Synthesis of Al-doping ZnO nanoparticles via mechanochemical method and investigation of their structural and optical properties

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In this study, pure and Al-doped ZnO nanoparticles were successfully synthesized by the mechanochemical method. The effect of doping on structural and optical properties was studied. The structural investigations of products confirmed the hexagonal wurtzite structure for all products and also it was observed that doping caused a little change in lattice parameters. The results obtained by SEM revealed that the average particle size of products increases by doping and nanoparticles have almost spherical morphology. UV–visible absorption and PL spectra showed that the maximum ultraviolet absorption wavelength of products increases and the optical band gap shifts from 3.15 eV to 3.11 eV, with increasing the Al concentration.

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1. Introduction

In recent years, semiconductor nanostructures due to their unique properties and applications have attracted much attention. Among many kinds of the metal oxide nanostructures that have been developed, ZnO is a material which is of great interest for a variety of applications [1,2]. Zinc oxide exhibits hexagonal wurtzite structure and has a direct band gap semiconductor around 3.37 eV at 300 K and the large exciton binding energy of 60 meV [3,4]. As an II–VI semiconductor, the ZnO is widely used in the gas sensors [5], solar cells [6], and luminescent, electrical and chemical sensors [7]. Doping affects the crystal growth when it is performed during the nanoparticles formation process and also makes some changes in its optical and electrical properties [8,9]. In order to improve the properties of the n-type ZnO semiconductor, it can be doped with metals such as Al, Ga and In [10,11]. The ZnO has some defects which can either be native (oxygen vacancies, zinc interstitials) or incorporated ones (such as hydrogen atoms) that these defects could affect optical properties of the ZnO by creating a donor levels in its band gap [12]. Therefore, it is worthwhile to investigate the optical properties of Al-doped ZnO. Al-doped ZnO (AZO) nanostructures could be synthesized by various methods such as sol–gel [13], hydrothermal [14], arc plasma [15] and magnetron sputtering [16].

As far as we know, producing the AZO nanoparticles by the simple and economic mechanochemical method is reported for the first time in the present work. The structural and optical properties of the samples were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TG), UV–visible absorption spectroscopy (UV–vis) and photoluminescence (PL).

2. Experimental

The starting materials were ZnCl₂, Na₂CO₃, NaCl and Al(NO₃)₃·9H₂O with high purity that were purchased from Merck. The NaCl was used as a dilute additive to the starting powder. The stoichiometric mixture of the starting powder was milled with the planetary mill for 9 h at 250 rpm then powder was calcined in air at 600 °C for 30 min [17]. The reactions are described in the following formula:

\[(1 - x)\text{ZnCl}_2 + 8.6 \text{NaCl} + x\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} \rightarrow \text{Al}_x\text{Zn}_{1-x}\text{O}_3 + 10.6 \text{NaCl}

\]

\[\text{Al}_x\text{Zn}_{1-x}\text{O}_3 \rightarrow \text{Al}_x\text{Zn}_{1-x}\text{O} + \text{CO}_2(\text{g}) + \text{...}

The amount of x was equal to 0, 0.01, 0.03 and 0.09. The diameter of the balls was 10 mm and ratio of the balls to the powder mass was 10:1. In continue the samples were washed with deionize water for a few times. Finally, AlₓZn₁₋ₓO nanoparticles were obtained from drying at 80 °C of washed powders.

3. Results and discussions

Thermogravimetry: Thermogravimetry analysis was carried out to determine the crystalline conditions. The obtained powder of milling was heated from the room temperature to 1000 °C with a
rate of 10 °C/min in the air. Fig. 1(a) shows a combined plot of dfTG and TGA. Notably, the TGA data plots the weight loss of the nanoparticles which is found to take place till 550–600 °C and is due to the release of CO₂, H₂O and N₂ gases. Therefore, the crystallization of AZO nanoparticles occurred at temperatures over 600 °C.

### Structural properties: Fig. 1(b) shows the X-ray patterns of AlₓZn₁₋ₓO with x=0, 0.01, 0.03 and 0.09. A comparison with the standard card demonstrates that the peaks can be indexed to know the hexagonal wurtzite structure of ZnO with lattice constants of a=3.250 Å, c=5.207 Å (JCPDF card: 79-2205). On the other hand, the samples are quite pure and no impurities such as Al₂O₃ are observed. In addition, negligible changes of all diffraction peak positions and lattice parameters of ZnO in all AZO samples compared to that of pure ZnO suggest that Al³⁺ ions substitute the Zn²⁺ ions and incorporate into the lattice of ZnO, that these results agree with the work reported by [18]. The lattice parameters and crystallite size, measured using Xpowder software, are listed in the Table 1. The results reveal that the lattice parameters decrease with doping, but with increasing the Al concentration, these parameters increase. It can be assumed that the Al-doping results in a decrease of the lattice parameters due to the fact that the ionic radius of Al³⁺ is smaller than ionic radius of Zn²⁺, but increasing the Al concentration leads to increase in Coulomb repulsion forces and expansion of the lattice parameters. As we know the grain boundary (GB) is the interface between two grains or crystallites. By increasing the Al doping, the average crystallites size was reduced and specific GB area (S_GB), which it introduces as the ratio of GB area to volume, was increased. By approximately, S_GB=1.65/D formula [19], where D is the average crystallites size, was used to determine the specific GB area that is shown in Table 1. The SEM image of products is illustrated in Fig. 2. A careful perusal of this image reveals that, nanoparticles have almost spherical morphology and the morphology of the nanoparticles stay the same after doping. Also, the SEM images show an increase in the average particle size of products after doping that their particle size displays in Table 1. It seems that the increasing of S_GB leads to the increment of average particle size.

### Optical properties: Optical properties were investigated using UV–visible and PL spectra. Fig. 3(a) displays the UV–vis absorption spectra and the plot of (αE)² versus E for pure ZnO and Al₀₉Zn₀₉O nanoparticles. Optical Band gap of nanoparticles was measured using the following formula [18]:

\[
(\alpha E) = A(E-E_G)^{1/2}
\]

Where \( \alpha \) is an optical absorption coefficient, \( E \) is a photon energy, \( A \) is a constant coefficient and \( E_G \) is the optical band gap energy. The maximum absorption wavelength and the optical band gap values of products, obtained by extrapolation method, were listed in Table 1. The PL spectrum of the pure and Al-doped ZnO nanoparticles is presented in Fig. 3(b). UV emission peak, related to the recombination of electron–hole in near band edge levels is observed at 389 nm for pure ZnO nanoparticles. One can see that, with increasing doping concentration, UV emission peak shifts to the longer wavelength that might be a sign of the optical band gap decreasing. It seems, Al-doping creates some energy donor levels in the band gap that leads to reduce the optical band gap of ZnO nanoparticles. These results are consistent with UV–visible results. The intensity of the UV emission peak decreases when the Al concentration is rose from x=0 to x=0.09 which represented the nonradiative emission.

### 4. Conclusion

In this study, the pure and Al-doped ZnO nanoparticles were synthesized via the mecanochemical method. According to the TG results, the appropriate temperature of calcinations is 600 °C. All products have the hexagonal wurtzite structure without any impurities such as Al₂O₃. The morphology of products was almost spherical and no changes were observed with Al doping. Moreover, the average particle size incremented with increasing the Al concentration. The optical studies showed a reduction in optical
band gap of Al$_{0.09}$Zn$_{0.91}$O nanoparticles in comparison with the ZnO nanoparticles.

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References


