# Elaboration and nanostructural study of pure and Al doped ZnO nanopowders

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In this work we present the results on the synthesis of zinc oxide nanostructured powders pure and doped with Al by different methods: hydrolysis, hydrothermal and physical vapor deposition in solar reactor. The fine nanostructural characterization of all powders has been performed by X-ray diffraction, SEM electron microscopy and BET analysis. From X-ray diffraction spectra performed on the nanopowders obtained the lattice parameters and the phase changes as well as the average grain sizes and the grain shape anisotropies have been determined. These results are supported by micrographics obtained by SEM. The results show that by combining the hydrothermal synthesis and the solar PVD method it is possible to obtain ZnO nanophases with controlled composition and morphology (from flower-like structure to nanowhiskers).

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## 1. Introduction

The nanometric field is governed by numerous surface phenomena (photosynthesis, catalysis, precipitation, reactivity, deformation, reflectivity, luminosity). This is so because in nanomaterials the number of atoms which are localized on free surfaces as well as on internal interfaces may be equal or higher than the number of atoms localized inside the grains. On this account the properties are strongly influenced by the interfaces present (surfaces, grain boundaries). Nanopowders consist of grains (unorganised aggregates, nanocristals or polycrystals) which have nanometric dimensions; they belong to the general class of "nanomaterials". The interest in the unique properties associated with materials having structures on a nanometer scale has been increasing at an exponential rate in last decade. From oxide class zinc oxide, due to its interesting physic-chemical properties, is a material of wide applications in many fields of industry**.** It is a wurtzite-type semiconductor with energy gap of 3.37 eV at room temperature [1]. Due to its large bandgap, ZnO is an excellent semiconductor material for applications considered for other wide bandgap materials such as GaN and SiC. Zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. Compared with other semiconductor materials, ZnO has higher exciton binding engery (60 meV) and has been studied as an optoelectronic, transparent conducting, and piezoelectric material. In the past few years, numerous studies have been made on both production and electronic and optoelectronic applications of one-dimensional ZnO, typically nanowires and ribbons. New processes for the synthesis and sintering are required to control and optimize the chemical composition, component distribution, crystalline and grain sizes. A number of investigations on the synthesis of ZnO nanostructures have been reported in the literature [1-8]. Different fabrication techniques such as metal organic chemical vapor deposition (MOCVD), spray pyrolysis, ion-beam-assisted deposition, laser ablation, sputter deposition, template-assisted growth, and chemical vapor deposition (CVD) have been employed to fabricate different types of ZnO nanostructures [1–8]. In parallel to the conventional solid-state processes, much attention was given to prepare micro- to nano-scaled ZnO particles in various synthetic routes, such as precipitation, hydrolysis, pyrolysis [1-8], and hydrothermal methods [1,4]. Among them, a simple and effective method to obtain significantly crystallized nanomaterials could be the better alternative for the future applications. In addition to this, selecting a cheap precursor with relatively low operating temperature may further tune simpler for the nanomaterial synthesis. In our paper we present the results on the synthesis of zinc oxide powders pure and doped with Al by different procedures: hydrolyze hydrothermal route and evaporation-condensation in a solar reactor. The influence of the synthesis parameters on the chemical and microstructural characteristics of synthesized nanophases has been systematically studied using XRD, BET and SEM.

## 2. Experimental procedure

### 2.1. Preparation of ZnO powders by hydrolysis

For obtaining ZnO nanostructured powders precursor Zn(II) aqueous solutions were prepared by dissolution of the corresponding nitrates into distilled water. The hydrolysis was performed in a hydrolyze reactor (fig.1a) at different temperatures and pH. The pH of the solution was adjusted to the desired values by mixing with a mineralizing agent (KOH). For obtaining Al doped ZnO nanostructured powders $AlCl_3$ aqueous solutions were utilized. The precipitates were filtrated, washed with distilled water to remove the soluble chlorides and ethanol to control agglomeration and dried in air at $110^0$C.

### 2.2. Preparation of ZnO powders by hydrothermal method

Hydrothermal synthesis has become in the last decade a very interesting route for the synthesis of different nanostructured materials (powders and thin films) having a controlled composition, grain size and texture. The principal advantages of the hydrothermal process concerning the mechanism and the homogenous kinetics of reactions consist in: versatility, reduction of technological operations number, minimizing the energy cost and chemicals agents consumption, elimination or reduction of effluents, fabrication of nanocristalline powders, with high reactivity, low cost and low energy consumption. The hydrothermal synthesis of zinc oxide nanopowders was performed in a 2L computer-controlled Teflon autoclave at $200^0$C and pH≈12, using KOH as a mineralizing agent (fig.1b) starting from precursor Zn(II) and Al(III) in aqueous solutions (prepared by dissolution of the corresponding nitrates and chlorides into distilled water). The hydrothermal synthesis is one step process, all the additional operations not being necessary.

### 2.3. Preparation of ZnO powders by the vapour condensation method with solar energy

The Solar Physical Vapor Deposition (SPVD) is an original process to prepare nanopowders. This method has been developed in Odeillo-Font Romeu in France using solar reactors working under concentrated sunlight in 2kW solar furnaces.The powders synthesized by hydrothermal method were the precursors for the physical vapor deposition on the solar reactor (SPVD). Fig. 1c presents the solar reactor. Materials are sublimated inside the evaporation chamber by using solar energy, focused on the sample by means of a 1 $m^2$ in surface parabolic mirror. The nanopowders were collected by aspiration on a nanoporous ceramic filter and by condensation on a cold finger.

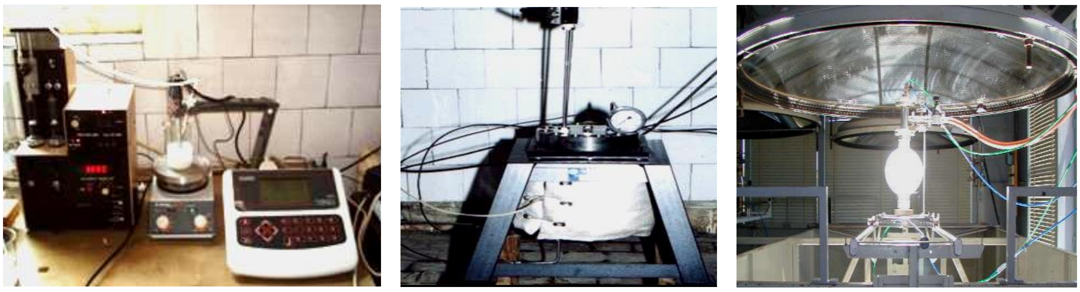


*Fig. 1. The hydrolyze reactor (a); hydrothermal reactor (b); and solar reactor (c).*

## 3. Powder characterization methods

The phase composition and lattice constants were determined from X-Ray Diffraction (XRD). X ray diffraction phase analysis relieved that the samples synthesized by hydrolysis at $90^0$C present only the corresponding zinc oxide peaks (according to JCPDS 5-664) (Fig. 2)

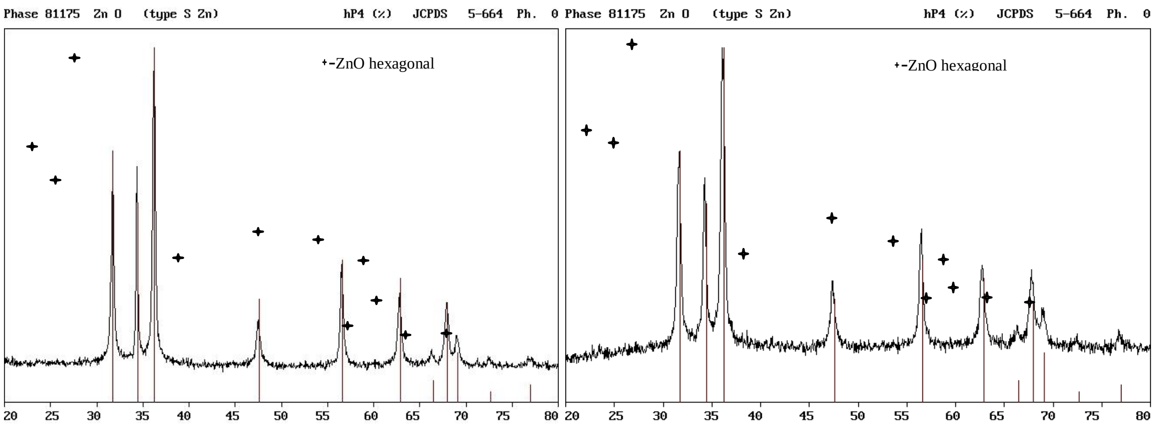



*Fig. 2. XRD patterns of powders synthesized by hydrolysis procedure: a) Zn(II), 0.1M and b) doped with 2.5at%Al, pH≈12, T=$90^0$C.*

X ray diffraction phase analysis relieved that the sample synthesized by hydrothermal route and vapour condensation method only the corresponding zinc oxide peaks (JCPDS 36-1451) (Fig. 3,4).

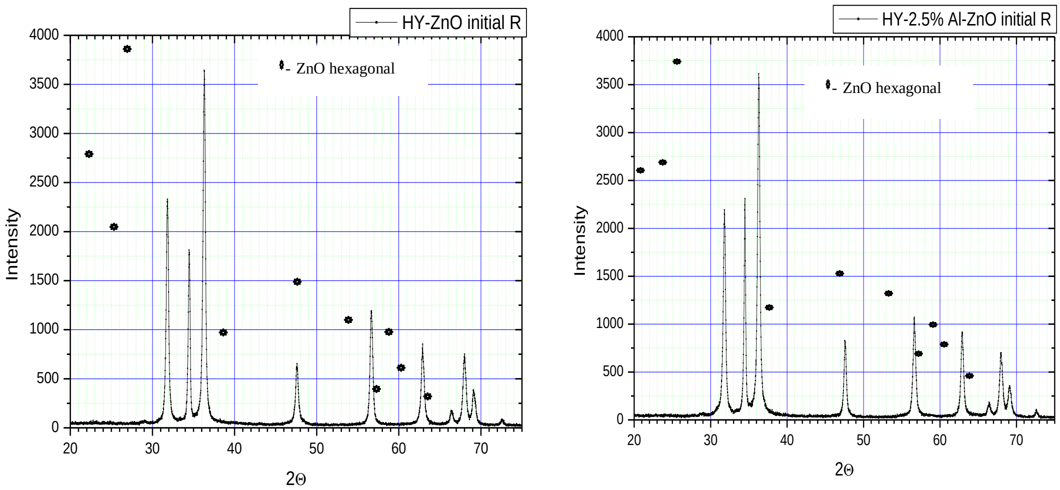



*Fig. 3. XRD patterns of powders synthesized by hydrothermal method: pure and doped with 2.5%at. Al.*

The X-ray diffraction phase analysis (Fig. 2, 3 and 4) has shown that all samples, independent of their aluminum content, contain only the zinc oxide peaks. The intensity of the peaks relative to the background signal indicates the high purity of the ZnO hexagonal phase in the products we have obtained. No characteristic peaks of impurities such as $Zn(OH)_2$ have been put in evidence in the obtained powders.

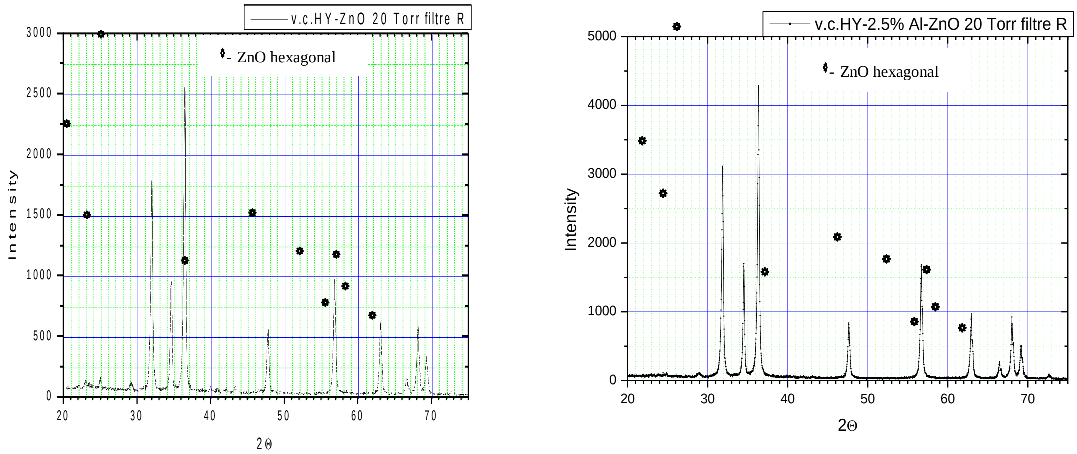



*Fig. 4. XRD specters of powders synthesized by solar physical vapor deposition: pure and doped with 2.5%at. Al.*

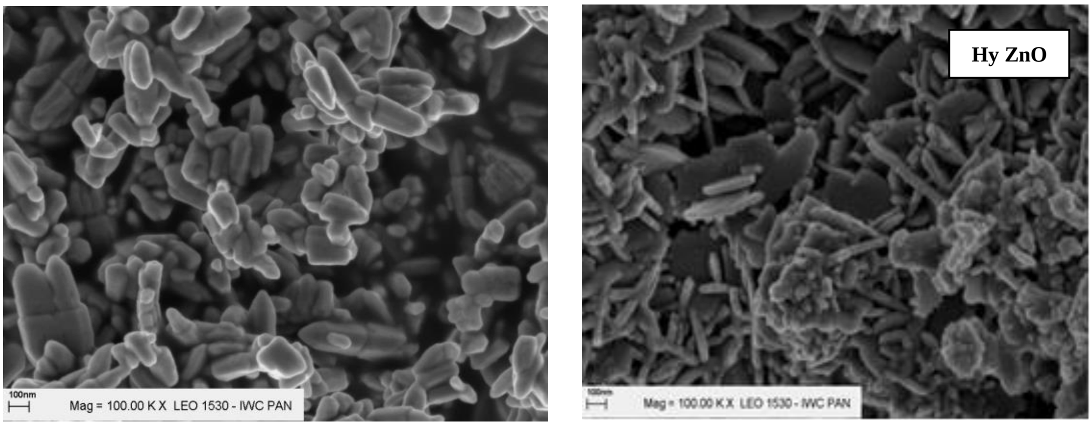
It can be observed that the *a* and *c* parameters decrease with the increase of temperature at pH constant, which corresponds to a diminution of cell size in the hydrolysis and hydrothermal processes (Table 1). The expansion of lattice of ZnO upon Al doping can be explained assuming predominantly interstitial positions of these ions. In the case of predominantly substitutional positions, we expected shrinkage of the lattice around the Al ions, caused by a smaller diameter of Al ions, as compared to Zn ions. After vaporcondensation process, starting from hydrothermal precursors, the cell parameters and the average grain size increase for the pure nanopowders and decrease in the doped one, as results of vaporization and rapid condensation in the reactor. The present results are consistent with Al ions being in part segregated to surfaces, and in part distributed in the interstitial positions in the interior of the particles.

*Table 1. The cell parameters and main grain size.*

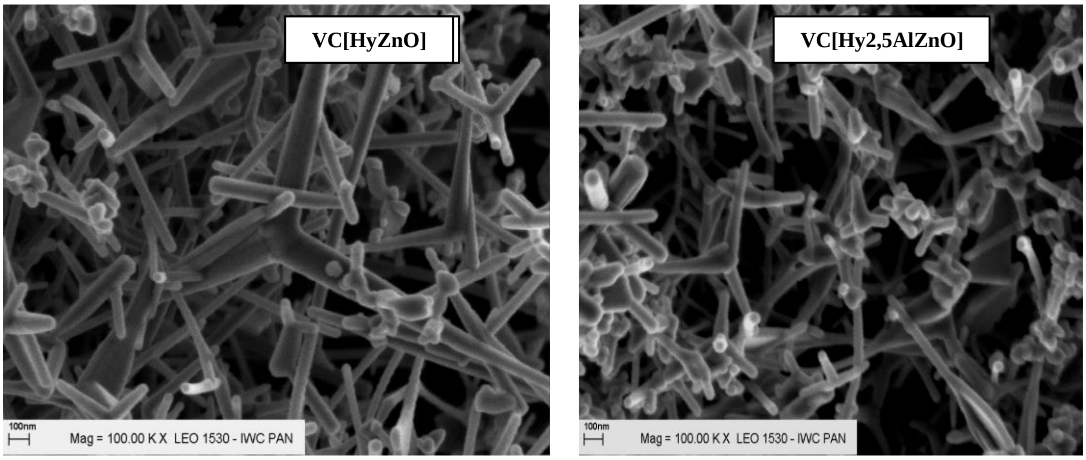
| Method | Al content (% at.) | a(nm) | c(nm) | Mean grain size (nm) |
|---|---|---|---|---|
| Hydrolyse (Hys) | none | 3.256 | 5.217 | 29.59 |
| | 2.5% | 3.251 | 5.220 | 32.31 |
| Hydrothermal (Hy) | none | 3,249 | 5,207 | 23.76 |
| | 2.5% | 3.253 | 5.213 | 24.22 |
| Vapor – Condensation (VC) | none | 3.254 | 5.214 | 26.64 |
| | 2.5% | 3.252 | 5.211 | 21.03 |

The relative fraction of Al ions on the surfaces and in the interior could not be determined using available methods. When the morphology of the nanophases is anisotropic, it is possible by XRD to determine their average form from the "average sizes" of the particles along the principal crystallographic directions (Table 1). It is however necessary to take into account that it is the average size of the coherence diffraction domains which are related to the size and morphology of the substructure. The determination of the size distributions and the morphology of the particles can be refined by observations in electron microscopy.

Scanning electron microscope analysis for the powders synthesized under hydrothermal conditions (Fig. 5 a) and b) show the influence of the aluminium dopant content and the influence of synthesis process. With aluminium content the morphology changes from spherical shape to pallets with a homogeneous distribution of the grain sizes.




*(a)*




*(b)*

*Fig. 5. SEM micrographs for Al doped ZnO nanopowders obtained by: a) hydrothermal method and b) solar physical vapor deposition.*

We can observe the formation of zinc oxide whiskers in the physical vapor deposition using solar reactor that demonstrates the influence of synthesis process. All the results from SEM support the XRD results. The realization of doping with aluminum was put in evidence by the EDS spectrum.

Energy Dispersive X-ray analysis (EDX) offers complementary information on the chemical state of the nanopowders (Fig.6).

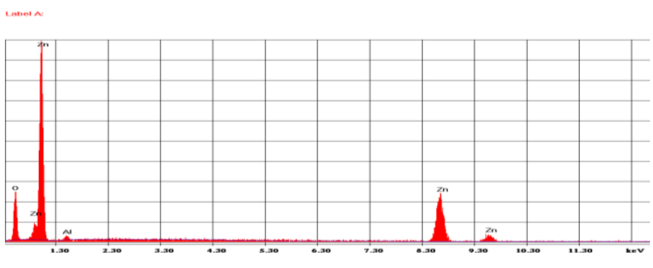



*Fig. 6. EDS spectrum for 2.5%at. Al doped zinc oxide.*

## 4. Conclusions

The ZnO nanoparticles can be obtained combining different methods. XRD results demonstrate that the obtained nanoparticles have the hexagonal wurtzite structure and the particle size is dependent of synthesis process. The analyzing of XRD spectres shows that in the case of hydrolyze procedure with the increasing of temperature only the ZnO phase is present. The hydrothermal route offers the possibility to synthesis only ZnO powders in the nanometric range with a better control of process parameters in one step by comparing with hydrolysis process. Obtaining nanopowders by physical vapor deposition in solar reactor starting from precursors synthesized by hydrothermal method represent an original method to produce nanomaterials in small quantities with solar energy. This is a powerful method to obtain pure and Al-doped ZnO nanophases with controlled composition and morphology (from flower-like structure to nanowhiskers). In many cases, it is on massive nanomaterials or in layers, that appear the new properties and the preparation of these nanomaterials is an important stage to develop.

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