THE ANNALS OF “DUNĂREA DE JOS” UNIVERSITY OF GALAȚI
FASCICLE V, TECHNOLOGIES IN MACHINE BUILDING, ISSN 1221-4566
2008

Microstructural Characterization and Properties of Some ZnO Based Nanopowders

Adriana Gabriela PLAIASU
University of Pitești

ABSTRACT:

In this paper we analyze the influence of some pure and Al doped ZnO nanopowders obtained by different methods: hydrolise, hydrothermal method and vapour condensation method. It is shown that the X-rays diffraction analysis allows a fine nanostructure characterisation of these powders while informing on their composition and on coherence diffraction domain (size and shape anisotropy).

Keywords: *nanopowders, ZnO, caracterisation, XRD.*

1. Introduction

All materials are composed of grains, which in turn comprise many atoms. Conventional materials have grains varying in size anywhere from hundreds of microns to centimeters. It is known in nanomaterials that properties are strongly influenced by the interfaces present (surfaces grain boundaries…. Nanopowders are formed of grains (unorganised aggregates, nanocristals or polycrystals) which have nanometric dimensions; they belong to the general class of “nanomaterials”.

ZnO is known to be one of the earliest discovered and the most widely applied oxide gas sensing material. Among the functional oxides with perovskite, rutile, CaF2,spinel, and wurtzite structures, ZnO is unique because it exhibits dual properties.[1] ZnO is a material that has diverse structures, whose configurations are much richer than any known nanomaterials including carbon nanotubes. 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. N-type conductivity of ZnO is relatively easy to be realized 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 methods routes to obtain ZnO materials were studied [2], namely:

- synthesis by mechanical method,
-synthesis using physical methods,
- synthesis by chemical way,
- mixed methods.

All zinc obtained oxide powders pure and doped present different morphology (prismatic, ellipsoidal, bi-pyramidal, dumbbell-like, nanowire, nanorod).

In our paper we present the results on the synthesis of pure and doped zinc oxide powders with different Al content obtained by three different procedures: hydrolise, hydrothermal route and evaporation-condensation in a solar furnace.

The principal advantages of hydrothermal process concerning the mechanism and the homogenous kinetic of reactions consist in:

- versatility, the process can be utilised for the synthesis of varied and complexes systems, from different materials;
- reduction of technological operations number, the energy cost and chemicals agents;
-elimination or reduction of effluents with nocive effect on medium;
- fabrication of nanocristallins powders, monodisperses whit high reactivity, sinterized at low temperatures.

The influence of the synthesis parameters on the chemical and microstructural characteristics of nanophases synthesized has been systematically studied using XRD.

2. Experimental methods

2.1. Synthesis methods

For obtaining ZnO nanostructured powders precursor Zn(II) aqueous solutions were prepared by dissolution of the corresponding nitrides into distilled water. The hydrolyze was performed in a hydrolyze reactor (fig.1) at different temperatures and pH≈8 or pH≈12 The pH of the solution was adjusted to the desired values by mixing with a mineralizer solution. As a mineralizing agent was used a KOH solution.

Figura 1. *Hydrolyse installation*

The hydrothermal synthesis of zinc oxide nanopowders was performed in a 2L computer-controlled Teflon autoclave (CORTEST, USA) at 200^{0}C and pH≈12, using KOH as a mineralizing agent (fig.2), starting from Zn(II) precursors.

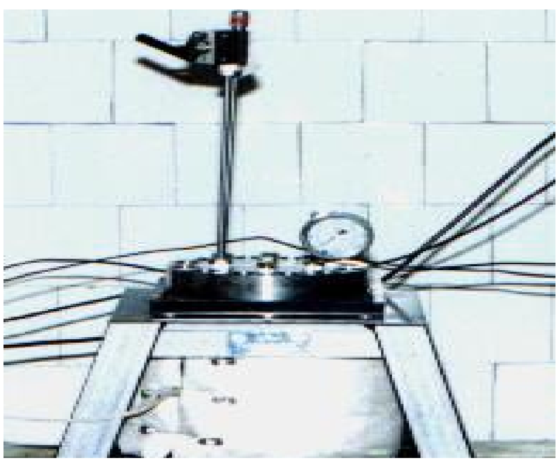


Figura 2. *Autoclave*

The precipitated were filtrated, washed with distilled water to remove the soluble chlorides and ethanol to control agglomeration and dried in air at 110^{0}C. The pH of the solution can be adjusted to the desired value mixing it with a mineralizer solution (ammonia for doped zirconia, sodium hydroxide for $BaTiO_3$, potassium hydroxide for ZnO or PZT).

A reactor powered with a solar energy was applied to evaporate the powder produced the hydrothermal method. Figure 3 shows the powders preparation chamber. 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.

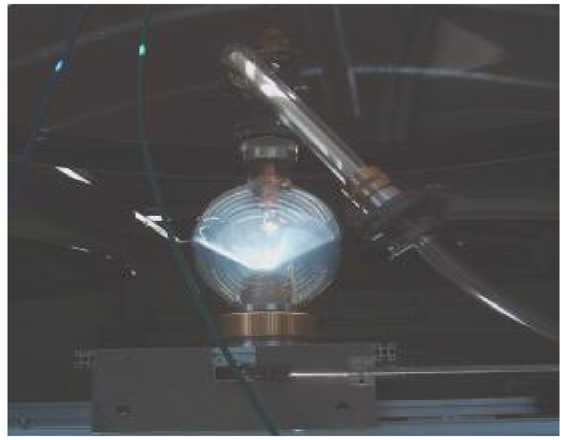


Figura 3. *Vapour condensation reactor*

2.2. Powder characterization methods

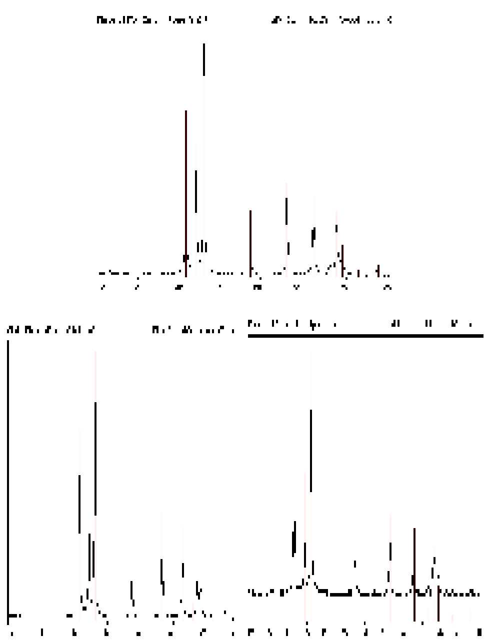
The phase composition and lattice constants were determined from X-Ray Diffraction (XRD) patterns obtained by means of a DROM-UM1 Diffractometer.

Figura 4. *Diffractometer DROM-UM1*

3. Results and Discussions

X ray diffraction phase analysis relieved that all the samples present only the corresponding zinc oxide peaks (JCPDS 36-1451).

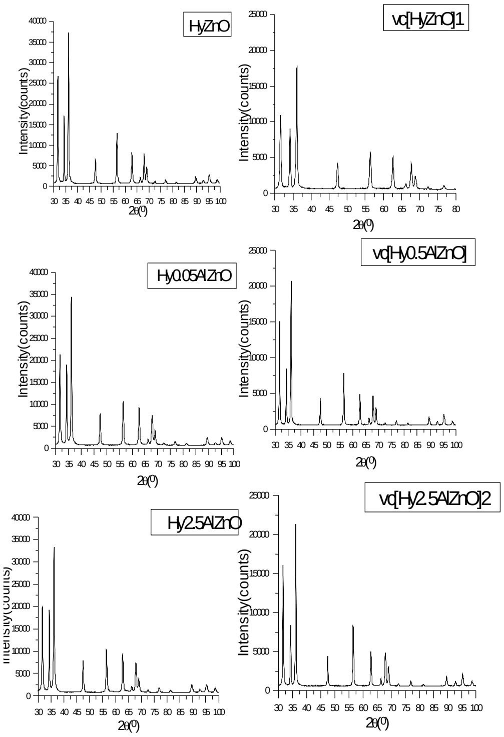
Method	Al content	Main grain size (nm)
Hydrolyse, 60^0C, pH≈12	0 %	28,28
Hydrolyse, 90^0C, pH≈8	0 %	28,59
Hydrolyse, 90^0C, pH≈12	0 %	29,59
Hydrotermal,	0 %%	70.6
	0.05 %	45.6
	1 %	29.3
	2.5 %	39.9
Vapour-condensation	pur	3.4.97
	0.05 %	36.70
	1 %	41.47
	2.5 %	37.63



a) hydrolyse

Table 1. *Properties of powders produced in the hydrothermal and in the solar reactor*

Method	Al content (% wt.)	a (nm)	c (nm)
Hydrothermal	pur	3,249	5,207
	0,05 %	3,258	5,219
	1 %	3.258	5.218
	2.5 %	3.253	5.213
Vapour condensation	pur	3.254	5.214
	0.05 %	3.252	5.210
	1 %	3.255	5.216
	2.5 %	3.252	5.211



b) hydrothermal method c) vapour-condensation

Figura 4. *Results of X-ray diffraction analysis*

4. Conclusions

In this work we studied influence of doping on, structural quality and light output properties of pure and Al doped ZnO nanopowders produced by three methods: hydrolyse, hydrothermal synthesis and evaporation/condensation in a solar reactor. 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 a 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.

Bibliography

[1]. **Norton** P., Heo Y.W., et al., “ ZnO:growth, doping&procesing “, Materials today, 34-40 (2004);

[2]. **Zhong** Wang Lin, “ Nanostructures of zinc oxide”, Materials today, 26-32 (2004);

[3]. **Jiemenez-Gonzalez** A.E. et al., "Optical and electrical characteristics of aluminium-doped ZnO thin films prepared bz solgel technique", Journal of Crystal Growth 192, 430-438 (1998)

[4]. **Michael** B. Kerber, Shafler, Erhard Michael J. Zehetbauer, "Processing and evaluation of X-ray line profiles measured from nanostructured materials produced by sever plastic deformation", Rev. Adv. Mater. Sci 10, 427-433 (2005)

Caracterizarea microstructurală şi proprietățile nanopulberilor pe bază de oxid de zinc

Rezumat

În această lucrare se prezintă influența condițiilor de reacție asupra nanopulberilor de oxid de zinc pur şi dopat cu Al, obținute prin trei metode: hidroliză, metoda hidrotermală şi vapocondensare. Analiza cu raze X permite o caracterizare a nanopulberilor oferind informații despre compoziție şi domeniul de difracție coerentă(dimensiune şi formă anizotropă).

La caractérisation microstructurelle et les propriétés des nanopudres à base d'oxyde de zinc

Résumeé

Dans notre travail on présence l'influence des conditions de réaction zur les nanopoudres d'oxyde de zinc pure mais aussi sur celui dopé avec de l'Al, obtenues par trois méthodes: la hydrolyse, méthode hydrothermale et vapocondensation. L'analyse à rayons X permet une caractérisation des nanopoudres en nous ofrant des informations sur la composition et sur le domaine de de diffraction cohérente (dimension et forme anisotropique).