Structural and morphological characterizations of pure and Ce-doped ZnO nanorods hydrothermally synthesized with different caustic bases

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This investigation concerns the synthesis as well as structural and morphological characterizations of pure and Ce-doped ZnO nanorods. The samples were synthesized by simple low-temperature hydrothermal process using respectively NaOH and KOH as caustic bases. The as-synthesized nanorods were characterized in terms of their morphological, structural, compositional and vibrational properties. The sizes of the rods were found to be 1.5 μm to 2 μm in length and 250 nm to 300 nm in diameter. The presence of Ce ions in ZnO (NaOH) favored the agglomeration of the rods to form flower-like nanostructures. EDAX measurements showed Zn rich materials with high oxygen vacancy concentration. XRD results indicated that the synthesized ZnO nanorods possess a pure wurtzite structure with good crystallinity. It has also been found that Ce doping deteriorates the crystalline quality of ZnO (NaOH) and improves that of ZnO (KOH). The insignificant intensities observed in FT-IR signals confirm that the synthesized nanorods are of high purity. The Raman spectroscopy studies showed that Ce ions shift the vibrational modes towards lower frequencies. The peaks related to E_2 (high) mode in ZnO (KOH) are relatively intense compared to those of ZnO (NaOH). The peaks are found to be shifted and asymmetrically broadened due to anharmonic effects originating from quantum-phonon-effect confinement.

Keywords: ZnO nanorods; hydrothermal synthesis; caustic base; cerium doping; structure; morphology

1. Introduction

As an important low-cost basic II-VI semiconductor material, zinc oxide (ZnO) nanostructures have attracted a great deal of interest for their unique characteristics such as n-type native conduction, wide and direct band gap energy (3.3 eV) at room temperature, large exciton binding energy (60 meV), excellent thermal stability, high electron mobility and specific electrical and optical properties [1]. ZnO can be used for several technological applications in electronics, optoelectronics, gas sensors, photonic devices and photocatalyst [2–6]. ZnO nanostructures have been synthesized by various methods. Some of them require complex processes and sophisticated equipment, such as magnetron sputter deposition (MSD), chemical vapor deposition (CVD) and pulsed laser deposition

(PLD) [7–9]. Others, which are based on chemical approaches, such as ultrasonic spray pyrolysis (USP), sol-gel, wet chemical etching (WCE) and hydrothermal methods [10–17], can be operated at low temperature and pressure, are economical, simple in synthesis and provide high quality products. A variety of morphologies including prismatic forms, nanorods, nanotorus, nanoflowers, nanowires, dumbbell-like, whiskers and spheres have been synthesized [3, 5, 7, 9, 13–18]. Due to their large surface area, ZnO nanorods have been the most frequently synthesized nanostructures. Doping is considered as an effective way to improve ZnO properties for various applications. Cerium is one of the rare earth metal elements that has a strong effect on structural characteristics of ZnO nanostructures [6, 13, 16–19]. Ce-doped ZnO nanorods have been synthesized by various methods: wet-chemical method [10], hydrothermal route [14, 16], CVD [7] and electrochemical

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process [18]. Hydrothermal method is preferred due to its better homogeneity, less energy consumption, inexpensive equipment, environment friendly (no solvents) and the possibility of incorporating extrinsic atoms into the metal oxides.

In this paper, we report the hydrothermal route synthesis of pure and Ce-doped ZnO nanorods using two different caustic bases (KOH and NaOH). The main objective is to study the influence of solutes on structural and morphological properties of pure ZnO nanorods and ZnO nanorods doped with rare earth element ions. The effect of Ce ions on the structural characteristics of ZnO nanorods elaborated in different basic media is also investigated.

2. Experimental

2.1. Preparation methods and conditions

Undoped ZnO powders were prepared by hydrothermal approach using zinc acetate dihydrate ($(\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})$, 99 %, Aldrich) as Zn^{2+} ions source, distilled water as a solvent, sodium hydroxide (NaOH) and potassium hydroxide (KOH) as caustic bases. In this procedure, two aqueous solutions of zinc acetate dihydrate (0.2 M) and sodium hydroxide (3 M) were mixed and stirred at ambient temperature until the appearance of a whitish precipitate in the solution. Then, the solution was heated up to 95 °C in a water bath for 1 h. The final alkaline solution, having pH equal to 12.82, was filtered and the precipitate was recovered. The recovered precipitate was repeatedly washed with distilled water and dried in ambient air for a few hours. ZnO powder was formed according to the following chemical reactions:

The sodium salt $\text{Na}(\text{CH}_3\text{COO})$ was removed by the water washing. Finally, the product was heat

treated in a furnace in air at 600 °C for 2 h to obtain ZnO powder. In a similar process ZnO powder was elaborated using the caustic base KOH instead of NaOH with the same molarity (3 M). In this case, the pH of the mixed solution was 13.26. Ce-doped ZnO powders were obtained in a similar manner as that described above by adding to the precursor solution an amount of cerium nitrate $[(\text{CeNO}_3, 6\text{H}_2\text{O})]$, Aldrich corresponding to atomic ratio $[\text{Ce}]/[\text{Zn}] = 0.01$ (1 %). All the powders were prepared in an identical way and under the same conditions.

2.2. Characterization techniques

All synthesized powders were characterized at ambient temperature. The crystalline structure of the samples was investigated by X-ray diffraction (XRD) with a PanAlytical diffractometer, operating at 40 kV and 30 mA using $\text{CuK}\alpha$ radiation (wavelength $\lambda = 1.54 \text{ \AA}$). Infrared spectra (FT-IR) were recorded with a Shimadzu IRAffinity-1 spectrometer. Scanning electron microscope (SEM) images were obtained by a Quanta 2000 microscope with energy dispersive X-ray (EDAX) spectroscopy. EDAX was used to identify the chemical composition of the products. The structural composition of pure and Ce-doped ZnO powders was studied using Horiba Jobin Yvon HR 800UV μ -Raman spectrometer.

3. Results and discussion

Fig. 1 and Fig. 2 show the low-magnification SEM images of pure and Ce-doped ZnO powders synthesized with NaOH and KOH, respectively. As can be seen from the micrographs, the synthesized powders have nanorod morphology. In undoped ZnO samples, the growth of nanorods is characterized with high density and a random distribution. In Ce-doped ZnO powders synthesized with NaOH (Fig. 1), the nanorods are gathered to form a flower-like nanostructures. It is shown that the distribution of these flowers-like structures is uniform. Moreover, the ZnO nanorods are randomly grown and they originate from the center of the flower. It seems that the central part of the flower-shaped structures provides a root for the growth

of these ZnO nanorods. In Ce-doped ZnO powder, prepared with KOH, the rods are still randomly distributed and no remarkable agglomeration has been observed. EDAX analysis was done to assess the elemental composition of the synthesized pure and Ce-doped nanorods; the results are mentioned in Fig. 1 and Fig. 2. EDAX spectra show numerous well-defined peaks related only to Zn, O and Ce atoms. This result indicates that the presently prepared nanorods are solely formed of Zn, O and Ce and no peaks related to other impurities have been detected in the EDAX spectra. Thus, these indications confirm that the synthesized nanorods are Ce-doped ZnO. From the compositional values, it can be noted that the rods are Zn rich. According to published data [20, 21], oxygen vacancies (V_O) should predominate in Zn-rich crystals, since their formation energy is lower than that of zinc interstitials (Zn_i). It is also observed that the total oxygen contribution drops from 29.84 at.% (undoped ZnO) to 15.99 at.% (ZnO (NaOH):Ce) and 22.96 at.% (ZnO(KOH):Ce). This result could be due to the creation of Ce–O clusters which is more favorable in NaOH medium. These clusters may play an important role in the agglomeration of ZnO (NaOH):Ce nanorods as described above. The calculated atomic ratio $[Ce]/[Zn]$ was found to be 3.7 % in Ce-doped ZnO synthesized with NaOH and 1.17 % in the nanorods prepared with KOH. This result indicates that cerium ions are more homogeneously distributed in KOH solution than in that of NaOH. As shown in the inset in Fig. 2, the enlarged SEM image shows that a typical length of the nanorods is in the range of 1.5 μm to 2 μm , while the diameters are in the range of 250 nm to 300 nm. The diameters of most of the synthesized rods are almost the same throughout their length with a slight reduction in the diameters at their tips. The inset also shows that the nanorods surfaces are very clean without any particle impurities. The droplets observed at the ends of the nanorods indicate that the obtained nanorods have grown following VSL mechanism [22, 23].

Fig. 3 shows XRD patterns of pure and Ce-doped ZnO nanorods synthesized by hydrothermal route using NaOH and KOH. All observed peaks between 30° and 72° ((1 0 0), (0 0 2), (1 0 1),

Fig. 1. SEM micrographs and EDAX spectra of undoped and Ce-doped ZnO nanorods synthesized with NaOH.

(1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 0), (1 1 2) and (2 1 0)) are those of the hexagonal wurtzite structure of ZnO (JCPDS Card No. 79-2205, $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$). The intense XRD peaks indicate that the ZnO nanorods are polycrystalline with a high degree of crystallinity. No peaks related to cerium or cerium based compounds crystalline forms are detected in XRD patterns. This indicates that the powders are pure and exhibit a single-crystal structure and confirms that the Ce ions uniformly substitute Zn sites in the ZnO lattice. The high peaks intensity, observed in pure ZnO (NaOH) spectrum compared to that of ZnO (KOH), are due to the pH and the high solubility of KOH in water compared to NaOH. Danishvar et al. [24] reported that dissolution of ZnO occurs in the presence of high OH^- concentration (high pH). The effect of pH on ZnO properties was widely investigated [10, 25, 26]; it was reported that the XRD peaks intensity increases with the increase of pH values from pH 9 to pH 14. The most crystallized structure of ZnO powder was obtained at pH 9 and the morphology of the products strongly depended on pH value [26].

The most pronounced XRD peaks ((1 0 0), (0 0 2) and (1 0 1)) shown in Fig. 4, put into evidence the incorporation of cerium ions into zinc ions sites or interstitial sites in ZnO lattice. As can

Fig. 2. SEM micrographs and EDAX spectra of undoped and Ce-doped ZnO nanorods synthesized with KOH.

be seen, the position of Ce-doped ZnO peaks is shifted toward lower angles compared to those of undoped ones, indicating an increase in the cell parameters after the introduction of Ce ions into ZnO lattice. The dopant does not alter the crystal structure but only introduces a slight variation in the lattice parameters, which is also reflected by the shift in the peak position. This shift is due to Zn^{2+} ions substitution by Ce^{3+} ions. The difference in ionic radii of Ce^{3+} (0.114 nm) and Zn^{2+} (0.074 nm) leads to variation in the lattice parameters. The cell parameters: $a = b = 1/(\sqrt{3} \sin \theta)$ and $c = 1/\sin \theta$ of pure and Ce-doped ZnO were calculated from the positions of the (1 0 0) and (0 0 2) peaks, respectively. The volume of the ZnO hexagonal cell V and the Zn–O or Ce–O bond length L were calculated using reported formulas [19]. The degree of crystallinity X_c is given by [27]:

$$X_c = \left(\frac{0.24}{\beta_{002}} \right)^3 \quad (4)$$

where β_{002} is the full width at half maximum (in degrees) of (0 0 2) Miller plane. The cell parameters a and c , c/a ratio, cell volume V , Zn–O bond length (L) and X_c , calculated for all samples, are shown in Table 1. Based on Table 1 data, we note that the cell parameters of pure ZnO synthesized

with KOH are lower than those of a standard ZnO powder (JCPDS Card No. 79-2205), while those of pure ZnO synthesized with NaOH are found to be higher. The introduction of cerium atoms into ZnO leads to an increase in the lattice parameters, the cell volume and the Zn–O length. The degree of crystallinity in pure ZnO (NaOH) is higher than that of pure ZnO (KOH). After the introduction of cerium ions into ZnO lattice, the crystalline quality of ZnO (NaOH) deteriorates and that of ZnO (KOH) improves (Table 1 and the inset of Fig. 4). This result indicates that Ce ions occupy only Zn ions sites in ZnO (KOH), but Zn ions sites and interstitial sites in ZnO (NaOH) due to the high concentration of cerium ions observed in ZnO synthesized with NaOH (EDAX results). The X-ray diffraction analysis of these powders gives the ratio of crystal lattice parameters $c/a \cong 1.60$, which is also characteristic of the ZnO hexagonal crystal lattice.

Fig. 3. XRD patterns of pure and Ce-doped ZnO nanorods synthesized with NaOH and KOH.

To confirm the chemical composition, the as-synthesized pure and Ce-doped ZnO nanorods were characterized by FT-IR spectroscopy at room temperature. FT-IR spectra of all samples are shown in Fig. 5. Various low intensity signals at 507 cm^{-1} , 881 cm^{-1} , 1019 cm^{-1} , 1436 cm^{-1} , 1627 cm^{-1} , 2373 cm^{-1} , 2940 cm^{-1} and 3444 cm^{-1} are observed in all the spectra. The very strong peak appearing at 507 cm^{-1} could be attributed to the

Table 1. Cell parameters a and c , c/a ratio, cell volume V , Zn–O bond length (L) and the degree of crystallinity X_c of the samples.

Sample	a [nm]	c [nm]	c/a	X_c	V [$\text{\AA}^3$]	L [nm]
Pure ZnO (NaOH)	0.3251	0.5208	1.6019	1.96	47.667	0.19783
Ce-doped ZnO (NaOH)	0.3255	0.5214	1.6018	1.45	47.839	0.19806
Pure ZnO (KOH)	0.3248	0.5204	1.6022	1.26	47.543	0.19763
Ce-doped ZnO (KOH)	0.3256	0.5215	1.6016	2.29	47.878	0.19806
JCPDS Card No. 79-2205	0.3250	0.5207	1.6020	/	47.629	0.19776

Fig. 4. XRD patterns of the most pronounced peaks of pure and Ce-doped ZnO nanorods synthesized with NaOH and KOH (inset: high magnification of (1 0 1) peak).

metal oxygen (Zn–O) bonds, confirming the formation of ZnO. The signal at 3444 cm^{-1} is due to the stretching mode of the O–H group which reveals the existence of a small amount of water absorbed by the ZnO nanorods. The signal at 1627 cm^{-1} corresponds to O–H bending vibration, while that at 2940 cm^{-1} shows the C–H stretching and that at 2373 cm^{-1} represents the stretching vibration of CO_2 [28]. The very small signal at around 881 cm^{-1} is caused by C–O bond stretching [29]. The small band at 1019 cm^{-1} indicates the stretching vibration of (NH) –C–O group, and that located at 1435 cm^{-1} is due to aromatic –CH stretching vibrations [30]. The low intensities of the observed signals confirm that the synthesized nanorods are of high purity. The Zn–O vibration band observed in pure ZnO at 507 cm^{-1} is shifted

to 510 cm^{-1} in Ce-doped ZnO nanorods. The decrease in the band intensity and the occurrence of a shoulder around 700 cm^{-1} in the doped samples spectra is probably due to the presence of cerium ions. It has been reported that the FT-IR spectrum of ceria exhibits strong broad band below 700 cm^{-1} which is due to $\delta(\text{Ce–O–C})$ mode [31]. It should be noted that all vibration bands detected in the FT-IR spectra, related to the carbonic bonds are very low, indicating the presence of very small quantity of C atoms originated from the atmosphere.

Fig. 5. FT-IR spectra of pure and Ce-doped ZnO nanorods synthesized with NaOH and KOH.

The micro-Raman spectroscopy has been used to complete the structural characterization of the prepared samples. The micro-Raman spectra of pure and Ce-doped ZnO nanorods, synthesized hydrothermally in NaOH and KOH caustic bases, are illustrated in Fig. 6. All the spectra were recorded at room temperature using a 785 nm excitation wavelength. It is well known that ZnO wurtzite structure

possesses 12 phonon active modes: three acoustic and nine optical modes [22]. As shown in Fig. 6, in the pure ZnO spectra, there are two more intense Raman peaks at 419 cm^{-1} and 438 cm^{-1} and five low intense peaks at 267 cm^{-1} , 335 cm^{-1} , 378 cm^{-1} , 405 cm^{-1} and 534 cm^{-1} . The sharp and strong peak at 438 cm^{-1} is assigned to E_2 (high) mode of the ZnO wurtzite structure. This vibrational mode indicates high crystallinity of wurtzite ZnO. This mode is typical of $P6_3mc$ symmetry and originates from the oxygen vibration in ZnO [19, 32]. The intense peak at 419 cm^{-1} is assigned to E_1 (TO) modes of ZnO nanorods, which is due to the presence of oxygen vacancies and/or the interstitials zinc or their complexes [33]. This peak was also observed in big ZnO crystals [34]. This result confirms the EDAX measurements of the synthesized ZnO nanorods. The low intensity band observed at 331 cm^{-1} is attributed to the second-order Raman spectrum arising from zone-boundary phonons (E_2 (high) – E_2 (low)) of hexagonal ZnO [35]. The peak of ZnO nanorods observed at 534 cm^{-1} , which is related to multi-phonon processes, can be assigned to the second order Raman spectrum arising from zone-boundary phonons (E_2 (low) + E_2 (high)) due to combination of first order modes. This peak was observed in ZnO nanorod at 542 cm^{-1} [33]. The observed phonon peak shift in Raman spectra may be attributed to phonon localization by defects such as oxygen deficiency, zinc excess and surface impurities [33, 36]. The peak located at 378 cm^{-1} can be assigned to A_1 (TO) vibration modes of wurtzite ZnO [37]. The peak around 405 cm^{-1} is assigned to A_1 (TO) phonon oxygen-dominated polar mode in which Zn and O atoms move parallel to the c axis in the ZnO hexagonal structure [38]. The peak at 267 cm^{-1} is assigned to laser plasma lines [33]. In Ce-doped ZnO nanorods micro-Raman spectra, an additional less intense peak is observed at around 461 cm^{-1} . This signal originates from the Raman active mode, characteristic of CeO_2 fluorite structured materials with F_{2g} symmetry, and corresponds to the ceria $\text{Ce}-\text{O}_8$ vibrational unit [37, 39, 40].

As can be seen from Fig. 6, the Raman peaks in Ce-doped ZnO slightly shift to lower

Fig. 6. Micro-Raman shifts of pure and Ce-doped ZnO nanorods synthesized with NaOH and KOH (inset: high magnification of E_1 (TO) and E_2 (high) modes).

frequencies compared to those of undoped ZnO, suggesting the existence of strain variations in Ce-doped ZnO nanorods. Generally, the red shift of E_2 (high) and A_1 (TO) modes towards lower frequencies may be attributed to optical phonon confinement [41]. Thus, we can suggest that Ce ions favor the amplification of optical phonon confinement when caustic bases are used in the hydrothermal synthesis route. The nanostructures length is much larger than the diameter, which means that the confinement effect mainly occurs along the diameter direction. Apart from Ce-doped ZnO (NaOH) spectrum, the 419 cm^{-1} peak intensity (E_1 (TO) mode of ZnO nanorods) remains almost unchanged in all the spectra. This indicates that the morphologies of the synthesized materials are all of nanorod type, which is confirmed by the SEM micrographs. The increase in the intensity of this peak in Ce-doped ZnO (NaOH) indicates the change in the morphology of the prepared nanostructures (inset in Fig. 6) and is confirmed the SEM analysis. In contrast, the intensity of E_2 (high) mode (438 cm^{-1}) strongly changes. In ZnO (KOH) the intensity of E_2 (high) mode peak is higher than that of E_1 (TO) mode, whereas an inverse behavior is observed in ZnO (NaOH). The peaks related to E_2 (high) mode in ZnO (KOH) are relatively intense compared to those of ZnO (NaOH). This may be explained by

the differences in crystalline quality of the different nanorods. It can also be seen that the E_2 (high) modes are not only shifted, but also broadened and have an asymmetric line shape. Samuel *et al.* [33] calculated the broadening and the shift of the Raman peaks of ZnO nanorods and nanotubes based on the confinement model. This study clearly showed that the shift, broadening and asymmetric broadening of Raman peaks were caused by the anharmonic effects originating from quantum phonon effect confinement.

4. Conclusion

In this paper, successful synthesis of undoped and Ce-doped ZnO nanorods with different solutes NaOH and KOH by simple hydrothermal method was reported. Structural and morphological properties of the samples were investigated. All synthesized materials have nanorods morphology with 1.5 μm to 2 μm in length and 250 nm to 300 nm in diameter. Ce-doped ZnO (NaOH) nanorods gather to form a flower-like nanostructures with uniform distribution. EDAX measurements show that the rods are Zn rich with high concentration of oxygen vacancies. XRD analysis put into evidence the hexagonal wurtzite phase with very good crystallinity of prepared samples. The introduction of cerium ions into ZnO lattice deteriorates the crystalline quality of ZnO (NaOH) and improves that of ZnO (KOH). The insignificant intensities observed in FT-IR signals confirm that the synthesized nanorods are of high purity. The micro-Raman measurements show that the peaks related to E_2 (high) mode in ZnO (KOH) are relatively intense compared to those of ZnO (NaOH). Raman peaks of Ce-doped ZnO nanorods shift towards low frequencies after the introduction of Ce ions into ZnO lattice. The Raman spectroscopy studies clearly show a shift, broadening and asymmetric broadening of Raman vibrational modes due to the anharmonic effects originating from quantum phonon effect confinement.

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