STUDIES REGARDING THE ELABORATION OF NANOMETRIC ZINC OXIDE POWDERS

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Abstract. *This paper focuses on the newer chemical synthesis of zinc oxide powders and the effects of reaction temperature and possible mechanism of ZnO formation. The study of the reaction mechanism at different temperatures has resulted in establishing the optimum condition for the hydrothermal process.*

Keywords: ZnO, reaction mechanism, powder.

INTRODUCTION

It is well known that the size range below 100 nm is of greatest interest for the Materials scientific community and represents the greatest application potential. Nanoparticles can be manufactured by four generic routes: wet chemical, mechanical, form-in-place and gas phase synthesis[1]. The classical ceramic routes in producing oxides through solid state reactions at high temperature has many disadvantages due to the large diffusion distances. New chemical methods such as hydrolysis, sol-gel process, hydrochemical synthesis or processes in gaseous phase have been developed to synthesize oxides nanopowders. The hydrolysis is the easiest way to produce oxides from aqueous solutions. Also a significant number of powders and films can be obtained in hydrothermal conditions at temperatures in the range 25–200^0 C and pressures <1.5MPa. Due to versatility.[2-5] such conditions are interesting for industry.
From the large family of oxides ZnO is the most interesting one for modern applications due to its wide direct band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV). In addition some interesting optical properties, for example room-temperature ultraviolet laser emission have been demonstrated in ZnO nanostructures. ZnO has also great potential in applications in solar cells, sensors, photocatalysis, optoelectronic devices and surface acoustic waveguides. As far as the morphology is concerned ZnO has probably the richest variety of different nanostructures. This includes highly ordered nanowire arrays, tower-like structures, nanorods, nanobelts, nanosprings, nanocombs, and nanorings.[3-4]

EXPERIMENTAL PROCEDURES

Precursor Zn(II) aqueous solutions were prepared by dissolution of the corresponding nitrates into distilled water. The hydrolysis was performed in a hydrolysis reactor at different temperatures and pH≈8. The pH of the solution was adjusted to the desired values by mixing with a mineralizer solution (KOH). The pure ZnO powders were obtained through hydrothermal synthesis using $Zn(NO_3)_2$ as a precursor and KOH as a hydrolysis agent in autoclave.

RESULTS

For studying the influence of temperature on the hydrolysis process for 10^{-1}M Zn(II) the hydrolysis curves have been considered. The optimum domains of hydrolysis are obtained from the $pH=f(V_{solKOH})$ dependence function and its derivate $\frac{dpH}{dV}$ showed in figures1,2 and 3.

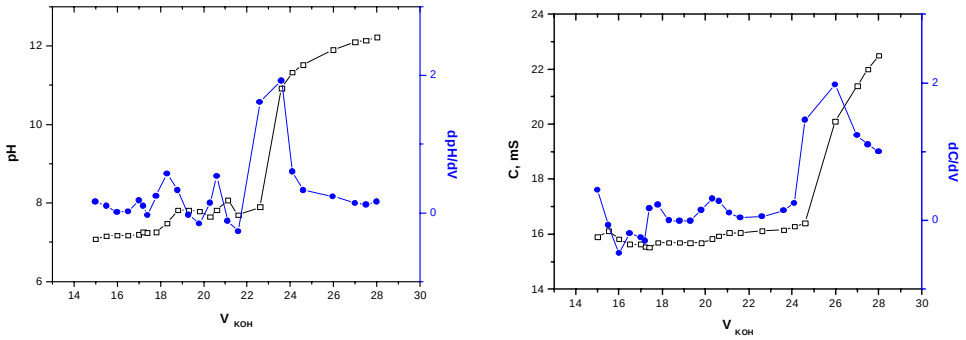

Fig.1. Evolution of pH and conductivity for Zn(II) 10^{-1}M at room temperature

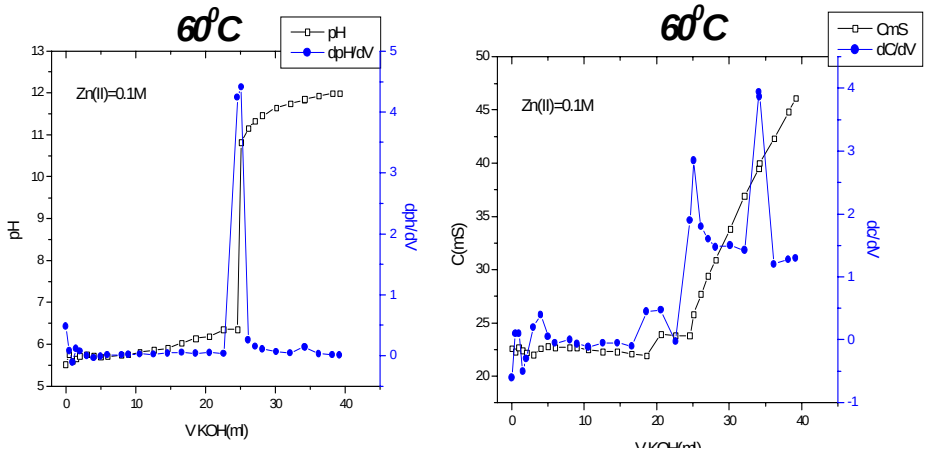

Fig.2. Evolution of pH and conductivity for Zn(II) 10^{-1}M at 60^0C

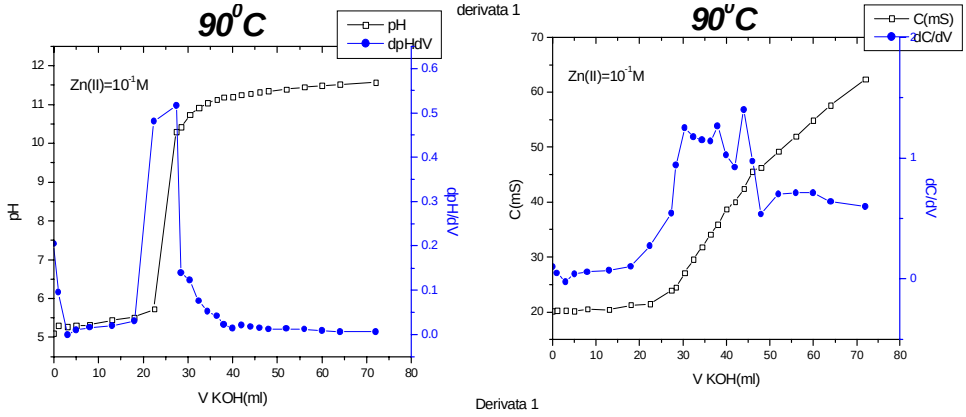

Fig.3. Evolution of pH and conductivity for Zn(II) 10^{-1}M at 90^0C

From $\frac{dpH}{dV}$ we have inferred that the optimum domain of precipitation is at pH_{PE} = 10, 3 -11.(fig.1-3). It is worth to mention that in the 8-12 u.pH range the experimental results from the precipitation curves agree with theoretical results from the Pourbaix diagrams for 10^{-1}M Zn(II) at room temperature. More specifically the optimum domain of precipitation is at pH_{PE} = 10,9 from $\frac{dpH}{dV}$. Taking into considerations the conclusions of our study on the influence of temperature from the

derivate $\frac{dpH}{dV}$ analyzed in the graphs, we have carried out the hydrothermal synthesis in a Cortest autoclave at the following parameters: temperature 200^{0}C, pressure 4.5 bars and time 120 minutes

For structural characterization all the precipitated products have been filtered, washed with distilled water to remove the soluble chlorides and with ethanol to control agglomeration and finally dried in air at 110^{0}C.

The X-ray powder diffraction patterns of the samples were recorded at room temperature with a DRON UM1 θ-2θ diffractometer using CuKα radiation and a graphite monochromator, operating at 36 kV and 30 mA in a step scan mode with a step size of 0,05° 2 θ and counting time of 10s per step. The morphology of the hydrothermal powders was analyzed by SEM.

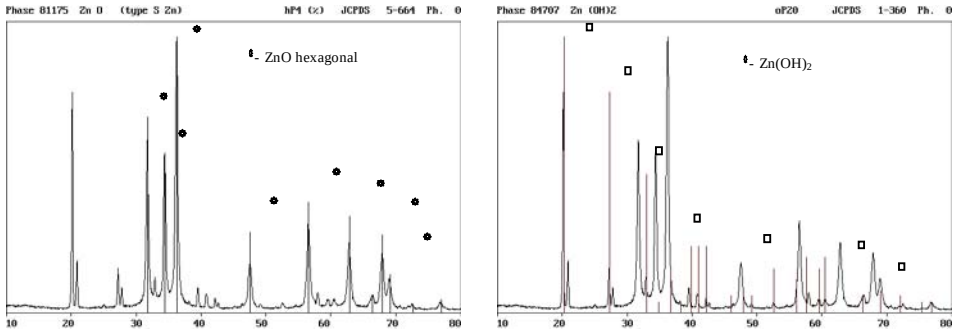

Fig.4. XRD patterns of powders synthesized at room temperature by the hydrolytic procedure, pH≈8

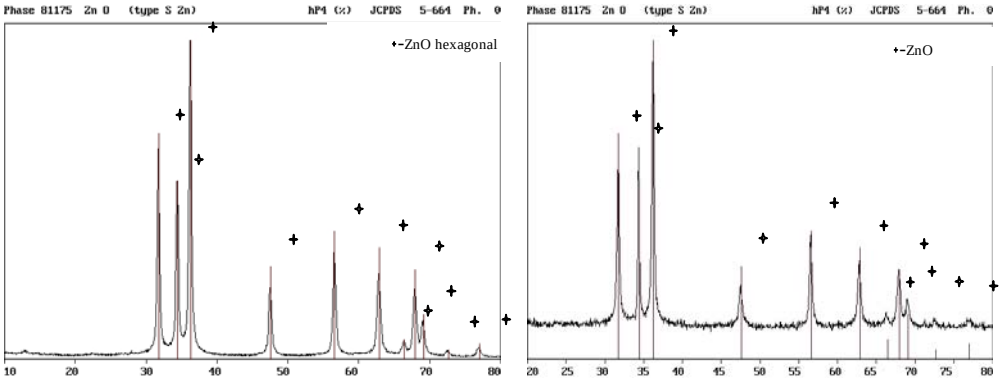

Fig.5. XRD patterns of the powders synthesized by the hydrolytic procedure ofZn(II) 0.1M at T=60^{0}C and 90^{0}C pH≈12

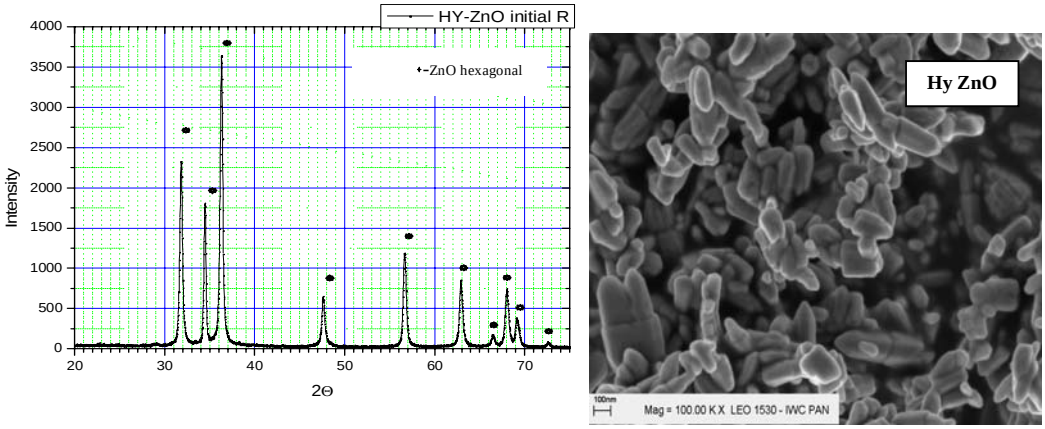

Fig6. XRD pattern of ZnO powders synthesized by the hydrothermal route and the SEM micrograph

The analyzing of XRD spectres shows that in the case of hydrolyze procedure with the increasing of temperature only the ZnO phase is present which is determined by the apparition of only the ZnO phase (JCPDS 5-664) while the phase $Zn(OH)_2$ disappears (JCPDS 1-360). The dimension of the crystallites is very fine if the process is carried out at room temperature (d=21,64nm) and it gradually increases with temperature reaching d=28,28nm at 60^0C and d=29,59 nm at 90^0C. The hydrothermal route offers the possibility to synthesis only ZnO powders in the nanometric range (d=23,76 nm) according to JCPDS 36-1451, with a better control of the process parameters (temperature - pH-presure). SEM examination of the morphology of the powders obtained by the hydrothermal process has shown that it is palled shaped.

DISCUSSION AND CONCLUSIONS

Several important facts have been put in evidence in the present research, namely:

- Hydrolysis is an easy process for obtaining zinc oxide nanometric powders.
- Examination of the X-ray diffraction patterns has shown that increasing the temperature of the process.
- The hydrothermal route offers the possibility to synthetize only ZnO powders in the nanometric range.
- The morphology of the powders obtained by the hydrothermal process has shown that it is palled shaped showed by SEM examination.

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