Synthesis of boron doped ZnO particles by hydrothermal method

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Boron doped ZnO particles were prepared by using zinc chloride precursors in an autoclave at 200 °C via a simple hydrothermal technique and the particles were annealed at 600 °C in air. Thermo-gravimetric and differential thermal analysis showed that endothermic peaks were observed between 100 °C and 200 °C accompanying with the water loss on the samples. X-ray diffraction measurements showed that boron doped ZnO particles have hexagonal wurtzite structure and boron atoms incorporate interstice in the ZnO lattice. Morphological characterization of the films were done by a scanning electron microscope and the results showed that by adding boron the morphology changes from hexagonal rod-like to particle-like structure. Optical measurements revealed that absorbance peak of boron doped ZnO particles were blue shifted.

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1. Introduction

ZnO, a wide band gap semiconductor material with an energy gap of 3.37 eV (300 K) and large excitation binding energy (60 meV), has attracted a great deal of attention for its potential application including surface acoustic wave filters, chemical sensors, transparent conductor, light-emitting diodes, solar cells and optical modulator wave-guides, etc.[1–5]. Studies show that the physical properties of ZnO particles depend on preparative methods, growth condition and its chemical composition. Moreover, doping in ZnO, such as Al, Fe, B, etc., offers an effective approach to adjust structural, optical and electrical properties [6-8].

Various synthesis methods have been used to grow such materials. They include thermal evaporation [1], chemical vapor deposition [3], sol-gel method [5], electrochemical deposition [9], rf magnetron sputtering deposition [10], spray pyrolysis [6] and hydrothermal deposition [7]. Among these methods, the hydrothermal method is promising for fabricating ideal material with special morphology because of the simple, fast, less expensive, low growth temperature, high yield and scalable process. Most of the previous research works have focused on boron-doped ZnO thin films [11–18]. In this paper, we have studied the boron doped ZnO particles (ZnO:B) prepared by hydrothermal technique and we have also investigated the thermal, structural, optical and morphological properties of boron doped ZnO particles obtained from zinc chloride salts.

2. Experimental details

The precursor solution was prepared by dissolving 0.1 M of zinc chloride, 0.01 M of hexamethylenetetramine (HMT) and 0.1M of boron oxide (B_2O_3) in 100 ml deionized water. Here, HMT and B_2O_3 were used as a complexing agent and the source of boron, respectively. The boron concentrations in precursor solutions were adjusted in term of atomic percentage (0, 1, 3, 5 and 7 at%) with respect to zinc. Hydrothermal growth was carried out at 200 °C in a teflon lined autoclave placed on a furnace for 4 hours and then cooled down to room temperature. After cooling naturally to room temperature, the transparent supernatant was removed by using a pipette and white ZnO:B precipitates were collected. The obtained particles were washed with distilled water several times and dried at room temperature in air for further characterization. All experimental conditions were kept the same for all samples.

The crystal structures of ZnO:B particles were investigated by Philips X'Pert Pro X-ray diffractometer (XRD), with Cu-K_α radiation, the surface morphologies were observed using a Zeiss EVO-LS10 scanning electron microscopy (SEM). Thermal gravimetric and differential thermal analysis (TG-DTA) was carried out

from room temperature to 1150 °C at a heating rate of 40 °C/min in air by a Perkin-Elmer Diamond TG-DTA 6300. Optical properties of particles were obtained by using a Shimadzu UV-1800 ultraviolet–visible spectrometer (UV–vis).

3. Results and discussion

Fig. 1 shows TG and DTA results of the as-synthesized ZnO:B particles (0, 3, 7 at%). The TG curves show two step weight losses. For the first step, the weight loss at around 100-200 °C has been attributed to the loss of water molecules on the surface and interlayer of the samples. The endothermic peaks seen around 200 °C are corresponding to the water loss on the surface and interlayer of the samples with 3 and 7 at %. The second step occurs at 200-600 °C due to the decomposition of hydroxide and residual organics in the precursor solutions. At high temperature, the weight loss might be due to complete crystallization of the samples. The results of thermal analysis indicate that the samples contain some hydroxyl and organic impurities. The XRD results (Fig.2a-b) confirm this idea, because some low intensity peaks other than wurtzite ZnO observed in Fig.2a disappeared after thermal treatment (Fig. 2b).

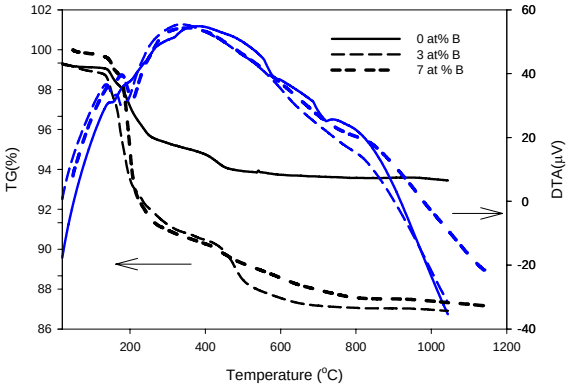

Fig.1. TG-DTA trace for the boron doped ZnO particles

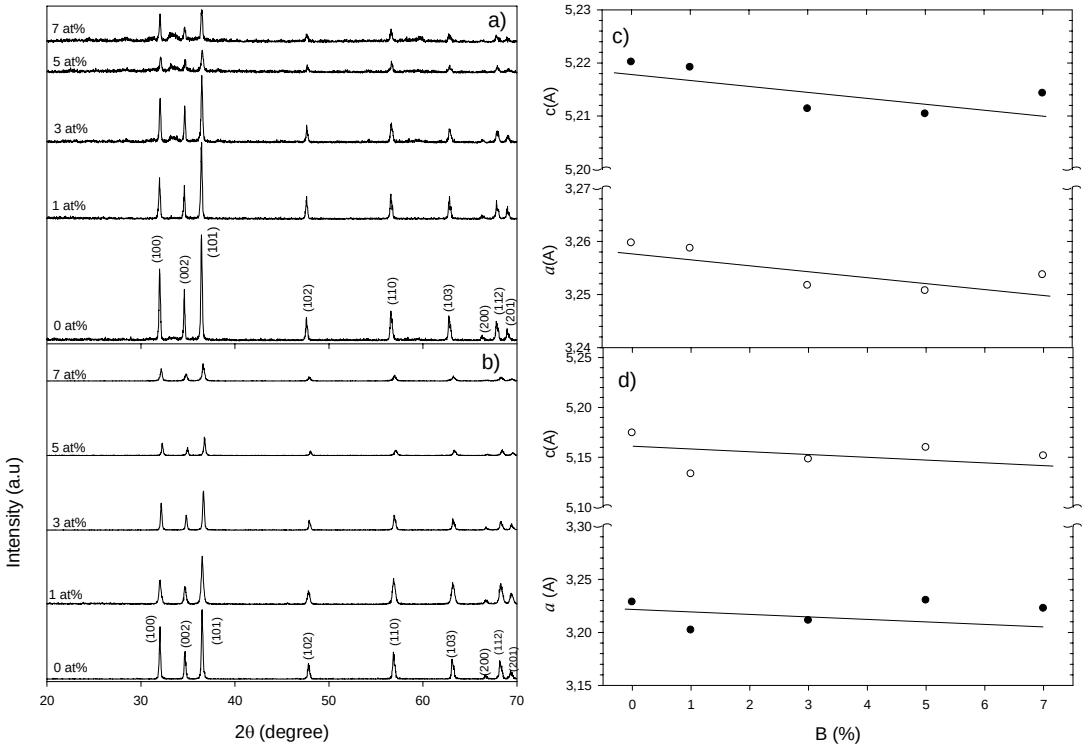

Fig2. XRD patterns of boron doped ZnO particles (a), annealed boron doped ZnO particles (b). Variation in lattice parameters with B doping concentration for the as-synthesized (c) and for annealed particles (d). The solid lines are a guide for the eye.

The XRD patterns of the as-synthesized and annealed ZnO:B particles with various boron doping concentration are presented in Fig.2a-b. In Fig.2a, in addition to peaks belonging to ZnO structure, some other broad and low intensity impurity peaks have been observed at 2θ values especially between 30° and 35°. The intensities of the

impurity peaks increase with increasing boron addition. These impurity peaks disappear with the thermal annealing at 600 ^{o}C. It is considered that these impurity peaks are originated from some hydroxide compounds and other organic compounds in the structure of prepared ZnO:B particles. Moreover, the peak intensities of ZnO planes are found to decrease with increasing boron doping concentration for the as-synthesized and annealed ZnO:B particles. This indicates that the crystalline quality of the powders degrades when the boron doping increases [19]. The incorporation of boron into ZnO lattice is evidenced by the shrinkage of the lattice parameters of ZnO. Fig. 2c-d shows the variation of lattice parameters (a, c) of the as-grown and annealed ZnO particles with the variation of dopant concentration. Although the variation of the lattice parameters with boron concentration is nonlinear, as seen in Fig.2c-2d, it is observed that the lattice parameters are decreasing with increasing boron concentration. The nonlinear behavior of the lattice constants could be due to the interstitial incorporation of boron atoms in the ZnO lattice. As for ZnO, the cell constant is estimated to be a = 0.3259 nm, c = 0.5220 nm (Fig. 2c). However, as for the annealed ZnO, the cell constant is estimated to be a = 0.3228 nm, c = 0.5174 nm (Fig. 2d). By thermal annealing, the decrease in the values of lattice parameters could be attributed to disappearances of the interstitial incorporation of residual ions such as Cl^- in ZnO matrix or could be originated from particle size and surface tension [19].

SEM images of as-synthesized and annealed ZnO:B particles with various boron doping concentration are presented in Fig.3 (a-f). As seen in Fig.3 (a-c) the distribution, size and microstructure of as grown ZnO particles change with the boron doping concentration significantly. It is seen that the ellipsoidal microstructure of ZnO particles transforms plate- like (3 at %) and rose-like (7 at%) structure with increasing boron concentration in the precursor solution. These plate-like and rose like structure could be assigned to one of the hydroxyl compounds of Zn. These results are in agreement with the XRD results. The annealed boron doped ZnO particles are presented in Fig. 3(d-f). As seen annealed images, plate-like and rose-like structures turn to particle-like structures and the sizes of rod particles decrease with increasing boron concentration in structure.

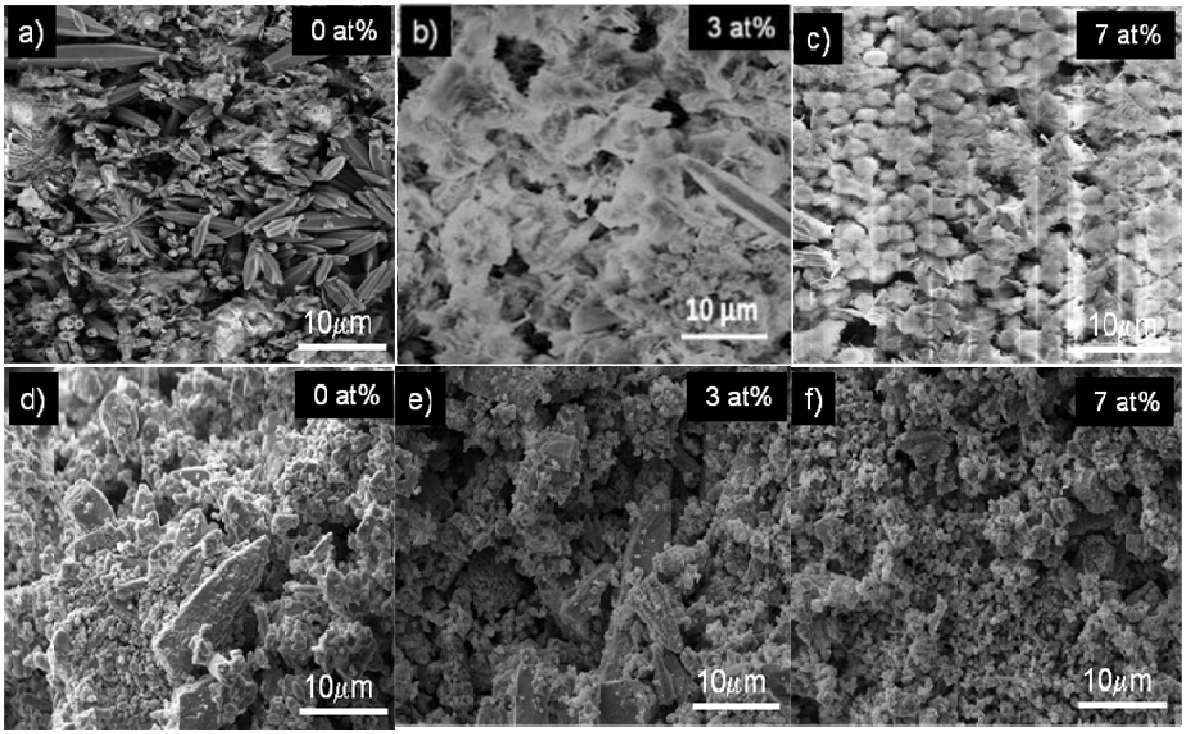

Fig.3 SEM images of boron doped ZnO particles (a-c) and annealed boron doped ZnO particles (d-f)

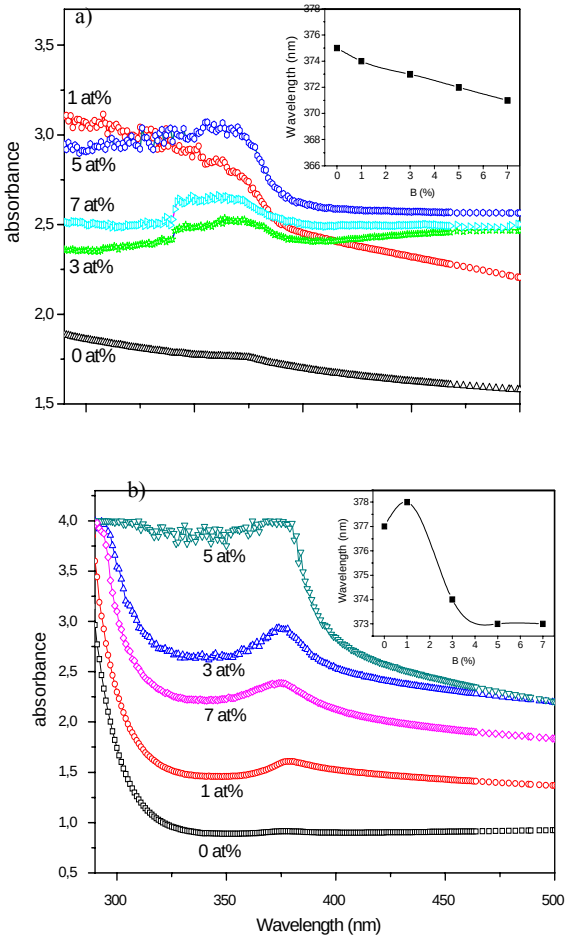

Fig.4. Absorption spectra of boron doped ZnO (a) and annealed boron doped ZnO particles (b). Insets show the change in wavelength with boron concentration.

Fig. 4a-4b shows UV–visible absorbance spectra of the as synthesized and annealed ZnO:B particles. All absorption curves exhibit an observable absorption with the wavelength between 370 and 380 nm, due to the large exciton binding energy. Insets of Fig.4a and 4b show wavelength shift of boron doped ZnO particles. After annealing the absorption peaks are observed much sharper and clear due to absence of hydroxyl groups and residual impurity. In addition, it is observed that the absorption peak decreases with increasing boron concentration for all samples. The movement of wavelength to the shorter wavelength (higher band gap) is the Burnstein-Moss shift [20], which is due to the increase of carrier concentration. It is expected, as a B^{+3} ions at Zn^{+2} ion sites creates one extra free electron acting as an electron donor.

4. Conclusion

Boron doped ZnO particles were prepared by hydrothermal method and they are characterized by TG, XRD, SEM and UV-Vis analysis. Measurements show that as-grown particles have some residual impurity and annealing at 600°C removes impurity in the structure. The XRD patterns and SEM measurements show that ZnO particles are influenced by addition of boron. For annealed samples, rode-like structure turn to particle-like structures and the size of rod particles decrease with increasing boron concentration. From UV -Vis spectrum, we find that wavelength of ZnO powders are decreasing with increasing boron concentration.

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