ANNALS of the ORADEA UNIVERSITY.

Fascicle of Management and Technological Engineering, Volume VII (XVII), 2008

RESEARCHES ON THE INFLUENCES OF THE REACTION CONDITIONS ON THE STRUCTURE OF NANO-OXIDES MATERIALS

ADRIANA GABRIELA PLAIASU
University of Piteşti, Department of Technologies and Management
plaiasugabriela@yahoo.fr

Key words: nanomaterials, synthesis, characterisation, structure.

Abstract: Nanomaterials possess many unique chemical, physical, and mechanical properties. Due to these beneficial properties, nanomaterials are being favorably considered for a wide variety of structural, non-structural, biomedical and microelectronic applications. The implementation and utilization of these new materials is strongly dependant on the microstructure and surface nanochemistry characteristics investigation and modelling. The present work discusses the determination of correlations between reaction parameters-grain size, for the hydrolyze and hydrothermal synthesis of nanostructured zinc oxide.

1. Theoretical considerations

ZnO is attracting attention for its application to UV light-emitters, varistors, transparent high power electronics, piezoelectric transducers, gas-sensing as a window material for display and solar cells.

`In the science and technology of zinc oxide several key issues have to be achieved: controlling the morphology and chemical composition of the zinc oxide powders; 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) were obtained. [1]

The classical ceramic routes in producing the oxides base on the solid state reactions at high temperature has many disadvantages due to the large diffusion distances. New chemical methods such as hydrolyze, sol-gel process, hydro-chemical synthesis or process in gaseous phase have been developed to synthesize oxides nanopowders. The hydrolysis is the easiest way to produce oxide from aqueous solutions. In the mean time significant number of powders and films can be obtained in hydrothermal conditions at temperatures in the range 25-200^{o}C and pressures ›1.5 MPa in conditions interesting for the industry, due to some advantages like: versatility, it is an environmentally friendly procedure due to the fact that it takes place at lower temperatures and pressures closely to the living conditions on Earth (other processes require higher temperatures and higher/lower pressures and therefore they are considered environmentally stressed); low reactions temperatures avoiding problems related to the volatilization of components and stress induced defects; the rate and uniformity of nucleation, growth and aging can be controlled; powders, fibbers, single crystals, monolithic bodies, coatings on metals, polymers, and ceramics can be prepared; the costs for energy, instrumentation and precursors are lower. A large quantity of energy is necessary to create melt, vapours, gas, plasma comparing to the formation of an aqueous solution at the same temperature. The time and energy consuming is lower for the hydrothermal processes due to the fact that mixing and milling steps are not necessary. [1-4]

2. Experimental

Precursor Zn(II) aqueous solutions were prepared by dissolution of the corresponding nitrides into distilled water. The hydrolysis reactions were performed in a laboratory glass reactor with magnetic stirring (see figure1) at different temperatures and different pH. The pH of the solution was adjusted to the desired values by mixing with a mineralise solution. As mineralizing agent was used a KOH solution. The hydrothermal synthesis of zinc oxide nanopowders was performed in a 2L computer-controlled Teflon autoclave (CORTEST, USA) at 200^0C and pH≈12, using KOH as a mineralizing agent.(see figure 2).

***Fig.1**: Hydrolysis installation*

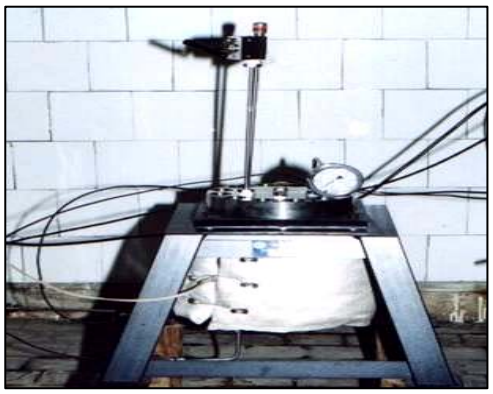

***Fig. 2**:Autoclave*

The obtained precipitates were filtered, washed with distilled water to remove the soluble chlorides and ethanol to reduce agglomeration and dried for several hours in air at 100^0C.

The phase composition the powders was investigated by XRD. The mean crystallite sizes of powders obtained by hydrolyse were by PROFILE program of diffractometer.

The mean crystallite sizes of powders obtained by hydrothermal method were determined using the Sherrer formula. The fundamental equation to determine the size of a crystallite at the intrinsic width of the diffraction ray was formulated by Scherrer:

$$d_m = \frac{k\lambda}{\delta \cos\theta}$$

where: d_m- mean crystallite sizes; k- constant which depend on the shape of the crystallite, Miller indexes and Bragg demonstrated that its value is near 0.9; θ- Bragg diffraction angle; λ- the wave length of the incident radiation; δ-intrinsic width of the diffraction ray.

3. Results and discussions

X-ray diffraction phase analysis relieved that the sample synthesizes by hydrothermal route and hydrolyze at 60^0C and 90^0C present only the corresponding zinc oxide peaks (according to JCPDS 5-664). The sample synthesize at room temperature, pH≈8, present zinc oxide peaks and $Zn(OH)_2$ peaks (according to JCPDS 1-360).

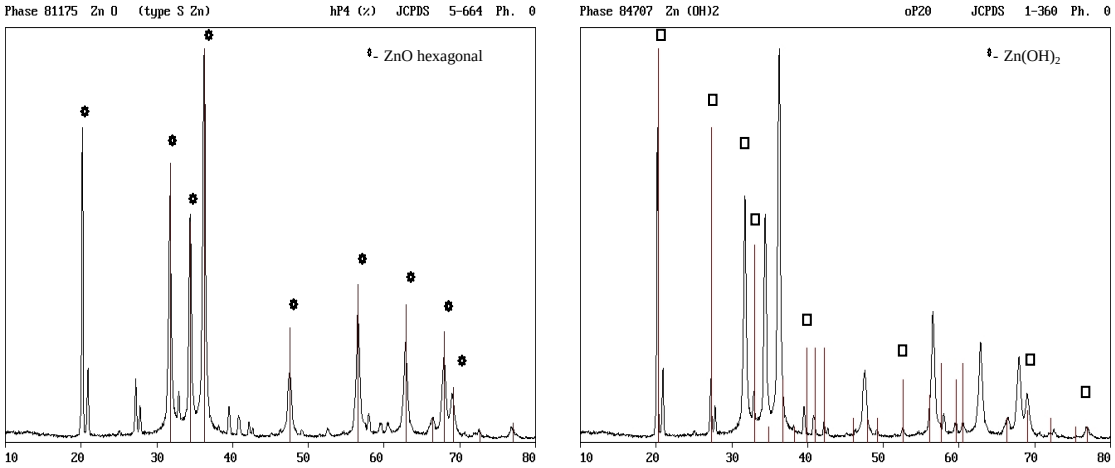

***Fig. 3**: XRD Spectres of powders synthesized at room temperature by hydrolyze procedure, pH≈8*

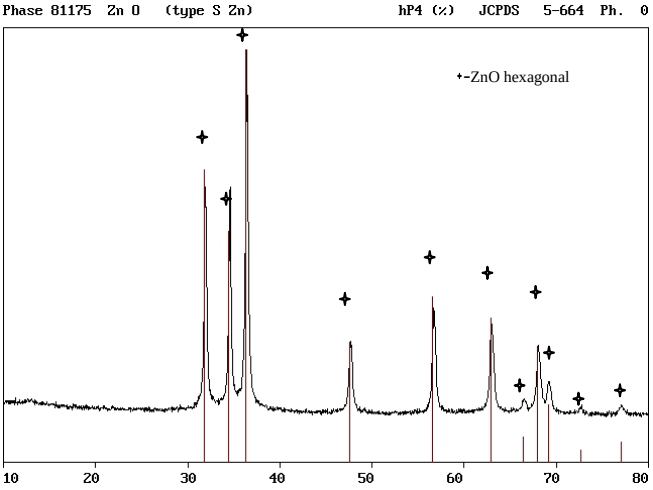

***Fig. 4**: XRD Spectres of ZnO powders synthesized at 60^{0}C by hydrolyze procedure, pH≈10*

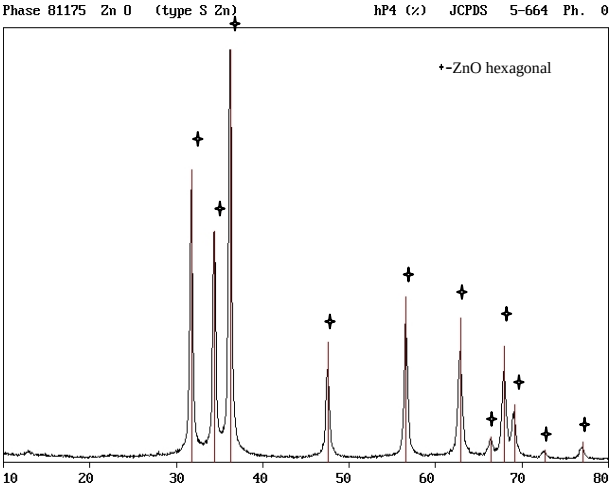

***Fig. 5**: XRD Spectres of ZnO powders synthesized at 60^{0}C by hydrolyze procedure, pH≈12*

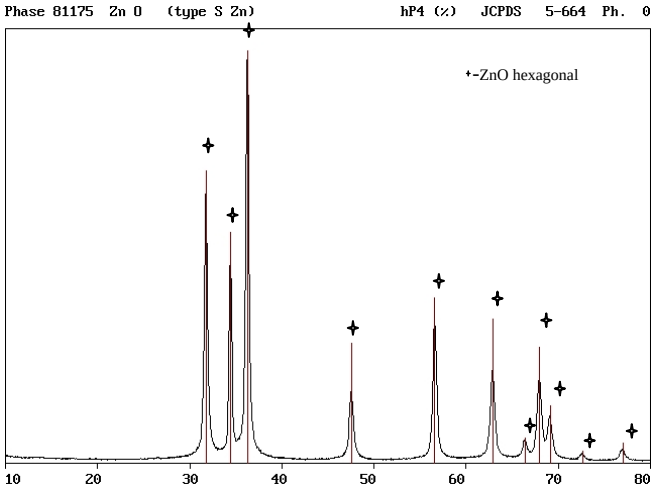

***Fig. 6**: XRD Spectres of ZnO powders synthesized at 90^{0}C by hydrolyze procedure, pH≈8*

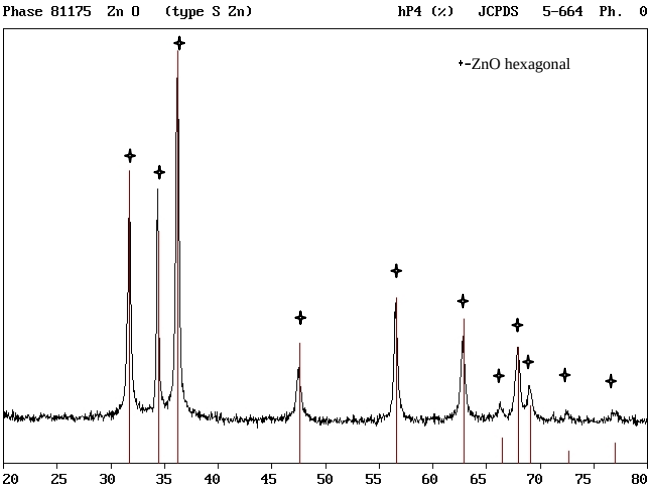

***Fig.7**: XRD Spectres of ZnO powders synthesized at 90^{0}C by hydrolyze procedure, pH≈12*

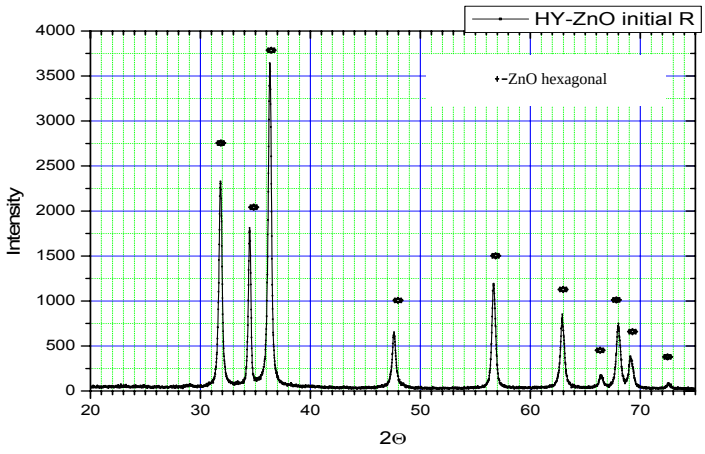

***Fig.8**: XRD Spectres of ZnO powders synthesized by hydrothermal route*

This means that the powders have crystallized in a hexagonal wurzite ZnO.

The cell parameters and crystallite sizes of nanopowders obtained by hydrolyze and hydrothermal route are presented in table 1.

Table 1. Powders parameters

Precursors	Hydrolyse agent	Synthesis method	Conditions	Phase	Cell parameters	Mean cristallite size
0,1M Zn (II)	1M KOH	Hydrolyse	pH≈8, t.cam.	ZnO	a=3,258 Å c=5,219 Å	21,64 nm
0,1M Zn (II)	1M KOH	Hydrolyse	pH≈12, t=60^{0}C	ZnO hexagonal	100% a=3,245Å c=5,200 Å	28,28 nm
0,1M Zn (II)	1M KOH	Hydrolyse	pH≈10, t=60^{0}C	ZnO hexagonal	100% a=3,249 Å c=5,205 Å	29,11 nm
0,1M Zn (II)	1M KOH	Hydrolyse	pH≈12, t=90^{0}C	ZnO hexagonal	100% a=3,256 Å c=5,217 Å	29,59nm
0,1M Zn (II)	1M KOH	Hydrolyse	pH≈8, t=90^{0}C	ZnO hexagonal	100% a=3,250 Å c=5,208 Å	28,59nm
0,1M Zn (II)	1M KOH	Hydtrothermal	pH≈12, t=200^{0}C	ZnO hexagonal	a=3,249 Å c=5,205 Å	23,76 nm

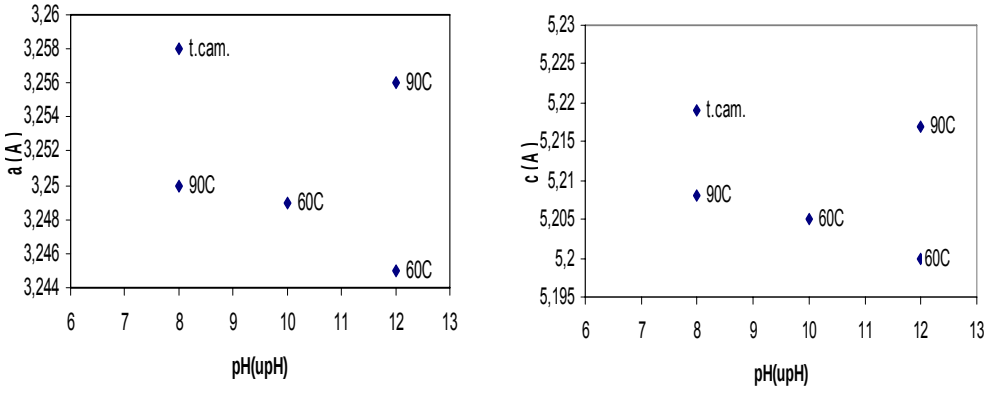

***Fig. 9**: Influence of parameters conditions of crystalline parameters*

The analyzing of XRD spectres shows that in the case of hydrolyze procedure with the increasing of temperature only the ZnO phase is present. 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.

The hydrothermal route offers the possibility to synthesis only ZnO powders in the nanometric range with a better control of process parameters.

3. Conclusion

The ZnO nanopowders can be successfully prepared by chemical route: hydrolyse and hydrothermal methods. The process parameters(temperature and pH) have a significant influence on phase composition and crystallite size. The powders crystallized in a hexagonal wurzite phase. The mean crystallite sizes of obtained was determined by XRD. The grains of powders are in the range of nanometric scale (d<50nm).

4. References

[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.
[5]. Cheng X.L., Zhao H., Huo L.H., Gao S., Zhao J.G., ZnO nanoparticulate thin film: preparation and gas-sensing property, Sensors and Actuators no.102, pag. 248-252, 2004.
[6]. Chittofrati A., Matijevic E., Uniform particles of zinc oxide of different morphologies, Coll. Surf. 48, pag. 65–78, 1990.