Structural Characterization of ZnO and Al Doped ZnO Powders Synthesis in Aqueous Solutions

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Undoped and Al-doped ZnO (AZO) powders have been synthesized by hydrolytic and hydrothermal synthesis from $Zn(NO3)_2$, $AlCl_3$ using KOH 1M concentraction like hydrolisis agent. The structural properties of prepared powders were studied using XRD and FTIR spectroscopy. Presence of aluminium in the hydrothermal powders is correlated with the presence of Zn-Al hydrotalcite like structure.

Keywords: ZnO, Al-doped, Attenuated Total Reflexion, X-ray diffraction

Functional oxides especially as nanocrystalline materials are of particular interest due to their specific properties related with miniaturization tendency of the technological applications. As a first example, nanocrystalline ZnO shows a blue shift in the absorption spectrum, unlike the microcrystalline equivalent [1]. The origin of this difference lies in the much larger surface-to-volume ratio of the sample for nanocrystalline compounds, which means that surface effects become more important and may even dominate the properties of the bulk. Moreover, due to the high value of this ratio, the nanocrystalline material exhibits a much higher reactivity in the solid state reactions, which is important for the catalysts, but also for the decomposition of the precursors in order to obtain functional oxides. It is well known from the literature that the size of crystallites in the final oxides depends on how they were synthesized. In addition to other factors, such as the temperature and duration of thermal treatment, the nature of the precursor material is of major importance [1-3].

Experimental part

In the case of obtaining zinc oxide powders by hydrolytic synthesis we used zinc nitrate as a soluble precursor because the solubility of the inorganic salts of the same metal increases in the order of the perchlorate-perchlorate-nitrate. As a hydrolysis agent we used a strong nucleophilic agent: potassium hydroxide (1M concentration) in very small quantities. It generates directly and at high velocity OH^- ions. *P*h has an important role to play in balancing the hydrolysis reaction and the nature of the hydrolyzed species. The dependence of the solubility product K electro-negativity according to the latter is shown in figure 1.

The co-precipitation process is based on the hydrolysis of mixed salt solutions: nitrates and chlorides, with hydrolysis agents (potassium hydroxide, KOH 1M), which allows molecular homogenization.

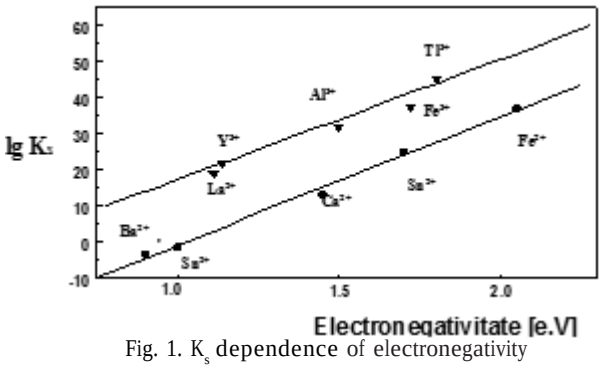

Fig. 1. K_s dependence of electronegativity

Precursor solutions were prepared by dissolving the pure salts: $Zn(NO_3)_2$ and $AlCl_3$ in distilled water and was mixed for obtaining 4% at. doping. Initially, a homogeneous mixed solution containing Zn^{2+} and Al^{3+} ions is obtained, from which doped ZnO is precipitated, with the basic hydrolysis agent.

Phase precipitation of basic salts is lower than that of hydroxides due to the influence of anion activity.

Table 1

SAMPLES BY HYDROLYTIC SYNTHESIS

SAMPLE	Dopant concentration	Condition
ZnO	-	25°C
4AlZnO25/135	4% at Al	25°C, 135 min.
4AlZnO85/135	4% at Al	85°C, 135 min
4AlZnO85/5	4% at Al	85°C, 5 min

Hydrothermal synthesis consists of a heat treatment under pressure in the presence of oxides and hydroxides in an autoclave containing an aqueous solution. In general, the reaction occurs at high temperatures and pressures. The aqueous solution of zinc nitrate was used as a precursor for obtaining unpacked powders, case of 4% at. doped powders was used zinc nitrate, $Zn(NO_3)_2$, and aluminium chloride ($AlCl_3$) dissolved in distilled water. The hydrolysis agent used is KOH 1M solution. Hydrolysis agent used is 1M KOH solution. Increasing temperature favours the displacement of the hydrolysis reaction equilibrium to the formation oxides by breaking the Zn-OH bonds with the increase in hydrothermal precipitation produce. Increasing pressure can even result in structures with large coordination numbers. Hydrothermal synthesis was completed into a CORTEST (USA) 2l autoclave. The whole process is computerized. The pressure used was 4.5 bar, temperature about 200°C and 40 min. After the process, the resulting powders were washed with distilled water to remove chlorine ions and ethyl alcohol to prevent agglomeration.

Table 2

SAMPLES BY HYDROTHERMAL SYNTHESIS

SAMPLE	Dopant concentration	Condition
ZnO	-	4.5 bar, 200°C, 40 min.
4AlZnO	4% at Al	4.5 bar, 200°C, 40 min

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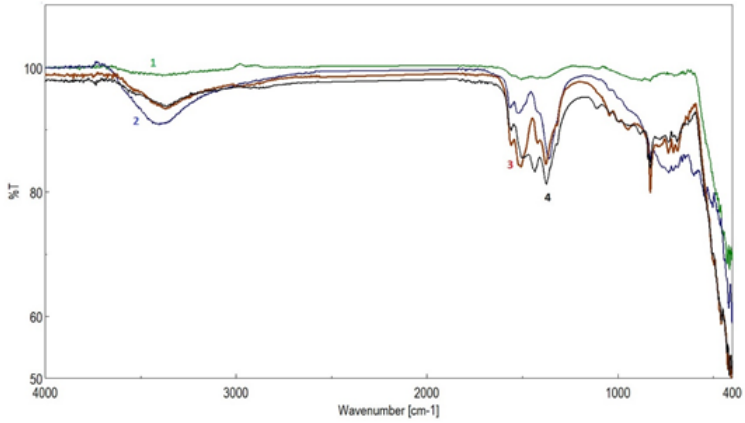

Fig. 2. FTIR spectra of undoped ZnO (1), 4AlZnO25/135 (2), 4AlZnO85/4 (3) and 4AlZnO25/135 (4) by hydrolysis synthesis

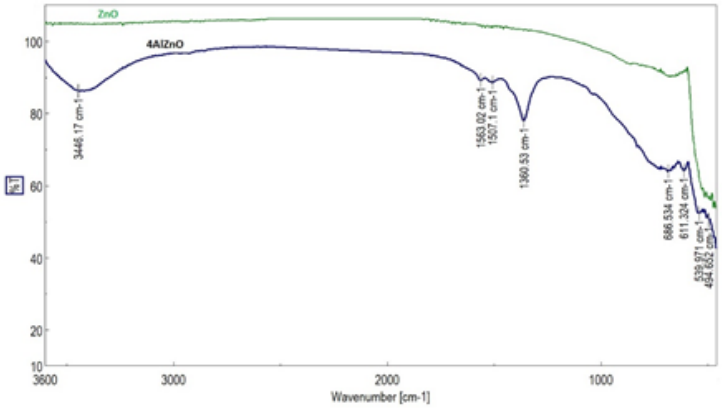

Fig. 3. FTIR spectra of undoped ZnO, and 4AlZnO by hydrothermal synthesis

The IR spectra were recorded using a Jasco 6300 FT-IR spectrometer in the region of 4000 -400 cm^{-1} with detector TGS, software Spectra Manager II. ATR spectra were obtained with an attenuated total reflection attachment Gladi ATR, apodization Cosine. The instrument had a spectral resolution of 4 cm^{-1}, which was used in all spectra determinations.

X-ray diffraction patterns were acquired on a Rigaku Ultima IV diffractometer in Bragg/Brentano geometry, using Cu-Kα radiation and a DTex Ultra detector. Scans were recorded in the 2θ range of 18° - 105° with a step of 0.02° and a counting time of 1 deg./min.

Results and discussions

FTIR analysis

Fourier transform infrared spectroscopy (FTIR) provides the information related to functional groups present in the sample, the molecular geometry, and intra or inter-molecular interactions. In this study, FTIR was used to study the vibrational mode of the samples. FTIR spectra of samples are shown in figures 2 and 3.

Infrared studies were carried out in order to ascertain the purity and nature of the metal nanoparticles. Metal oxides generally give absorption bands in fingerprint region i.e. below 800 cm^{-1} arising from inter-atomic vibrations.

The figures 2 and 3 show FTIR spectra of nanostructured ZnO particles.

The peaks observed at 3360-3404 cm^{-1} and 1110 cm^{-1} are may be due to O-H stretching and deformation, respectively assigned to the water adsorption on the metal surface.

The transmission band at 1553-1563 cm^{-1} in all the samples is due to the carbonyl group of the carboxylate ions which might remain adsorbed on the surface of ZnO.

The peaks around 1350 cm^{-1} correspond to the C-O absorption of ZnO surface.

For the AlZnO sample, the band around 1 360 - 1374 cm^{-1} can be attributed to the anti-symmetric stretching mode of carbonate, and bands observed about at 830 and around 680 cm^{-1} are attributed to the weak non-planar bending mode and the angular bending mode of carbonate, respectively [4].

The peaks at 649-689 cm^{-1} are correspond to Zn-O deformation vibration, respectively and confirms the formation of rod shaped ZnO particles. The peaks appearing between 400 and 600 cm^{-1} are assigned to the Meta-Oxygen stretching mode from Table 3. The metal-

Table 3

IR PEAKS AND ASSIGNMENTS OF NANOSTRUCTURED ZnO PARTICLES

Assignments	Wave number (cm^{-1})					
	ZnO Hydrothermal	4AlZnO Hydrothermal	ZnO Hydrolysis	4AlZnO25/135 Hydrolysis	4AlZnO85/5 Hydrolysis	4AlZnO85/135 Hydrolysis
O–H stretching		3346	3386	3404	3369	3360
Symmetric stretching of C-O		1360		1359	1376	1374
Zn-O stretching	653	656	649	662	687	689

Sample code	Synthesis method	Phase analysis
ZnO	Hydrolytic	ZnO hexagonal
		$Zn(OH)_2$
ZnO	Hydrothermal	ZnO hexagonal
4%AlZnO	Hydrothermal	ZnO hexagonal
		Zn-Al hydrotalcite-like structure
4%AlZnO/85/135	Hydrolytic, T = 85°C, t = 135 min	ZnO hexagonal
		$4ZnO*CO_2*4H_2O$
		traces of ZnO cub
4%AlZnO/85/5	Hydrolytic, T = 85°C, t = 5 min	ZnO hexagonal
		$4ZnO*CO_2*4H_2O$
		traces of ZnO cub ZnO cub
4%AlZnO/25/135	Hydrolytic, T = 25°C, t = 135 min	ZnO hexagonal
		Zn-Al hydrotalcite-like structure
		$4ZnO*CO_2*4H_2O$
		traces of ZnO cub

Table 4
QUALITATIVE PHASE ANALYSIS BY XRD

oxygen frequencies observed for the respective metal oxides are in accordance with literature values [5-8]. The appearance of peaks in different position depends on shapes of ZnO have reported by Verges et al. [9]. The shape affects the position and intensity of the peaks. As Figures 2 and 3 show the FT-IR spectra of Al doped ZnO which are almost similar to ZnO undoped in region 400-650 cm^{-1}. The vibration mode at wave number 655 cm^{-1} slightly changes.

The stretching of band appearing at 653-689 cm^{-1} suggests the formation nanostructured ZnO particles. Aluminum doped ZnO leads to the higher wavenumber for Zn-O stretching vibration (table 3).

The structure of the powders developed by hydrolytic and hydrothermal synthesis were characterized by X-ray powder diffraction for qualitative phase analysis (table 4) [10, 11].

All the resulting powders obtained by both synthesis routes exhibit diffraction peaks of ZnO (JCPDS 36-1451). The two samples obtained by hydrothermal route (fig. 4) were pure ZnO and 4% Al doped ZnO. The addition of Al salt in the hydrothermal process is correlated with the presence of Zn-Al hydrotalcite like structure (JCPDS 38-486) in the diffraction pattern.

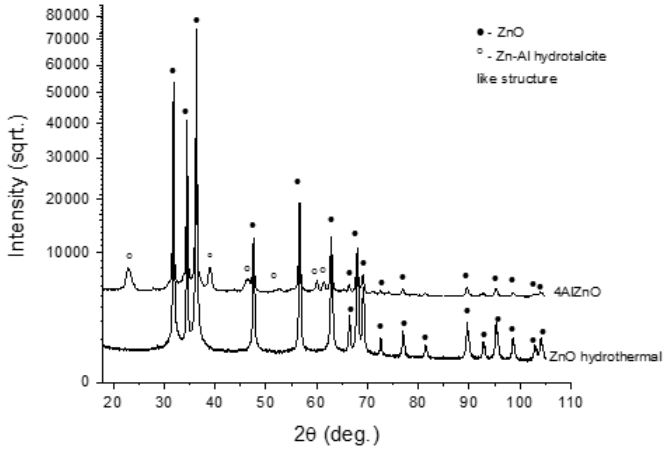

Fig. 4.XRD patterns of pure ZnO and 4%Al doped ZnO by hydrothermal route

Those hydralcite phases are layered hydroxides held each other by weak intermolecular forces or hydrogen bondings. In the case of this kind of structure the substitution of a divalent cation by a trivalent cation in brucite structure induces the presence of an interlayer anion in order to conserve the electroneutrality of the structure [12].

This structure is observed also in a sample obtained by hydrolytic route, but only at room temperature (fig. 5). The undoped sample exhibits also peaks related to $Zn(OH)_2$ structure (JCPDS 38-0345), an intermediate reaction product incompletely transformed and also some carbonate peaks (JCPDS 11-287).

The Zn-Al hydrotalcite like structure is not present in the samples obtained at 85^0 C. Also, the carbonate phase peaks intensity increases with temperature.

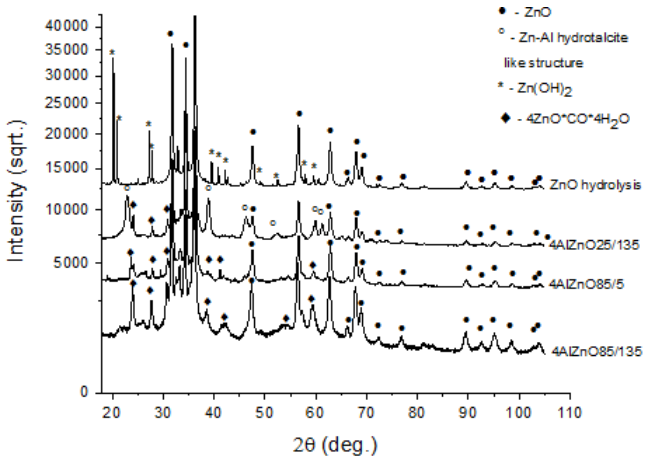

Fig. 5.XRD patterns of pure ZnO and 4%Al doped ZnO by hydrolytic route at different reaction temperature and time

Conclusions

Nanostructured ZnO and at 4% Al dopped ZnO have been synthesized by hydrothermal and hydrolytic synthesis. The XRD measurement results conclude that ZnO particles are with single phase hexagonal structure whereas for Al doped ZnO there is a mixture of hexagonal ZnO phases, hydrotalcite-like structure and carbonate phase. The presence of functional groups and the chemical bonding with Al is confirmed by FT-IR spectra.

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