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# Raman study of surface optical phonons in ZnO(Mn) nanoparticles

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ABSTRACT

Nanocrystalline samples of ZnO(Mn) were characterized by X-ray diffraction to determine composition of the samples (ZnO, $Mn_3O_4$, $ZnMn_2O_4$ and $ZnMnO_3$) and the mean crystalline size (between 9 and 13 nm for $ZnMnO_3$ phases, from 24 to 47 nm for $Mn_3O_4$ phases and above 100 nm for ZnO and $ZnMn_2O_4$ phases). In this paper we report the experimental spectra of Raman scattering (from 200 to 1600 $cm^{-1}$) with surface optical phonons (SOP) in range of 520–575 $cm^{-1}$. The phonon of registered phases exhibits effects connected to phase concentration, while the SOP phonon mode exhibits significant confinement effect.


## 1. Introduction

The synthesis and the properties of nanoscale inorganic materials have been attracted great interest, especially nanostructures made of ZnO and ZnO-related compounds due to their large expected spectra of applications. Some of them are in the quality of transparent conducting electrodes for solar cells and flat panel displays, in spintronic devices, transparent ultraviolet protection films and low-voltage and short-wavelength electro-optical devices [1,2].

It has been observed that ZnO is most promising host semiconductor material for high temperature ferromagnetism, because he exhibits ferromagnetism when is doped with most of the transition metals such as Co, Ni, Cr, Fe, and V [3].

Raman scattering has been method of choice for many studies of vibration properties of ZnO, for bulk, thin films and nanostructure samples, pure and doped due to his characteristics of an ideal sensitive, non-destructive tool. He permits obtain information about sample quality, the presence of impurities and their position in host lattice as well as information about phonon lifetimes and isotopic effects [4,5]. Local atomic arraignment, dopant incorporation, electron–phonon coupling, multi-phonon process, influence of annealing process, temperature dependence of Raman modes and others have been studied in ZnO and ZnO-related compounds using Raman scattering [6–11].

For nanostructures of ZnO is expected the appearance of surface optical phonon (SOP) modes in Raman spectra because of their large surface-to-volume ratio. This is the reason why the state of surface atoms has play important role in determining their properties. Surface modes are only modes that persist when dimensions become extremely small. With this we can say that SOP modes are Raman forbidden modes whose presence is related to loss of long-range order and symmetry breakdown in ZnO shell [12]. All this can be found in many papers predicted theoretically and/or detected experimentally for ZnO nanostructures [13].

In our previous paper [14] we have done analysis of vibrational modes and detailed study SOP mode in ZnO(Co) samples, while with this paper we want to continue completing the picture about the impact of doping with the transition elements on vibrational properties of doped ZnO.

The aim of this work is to study the influence of preparation method on sample's characteristics, by applying micro-Raman spectroscopy to study SOP, the Mn ion position in ZnO lattice, the formation of existing phases, and the samples quality in dependence of MnO concentration.

## 2. Samples and characterization

The nanocrystalline samples of ZnO doped with MnO were synthesized by use of the wet chemical method. First, the mixture of manganese and zinc hydroxides was obtained by the addition of an ammonia solution to the 20% solution of proper amount of Zn $(NO_3)\cdot 6H_2O$ and $Mn(NO_3)\cdot 4H_2O$ in water. Next, the obtained hydroxides were filtered, dried at 70 °C and calcined at 300 °C during one hour. Nanopowders obtained on this way were pressed into indium panel.

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This method allowed to obtain the series of samples with nominal concentration of MnO from 5% to 95%. In this paper we present the results of micro-Raman spectroscopy for representative samples as well as changes in relative intensity of modes with concentration of MnO.

Morphology of the samples was investigated using scanning electron microscope (SEM). SEM images for four representative samples doped with 5, 20, 50 and 95 wt.% of MnO are shown in Fig. 1. In Fig. 1(a–c) two types of particles can be easily distinguished: one is bigger than 100 nm and it belongs to ZnO phase (marked with Z), and the other is much smaller and it belongs to $ZnMnO_3$ phase (marked with $M_3$). Also it is notable that the dominance of big ZnO particles decreases with the increase in concentration of MnO. On the other hand in Fig. 1(d) we can notice approximately equal size particles that belong to $Mn_3O_4$ phase.

The phase composition of the samples was determined by X-ray diffraction (Co K$\alpha$ radiation, X'Pert Philips). The detailed phase composition investigation revealed the presence of hexagonal ZnO, along with spinel structures of $Mn_3O_4$, $ZnMn_2O_4$ and $ZnMnO_3$. In order to demonstrate this fact, the characteristic X-ray diffractogram for representative samples is shown in Fig. 2 while Fig. 3 gives the enlarged part of Fig. 2 with highest concentration of peaks of all registered phases. XRD data allowed to determine a mean crystallite size in prepared samples by use of Scherrer's formula [15]. The mean crystalline size $\tilde{a}$ of these phases is between 9 and 13 nm for $ZnMnO_3$ phases, from 24 to 47 nm for $Mn_3O_4$ phases and above 100 nm for ZnO and $ZnMn_2O_4$ phases. The results of XRD measurements are gather in Table 1. Sign "+" in this table means that it has been register the presence of these particles but it was not possible to determinate their size.

Here the diversely grain size is the consequence of production of samples with different concentrations of MnO not the principle aim of the work. As it is obvious surface of these samples is not mirror-like as it was for the samples used in work of C.M. Julien at al. [16] and cannot be compared with it or with samples obtained by epitaxially grown nor bulk crystal samples.

In this work we present the investigation of samples doped with 5, 20, 30, 50, 60, 70, 80 and 95 wt.% MnO. No other crystal phases are observed in these samples.

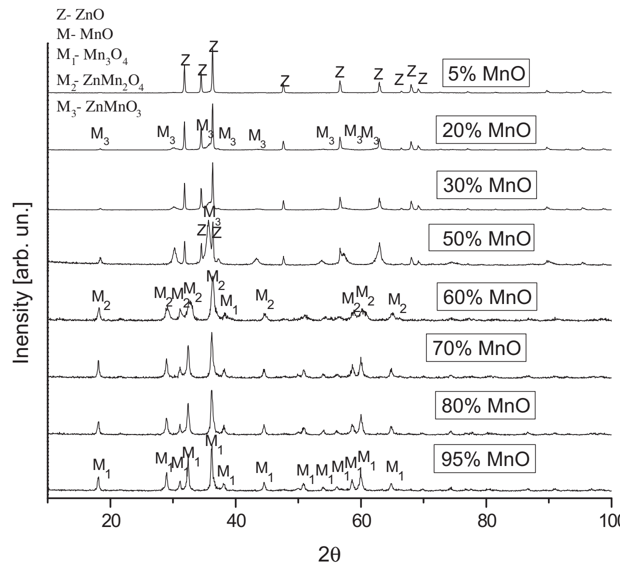


**Fig. 2.** XRD spectra of representative samples all register crystalline phases are marked and evident.

## 3. Surface optical phonons

Here we will give a brief concept of surface optical phonons (SOP). Reduction in the particle dimensions to nanoscale, as in our case, and the presence of imperfections, impurity and others, results in breakdown of phonon momentum selection rules, that is why some new forbidden vibration modes whose phonons have $l \neq 0$ contribute to Raman scattering [6,7,17,18]. Also we can mention that SOP modes appear in samples whose particles size is smaller than the wavelength of incident laser beam and that these modes arise in polar crystals [12]. From the literature dielectric function for the case of polar semi-insulating semiconductor [see for example Ref. [13] and literature cited there], many mixing models for the effective dielectric permittivity [19], as well as Maxwell–Garnet mixing rule can be found [20,21]. However the Maxwell–Garnet approximation is only valid for small volume fraction of inclusions and is not appropriate in our case. That is why we will be focused on Bruggeman formula and it mixing rule [22–24] which is much more appropriate in our case. In Bruggeman model does not exist restrictions for volume fraction that is why it is suitable for high concentration of inclusions. The effective dielectric function according to the Bruggeman mixing rule is given as follows:

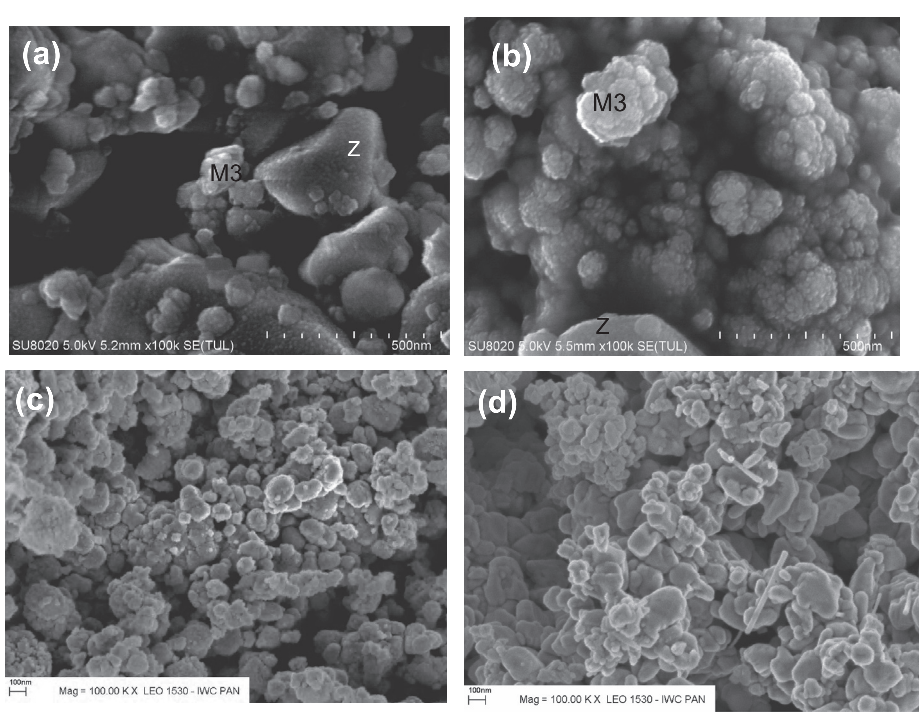


**Fig. 1.** SEM images of four samples of nanosized ZnO doped with MnO, (a) correspond to sample doped with 5 wt.% of MnO, (b) correspond to sample doped with 20 wt.% of MnO, (c) correspond to sample doped with 50 wt.% of MnO while Fig. 1 and (d) correspond to sample doped with 95 wt.% of MnO.