CHARACTERIZATION OF Al DOPED ZnO NANOPOWDERS OBTAINED BY HYDROTHERMAL SYNTHESIS AND SOLAR PHYSICAL VAPOR DEPOSITION

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Abstract: *The paper presents the results of the experimental researches concerning the synthesis of ZnO nanopowders by solar physical vapor deposition (SPVD) starting from precursors obtained by hydrothermal synthesis. The SPVD was carried out by using a solar reactor consisting of a glass balloon placed in the focus of a solar PVD furnace. The fine nanostructural characterization of all powders has been performed by X-ray diffraction, SEM electron microscopy and BET analysis .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).*

Key words: nanopowders, ZnO, hydrothermal synthesis, SPVD.

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" [1,2]. Among the functional mineral compounds such as perovskite ($CaTiO_3$), rutile (TiO_2), CaF_2 ,spinel ($MgAl_2O_4$), wurtzite (ZnS) and zincite (ZnO), the last one is unique because it exhibits dual semiconducting and piezoelectric properties [1]. Due to the combination of interesting piezoelectric, electric, optical and thermal properties, ZnO-doped nanomaterials are of high interest for multifunctional applications in gas sensors, ultrasonic oscillators or transparent electrodes in solar cells.
Nanostructured ZnO is a material that may present various structures, whose configurations are much richer than for any known nanomaterial including carbon nanotubes. The n-type conductivity of ZnO is relatively easy to be obtained by using Zn in excess or by doping zinc oxide with Al, Ga, In [1]. The most promising dopants for obtaining p-type conductivity are the elements from the V^{th} group. Different routes to obtain doped ZnO have been studied as yet: the incorporation of transition metal ions (e.g. V or Cr ions) into a semiconductor photo catalyst by ion implantation or by co-precipitation; introduction of oxygen vacancies by treating a photo catalyst with hydrogen plasma or X-ray irradiation; coupling semiconductors (ZnO or TiO_2) with oxides or sulfides that enable visible light absorption (WO_3, Fe_2O_3, CdS) by co precipitation or impregnation; doping of N-atoms into the substitution sites in the crystal structure of a photo catalyst. In the science and technology of zinc oxide several key issues have to be achieved [3-5]: controlling the morphology and chemical composition of the zinc oxide powders; controlling the purity and particle size during the synthesis process of zinc oxide powders; controlling the level amount of the dopants. Zinc oxide powders with different morphology (prismatic, ellipsoidal, bi-pyramidal, dumbbell-like, nanowire, nanorod) have been obtained as yet [6].

This paper is aimed at presenting the results we have obtained by synthesizing nanostructured zinc oxide powders with different Al content (as a dopant) by two different procedures: the hydrothermal route and the evaporation-condensation in a solar furnace .

EXPERIMENTAL METHOD APPLIED TO OBTAIN Al DOPED ZnO POWDRES BY HYDROTHERMAL SYNTHESIS

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.

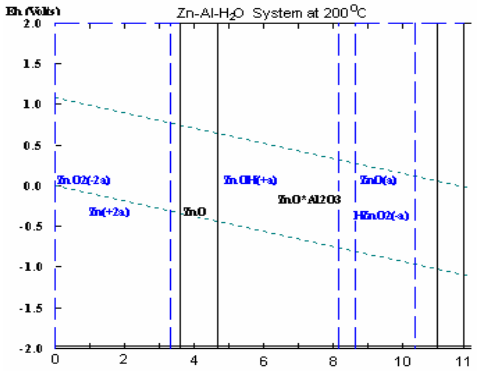


Fig.1. The Zn-Al-H2O Pourbaix diagram

In our experiments we have carried out the hydrothermal synthesis of zinc oxide nanopowders in a 2L computer-controlled Teflon autoclave at 200^0C and pH≈12. For obtaining Al doped ZnO nanostructured powders $Zn(NO_3)_2$ and $AlCl_3$ aqueous solutions were utilized. The pH of the solution was adjusted to the desired values by mixing with a KOH solution. All of the chemical reagents used in the experiments were analytical grade.
The precipitates obtained were filtered, washed with distilled water to remove the soluble chlorides and with ethanol to reduce agglomeration and finally dried for several hours in air at 110^0C. The synthesis corresponds to the Pourbaix diagram for the system Zn-Al-H2O as presented in figure 1.
The dried ZnO nanopowders have been further processed by solar physical vapor deposition (SPVD).

EXPERIMENTAL METHOD APPLIED TO PROCESS THE Al DOPED ZnO POWDRES BY SOLAR PHYSICAL VAPOR DEPOSITION

The solar physical vapor deposition is an original process to prepare nanopowders. Indeed the solar furnaces make it possible to implement high temperature material processing. A reactor powered with solar energy was used in our research to evaporate the powder produced by the hydrothermal method. The density of the solar flux and the pressure in the reactor are presented in table 1.

Table 1. Conditions of vaporization-condensation process in the solar furnace applied to the investigated samples

Sample code	Precursor	Solar flux density W/m^2	Pressure (Torr)
VC[HyZnO]	HyZnO	777	20
VC[Hy0.05AlZn]	Hy0.05AlZnO	910	20
VC[Hy1AlZnO]	Hy1AlZnO	937	20
VC[Hy2.5AlZn]	Hy2.5AlZnO	916	20
VC[Hy10AlZnO]	Hy10AlZnO	853	20

By using the solar energy, focused on the sample by means of a 1 m^2 in surface parabolic mirror the materials inside the evaporation chamber were subject to a sublimation process. Figure 2 shows the solar reactor. The nanopowders were collected by aspiration on a nanoporous ceramic filter and by condensation on a cold finger.

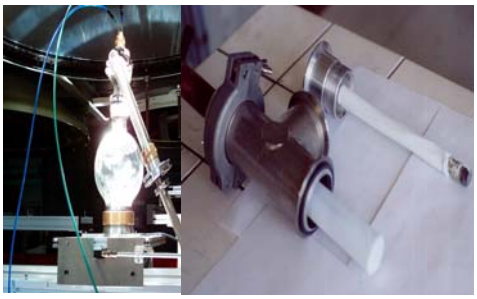


Fig. 2. a) Vapour condensation reactor; b) Filter and cold finger

EXPERIMENTAL METHODS APPLIED TO CHARACTERIZE THE Al DOPED ZnO POWDERS

The powders structure was investigated by X-ray diffraction analysis using a Phillips Analytical X-ray RV type PW3710700 instrument. In order to determine the grain size of the crystallites in the powders we have applied the usual Scherrer equation based on the measurement of the intrinsic width of the diffraction lines:

$$L = \frac{K\,\lambda}{\beta \cos \theta} \quad (1)$$

where L is the mean crystallite size, K is a constant which depends on the shape of the crystallite (usually taken equal to 0.9), θ is the Bragg diffraction angle for the selected line, λ is the wave length of the incident radiation, β is the intrinsic width of the diffraction line.
The BET specific surface area of the powders was determined on a Gemini 2360 Micrometrics Instruments apparatus. The picnometric density was determined by means of a AccuPyc 1330 Micrometrics apparatus. The equivalent mean particle sizes (in nm) were calculated from:

$$d = 6000/(S \times \rho) \quad (2)$$

where S is the specific BET surface area (in m^2/g) and ρ the picnometric density (in g/cm3) of the nanopowders.
The powder morphology was investigated by scanning electron microscopy by means of a SEM Gemini LEO 1530 instrument.

RESULTS AND DISCUSSION

The intensities of the diffraction peaks in the recorded XRD diagrams were shown to agree with the ICDD reference file (36-1451) from the American Mineralogist Crystal Structure Database pointing to the zincite structure. The diffraction peaks in the pattern have been be indexed to the hexagonal wurtzite structured ZnO (space group: P63mc; a =0.3249 nm, c =0.5206 nm).

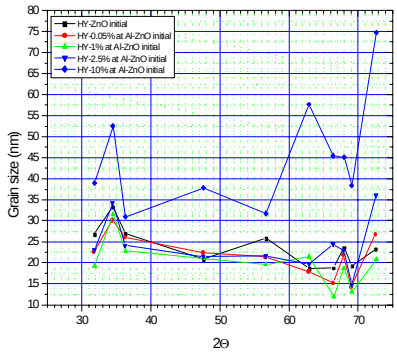


Fig.3. Variation of grain size in function of the crystallographic direction of the powders synthesized by the hydrothermal method

The X-ray diffraction phase analysis (Fig.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 powders obtained by hydrothermal synthesis. Thus, the result showed that the prepared product is single phase hexagonal ZnO.

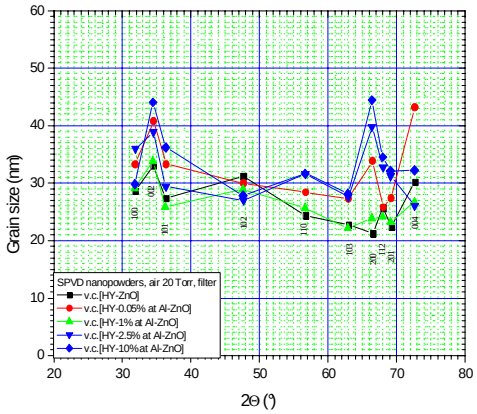


Fig.4. Variation of grain size in function of the crystallo-graphic direction of the powders processed by SPVD

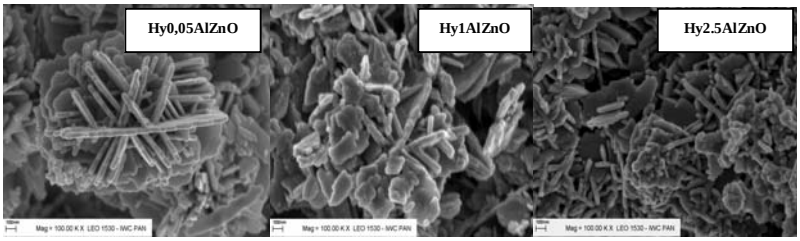
The lattice constants and the grain size for the powders synthesized by the hydrothermal method and for those processed in the solar reactor were determined from the recorded X- ray diffraction patterns and they are presented in table 2.

Table 2. Values of the lattice parameters a and c as function of the Al content

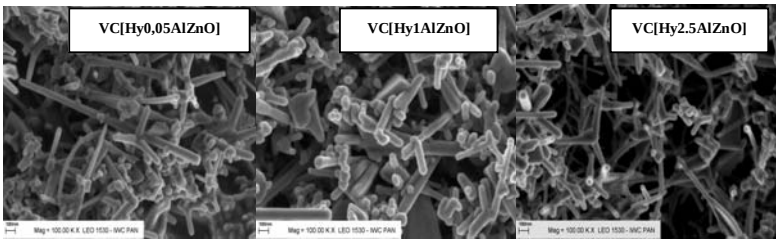
Method	Al content (% wt.)	a(nm)	c(nm)	Mean grain size(nm)
Hydrothermal (Hy)	none	3,249	5,207	23.76
	0,05%	3,258	5,219	21.90
	1%	3.258	5.218	20.03
	2.5%	3.253	5.213	24.22
Vapor – Condensation (VC)	none	3.254	5.214	26.64
	0.05%	3.252	5.210	32.32
	1%	3.255	5.216	26.33
	2.5%	3.252	5.211	32.03

The grain sizes derived from the recorded XRD patterns vary with the crystallographic direction. It is to be noted that the (002) peak indicates that the coherency domains are lengthened in the direction of the c axis. A similar phenomenon seems to appear for the (200) peaks of the nanopowders, corresponding to a direction perpendicular to the c axis which is also enlarged. These results, apparently contradictory, could be interpreted as due to a mixture of particles, a part of them being elongated in a direction perpendicular to the c axis, another part parallel to the c axis [7]. Figure 5 shows the SEM micrographs for the nano-powders.

The scanning electron microscopy examination of the powders synthesized under hydrothermal conditions (Fig. 5a) show the influence of the aluminum dopant content and those in Fig. 5b point to the influence of the synthesis process. With increasing aluminum content the morphology changes from flower like to spherical shape with a homogeneous distribution of the grain size. The formation of zinc oxide whiskers has been put in evidence in the products processed by solar physical vapor deposition, demonstrating the influence of the synthesis process.



a



b

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

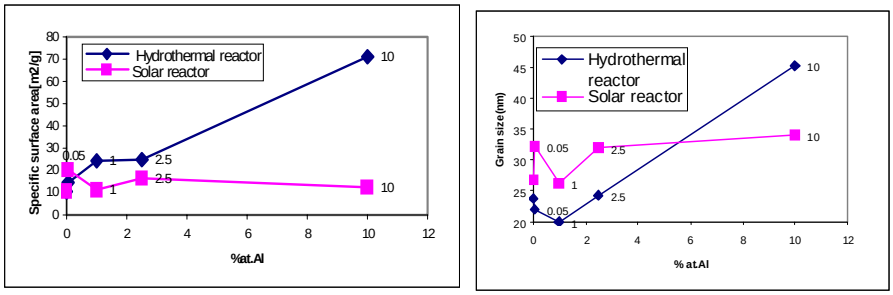


Fig.6. a)Variation of specific area in function of the synthesis method b)Variation of grain size in function of the synthesis method

All results obtained by BET analysis and XRD grain size determination (Fig. 6) indicate a very fine powder resulting after the vaporization-condensation processing in the solar furnace.

The Al doped zinc oxide powders obtained by hydrothermal synthesis and further processing by solar chemical vapor deposition (SCVD) have demonstrated a lower grain size at high aluminum percent.

CONCLUSIONS

Several important facts have been put in evidence in the present research, namely:
- The hydrothermal route offers the possibility to synthetize ZnO powders whose size is only in the nanometric range with a good control of the process parameters.
- The expansion of the lattice of ZnO upon Al doping was clearly demonstrated and it can be explained assuming predominantly interstitial positions of these ions. Indeed for predominantly substitutional positions, a lattice shrinkage around the Al ions, was to be expected and not an expansion, because of a smaller diameter of Al ions, as compared to Zn ions. 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. However the relative fraction of Al ions on the surfaces and in the interior cannot be determined using available methods.
- Combining hydrothermal synthesis and solar PVD method is a powerful method to obtain Al-doped ZnO nanophases with controlled composition and morphology (from flower-like structure to nanowhiskers).

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