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Influence of Ti doping on ZnO nanocomposites: Synthesis and structural characterization

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ABSTRACT

In this study, pure phase titanium (Ti) doped zinc oxide (ZnO) nanocomposites were successfully synthesized through facile and effective high energy ball-milling method using suitable precursors. Different Ti concentrations ($Zn_{1-x}Ti_xO$, x = 0, 0.03, 0.05 and 0.1) were doped into ZnO. Detailed crystal and local atomic structures of synthesized samples were characterized via X-ray diffraction (XRD) and non-destructive synchrotron based X-ray absorption spectroscopy (XAS). Obtained results revealed that substitution of Zn sites by Ti ions in $Zn_{1-x}Ti_xO$ did not cause any alteration in the hexagonal wurtzite phase of ZnO with increasing doping concentrations. This study clearly suggests that ball-milling is a quite simple, cost effective, eco-friendly method to synthesize highly crystalline nanosized Ti doped ZnO composites for future nanotechnological applications, spintronic devices in particular.

1. Introduction

Synthesis of nanostructured materials has been opened possibilities for production and rational design of novel functional devices and technologies. Nanomaterials are used in today's environmental, biomedical, agricultural, food safety, security, energy conversion, and aerospace applications etc. [1–3]. Physical properties of materials in nanoscales are remarkably different from those of other bulk materials due to quantum size effects. From this point of view, development of new methods for preparation of materials with a nanometer-sized microstructure have become crucial for designing and fabricating next generation new devices based on nanostructures. Recently, nanostructured metal oxide semiconductor materials such as zinc oxide (ZnO), titanium dioxide (TiO_2), copper oxides (CuO and Cu_2O), cobalt oxides (CoO and Co_3O_4) etc. have been a popular subject of extensive research for nanotechnological applications [4–10]. Among them, ZnO is one of the primary and versatile functional semiconductor materials used in nanoscience research applications including optoelectronics, solar cells, and spin-transport electronics (spintronics) due to its wide direct bandgap (3.37 eV), large free-exciton binding energy (60 meV), high transparency, non-noxious nature, excellent chemical stability, low cost fabrication and electrical and optical characteristic features at room temperature. ZnO is generally crystalized in the hexagonal wurtzite structure under ambient condition [11]. However, structural properties of the nanostructured ZnO could be tuned by doping elements into the host structure leading to remarkable changes in the electrical and optical properties of ZnO. Moreover, ferromagnetic characteristics can be obtained by doping ions into the non-magnetic ZnO nanostructures at room temperature which demonstrates enhanced performance for the spintronic applications. The information is carried by electron spin instead of electron charge in emerging spintronic technique. Different doping elements especially transition metals (TM) have been used for incorporation with ZnO to observe the application possibility of ZnO based devices [12–17]. Wurtzite type ZnO is generally occurred by tetrahedral (s-p^3) bonding between Zn and O atoms. When TM ions are replacing the Zn sites in the wurtzite ZnO crystal, ions make a contribution their $4s^2$ electrons to the s-p^3 bonding. Therefore, doped TM takes place usually tetrahedral sites in the host ZnO semiconductor. Fabrication of TM doped ZnO nanostructures via ball-milling is considered a promising method due to low cost, environmental friendly and quite simple process. In this technique, properties of the TM doped ZnO nanostructures can be modified or controlled by doping and milling parameters [18]. For instance, ball to powder weight ratio, speed and time of milling and type and size of milling balls affect the physical properties of resulting nanosamples. However, motivation of the present study was fabrication and characterization of the pure phase titanium (Ti) doped ZnO nanocomposites via ball-milling route rather than optimization of milling parameters.

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Ti which is one of the TM ions has partially filled *d* shells, and thus can be easily substituted for ions of the host semiconductors. In addition, Ti^{4+} has closest ionic radius (0.61 Å) and covalent radius (1.36 Å) to those of Zn^{2+} (0.60 Å and 1.31 Å) comparing to other dopant elements. Hence, Ti seems to be a good appropriate choice among other dopants to be used. Accordingly, properties of ZnO nanostructures could be easily tuned and controlled by doping ZnO with Ti in order to make it suitable for modern applications in spintronic or microelectronic. In this study, Ti doped ZnO nanocomposites have been synthesized through conventional ball-milling method and resulting samples characterized by typical X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) methods. Obtained results revealed that highly crystalline Ti doped ZnO nanocomposite samples can be achieved with the use of ball-milling method without requiring expensive solvents and complicated and costly equipments. Accurate determination of the crystal and local structure of synthesized nanocomposites become strongly important because they play crucial role in evolving technological applications. Apart from XRD measurements, local structural characterization of the fabricated composites as a function of doping concentration have been intensively investigated through a non-destructive synchrotron based XAS. Results of absorption spectroscopy provided that no remarkable doping induced changes in ZnO structure for all doping concentrations of Ti were occurred. Within our knowledge, no detailed experimental studies have not been reported on local atomic structural analysis of Ti doped ZnO so far. Therefore, the obtained results will be significant to explore the prospects and future challenges for the development of practical applications based on TM doped ZnO nanocomposites.

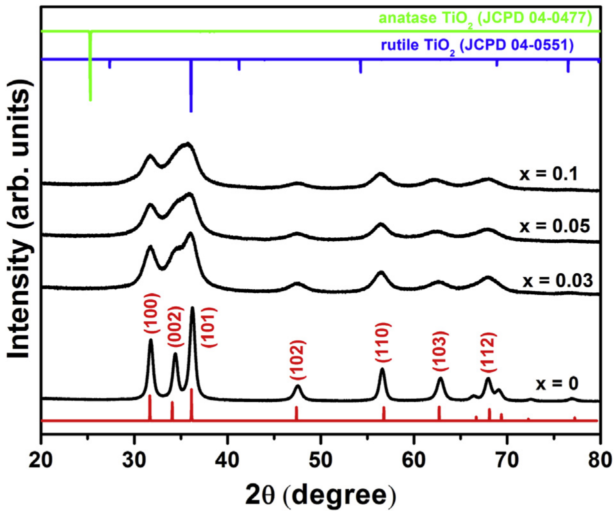

Fig. 1. XRD patterns of Ti doped ZnO nanocomposite samples with different doping concentrations. Reference data of TiO_2 in anatase and rutile form and ZnO are also given for comparison.

2. Experimental methods

Inorganic precursor ZnO (97%) and TiO_2 (anatase, 99.7%) powders were purchased from Merck and used without any further purification. It should be noted that the milling process parameters (ball-to-powder ratio, ideal type of ball, milling speed and time) were previously optimized. Namely, powders were weighed to achieve mixtures of ZnO with 3, 5, 10 mol% of TiO_2. A Fritsch Planetary premium line P7 mill was used for milling process and ball-to-powder weight ratio (10:1) was kept constant in all cases. The milling speed was set to a rotation rate of 500 rpm and each powder mixtures were milled with 5 mm diameter zirconia balls for 20 h in clean room conditions in order to observe effect of Ti contents on doped ZnO powders formation. As soon as the milled time finishes, milling was stopped to collect the resulting samples. Finally, milled granules were pressed into the form of disks with 10 mm in diameter and 0.5 mm in thickness by applying different compacting pressures. Following the pressing process, resulting samples were immediately subjected to structural characterizations.

Crystal structure and phase purity of the synthesized nanocomposites were determined via X-ray diffraction (XRD) technique (Rigaku Miniflex XRD system with wavelength of 0.154 nm). Data were collected in the wide angle region from 10° to 80° with a scan

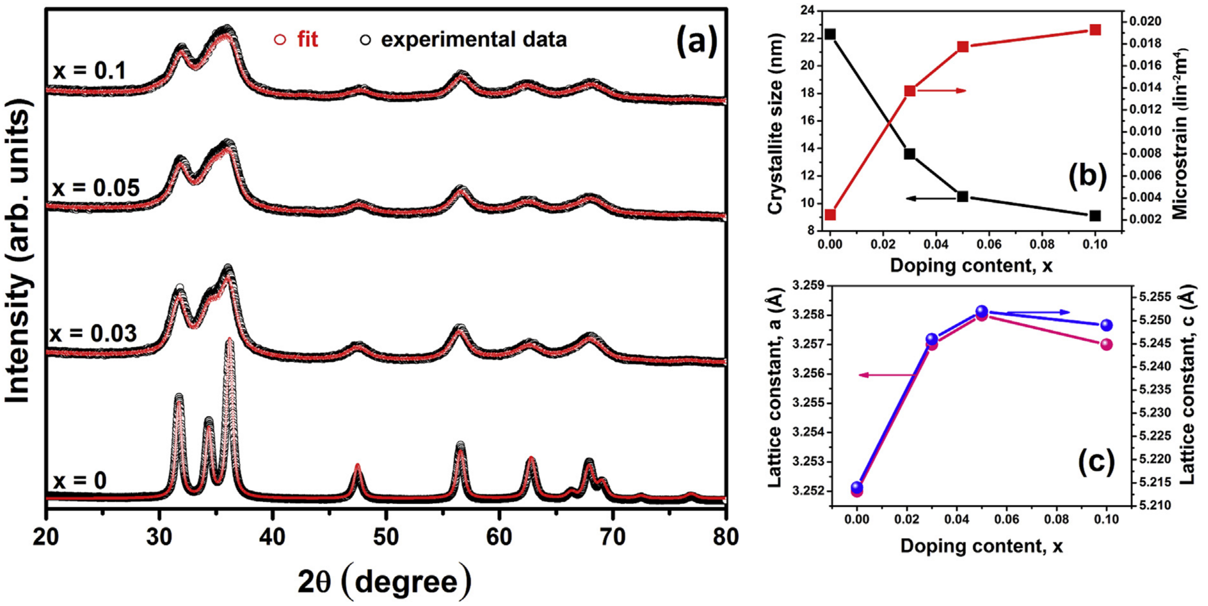

Fig. 2. (a) Rietveld refinement fits of XRD data, (b) crystallite size and microstrain, and (c) lattice parameters of Ti doped ZnO nanocomposite samples with different doping concentrations.