Simple route synthesis of (Al, Ni) co-doped ZnO nanoparticles and their characterizations

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The codoped nanoparticles by Aluminium and Nickel were prepared by sol–gel method and theirs different physical properties were studied. The obtained nanoparticles were undergoes a heat treatment in air at different temperatures ranging from 500 °C to 1000 °C in 2 hours. The structural results revealed that the structure is wurtzite with an average crystallite around 30nm, and the appearance of NiO second phase. The optical spectroscopy (UV-Vis) shows a red shift in band gap values with increasing of heat treatment temperature. Photoluminescence (PL) results indicate the effects of oxygen vacancies on emission spectra and confirms the shift of band gap energies. Magnetic measurements at 300K showed a superparamagnetic behaviors.

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1. Introduction

Nanotechnology has been an important focus for researchers, specifically after advancements of research and technology, in the semiconductor field. The doping of semiconductors is a proven technique to empower the use and control their physical properties [1,2]. Due to their particular physical and chemical properties, nanoparticles (NP) of zinc oxide (ZnO) have been able to play a very important role in various domains, such as sensors, light-emitting diodes, photocatalysis and solar cells [3-5]. The doping of ZnO with different transition metals (TM) has been well studied, as a dilute magnetic semiconductor (DMS). This makes him an essential candidate in magneto-electronics and magneto-optics. By doping with various elements, including TM (e.g., Co, Fe, Ni), rare earths (RE) (e.g., Gd, Eu, Tb) and non-magnetic element (e.g., Li, Al, C), room temperature ferromagnetism (RT-FM) of ZnO can be achieved [6-13]. Yi et al. [14] suggested that the improvement of ZnO FM properties is related to doping with appropriate elements due to cation vacancies stabilization and hole formation [15–19]. It has been reported that the Ni and Al co-doped ZnO nanostructure and nanoparticles can be prepared by several chemical and physical techniques [20-25]. According to some research groups, the room temperature ferromagnetism of ZnO films co-doped Ni and Al prepared on glass substrates by magnetron co-sputtering depends on the deposition temperature and the Ni concentration [26, 27]. On the other hand, doping with a metal ion improves the electronic properties of ZnO due to the increase in the number of free electrons in the crystal lattice structure. It was previously suggested that the conductivity of ZnO doped with metal ions Al^{3+}, In^{3+} and Ga^{3+} is due to oxygen vacancies and interstitial zinc defects [28]. Hence, a correlation is evident between the doping of semiconductors with MT and the electronic structure of metals in d orbitals [29].

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In the present work, the nanoparticles of (Al, Ni) codoped ZnO have been prepared by sol-gel method. The effects of heat treatment on the structural, optical and magnetic properties were studied.

2. Experimental details

2. 1. Nanoparticles preparation

Al and Ni co-doped ZnO aerogel nanopowders were prepared using zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), aluminum nitrate-9-hydrate ($Al(NO_3)_3\ 9H_2O$) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), as precursors purchased from sigma Aldrich. After 15 min of magnetic stirring in methanol, the mixture was dried under supercritical conditions of ethyl alcohol (EtOH) as described in our previous papers [1,5 ,11]. The obtained powders were heated at different temperatures ranging from 500 °C to 1000 °C in air for two hours.

2.2. Characterization techniques

The Bruker D8 Discover diffractometer (θ-2θ) with Cu-Kα radiation (λ=1.5406 Å) was used for XRD study. A JEM-2200 scanning electron microscopy (SEM) and JEM-200CX transmission electron microscope (TEM) were used to the morphology studies. We used a UV-Vis-IR spectrophotometer (Shimadzu UV-3101 PC) attached to an integrating sphere, desired for the powder samples, for absorbance measurement. Quantum Design MPMS-5S SQUID magnetometer was used for the magnetization (M–H) analysis.

3. Results and discussion

3.1. Structural analysis

XRD patterns of nanoparticles heated at different temperatures are illustrated in Fig.1 showing presence of strong and narrow reflected peaks of ZnO. The hexagonal ZnO with polycrystalline wurtzite structure is the most dominant crystalline phase (marked ●) [1, 10].

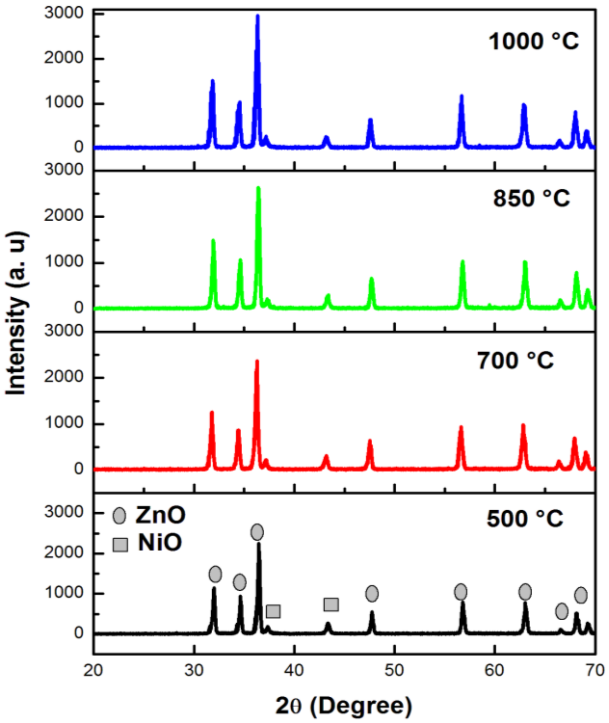

Fig.1. X-ray patterns of $Zn_{0.875}Ni_{0.1}Al_{0.025}O$ heated at different temperatures.

No secondary phase linked to Al element appeared in XRD results showing the good insertion of Al ions in the ZnO matrix. On the other hand, another secondary phase attributed to NiO (ICDD396-432-0500) was detected [30]. An increase in the intensity of the first three peaks is noted when the annealing temperature increases. This is accompanied by the decrease of full-width half maximum (FWHM) values. After fitting the all reflected peaks, we deduce the FWHM for each peak and the crystallites size for all samples are estimated using the known Debye–Scherer relation [32]:

$$D = 0.9\lambda/\beta \, \mathrm{Cos}\theta \quad (1)$$

The average crystallites sizes evaluated from this equation were between 30 and 70 nm, indicating a growth in size with temperature which is explained by agglomeration of the nanoparticles.

3.2. TEM analysis

Figure 2 show the TEM images for all samples. This images indicated that, the dominant structure is hexagonal shape and the average size increase with temperature, which confirms the XRD result. From EDX analysis, presented in Figure 3, the appearance of all elements present in the sample is confirmed with where amount showing the good preparation of sample.

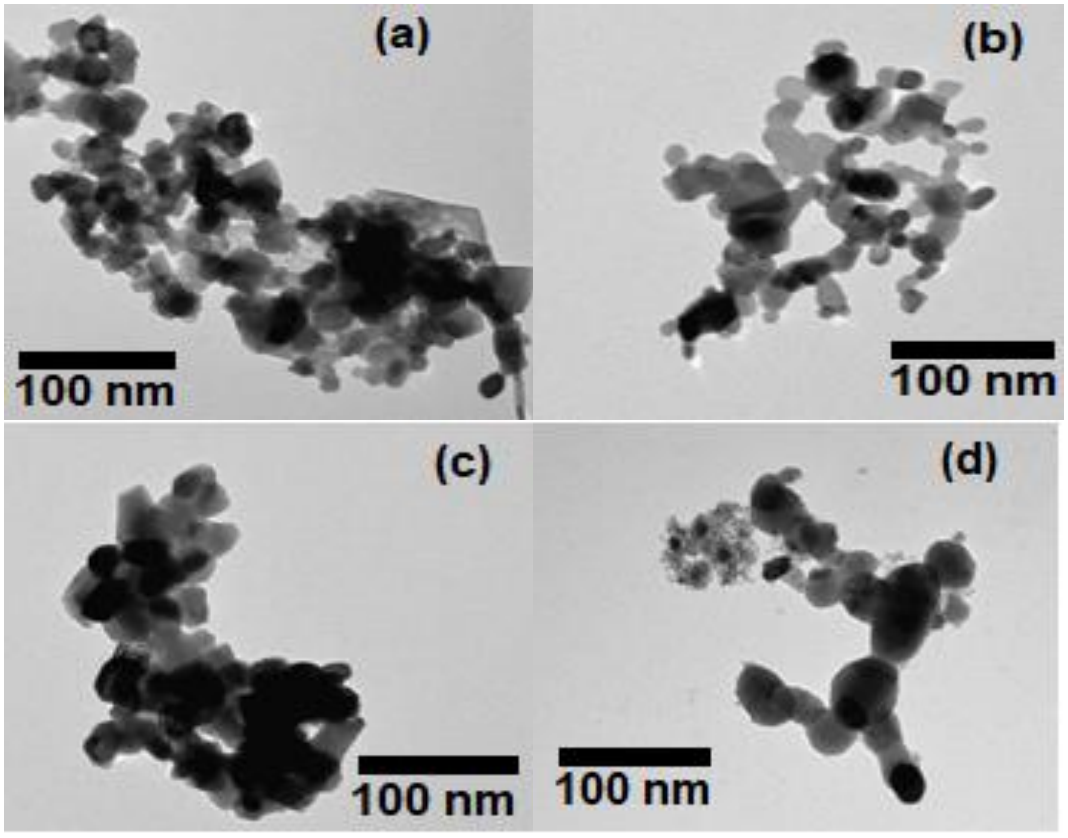

Fig. 2. TEM images $Zn_{0.875}Ni_{0.1}Al_{0.025}O$ nanoparticles heated at (a):500 °C, (b):700 °C, (c):850 °C and (d):1000 °C.

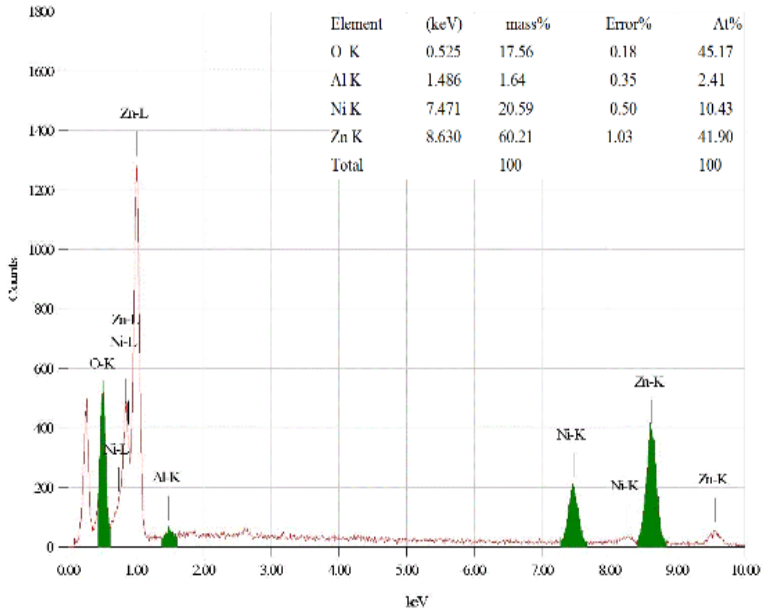

Fig. 3. EDX analysis of $Zn_{0.875}Ni_{0.1}Al_{0.025}O$ nanoparticles heated at 500 C.

3.3. Optical properties

Fig.4 shows the absorbance spectra revealing a high absorption in the UV spectral range indicating the good optical properties of the prepared nanoparticles.

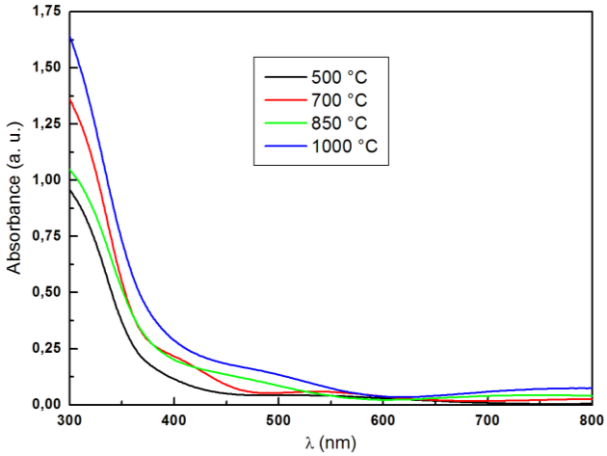

Fig. 4. Absorbance spectra of all samples.

The equation linking the absorption coefficient α to the optical energy Eg is given by [33]:

$$\alpha(h\nu) = C\left(h\nu - E_g\right)^{\frac{1}{2}} \tag{2}$$

where C is the constant of direct transition, and hν is the intensity of incident energy. The band gap Eg is deduce by extrapolating the straight portion, revealing the direct transition type of our semiconductors, of the plot $(\alpha h\nu)^2$ vs. (hν) to the x-axis. The spectra shown in Fig. 5 present a decrease of bandgap (Eg) values with increasing heat temperature. This red shift can be linked to the quantum confinement effects [34, 35].

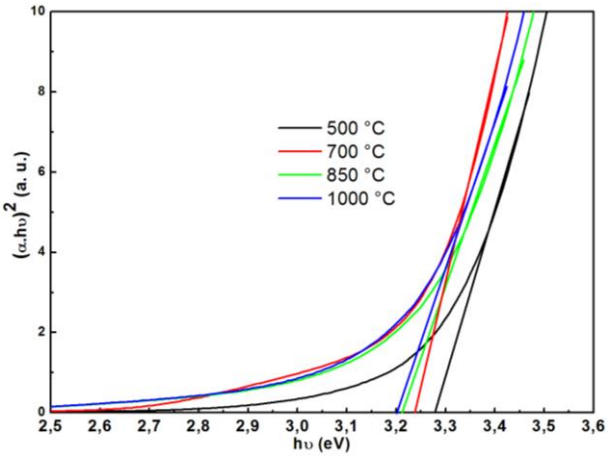

Fig. 5. Plot of $(\alpha h\nu)^2$ vs. $h\nu$.

3.4. Magnetic studies

Generally the small grain size or the presence of defects in the structure are the main causes of paramagnetic and weak ferromagnetic character of nano-ZnO at room temperature [36-38]. The doping of ZnO by a non-magnetic element and the grains boundaries may be responsible to improvement of ferromagnetic characteristics [39, 40].

Figure 6 shows the magnetization (M–H) of our samples at 300 K, revealing a decrease in magnetization as a function of the heat treatment with low coercivity and the absence of saturation. The observed decrease in magnetization may be due to the incorporation of Zn ions into the octahedral sublattice or to the formation of a spin glass structure or the existence of surface spins [41]. It's known that NiO is superparamagnetic material at room temperature, while, it is antiferromagnetic with a Neel temperature of 520 K [42]. The existence of NiO as a secondary phase is confirmed by XRD study in our case. The characteristic of super-antiferromagnetic/superparamagnetic behaviour appeared in our samples suggests this hypothesis.

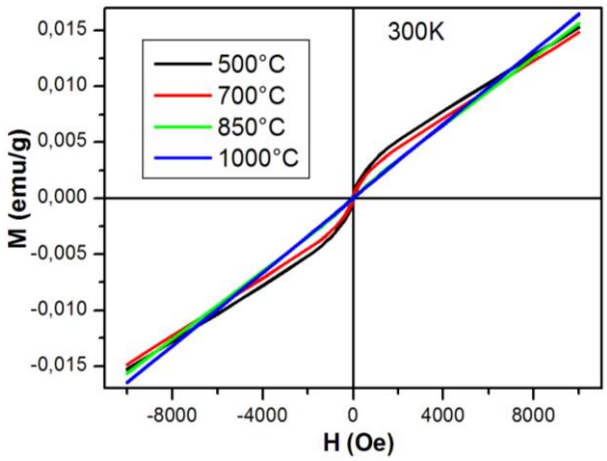

Fig. 6. Room temperature magnetization (M-H) spectra of all samples.

4. Conclusion

In this work, ZnO nanoparticles co-doped with nickel and aluminium are synthesized using the sol-gel method. The wurtzite structure of ZnO with hexagonal phase of the samples is demonstrated by structural and morphological studies. XRD results reveal the existence of small extent of NiO as a secondary phase. TEM images revealed the good purity of the synthesized co-

doped ZnO nanoparticles, which is a very advantage of sol gel technique. The optical absorbance shows a decrease of band gap energies with increase of heat treatment. The magnetic analysis shown a superparamagnetic behaviors.

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