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Effect of cerium on structural and optical properties of ZnO aerogel synthesized in supercritical methanol

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Pure ZnO and Ce-doped (5 at.%) ZnO aerogels were prepared by dissociation of dihydrate zinc acetate and cerium nitrate in methanol, followed by drying in supercritical conditions of the solvent. The concentration of zinc acetate solution and the atomic ratio Ce/Zn were fixed at 0.2 mol/L and 0.05 mol/L, respectively. XRD results showed a hexagonal wurtzite structure of ZnO aerogel crystallites and a formation of a separate second phase of ceria cubic phase with fluorite structure and 7.4 nm in size. The introduction of cerium in the solution had a negative effect on the aerogel crystalline quality. The crystallites size was found to be 16 nm in pure ZnO and 27 nm in Ce-doped ZnO aerogels. The grains of Ce-doped ZnO aerogel had torus shaped morphology with hollow centers, but those of pure ZnO were flattened semispheres. The calculated values of different structural parameters showed that cerium ions introduced into the ZnO lattice occupied interstitial sites and Zn ions substituted Ce ones in ceria lattice during the formation process. FT-IR and UV-Vis absorption spectra have not revealed any particularities due to the presence of cerium atoms in ZnO, indicating that Ce (5 at.%) doping of ZnO crystallites synthesized in supercritical methanol did not strongly affect the optical gap of the semiconductor. Micro-Raman studies confirmed the formation of cubic fluorite structure ceria in ZnO aerogel and showed that Raman active modes of ZnO are amplified with the presence of ceria.

Keywords: *ZnO aerogel; supercritical methanol; cerium; XRD; FT-IR*

1. Introduction

Metal oxides nanoparticles have received considerable importance in many technological applications. The search for new methods and processes to synthesize functional nanometric materials for specific applications in different areas, such as catalysis, paint and cosmetics is one of many laboratories priorities. The physical properties of nanomaterials are highly sought and used in pigments, plastics and lubricants. Zinc oxide (ZnO) is a semiconducting material characterized by a wide gap (3.37 eV) and a large exciton binding energy (60 meV) at room temperature. The importance of this semiconductor lies in its potential applications in gas detection [1], varistors [2] and luminescent devices [3]. A considerable number of methods have been developed to improve the properties of ZnO nanopowders. Among these processes, the sol-gel process synthesis in a supercritical fluid medium is the most advantageous. It is simple, less expensive and allows the production of highly pure and ultrafine nanoparticles with a high degree of transparency [5–7]. Doping ZnO particles is generally carried out with transition metals or rare earths atoms to exalt the physical properties of the material. Among these, doping rare earth elements, cerium is the most interesting one since the energy transfer from ZnO to the cerium ions can significantly alter its optical properties, in particular the UV emission [8]. In our previous work [9], we have synthesized ZnO aerogel particles in supercritical methanol with Ce/Zn ratio equal to 0.02 and observed that no composite cerium oxides was detected in the powders. The c parameter of Ce doped ZnO samples was found to be greater than in the pure ZnO. Panda et al. [10] have synthesized ZnO nanopowders doped with cerium ions (1.2 at.% and 1.5 at.%) through soft solution route using ultrasound and found that cerium ions substitute Zn sites in ZnO structure.

In this work, pure and highly cerium doped ZnO (5 at.%) aerogels were elaborated by sol-gel process associated with supercritical drying in

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methanol. The effects of cerium ions on the structural, morphological and optical properties of ZnO aerogels were investigated.

2. Experimental

Zinc oxide aerogel powder was obtained by dissociation of zinc acetate dihydrate ($(Zn(COOCH_3)_2{\cdot}2H_2O$):95 %) in methanol ($CH_3OH$) under continuous magnetic stirring for 10 min at room temperature. For Ce-doped ZnO (5 %) aerogel, an amount of cerium nitrate ($CeNO_3{\cdot}6H_2O$), corresponding to the atomic ratio Ce/Zn = 0.05, was added to the solution. The prepared solutions were placed in an autoclave and subjected to drying in supercritical conditions of methanol (Tc = 240 °C, Pc = 7.9×10^6 Pa). Once the supercritical conditions were reached, the solvent was removed and the autoclave was allowed to cool spontaneously to room temperature. The obtained powders were characterized without any chemical or heating treatments.

The crystalline structure of the as-prepared aerogels was studied using a PANalytical diffractometer where the X-rays are produced from a radiation source CuKα (λ= 1.54 Å), with an acceleration voltage of 40 kV and a current of 30 mA. Infrared spectra (FT-IR) were recorded with a Shimadzu's IRAffinity-1 spectrometer by KBr pellet technique. SEM images were obtained with a JSM-840A JEOL microscope type. UV spectra were recorded at room temperature with a spectrometer type Safas UVmc^2. The structural composition of aerogels was studied using the HORIBA Jobin-Yvon Raman spectrometer.

3. Results and discussion

Fig. 1 shows the XRD spectra of the as-prepared ZnO and Ce-doped ZnO aerogel powders. All the observed peaks are close to those of the polycrystalline ZnO hexagonal wurtzite structure. In the doped aerogel, a peak located at 2θ = 28.6°, related to the formation of a second phase caused by cerium atoms is observed. This new peak position is close to the most intense plane (1 1 1) of CeO_2 cubic phase with fluorite structure (JCPDS Card No. 34-394). CeO_2 is a stable form of bulk cerium oxide. The ceria parameter lattice and particle size of nanoceria crystallites are found to be 0.5394 nm and 7.4 nm, respectively. The introduction of cerium atoms in ZnO has significantly decreased the intensity of the diffraction peaks. This shows that doping with a content of 5 % cerium atoms deteriorates the crystalline quality of ZnO aerogel as confirmed by the degree of crystallinity values (Table 1). The value of nanoceria structure parameter is found to be lower than that of the standard JCPDS (Card No. 898436) pattern of CeO_2 (a = 0.5411 nm) [11]. As the ionic radius of Ce^{3+} (0.114 nm) is larger than that of Zn^{2+} (0.072 nm), we can suggest that Zn ions substitute the Ce ones in nanoceria crystallites during the elaboration process [12].

The XRD spectra of the most pronounced peaks of Fig. 1, from which the principal structural properties of ZnO aerogels were determined, are shown in Fig. 2.

The lattice parameters a and c of ZnO were calculated from the positions of the (1 0 0) and (0 0 2) peaks, respectively using the formulas [13]:

$$a = \lambda / (\sqrt{3} \sin\theta) \tag{1}$$

and

$$c = \lambda / \sin\theta \tag{2}$$

The average crystallite size was calculated using the Scherrer formula:

$$D = 0.89\lambda / (\beta \cos\theta) \tag{3}$$

where λ is the X-rays wavelength (λ= 1.54 Å), θ is the diffraction angle and β the full width at the half-maximum of the XRD line (in radians).

The volume of the ZnO hexagonal cell was calculated using the formula [9]:

$$V = 0.866 a^2 c \tag{4}$$

The Zn–O bond length was calculated from the formula [13]:

$$L = \sqrt{a^2/3 + (0.5 - u)^2 c^2} \tag{5}$$

In wurtzite structure, the parameter u is given by [13]:

$$u = a^2/3c^2 + 0.25 \tag{6}$$

The degree of crystallinity Xc was calculated using the following equation [14]:

$$X_C = \left(\frac{0.24}{\beta_{002}}\right)^2 \tag{7}$$

where β_{002} is the full width at half maximum (in degrees) of (0 0 2) Miller's plane.

All the calculated parameters are summarized in Table 1. Based on these data, we can note that the introduction of cerium atoms into ZnO increases the grains size and slightly decreases the lattice parameters. The result indicates that cerium atoms promote the little crystallites agglomeration and, on the other hand, the presence of ceria crystallites. For low Ce doping ZnO (2 % and less), Ce^{3+} ions occupy Zn sites and lead to an increase in ZnO cell parameters [3, 9]. In our work, with high Ce doping level (5 at.%), the introduced cerium atoms occupy interstitial sites in ZnO lattice. Consequently, the volume cell and the Zn–O bond length slightly decrease. The decrease in ZnO structural parameters is generally caused by the compression stress exerted by the solvent on ZnO crystallites and, in our case, this phenomenon is amplified by the presence of cerium ions during the synthesis process. The high pressure exerted on ZnO cells during supercritical drying (7.9×10^6 Pa) can also contribute to the decreasing of the lattice parameters. On the other hand, the same procedure has been followed to synthesize Ce (2 at.%) doped ZnO aerogel and, as a result, cerium ions have been found to substitute Zn sites in ZnO lattice [8, 9]. Since the Zn^{2+} ionic radius is 0.072 nm, it is more likely that Zn^{2+} will be replaced by Ce^{3+} (0.114 nm) or Ce^{4+} (0.101 nm) ions thus dilating the lattice parameters in ZnO. In our synthesized aerogels opposite results have been found. This can be explained by the fact that the introduced Ce atoms can occupy interstitial sites in ZnO lattice and simultaneously form the nanostructured ceria during the synthesis process. Then, it can be concluded that Ce ions would uniformly substitute into the Zn vacancies or interstitial sites in the ZnO lattice.

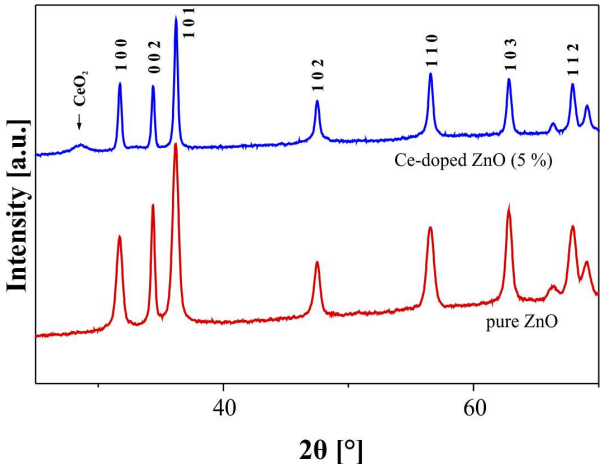


Fig. 1. XRD spectra ZnO and Ce-doped ZnO (5 at.%).

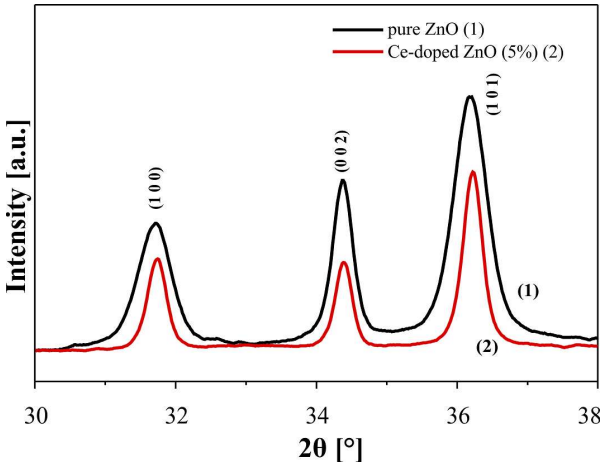
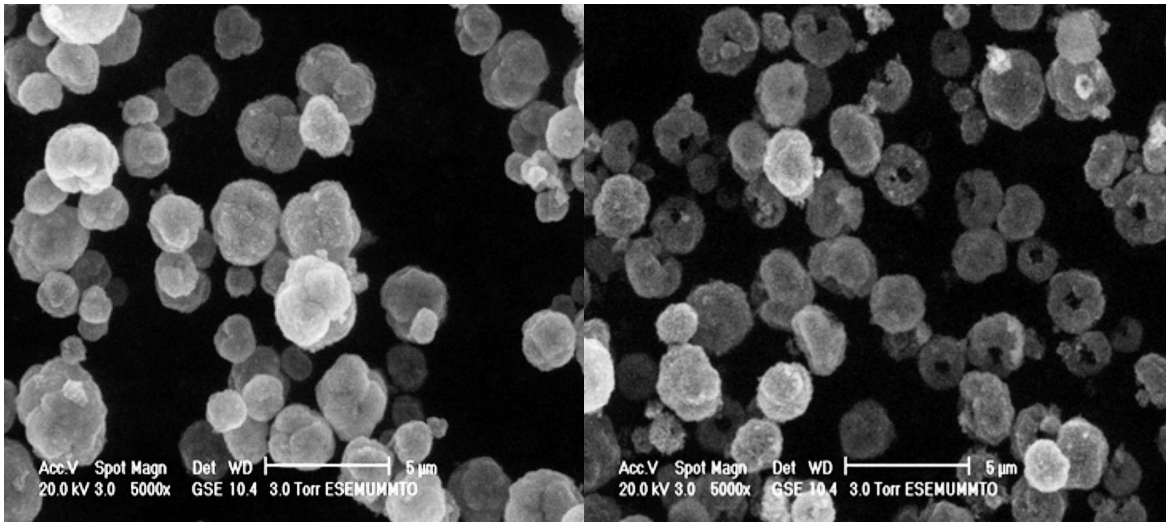


Fig. 2. XRD spectra of the strongest peaks of aerogels ZnO and ZnO: Ce (5 at.%).

Clinton [15] demonstrated that it is always possible to have point defects in CeO_2 caused by oxygen vacancies and these Ce^{3+} ions co-exist as defect states in the band gap and it is well established that in the case of rare earth oxides like ceria, having fluorite structure, Ce^{3+} ions occupy interstitial spaces as Frenkel defects [16]. George et al. [17] have reported that a decrease in lattice parameters is due to replacement of Zn ions with Ce ions while the increase in lattice constant is due to interstitial position of Ce ions in ZnO lattice.

Table 1. Lattice parameters a and c, c/a, D, V, X_C and L for different aerogels.

Aerogel	D [nm]	a [Å]	c [Å]	c/a	V [Å^3]	L [Å]	X_C
pure ZnO	16	3.2551	5.2113	1.600	47.8	1.9806	0.9531
Ce-doped ZnO (5%)	28	3.2519	5.2096	1.602	47.7	1.9791	0.5811



(a) (b)

Fig. 3. SEM images of pure ZnO (a) and Ce-doped ZnO (b) aerogels.

SEM images of pure and Ce-doped (5 at.%) ZnO aerogels are shown in Fig. 3. The pure ZnO aerogel grains have quasi-spherical or full-center torus shaped morphology. However, the doped ZnO aerogels have toroidal shape with hollow center morphology. The images indicate that cerium atoms have considerable influence on the shape of the ZnO grains. This result indicates that the presence of ceria phase with fluorite structure modifies the manner of the agglomeration of ZnO crystallites.

Recorded FT-IR spectra of pure ZnO and Ce-doped ZnO aerogels are shown in Fig. 4. The same bands are observed in both spectra. The only difference of these bands is in their intensities. No bond related to cerium or cerium-based compounds has been observed in the FT-IR curves. In addition, we remark a little shift of Zn–O band towards low wavenumbers after the introduction of Ce atoms into ZnO lattice.

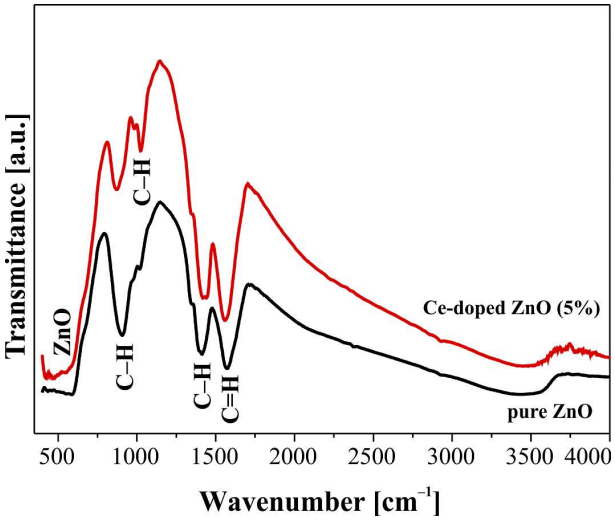


Fig. 4. FT-IR spectra of pure and Ce-doped (5 at.%) ZnO aerogels.

The normalized optical absorption spectra of pure and Ce-doped ZnO aerogels are illustrated

in Fig. 5. The ZnO crystallites begin to absorb at 350 nm. The absorption band intensity is more intense in the presence of cerium atoms. This amplification of the absorption intensity is probably due to the absorption of ceria (Eg = 4 eV) in the synthesized aerogel. The optical gaps of the samples calculated by the second derivative method are identical. The optical band gap is about 3.48 eV in both samples (inset in Fig. 5). As a result, it can be concluded that the introduction of cerium atoms in the aerogel does not strongly affect the optical gap of the ZnO crystallites.

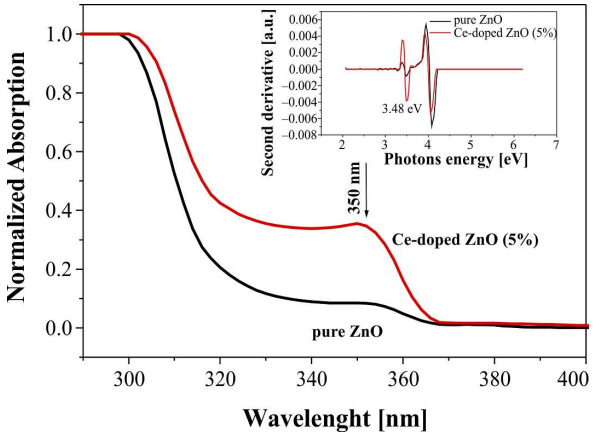


Fig. 5. Normalized absorption spectra of pure and Ce-doped (5 at.%) ZnO aerogels.

The micro Raman spectroscopy, which has been extensively used to discriminate different structures, has been employed to complete the structural characterization of Ce doped ZnO aerogel. The micro Raman spectra of the pure and Ce doped ZnO aerogels are shown in Fig. 6. The pure ZnO spectrum shows two Raman peaks at 99 cm^{-1} and 437 cm^{-1} ascribed respectively to the E_2 (low) and E_2 (high) phonon frequencies. These Raman active modes are attributed to the nonpolar E_2 vibrational modes due to the vibration of the zinc sublattice in ZnO (E_2 low) and oxygen vibration (E_2 high). These two bands are also observed in Ce-doped ZnO aerogel spectrum but with higher intensity [18]. The very low intensity band observed at 331 cm^{-1} is attributed to the second-order Raman spectrum arising from zone-boundary phonons of hexagonal ZnO [19]. In addition, we also observed a broader and relatively less intense peak at 462 cm^{-1}. This band, observed only in Ce doped ZnO, corresponds to the F2g Raman active mode of fluorite cubic CeO_2 [20, 21].

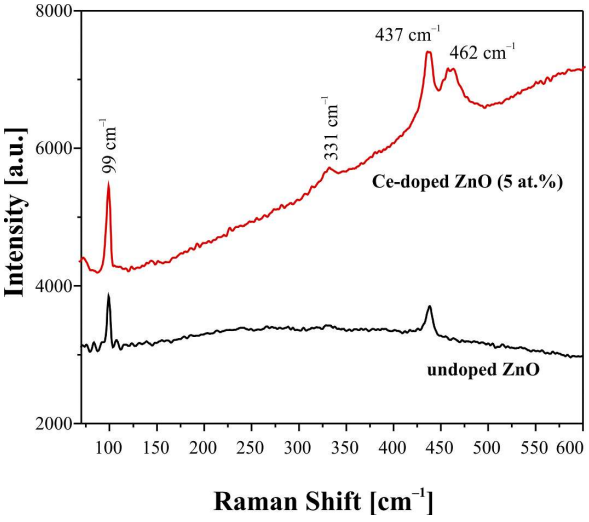


Fig. 6. Raman shift of pure and Ce-doped (5 at.%) ZnO aerogels.

4. Conclusions

Pure ZnO and Ce-doped (5 at.%) ZnO aerogels have been synthesized by sol-gel process in supercritical methanol. XRD spectra showed hexagonal wurtzite structure of ZnO crystallites and formation of ceria as a second phase. After the introduction of Ce ions into ZnO aerogel, a degradation of the crystalline quality with an increase in the crystallites size and a decrease in the lattice parameters values were observed. The size of the formed ceria crystallites was found to be around 7 nm with a lattice parameter lower than the standard one. This decrease is due the occupation of Ce sites by Zn ions in the CeO_2 lattice. On the other hand, Ce occupies interstitial sites in ZnO lattice. SEM images showed that the Ce-doped ZnO grains have torus morphology with hollow center, while the grains of pure ZnO are flattened semispheres. FT-IR spectra confirmed the presence of the absorption band of Zn–O bond and showed no bands related to cerium atoms. The micro-Raman shift confirms the formation of nanoceria in the ZnO aerogel. The optical absorption curves showed that the introduction

of cerium atoms in the aerogel did not strongly affect the optical gap of the ZnO crystallites.

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