Structural and Optical Characterization of Ni and Al Co-Doped ZnO Nanopowders Synthesized via the Sol-Gel Process

Amor Sayari¹,²* and Lassaad El Mir³,⁴

¹ Department of Physics, Faculty of Science, King Abdulaziz University, North Jeddah Branch, Saudi Arabia
² Équipe de Spectroscopie Raman, Département de Physique, Faculté des Sciences de Tunis, Campus Universitaire, Tunisia
³ Al Imam Mohammad Ibn Saud Islamic University (IMSIU), College of Sciences, Department of Physics, Saudi Arabia
⁴ Laboratoire de Physique des Matériaux et des Nanomatériaux appliquée à l’Environnement, Faculté des Sciences de Gabès, Tunisia

Abstract

We have successfully synthesized (Ni,Al) co-doped ZnO nanostructured powders via the sol-gel technique at low temperature. The elemental analysis confirms the incorporation of the Ni and Al ions into the ZnO matrix. The structural study revealed that the nanopowder samples are assembled in flower-shaped Zn₀.₉₋ₓNiₓAlₓO nanostructures with average crystallite sizes ranging from 39 to 53 nm. The XRD patterns show that the Zn₀.₉₋ₓNiₓAlₓO nanopowders have a hexagonal wurtzite polycrystalline structure. Weak diffraction peaks related mainly to nickel oxides are also detected in the samples. The highest crystallite size, lowest lattice parameters and unit cell volume are obtained for the nanopowder samples that contain 1.5 at.% of aluminum. The decomposition process of the dried gel system is investigated by thermogravimetric analysis (TGA). Raman scattering and FT-IR measurements confirm the wurtzite structure of the synthesized Zn₀.₉₋ₓNiₓAlₓO nanopowders. The energy band gap of the synthesized nanopowders (~3.32 eV) was estimated by using the Brus equation and the crystallite sizes obtained from XRD data, for comparison. The strain in the nanopowder samples (~2.7 × 10⁻³) was also calculated according to the Stokes-Wilson equation.

Keywords: ZnO, sol-gel, Ni and Al co-doping, SEM, XRD, Raman scattering

1. Introduction

Recently, semiconductor nanoparticles have attracted much attention due to different physical and chemical properties compared to their bulk materials. When the size of a nanostructure approaches the Bohr radius of exciton, optical, electronic and structural properties are greatly affected by the quantum confinement effect, meaning that nanosized materials are very different from their bulbs. Therefore, semiconductor particles are viewed as promising candidates for many important technological future applications. Among various semiconductor nanoparticles, nanosized zinc oxide (ZnO) particles are the most frequently studied due to their frequent applications in industrial areas. ZnO nanoparticles which have great potential for use as efficient UV light absorbers were recently applied to improve the finishing of textile products and are being utilized for improved cosmetic products. To synthesize uniform nanosized ZnO particles and control their sizes and morphology, a variety of techniques has been used such as thermal decomposition, chemical vapor deposition, sol-gel, spray pyrolysis, and precipitation.

It is well known that adding impurities into a wide gap semiconductor such as ZnO induces great changes in the optical, electrical and magnetic properties. Thus doping certain elements into ZnO has become an important route to control and optimize its optical, electrical and magnetic performance. It was reported that ZnO has been doped with elements of the groups IA such as Li, IIIA such as Al, VA such as N and VIII such as Ni, Co, etc. Doping of ZnO with magnetic ions such as Ni introduces magnetic properties ultimately forming dilute magnetic semiconductors, which are interesting materials for application in the spintronic domain. In addition, nanosized nickel oxide has demonstrated other excellent properties such as catalytic, electrochromic, optical and electrochemical properties. There is considerable interest in the development of zinc-oxide-based (ZnO: transition metal) diluted magnetic semiconductors because of their high Curie temperature which is essential for spintronic devices. Recently, co-doped ZnO nanomaterials

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3. P.O. Box 80203, Jeddah 21589, Saudi Arabia
4. Riyadh 11623, Saudi Arabia
5. Cité Erradi Manara Zrig, 6072 Gabès, Tunisia
6. Corresponding author: Amor Sayari; E-mail: amor.sayari@laposte.net
7. Tel: +966(2)6952287 Fax: +966(2)6952278

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with Al and transition metals have been investigated for scientific and practical interests. It was found that for the Ni and Al co-doped ZnO (Zn(Ni,Al)O) film, the ferromagnetic behavior was enhanced by increasing the Ni content. However, the co-doping of ZnO with metallic ions such as nickel (Ni$^{2+}$) and aluminum (Al$^{3+}$) is not widely investigated. The Zn(Ni,Al)O semiconductor is an interesting material due mainly to its ferromagnetic behavior with a high Curie temperature.

It is a significant task to prepare Zn(Ni,Al)O nanomaterials with better electrical, optical and ferromagnetic behavior for potential applications in magnetoelectronic and optoelectronic devices. The aim of the present contribution is the elaboration as well as the structural and optical characterization of Zn(Ni,Al)O nanoparticles synthesized by the sol-gel process where many environmental parameters such as temperature, pressure and doping concentration can be varied to control the growth of the crystal. This study is a prerequisite to investigate the ferromagnetic behavior in these powdered samples. The prepared Zn$_{0.9-x}$Ni$_x$Al$_x$O samples have an Ni composition fixed at 10 at.% and various Al contents ranging from 0.0 to 2.5 at.%.

The composition and structure of the Zn(Ni,Al)O nanoparticles are studied using energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The optical property and thermal analysis characteristics of the synthesized Zn$_{0.9-x}$Ni$_x$Al$_x$O nanopowders are retained but are accompanied by the existence of Zn, Ni, Al and O in the powdered samples, indicating the incorporation of Ni and Al ions into the ZnO matrix. It is clear from the elemental analysis that the percentage of Ni atoms is almost constant (around 11 at.%) for all the doped samples (Table 1). The intensity of the characteristic Al peak increases with increased dopant level. The average Al concentrations in the doped nanopowders are 0.0, 0.025 and 0.38 at.% for 0, 1.5 and 2.5 at.% Al doped Zn(Ni)O nanocrystals, respectively (Table 1).

2. Experimental details

Zn(Ni,Al)O nanocrystals were prepared by the sol-gel method using 16 g of zinc acetate dehydrate as a precursor in 112 ml of methanol. After 10 min magnetic stirring at room temperature, 2.8 g of nickel chloride hexahydrate corresponding to [Ni]/[Zn] = 10 at.% and an adequate quantity of aluminum nitrate-9-hydrate corresponding to [Al]/[Zn] ratios of 0.0, 1.5 and 2.5 at.% were added. After an additional 15 min magnetic stirring, the solution was placed in an autoclave and dried under supercritical conditions of ethyl alcohol (EtOH).

The phase identification of nanopowders was analyzed by X-ray diffraction using a Philips X’pert diffractometer equipped with copper X-ray tube ($\lambda_{K\alpha1}$ = 1.5406 Å), nickel filter, graphite crystal monochromator, proportional counter detector, divergence slit 1° and 0.1 mm receiving slit. The working conditions were 40 kV and 30 mA for the X-ray tube, scan speed 0.05° and 2 s measuring time per step. The morphology of the Zn(Ni,Al)O nanoparticles was observed by scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX). FT-IR spectroscopy (Thermo Scientific Nicolet iS10 FT-IR Spectrometer) was used at room temperature in the range of 500–4000 cm$^{-1}$ to study the optical properties of the synthesized Zn$_{0.9-x}$Ni$_x$Al$_x$O nanopowders. Thermal gravimetric analysis (TGA) curves of the (Ni,Al) co-doped ZnO nanopowders was performed using a TGA apparatus (Perkin Elmer). Approximately 2.9 mg of a sample was placed in a platinum crucible on the pan of the microbalance and heated from 35 to 950°C at a rate of 10°C/min$^{-1}$. The Raman spectra were performed at room temperature with a Labram system equipped with a microscope in back-scattering configuration. The excitation line was at 514.5 nm from an Ar$^+$ laser.

3. Results and discussion

3.1 Composition and structure

Fig. 1 shows typical EDX spectra of the (Ni,Al) co-doped ZnO nanopowders. The spectra in Fig. 1 show the existence of Zn, Ni, Al and O in the powdered samples, indicating the incorporation of Ni and Al ions into the ZnO matrix. It is clear from the elemental analysis that the percentage of Ni atoms is almost constant (around 11 at.%) for all the doped samples (Table 1). The intensity of the characteristic Al peak increases with increased dopant level. The average Al concentrations in the doped nanopowders are 0.0, 0.025 and 3.88 at.% for 0, 1.5 and 2.5 at.% Al doped Zn(Ni)O nanocrystals, respectively (Table 1).

Fig. 2 shows the X-ray diffraction spectra (vertically offset for clarity) of the prepared Zn(Ni,Al)O nanopowder samples. The crystal structure of Zn$_{0.9-x}$Ni$_x$Al$_x$O ($x = 0.00, 0.015$ and $0.025$) was wurtzite with preferred orientation along [101], [100] and [002] directions for all the samples. The reflection peak positions of the products coincide well with JCPDS data for the wurtzite structure of bulk ZnO. With Ni and Al incorporation, the dominant peaks of ZnO are retained but are accompanied by extra peaks marked by asterisks. The intensity of these extra peaks is seen to decrease with Al concentration due to incorporation of Al ions in the ZnO lattice. The occurrence of extra peaks and the intensity dependence on the Al concentration signifies that these peaks are due to the presence of additional phases in wurtzite ZnO mainly related to metallic Ni and NiO-like crystalline structures. It is known that Ni is very unstable in the ZnO matrix and has the tendency to form clusters of metallic Ni or NiO. The dominant phase is, however, the wurtzite because of smaller concentrations of Ni (10%) and Al (0–2.5%) atoms in the prepared samples. The results show that the addition of Ni and Al atoms as dopants did not affect the lattice patterns of ZnO nanocrystals.
The Zn$_{0.9-x}$Ni$_{0.1}$Al$_x$O crystallite sizes (D), calculated from the widths of the major diffraction peaks observed in Fig. 2 using the Scherrer formula$^{30}$, are given in Table 2. The average crystallite sizes range from 39 to 53 nm. The slight changes in the lattice parameters (Table 3) are expected due to the ionic radii mismatch. Both ionic radii of Al$^{3+}$ (0.57 Å) and Ni$^{2+}$ (0.69 Å) are smaller than the ionic radius of Zn$^{2+}$ (0.74 Å)$^{24}$. Fig. 3 illustrates the shift occurring in the (101) peak of ZnO with increase in Al concentration. It is clear from Fig. 3 that the (101) peak of ZnO shifts to higher angles for $x = 0.015$ and 0.025 compared to $x = 0$. However, for the higher doping concentration ($x = 0.025$), a smaller shift is detected. The lattice parameters (a and c) and the unit cell volume decrease (Table 3) with the introduction of Ni and Al ions; this can be attributed to the larger ion radius of Zn$^{2+}$ compared with that of Ni$^{2+}$ and Al$^{3+}$ $^{31}$. Therefore, Al atoms are more incorporated into the ZnO lattice at $x = 0.015$. The lattice strain of the Zn$_{0.9-x}$Ni$_{0.1}$Al$_x$O nanopowder samples is also calculated according to the Stokes-Wilson equation. The different values of the strain are $2.7 \times 10^{-3}$, $2.3 \times 10^{-3}$ and $2.9 \times 10^{-3}$ for $x = 0$, 0.015 and 0.025, respectively.

Fig. 4 shows SEM images of the Zn(Ni,Al)O nanopowders prepared with different nominal concentrations of aluminum. The nanoparticles have flower-like shapes consisting of a large number of primary nanocrystallites which are detected by XRD. No appreciable change either in shape or in size of the ZnNiO particles could be observed on Al-doping (Fig. 4(a–c)). From SEMmicrographs, a non-uniform distribution of particles is observed. It consists of either several single particles or a cluster of particles. The magnified image shows that flower-shaped structures are constituted by the accumulation of
several hundred sharp sheets of Zn(Ni,Al)O nanoparticles. The typical diameters of these individual nanosheets are in the range of 0.5–1 μm with a thickness of 50–100 nm. We note that similar morphologies of the nanostructured materials, consisting of nanometric homogeneous subunits aggregated into larger particles, have been reported previously for materials prepared by controlled precipitation or thermal decomposition of metalorganic precursors.

In order to compare the energy band gap ($E_g$) of the different Zn$_{0.9-x}$Ni$_{0.1}$Al$_x$O samples, we used the Brus equation derived from the effective mass model and the crystallite sizes obtained from XRD data. The parameters of ZnO bulk used in the calculations were taken from Ref. 35. The different values of $E_g$ are given in Table 3. We note that $E_g$ is almost constant (~2.2 eV) when the Al content increases from 0 to 2.5 at.%. 

### 3.2 Thermal properties

The thermal behavior of dried Zn(Ni,Al)O gel has been investigated by thermogravimetric analysis (TGA). Fig. 5 depicts the results of the TGA measurements on the nanosized Zn$_{0.9-x}$Ni$_{0.1}$Al$_x$O particles. It can be seen that the sample weight decreases continuously with increase in temperature in the interval 25–450°C. However, for temperatures up to 450°C, the weight loss decreases albeit at a small rate, which corresponds to the release of entrapped gases formed during the decomposition of acetate ions. The TGA curves show four main regions. The first weight loss is from room temperature up to 150°C due to the dehydration of Zn$_{0.9-x}$Ni$_{0.1}$Al$_x$O nanopowders. The second weight loss is from 150 to 220°C, which is attributed to the decomposition of chemically bound groups. The third step from 220 to 350°C is related to decomposition of the organic groups. The last weight loss from 350 to 450°C is attributed to decomposition of the impurity ions from the ZnO lattice and the formation of ZnO pure phases. The TGA study also shows the stability of the Zn$_{0.9-x}$Ni$_{0.1}$Al$_x$O nanopowders. We note that for $x = 0$, the weight loss is more important compared to samples with $x > 0$; this can be related to the addition of Al atoms.

### 3.3 Raman scattering

Room temperature Raman spectra of Zn(Ni,Al)O nanoparticles, synthesized by the sol-gel process, are reported in Fig. 6. The intense Raman peak located at about 502 cm$^{-1}$ could be assigned to multiphonon scattering of the transverse optical (TO) $E_1$ and $E_2$ (low) modes. The peak at 708 cm$^{-1}$ can be assigned to combinations of longitudinal acoustic (LA) and TO modes at the M point. In the low-frequency region, the peaks at 190, 330, 384 and 409 cm$^{-1}$ are attributed to 2E$_2$ (low), 2E$_2$ (M), A$_1$ (TO)
and $E_2$ (TO) modes\(^{37}\), respectively. Phonons in a nanocrystal are confined in space and all types of phonons over the entire Brillouin zone will contribute to the Raman spectrum. The intense peak at $\sim 434$ cm\(^{-1}\) is the $E_2$(high) mode, characteristic of the ZnO crystallinity\(^{38}\). Observation of the later modes indicates that the Zn(Ni,Al)O product has the wurtzite structure as confirmed by XRD analysis. The broad Raman peak at around 573 cm\(^{-1}\) may be due to the $A_1$(LO) mode\(^{39}\). Recent reports related the appearance of this mode to lattice defects, namely either oxygen vacancies or zinc interstitials or their combination\(^{40,41}\).

3.4 FT-IR measurements

Fig. 7 illustrates the FT-IR spectra of nanosized Zn\(_{0.9-x}\)Ni\(_x\)Al\(_x\)O powders in the range 500–4000 cm\(^{-1}\). FT-IR spectra of the synthesized products show a significant spectroscopic band at around 500 cm\(^{-1}\), which is the characteristic band of ZnO\(^{42}\). The broad OH band (3574, 3447) cm\(^{-1}\) appears in all the FT-IR spectra\(^{43}\). Theoretical calculations predict O-H vibrations in ZnO ranging from...
3216 to 3644 cm\(^{-1}\), depending on the configuration and number of hydrogen atoms in the complex\(^{44}\). The transmission bands at \(\sim 1576\) and 1412 cm\(^{-1}\) in all the samples are due to the carbonyl groups of the carboxylate ions which might remain adsorbed on the surface of nanoparticles\(^{45}\). The peak at 887 cm\(^{-1}\) is probably due to the nitrate (NO\(_3^–\)) group which is not completely removed during the sol-gel process\(^{46}\). Inclusion of Ni and Al ions in the ZnO lattice is confirmed by the emergence of the bands at 1038 and 582 cm\(^{-1}\)\(^{45}\).

### 4. Conclusions

In summary, Zn\(_{0.9-x}\)Ni\(_{0.1}\)Al\(_x\)O nanopolvers with crystallite sizes ranging from 39 to 53 nm were successfully synthesized by the sol-gel process and investigated by a variety of techniques for changes in microstructure and optical properties. The XRD patterns indicate high crystallinity in the hexagonal lattice of Zn\(_{0.9-x}\)Ni\(_{0.1}\)Al\(_x\)O nanoparticles; such a result is also confirmed by Raman measurements. The lowest lattice parameters and unit cell volume are obtained for the nanopowder samples that contain 1.5 at.\% of aluminum, which indicates that Al is better incorporated into the ZnO lattice at this Al content. The main weight losses showed by TGA curves occurring in the range between room temperature and 450°C are associated with water emission and the decomposition of organic groups and impurity ions. The TG trace shows
the formation of ZnO pure phases up to 450°C. The estimated band gap (~3.32 eV) from the Brus equation and the average crystallite sizes deduced from XRD data is not strongly dependent on the Al composition of the Zn$_{0.9-x}$Ni$_x$Al$_x$O nanopowders in our range of Al content ($x = 0–0.025$). The synthesized materials have potential applications in photocatalytic, optoelectronic and magnetoelectronic devices.

References


Amor Sayari

Amor Sayari received his bachelor’s degree in physics in 1989 and his Master of Science and PhD graduate degree in solid-state physics in 1991 and 1998, respectively, from Al Manar University, Tunisia. He obtained the habilitation qualification in physics (HDR) at Al Manar University in July 2012, and became an associate professor in 2013. After obtaining his PhD on “Study of folding, confinement and interface effects in GaAs/AlAs superlattices and quantum wells by Raman spectroscopy”, Dr. Sayari combined teaching activities with experimental research in the field of solid-state physics at Al Manar University. He is a member of the Raman Group, Faculty of Science Tunis.

His research interest is vibrational, optical and structural properties, especially for III/V and II/VI semiconductors heterostructures.

In 2006, he joined the King Abdulaziz University, Saudi Arabia, where he became interested in ZnO nanoparticles and their applications in nanotechnology.

Lassaad El Mir

Lassaad El Mir completed his PhD in 1995 at the College of Sciences in Tunis in collaboration with the University of Paris VI in the field of electronic transport in semiconductors and his “HDR” (accreditation to supervise research) in the field of nanotechnology in 2007 from the College of Sciences in Sfax, Tunisia. From 1992 to 2010 he spent several periods of research at the University of Paris VI and in the Institute of NanoSciences in Paris (France). Since 2012 he has been a full professor of physics.

From 1997 to 2002 he was head of the Physics Department of the College of Sciences in Gables University. His main research interest covers the synthesis and characterization of nanoparticles, thin films and nanocomposites for a variety of applications such as solar cells, transparent electrodes, advanced catalyst supports, water treatment, energy storage and gas sensors. Since 2012 he has been a guest professor at the College of Sciences at Al-Imam Muhammad Ibn Saud Islamic University, Saudi Arabia.