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RAPID SYNTHESISOF ZnO MICRO AND NANOSTRUCTURES

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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.

1. Introduction

It is well known that the size range below 80 nm is of greatest interest for the materials scientific community and represents the greatest application potential. Nanostructured materials 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 synthesis 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 such conditions are very interesting for industry [2-5].

ZnO is the most interesting one from the large family of oxides for modern applications due to its wide direct band gap (3.37 eV at room temperature) and large exciting 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.[3-5]

2. Experimental procedures

Precursors aqueous solutions were prepared by dissolution of the corresponding nitrates (ZnII) 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 mineralized solution (KOH). 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 for obtaining zinc oxide final powders.

The pure ZnO powders were obtained through hydrothermal synthesis in one step using $Zn(NO_3)_2$ as a precursor and KOH as a hydrolysis agent, without drying.

3. Results and discussions

3.1. Efects of temeparture of the oprtimum domain of hydrolyze

For studying the influence of temperature on the hydrolysis process the hydrolysis curves have been considered for 10^{-1}M Zn(II) solutions

The optimum domains of hydrolysis are obtained from the $pH=f(V_{solKOH})$ dependence function and its derivate $\frac{dpH}{dV}$ are represented in figures 1,2 and 3.

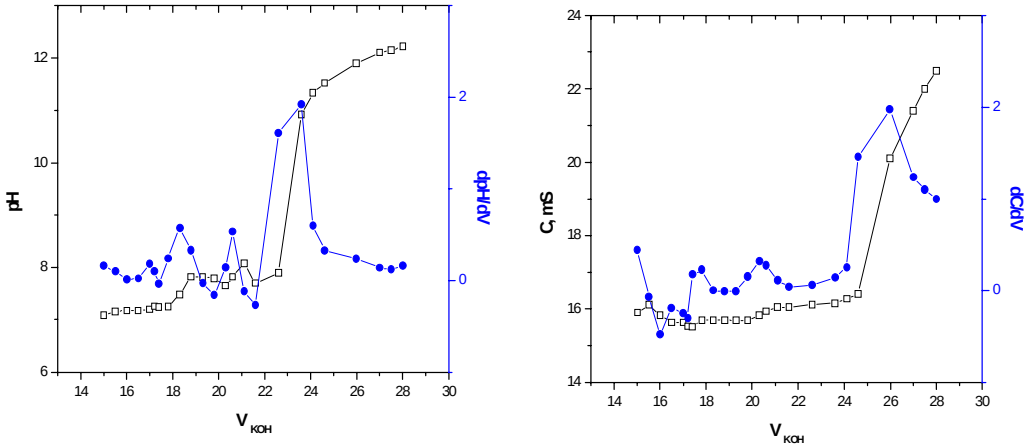

Fig.1. *Evolution of pH and conductivity for Zn(II) 10^{-1}M solution at room temperature*

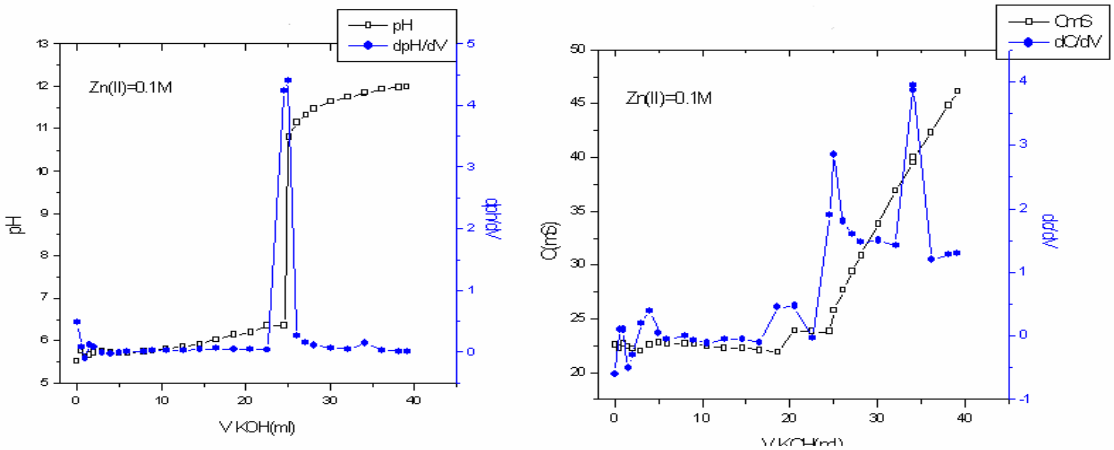

Fig.2.*Evolution of pH and conductivity for Zn(II) soluton 10^{-1}M at 60^{0}C*

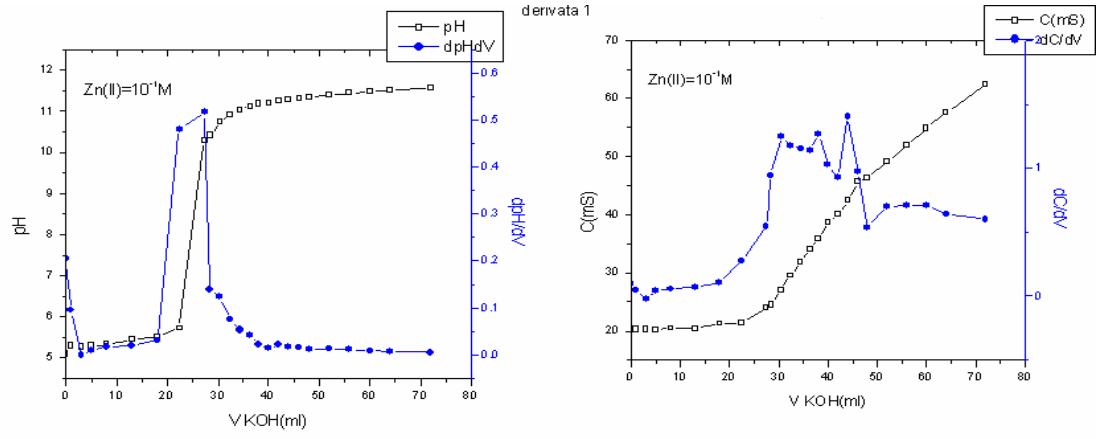

Fig.3.*Evolution of pH and conductivity for Zn(II) solution 10^{-1}M at 90^{0}C*

From $\frac{dpH}{dV}$ we have inferred that the optimum domain of precipitation is at pH_{PE} = 10, 3 -11.

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 $\frac{dpH}{dV}$.

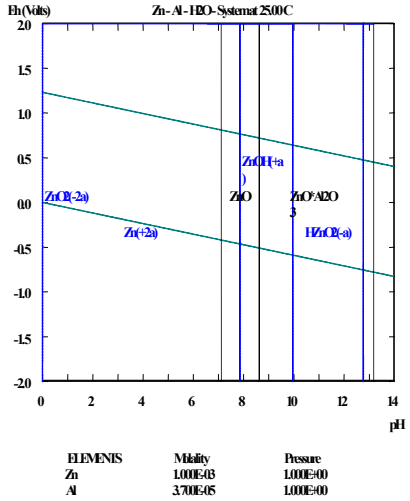

Fig.4. *The Zn-Al-H2O Pourbaix diagram at room temperature*

Taking into considerations the conclusions of our study on the influence of temperature, 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.

3.2. The microstructural and morphological characterization of ZnO nanoparticles

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

Figure 5 and 6 present the XRD pattern of ZnO synthesized at pH=8 at room temperature and pH=10 at 60^{0}C and 90^{0}C respectively. The powders obtained at height temperature present only the ZnO phase. Figure 7 present only ZnO phase obtained by hydrothermal method and the palled shape of powders.

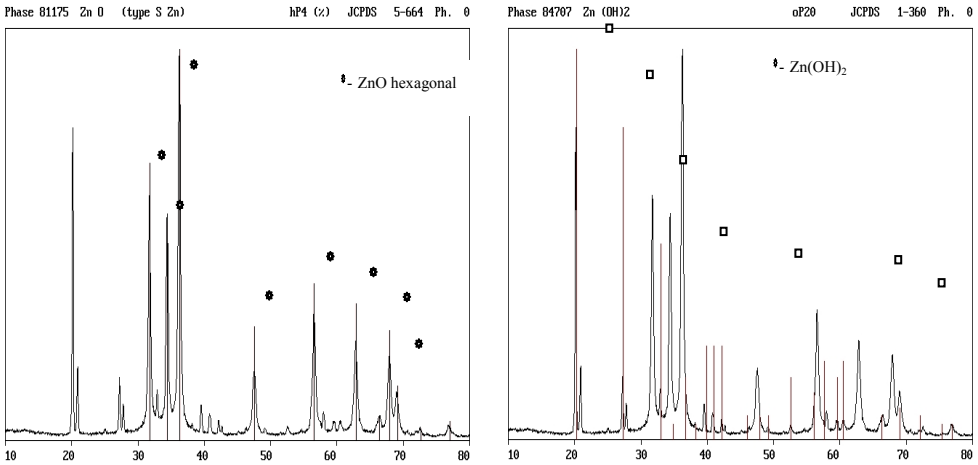

Fig.5. *XRD patterns of powders synthesized at room temperature by the hydrolytic procedure, pH≈8*

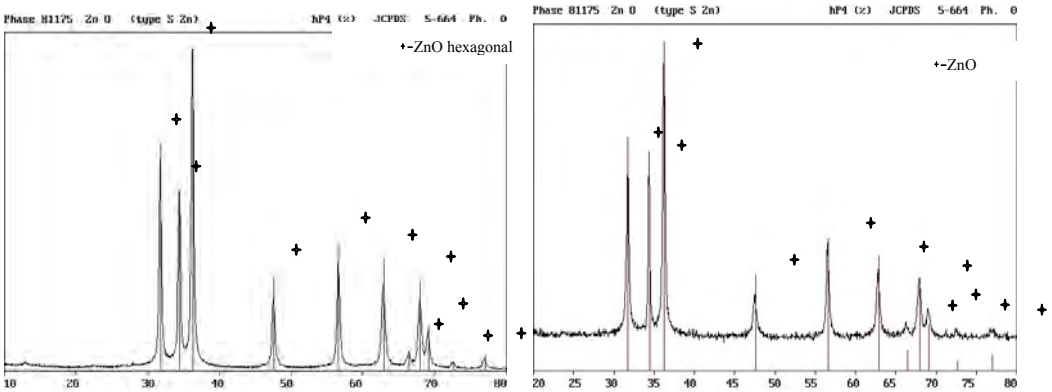

Fig.6. *XRD patterns of the powders synthesized by the hydrolytic procedure ofZn (II) 0.1M at T=60^{0}C and 90^{0}C pH≈12.*

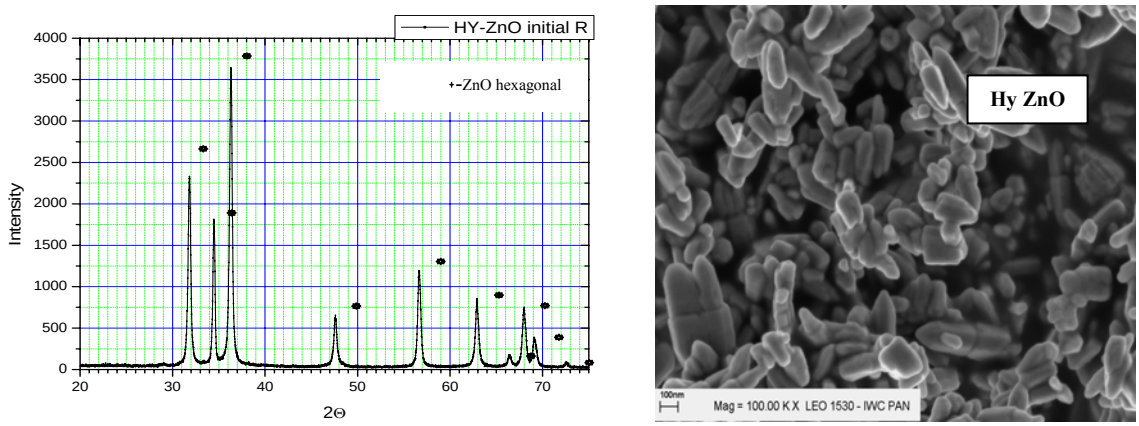

***Fig.7**. XRD pattern of ZnO powders synthesized by the hydrothermal route and the SEM micrograph.*

4. Conclusions

Several conclusions 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 and corroboration with the X-ray diffraction structure files has shown that increasing the temperature of the process determines the apparition of the only 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^{0}C and d=29,59 nm at 90^{0}C.
- The hydrothermal route offers the possibility to synthesize only ZnO powders in the nanometric range (JCPDS 36-1451, d=23,762 nm) with a better control of the process parameters (temperature-pH-presure).

From the SEM examination, the morphology of the powders obtained by the hydrothermal process has shown to be palled shaped.

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