead to the appearing of cobalt secondary phases for moderate cobalt concentration (depending on the authors); so, the preparation of deep green hues is compromised. To prevent metal oxide dissolution and their subsequent toxicity effects, numerous coating strategies involving a thin silica layer have been developed to create colloiddally stable surface-protected nanoparticles [17]. For instance, ZnO nanoparticles have shown a significant reducing of dissolution in acidic digestive media such as gastric media after coating with a 28 nm thick silica shell [18]. This increased chemical stability was directly related to the decrease in cytotoxicity when $\text{ZnO} @ \text{SiO}_2$ nanoparticles were incubated with colorectal cell lines.

In this study, we propose a simple and low cost process: polyol co-precipitation route in order to obtain pure nanometric $\text{Zn}_{1-x}\text{Co}_x\text{O}$ with x that can be varied in a wide range. The easy obtaining of $\text{ZnO}:\text{Co}@\text{SiO}_2$ core-shell powers is also reported, these latter materials exhibiting a decreased solubility into acidic solution and avoids the possibility of environment pollution with Co^{2+} ions.

II. Experimental

II.1. Powder from polyol synthesis

All of the chemical reagents were purchased from Aldrich and used without further purification steps. Zinc acetate dihydrate: $\text{Zn}(\text{CH}_3\text{OO})_2 \cdot 2\text{H}_2\text{O}$ and cobalt nitrate: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as zinc and cobalt sources and diethylene glycol ($\text{H}_{10}\text{C}_4\text{O}_3$) as template. In a typical synthesis, zinc and cobalt precursors are introduced in stoichiometric proportion in order to get 1 g. of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ powder (2.924 g) and added to 250 mL $\text{H}_{10}\text{C}_4\text{O}_3$. The resulting mixture was heated under continuous stirring to obtain a green sol refluxed at 180 °C for 1 h. At the end of the reaction, the precipitate was separated by centrifugation, washed several times with ethanol to remove the organic product and dried in an oven at 80 °C.

In a second step $\text{Zn}_{1-x}\text{Co}_x\text{O}@\text{SiO}_2$ core-shells were obtained by controlled hydrolysis-condensation of tetraethoxysilane (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) in alcohol medium (EtOH) from a derived Stöber process. Typically, 100 mg of powder were dispersed in 150 mL of EtOH, and 6.4 mL of NH_4OH as hydrolysis-condensation catalyst. TEOS with various quantities calculated to obtain different SiO_2 shell thicknesses was then added drop by drop to the as-prepared suspension. The suspension was then maintained under agitation at room temperature, 2hrs. Additionally, few drops of HCL aqueous solution (0.2M) can be added at the end of the maturation step in order to dissolve ZnO cores in case the silica shell is porous.

II.2. Characterization techniques

The powder structure was characterized by X-ray diffraction analysis (Philips PW 1820, PANalytical X'Pert instrument, 2θ range from 8 to 60° and λ -Cu ($K_{\alpha 1}$ - $K_{\alpha 2}$). The unit cell parameters were refined by structural pattern matching using the Fullprof® program package. The powder patterns were firstly analyzed using the Caglioti function (function N°5), i.e. the

isotropic peak profile function for which the u , v , w and shape parameters are refined; in a more appropriate model, the powder patterns were also refined using anisotropic peak profile (function N°7) that allows the crystallite size determination for each (hkl) crystallographic directions.

ICP measurements allow the determination of the Co/(Zn+Co) molar ratio of the Co-doped ZnO powder samples. Measurements were carried out on aqueous solutions obtained after complete dissolution of the powder into HCl with high purity using the Varian ICP-OES 720ES apparatus.

Scanning electron microscope used for morphological investigations of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ as-prepared particles is a Jeol-6700F SEM apparatus (using for chemical characterization, 15 kV as probe potential - 15 mm distance). For the $\text{Zn}_{1-x}\text{Co}_x\text{O}@\text{SiO}_2$ morphological characterization, transmission electron microscopy (TEM) images were recorded with JEOL JSM-6700F (operating at 5 kV) microscope.

The diffuse reflectance of our pigment particles were measured using a Varian Cary 5000 UV-Vis-NIR spectrophotometer in 250 nm - 2500 nm range. From the diffuse reflectance spectra, the determination of colorimetric parameters in the CIE $L^*a^*b^*$ colorimetric space for each compound was made using $x(\lambda); y(\lambda); z(\lambda)$ color matching functions which are the numerical description of the chromatic response of the observer (herein, CIE 1931 Standard Observer function).

III. Results and Discussion

III.1. Physico-chemical characterizations of as-prepared Co^{2+} -doped ZnO powder

All of the chemical reagents were purchased from Aldrich and used without further purification steps. $\text{Zn}_{1-x}\text{Co}_x\text{O}$ compounds with targets for x concentrations equal to 0.5 mol%, 10 mol%, 20mol% and 30 mol% are prepared by our polyol-mediated precipitation process.

These five compounds named here after ZC0, ZC05, ZC1, ZC2, and ZC3 were analyzed on a structural point of view by X-ray diffraction and on a chemical point of view by ICP measurements. In **Figure 1** are reported the X-ray diffraction patterns of the 5 as-prepared compounds. The compounds exhibit a pure würtzite structure, *i.e.* a single ZnO-type solid solution is obtained whatever the target composition. The efficient doping concentration, which was previously shown to differ from the target concentration in such a process used for the obtaining of $\text{Zn}_{1-x}\text{Al}_x\text{O}$ or $\text{Zn}_{1-x}\text{Ga}_x\text{O}$ phases, [19, 20] was titrated using ICP measurements.

Figure 1. X-ray diffraction patterns for various Co^{2+} -doped ZnO oxides obtained by hydrolysis-condensation in DEG. a) ZC0, b) ZC05, c) ZC1, d) ZC2 and e) ZC3.

The evolution of the efficient cobalt concentration versus the target one is plotted in **Figure 2**. The dependency of the efficient concentration versus the target concentration is clearly linear and the curve' slope indicates that half the cobalt ions in the raw polyol medium are efficiently

introduced in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ compounds: there is a constant factor of 2 in between the efficient and target cobalt concentrations.

Figure 2. Co^{2+} concentration efficiently introduced in Co-doped ZnO particles versus the Co^{2+} target concentration (corresponding to the ratio between Zn^{2+} and Co^{2+} ions introduced in the DEG synthesis medium).

Full pattern matching was performed on the X-ray pattern of the various $\text{Zn}_{1-x}\text{Co}_x\text{O}$ compounds. Two models were used for the full-pattern matching process: (i) a model using for the peak profile an isotropic peak profile function (Caglioti function, N°5 in FullProf package); (ii) an anisotropic peak profile function (N°7 in FullProf package). Indeed, previous works have already shown that ZnO particles obtained from the polyol process are constituted of anisotropic crystallites shape: olive shapes, with a (001) crystallographic orientation (large diameter direction). Consequently, the peak width has to be correlated to the peak's Miller indexes, using an anisotropic model for X-ray peak profile description. For illustration, the results obtained using these two different refinement processes on the ZC2 compound are reported in **Figure 3**. One can see that the correlation factors: R_p , R_{wp} , R_{exp} are both significantly decreased while an

anisotropic peak profile is taken into account, in comparison pattern matching with the use of an isotropic peak profile. Hence, the cell parameters and correlation factors (R_p , R_{wp} and R_{exp}) reported in the **Table 1** are extracted from the refinements using the anisotropic peak profile function. Also, the evolutions of the unit-cell parameters versus the cobalt concentration (efficient concentration in the mixed oxide) are plotted in the **Figure 4**. The proximity of Co^{2+} and Zn^{2+} Shannon ionic radii: Co^{2+} in (IV) coordination site equals 0.58 Å while ionic radius of Zn^{2+} in (IV) coordination site equals 0.60 Å, makes the variation of the cell parameters with composition very light. Nevertheless, a clear tendency of a decrease of the unit-cell volume can be observed. This unit-cell volume decrease is due to the decrease of the a cell parameter (**Figure 4a**) and c cell parameter (**Figure 4b**) into the same proportion (i.e., an homothetic decrease of both unit-cell parameters is observed). Indeed, the c/a ratio remains in a very narrow range: in between 1.6023 and 1.6026 values (**Figure 4c**).

Table 1. Unit-cell parameters and reliability factors obtained on the various Co^{2+} -doped ZnO oxides.

Target compound	Effective compound	a	c	R_p	R_{wp}	R_{exp}
ZnO-Co 0%	ZnO-Co 0%	3.25286(16)	5.21277(30)	3.0	3.5	2.0
ZnO-Co 5%	ZnO-Co 1.5%	3.25256(35)	5.21258(55)	3.8	3.8	2.1
ZnO-Co 10%	ZnO-Co 5.5%	3.25269(17)	5.21204(28)	2.8	3.2	1.9
ZnO-Co 20%	ZnO-Co 12%	3.25238(16)	5.21162(27)	2.6	3.9	1.9
ZnO-Co 30%	ZnO-Co 16%	3.25238(22)	5.21182(22)	2.9	3.6	1.9

Figure 3. (a) Full-pattern matching using isotropic peak profile function on the $\text{Zn}_{0.88}\text{Co}_{0.12}\text{O}$ (ZC2) oxide composition ; (b) full-pattern matching using an anisotropic peak profile function on same compound.

Figure 4. Evolution of the unit-cell-parameters of Co-doped ZnO powders versus the cobalt concentration.

From anisotropic peak profile refinements, it is possible to extract directly the crystallite shape of the as-prepared $\text{Zn}_{1-x}\text{Co}_x\text{O}$ crystallites with great accuracy. The crystal shapes are drawn in **Figure 5**. The pure ZnO compounds, already studied using same polyol route and using same experimental condition exhibits the same crystal shape and size than the first ZC05 compound (i.e. the impact of the doping for such low cobalt concentration is negligible). However, a significant evolution of the crystal size (volume) and shape (needle-like anisotropic distortion) is shown with increasing cobalt concentration. From an olive shape with a large diameter along the (001) axis, a length of 11 nm/ a width of 8.6 nm, the particles with increasing the cobalt concentration tend to become more spherical and with a smaller crystallite size. Even, a reversal of the anisotropy is observed for the ZC3 compound, with a width along (hk0) direction becoming larger than the length along (001) direction. Besides the monotonic evolution of the cell parameters versus the cobalt concentration, the monotonic modification in the crystallite shapes supports the efficient and homogeneous introduction of cobalt ions inside the würtzite crystallographic network.

Figure 5. Crystallite's average morphology obtained from X-ray diffraction pattern refinements using anisotropic peak profile function.

SEM images were also made on various ZCX powders. The images reveal Co^{2+} -doped ZnO particles are made of spherical aggregates with sub-micron diameter in good agreement with our previous reports on the synthesis of Ga^{3+} -doped ZnO particles from polyol synthesis (**Figure 6**) [19, 20]. The obtaining in a reproducible way of spherical aggregates is shown, *i.e.* whatever the cobalt concentration very similar powder architecture is observed. Nevertheless, an accurate study of the aggregate (particle) size distribution from image treatment has allowed a significant evolution versus the cobalt concentration to be shown. Indeed, in the case of low cobalt concentration a bimodal distribution for the particle size, with approximatively half-half concentration, with centers located at 225 nm and 425 nm, is evidenced whereas, for high cobalt concentration, a single mode centered on 225 nm is observed (*i.e.* the biggest aggregates have disappeared) (**Figure 7**). Maybe, the change of the aggregate size can be correlated positively with the change of crystallite size versus cobalt distribution, since for both scales a slight tendency to the size decrease is noted. Considering that the aggregates have an average diameter of about 200-400 nm and are constituted of a random pack (with about 40% of porosity) [19] of olive-like crystallites (about 10 nm size), the aggregates are constituted of about 10^4 crystallites.

Figure 6. SEM photographs of the various Co^{2+} -doped ZnO spherical particles obtained by hydrolysis-condensation in DEG (SEM microscopy). a) ZC0, b) ZC05, c) ZC1, d) ZC2 and e) ZC3.

Figure 7. Particle size distribution for ZC05 (red lines) and ZC2 (blue lines) particles

III.2. Co^{2+} -doped $\text{ZnO}@\text{SiO}_2$ core-shell powder

Three different amounts of TEOS were used in order to vary the shell thickness deposited via sol-gel process on the Co-doped ZnO powder, the experiments being performed on the ZC20 sample. The three as-prepared core@shell samples, from the thinner to the thicker silica shell, are noted ZC20@SiO₂-1, ZC20@SiO₂-2 and ZC20@SiO₂-3. TEM images for the ZC20@SiO₂-1 sample, before and after acid attack are reported on **Figure 8**. The silica shells are evidenced by the acid attack which leads to a total dissolution of the ZC20 cores. It can be seen, that quite homogeneous shells are obtained with just few silica nuclei due to the competition between shell growth and secondary germination. TEM pictures on the three ZC20@SiO₂-1, ZC20@SiO₂-2 and ZC20@SiO₂-3 samples are compared in **Figure 9**, all the pictures being taken after acid attack. Three main results can be extracted from these TEM observations: (i) the silica shell thickness well increases from ZC20@SiO₂-1 to ZC20@SiO₂-2 and ZC20@SiO₂-3, (ii) the agglomeration of the spherical aggregates increases with the amount

of TEOS used, certainly in correlation with the appearing of more and more silica colloids, (iii) the silica shell becomes resistant to the acid attack and protect the core particle while the thickness of the shell increases.

Figure 8. TEM photographs on the 12 mol% Co^{2+} -doped ZnO core-shell compound ($\text{ZC2@SiO}_2\text{-1}$) before acid attack (a) after acid attack (b).

Figure 9. TEM photographs on the ZC2@SiO_2 compounds with various average shell thickness (after acid attack): $\text{ZC2@SiO}_2\text{-1}$, $\text{ZC2@SiO}_2\text{-2}$, $\text{ZC2@SiO}_2\text{-3}$ from top to bottom.

III.3. Optical properties

In a first step, the optical properties were studied on the Co-doped ZnO powders. The diffuse reflectivity K/S Kubelka-Munk transforms are plotted in **Figure 10**. For tetrahedral symmetry, with regard to Tanabe–Sugano diagrams established for a $3d^7$ electronic configuration, three transitions corresponding to ν_1 ($^4A_2(F) \rightarrow ^4A_1(F)$), ν_2 ($^4A_2(F) \rightarrow ^4T_1(F)$), and ν_3 ($^4A_2(F) \rightarrow ^4T_1(P)$) are allowed [21]. For cobalt(II) ions the first two transitions are known to be located in the infrared with a wavelength of about 1400 and 1600 nm, respectively. The third one is known to appear as a triplet due to the L–S Russel–Sanders coupling for which the maximal absorptions, for instance, in $CoAl_2O_4$ where the punctual symmetry of the tetrahedral site is T_d , are around 540, 590, and 640 nm.¹² The visible triple transition, centered in the orange region, leads to blue coloration when the material color is only due to the cobalt (II) ion located in a tetrahedral site as a unique chromophore. The reported diffuse reflectance spectra for the different cobalt rates clearly show that the visible range triple transition as well as a large infrared peak between 1200 and 1700 nm associated to the convolution of ν_1 ($^4A_2(F) \rightarrow ^4A_1(F)$) (located here at 1640 nm: Figure 10b), ν_2 ($^4A_2(F) \rightarrow ^4T_1(F)$) (located here at 1310 nm) low energy transitions, both characteristic of cobalt in a tetrahedral site, are well taking place whatever the cobalt rate studied. Furthermore, the positions of the triple ν_3 transition, calculated from raw the K/S transform, remain about the same whatever the cobalt content at 565, 610, and 660 nm (Figure 10b). Hence, one can assume that from the remarkable stability of the 3 (ν_1 , ν_2 , ν_3) absorption bands positions versus cobalt concentration, that cobalt adopts in all cases, at room temperature, its thermodynamically stable environment; *i.e.*, as already assumed from X-ray diffraction analyses, cobalt is located in a nearly isotropic tetrahedral site. The evolution of the K/S intensity of the cobalt $d-d$ absorption bands (focusing on ν_1 and ν_3 transitions) are plotted in **Figure 11** (evolution of the 660 nm peak intensity reported in **Figure 11a**, evolution of the 1640 nm peak intensity reported in **Figure 11b**).

Figure 10. Diffuse reflection spectra ($R_{\text{diff}}\%$) (a) and K/S absorption spectra (b) of the various Co^{2+} -doped ZnO oxides.

Figure 11. Intensity at the maximum of the two absorption triplets in the visible range (c) and the infrared range (d) associated with the d-d Co^{2+} transition versus cobalt concentration in the various Co-doped ZnO compounds.

In a remarkable manner, the intensity of both transitions in visible range as well as in infrared range evolves in a linear way versus cobalt concentration. That is a new evidence for the efficient introduction inside the würtzite crystal of the cobalt previously titrated by ICP in the powder. Thanks to the control of the d-d transitions intensity versus cobalt concentration a large scale of green compounds can be obtained. The $L^*a^*b^*$ parameters, extracted from the diffuse reflectance curve, using x_λ , y_λ , z_λ color space system defined from CIE (1961), are regrouped in **Figure 12**. Obviously, for low cobalt concentration the green pigment exhibits a

less saturated green color that for higher doping rates. Hence, the L^* luminosity parameter gradually decreases versus the cobalt concentration from 80.2 for 1.5 mol% of cobalt efficiently introduced in ZnO down to 62.8 for the 16 mol% Co-doped ZnO. Interestingly, the green hue, which is directly characterized by the a^* value (red hue - green hue axis), shows a saturation maximum for intermediate cobalt concentration: the most saturated green color is obtained for the 12mo% Co-doped ZnO pigment (ZC2 sample). That is why the coatings of the pigment particles by silica shell were made on this sample.

$x_{Co}=1.5$ mol%	$x_{Co}= 5.5$ mol%	$x_{Co}=12$ mol%	$x_{Co}=16$ mol%
$L^*= 80.2$ $a^*= -14.6$ $b^*= 2.8$	$L^*= 76.2$ $a^*= -17.0$ $b^*= 0.2$	$L^*= 63.5$ $a^*= -21.8$ $b^*= 1.1$	$L^*= 62.8$ $a^*= -18.6$ $b^*= -1.5$
$x_{Co}=12$ mol% SiO ₂ shell 15-20 nm		$L^*= 65.2$ $a^*= -20.8$ $b^*= 2.5$	
$x_{Co}=12$ mol% SiO ₂ shell 35-45 nm		$L^*= 75.2$ $a^*= -16.8$ $b^*= 4.5$	
$x_{Co}=12$ mol% SiO ₂ shell 50-55 nm		$L^*= 75.9$ $a^*= -18.9$ $b^*= 1.7$	

Figure 12. $L^*a^*b^*$ parameters and coloration of the different Co-doped ZnO compounds and Co-doped ZnO@SiO₂ core-shell compounds prepared in this publication (corresponding to the ZC2@SiO₂-1, ZC2@SiO₂-2, ZC2@SiO₂-3 samples).

The diffuse reflectance focusing on the UV-visible range of the various core@shell materials are joined in **Figure 13**. It can be seen an increase in the visible reflectivity while the silica shell thickness increase. The comparison of the obtained colours of the three core@shell compounds and the core compound are also reported in **Figure 12**. Consequently to the addition of silica shells, the Luminosity parameter tends to increase versus the shell thickness. However, the green hue is only slightly impacted by the shell, and very beautiful green hue: $a^* = -18.9$,

$b^* = 1.7$ remains for the ZC2@SiO₂-3 sample. For this sample, the combination of optimal color properties and of a chemical stability (for illustration besides acid attack) is so reached.

Figure 13. Diffuse reflection spectra ($R_{diff}\%$) of the ZC2@SiO₂ compounds with various average shell thickness : a)ZC2@SiO₂-1, b) ZC2@SiO₂-2, c)ZC2@SiO₂-3.

IV. Conclusion

In this paper, the polyol synthesis route has allowed the obtaining of Zn_{1-x}Co_xO compounds, with nanometric crystallites (olive shape) / micrometric spherical aggregates, a large range of cobalt concentration associated to a large deep green – pale green scale of colorations. The color of the as-prepared powders is attributed to the efficient substitution of the zinc ions by cobalt (II) ions inside the tetrahedral sites of the würtzite phase. The spherical aggregates can be easily coated via sol-gel process by silica shells with tuned thickness in order to limit pigment's toxicity; this, without a significant decrease of the colorimetric properties.

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