RESEARCHES CONCERNING THE ELABORATION AND CHARACTERIZATION OF NANO-OXIDE POWDERS

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Abstract: *In this work we present the results on the synthesis of zinc oxide powders pure and doped with different Al content by different methods: hydrolysis, hydrothermal and physical vapor deposition in solar reactor. 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.*

Keywords: nanopowders, elaboration, doping, characterization, hydrothermal method

INTRODUCTION

Nanocrystalline ceramic and composite materials present a set of highly improved and novel mechanical, electronic, optical, catalytic or bioactive properties over the traditional materials. The implementation and utilisation of these new materials is strongly dependant on the microstructure and surface nanochemistry characteristics investigation and modelling. New processes for the synthesis and sintering are required to be developed to control and optimize the chemical composition, component distribution, crystalline and grain sizes [1-3].
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. In our paper we present the results on the synthesis of zinc oxide powders with different Al content by hydrothermal route The influence of the synthesis parameters on the chemical and microstructural characteristics of nanophases synthesized by hydrothermal method has been systematically studied using XRD, EDS and SEM.

EXPERIMENTAL STUDIES

1. Synthesis of ZnOdoped with Al by the hydrothermal method

Hydrothermal synthesis became in the last decade a very interesting route for the synthesis of different nanostructured materials as powders and thin films controlled composition, grain size, texture. The principal advantages of hydrothermal process concerning the mechanism and the homogenous kinetic of reactions consist in: versatility, reduction of technological operations number, the energy cost and chemicals agents, elimination or reduction of effluents, fabrication of nanocristallins powders, whit high reactivity, low cost and energy. The hydrothermal synthesis of zinc oxide nanopowders was performed in a 2L computer-controlled Teflon autoclave at 200^0C and pH≈12.For obtaining Al doped ZnO nanostructured powders were utilized $Zn(NO_3)_2$ and $AlCl_3$ aqueous solutions. The pH of the solution was adjusted to the desired values by mixing with a KOH solution. All of the chemical reagents used in this experiment were analytical grade.The precipitates obtained were filtered, washed with distilled water to remove the soluble chlorides and ethanol to reduce agglomeration and dried for several hours in air at 110^0C. The synthesis correspond to the Pourbaix diagram for the system Zn-Al-H2O how is presented in the figure 1.

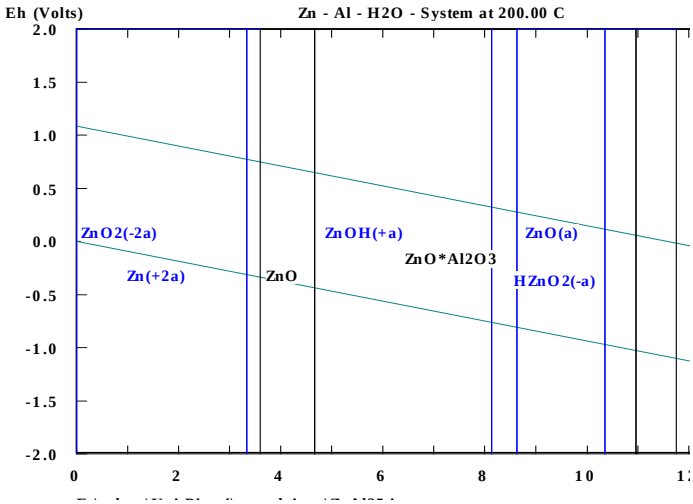

Fig. 1. The Pourbaix diagram

2.2. CHARACTERISATION OF POWDERS

Powder phase analysis was investigated by X-ray diffraction analysis using a Phillips Analytical X-ray RV type PW3710700. The fundamental equation to determine the size of a crystallite at the intrinsic width of the diffraction ray was the usual Scherrer equation:

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

where L is the mean crystallite size, k the constant which depend on the shape of the crystallite, Miller indexes and Bragg demonstrated that its value is near 0.9, θ the Bragg diffraction angle, λ the wave length of the incident radiation, the intrinsic width of the diffraction ray. Powder morphology was analyzed by scanning electron microscopy (SEM, Gemini LEO 1530).

RESULTS AND DISCUTION

Crystalline powder structure was recorded by X-ray diffractionwith Cu K_ radiation (λ = 1.54056A°) using the Philips diffractometer. Each diffraction peak was deconvoluted by two Lorentz functions each one corresponding to the radiations λK_1 (1.540656) and λK_2 (1.54438) of Cu (ORIGIN 6.0 software). The spectra were scanned over the 2θ angular range 10–70°. From XRD peaks width it is possible to determine an “average grain size” (in fact the “coherent diffraction domains” average size) of the nanopowders by applying the Scherrer (see eq. nr.1) The intensities of the diffraction peaks correspond to the XRD diagrams of the JCPD reference file (36-1451) and to the zincite structure from the American Mineralogist Crystal Structure Database. The diffraction peaks in the pattern can be indexed to hexagonal wurtzite structured ZnO (space group: P63mc; a =b=0.3249 nm, c =0.5206 nm).
X-ray diffraction phase analysis (Fig.2) showed that all the samples, independent of aluminum content, present only the corresponding zinc oxide peaks. The intensity of the peaks relative to the background signal indicates the high purity of the ZnO hexagonal phase of the products. No characteristic peaks of impurities such as $Zn(OH)_2$ were observed in the case of hydrothermal synthesis.
Thus, the result showed that the prepared product is single phase hexagonal ZnO. The grain sizes from XRD vary with the crystallographic direction like in figure 2.

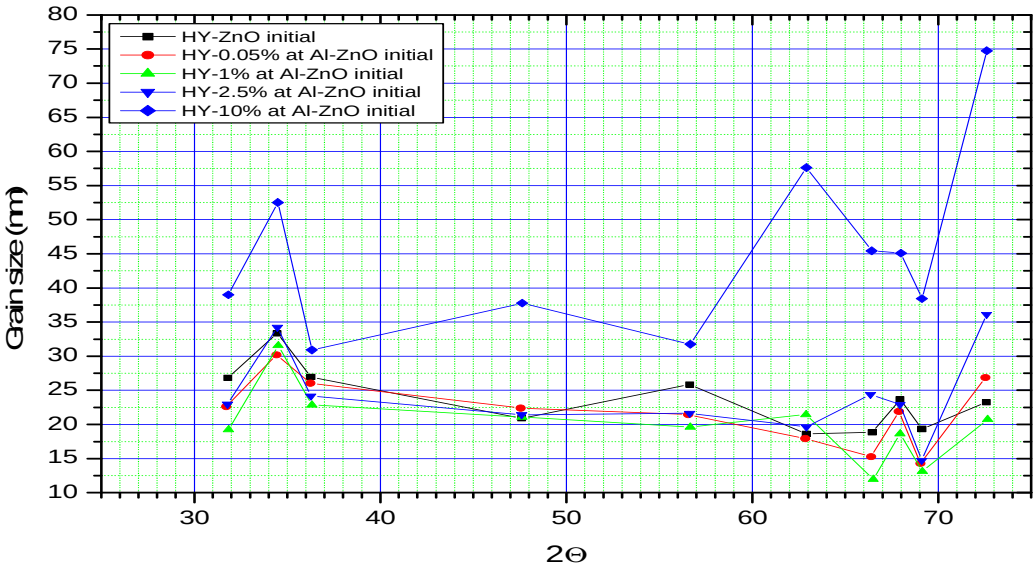

Fig.2. Variation of grain size in function of the crystallographic direction of the powders synthesized by hydrothermal method

The lattice constants and the grain size for powders made using the hydrothermal method and in the solar reactor were determined from X-Ray Diffraction and are presented in table 1.

Table 1. Values of the lattice parameters a and c as function of Al content

Method	Al content (% wt.)	a(nm)	c(nm)	Mean grain size(nm)
Hydrothermal (Hy)	pur	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

The parameters *a* or *b* and *c*, as well as the cell volume, computed from the XRD spectra (such as those shown in Fig. 2) have been reported in table 1. The parameters a or b are practically the same while the c parameter is practically independent on the Al content and is strongly higher compared to the literature data for pure ZnO, to annealed ZnO powders and to the pure ZnO nanopowders. As a consequence, the cell volume is also higher.
To put in evidence the presence of Al like dopant the specters from EDS are represented in figure 3.

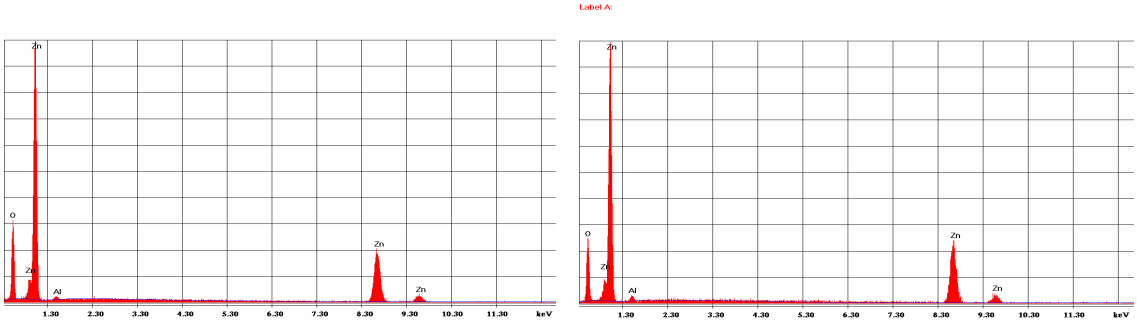

Fig. 3. Specter from EDS for Hy1AlZnO and Hy2.5AlZnO

The EDS specter confirm the results from XRD such as the presence of Al like dopant. Scanning electron microscope analysis for the powders synthesised under hydrothermal conditions (Fig. 4) shows the influence of the aluminium dopant content and the influence of synthesis process.

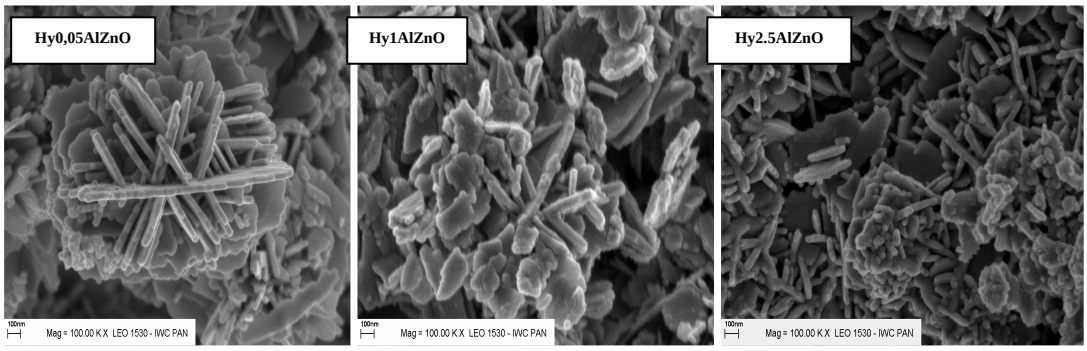

Fig.4. SEM micrographs for Al doped ZnO nanopowders obtained by hydrothermal method

With increasing aluminium content the morphology changes from flower like to spherical shape with a homogeneous distribution of the grain sizes. 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.
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. The relative fraction of Al ions on the surfaces and in the interior could not be determined using available methods.

CONCLUSIONS

The work relieve that the hydrothermal is an easy process for obtaining zinc oxide nanometric powders and it offers the possibility to synthesis only ZnO powders in the nanometric range with a better control of process parameters.. The principal advantages of hydrothermal process concerning the mechanism and the homogenous kinetic of reactions consist in: versatility, reduction of technological operations number, the energy cost and chemicals agents, elimination or reduction of effluents, fabrication of nanocristallins powders, whit high reactivity, low cost and energy.

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