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

Funda Aksoy Akgül

Department of Physics, Nigde University, 51240 Nigde, Turkey

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 ($\text{Zn}_{1-x}\text{Ti}_x\text{O}$, $x = 0, 0.03, 0.05$ 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 $\text{Zn}_{1-x}\text{Ti}_x\text{O}$ 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.

Keywords: A. Nano-structures, B. Microstructures, E. Powder processing

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 (TiO₂), copper oxides (CuO and Cu₂O), cobalt oxides (CoO and Co₃O₄) 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-toxic 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.

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.

2. Experimental Methods

Inorganic precursor ZnO (97%) and TiO₂ (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 TiO₂. 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 speed of 2° min⁻¹ and carefully analyzed by Rietveld refinement using MAUD program [19]. Generally, XRD is not a sensitive method to examine the formation of small precipitates of a second phase that could be at low concentration in the form of nanoparticles within synthesized composites. Moreover, the amount of precipitates of a second phase as compared to bulk could be negligible and/or the crystallite size of precipitates of a second phase could be too small to be detected by XRD. Because of this reason, the fabricated nanosamples were also characterized by synchrotron radiation based XAS in order to further substantiate their structural properties. XAS is quite sensitive and a valuable method to examine doping induced changes in such nanostructured samples. Absorption experiments were conducted at beamline 4-3 of Stanford Synchrotron Radiation Laboratory (SSRL). Beamline 4-3 is a wiggler magnet beamline dedicated to X-ray absorption spectroscopy experiments and has energy range between 2.4 and 14 keV. Measurements were recorded at Zn and Ti K edge for each samples. In order to get consistent comparisons, all measurements were collected in transmission mode using two ionization chambers as incident and transmitted beam intensity detectors at room temperature. Prior to nanocomposites measurements, photon energy calibration was done using the first inflection point of the spectrum at 9659 and 4966 eV of the 2 µm thick metallic zinc and titanium foil in each scan, respectively. Twenty independent scans were taken and averaged to eliminate the statistical noise and improve statistics for all synthesized nanosamples. During measurements, any energy drift of the monochromator were not observed. A commercial sample of anatase TiO₂ was also subjected to XAS measurement in transmission mode at Ti K edge as a reference sample. The collected experimental data were processed and meticulously analyzed using the programs Athena and Artemis interface to IFEFFIT software package [20].

3. Results and Discussion

Figure 1 shows XRD patterns of the fabricated nanosamples as a function of Ti doping contents, together with the reference diffractograms of possible TiO_2 phases. Only a single ZnO wurtzite phase was detected in all samples and doping with Ti did not create any separated phase such as anatase and rutile TiO_2 for all concentrations. It is evident that all fabricated samples have polycrystalline structure and the existence of all peaks of ZnO structure means there is no preferential growth direction. The solid vertical reference peak for the hexagonal wurtzite ZnO structure (JCPD card no. 36-1451) below the XRD pattern of the pristine ZnO ($x = 0$) was also evidenced that a single hexagonal wurtzite phase was occurred in the fabricated samples for all Ti doping contents. No trace of other impurities or phase(s) was observed within the detection limit of instrument. It can be seen from Figure 1 that all XRD diffraction peaks of the resulting samples become wider with increasing doping concentration of Ti. This result clearly proves a decreasing crystallite size of the wurtzite type nanocrystals as dopant concentration increases. Rietveld refinement was evaluated in order to determine microstructural parameters of the synthesized nanosamples. The obtained refinement fits for all the fabricated nanosamples are provided in Figure 2 (a). Refinement procedure exhibited that crystallite size alters from 22.3 nm for pure ZnO ($x = 0$) to 9.1 nm for Ti doped ZnO ($x = 0.1$) nanosample. The lattice parameters (a and c) and microstrain of the doped ZnO samples significantly increased with increasing Ti doping concentration while the crystallite size decreased, as would be expected with the substitution of Ti^{4+} for Zn^{2+} . The obtained microstructural parameters extracted from the refinement process are shown in Figure 2 (b) and (c) as a function of doping content of Ti. Table 1 also summarizes the detailed microstructural parameters. The basic lattice constants for pristine ZnO found here is in good agreement with previously reported values in the literature [21]. These results clearly provide that the Ti^{4+} ions are substituted for Zn^{2+} ions in ZnO lattice without changing the

wurtzite crystal structure. Because the increase of the lattice parameters and microstrain can be due to the incorporation of Ti into the wurtzite lattice. Moreover, difference between the ionic radius of Zn^{2+} (0.60 Å) and Ti^{4+} (0.61 Å) allows incorporation of Ti^{4+} into ZnO with only a slight change in the microstructural parameters which cause a small shift all the peaks to lower or higher angles (see Table 1).

Complementary to XRD, synchrotron based XAS technique was adopted to further examine the local atomic structure of the fabricated nanosized composite samples for clarifying existence of a second phase(s) in the structure if occurs. Distribution and location of incorporated ions in parent compounds can be determined by utilizing element specific XAS method including both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). This specific characteristic of XAS allows to determine local structure of dopant element in the host ZnO environment. The normalized Zn and Ti K edge experimental XANES spectra for the all prepared samples having doping concentrations of $x = 0 - 0.1$ are provided in Figure 3 (a) and (b), respectively. XANES spectra for Zn and Ti metals are also shown for comparison. As obviously evidenced from Figure 3 (a) and (b), the XANES spectra for the all fabricated nanocomposite samples look quite similar for each Zn and Ti K edge. These observations are in good agreement with the XRD data as shown in Figure 1. Note that no energy position shift was observed for Zn K edge XANES spectrum of the fabricated nanosamples. Any traces of Zn metallic precipitates after doping process did not observe in the XANES spectra. It can be also seen from Figure 3 (a) that Zn K edge of all fabricated composites do not have any pre-edge peaks due to all 3d band of Zn is occupied by 3d electrons. In addition, energy difference between maximum XANES edge of the fabricated nanosamples and Zn metal was found to be approximately 10 eV. This energy difference could be due to the oxidation state and bonding characteristics of the atoms. Since zinc atoms

linked to oxygen atoms reveals stronger bonding in the case of ZnO structure, the absorption edge of ZnO therefore shifts to higher photon energy side of the XANES spectrum.

Ti K edge XANES spectra of ZnO nanosamples doped with different Ti contents are provided in Figure 3 (b). Obviously, all the samples exhibit significantly different XANES spectrum than that of the reference Ti foil. Contrary to those in Zn K edge XANES spectra, Ti K edge of the fabricated composites has a distinguishable pre-edge peaks around 4.968 keV before the main edge peak. Electron transitions from a core level to the higher unfilled or hybridized orbital generate the pre-edge features providing useful information on chemical environment of the X-ray absorbing atom. Therefore, the origin of this characteristic peak is due to the transition of Ti 1s electron to the *p* component in *p-d* hybridized states. This pre-edge feature clearly indicates that the majority of Ti⁴⁺ ions are situated at available tetrahedral coordinated site within host ZnO structure for all Ti concentrations [22]. Moreover, main edge energy position of the fabricated nanosamples slightly shifts to higher energy side of the spectrum due to the oxidation state of Ti that is likely +4. Based on the obtained results, it could be concluded that Ti⁴⁺ ions are incorporated into ZnO hexagonal wurtzite lattice at all Ti concentrations (*x* = 0.03 - 0.1).

The experimental EXAFS data were recorded at Zn and Ti K edge in order to further investigate changes in local atomic structures for different doping concentration of Ti. Figure 4 (a) and (b) shows Zn K edge EXAFS signals and Fourier Transforms (FT) magnitude of k^3 -weighted data for all the fabricated nanosamples, respectively. EXAFS region ($k = 2 - 12 \text{ \AA}^{-1}$) was transformed to FT and fitted in real space to get the best fitting results applying a Hanning window. FEFF8 code was used in order to perform data analysis of EXAFS measurements [20]. FEFF8 is a self-consistent real space multiple scattering code for simultaneous calculations of X-ray absorption spectra and electronic structure. FEFF input files were created using database of ATOMS package [20]. As seen in Figure 4 (a), similar

EXAFS signals were collected from ZnO compounds doped with different Ti concentrations ($x = 0.03, 0.5$ and 0.1), and undoped ZnO ($x = 0$) sample as well. This finding evidently suggests that Ti^{4+} ions for all doping concentrations are largely substitutionally incorporated into Zn sites in the host wurtzite ZnO lattice. As shown in Figure 4 (b), three main types of nearest neighbors (oxygen, titanium and zinc) bonded to zinc atoms were observed for the doped ZnO nanosamples. The first, second and third peak corresponds to Zn-O coordination in the first shell, Zn-Ti coordination in the second shell, and Zn-Zn in the third coordination shell, respectively. The position of the FT peaks at Zn K edge did not change and the peak magnitudes of the FT were quite similar for the doped ZnO samples with each other. Therefore, these results prove the existence of an ordered environment in the fabricated nanocomposite samples.

Ti K edge EXAFS and FT spectra for all the doped nanosamples together with anatase TiO_2 powder as reference are provided in Figure 5 (a) and (b), respectively. It is quite apparent from Figure 5 (a) that the similar EXAFS oscillations for ZnO samples doped with Ti at various concentrations ($x = 0.03, 0.5$ and 0.1) were recorded, contrary to the reference material. Moreover, no remarkably changes were found for the positions of peaks with increasing Ti content. In Figure 5 (b), the first and second peaks are due to Ti-O and Ti-Zn coordination in the first and second shell, respectively. The third weak peak could be attributed to Ti-Ti coordination. It must be noted that fitting results of Ti-O distance ($1.92 - 1.95 \text{ \AA}$) for all the Ti doped ZnO nanosamples is less than those of Zn-O ($1.97 \text{ \AA}$) in pure ZnO. This shorter Ti-O distance reveals that Ti has +4 valence state and in a tetrahedral coordination since the atomic radius of Ti^{4+} in tetrahedral sites is shorter than in octahedral sites. The short Ti-O distance also exhibits strong local interaction in Ti-O in the ZnO.

In the present study, detailed analysis was performed on the EXAFS data of the fabricated nanosamples using IFEFFIT method. Artemis was utilized for the fitting of

experimental EXAFS and FT data to estimate the local atomic parameters of the prepared samples. Since an accurate determination of local atomic order in the doped nanostructured materials is very important in order to understand their behavior in the spintronic devices, both single and multiple scattering model paths were included in the fitting procedures of this work to obtain best fitting results for all nanocomposite samples. An example for the best fit of ZnO compound doped with 10% Ti concentration at Zn and Ti K edge is provided in Figure 6 and 7, respectively. The experimental EXAFS data (insets of Figure 6 and 7) and their FT were fitted in the $k = 2 - 12 \text{ \AA}^{-1}$ and $R = 1 - 6 \text{ \AA}$ region, respectively. The obtained fitting results are fully in good agreement with the experimental data up to about $6 \text{ \AA}$ in both real space (R) and k-space. Values of the structural atomic parameters extracted from the fitting procedure are listed in Table 2. It is clearly seen in Table 2 that the bond distances of Ti-O and Ti-Zn in all Ti doped ZnO samples are very close to Zn-O and Zn-Zn distances in undoped ZnO. This result strongly suggests that Ti ions are incorporated into ZnO wurtzite lattice in the oxidation state of +4 with a tetrahedral coordination for titanium contents between $x = 0.03$ and $x = 0.1$.

4. Conclusions

In summary, present study was focused on the synthesis of highly crystalline pure phase ZnO nanocomposites doped with different concentrations of Ti ($x = 0, 0.03, 0.05$ and 0.1). High energy ball-milling method was applied to fabricate nanocomposite samples. In contrast to the previously reported fabrication methods, ball-milling processing technique offers several advantages such as simplicity, low cost and eco-friendly nature for the production of highly pure nanoparticles for various technological applications. XRD measurements clearly exhibited that crystalline Ti doped ZnO nanocomposite samples with small particle sizes can be simply obtained using ball-milling method. Local atomic structures

of the fabricated nanocomposites were examined by diagnostic synchrotron radiation based XAS. No evidence of any residue of metals and secondary phase or phases was found by XRD and XAS measurements. A comprehensive EXAFS analysis was executed to get qualitative information about the local structural parameters of the resulting samples. The present results evidently demonstrated that majority of Ti^{4+} ions occupied Zn^{2+} sites in the wurtzite ZnO lattice for all Ti doping concentrations. This is the first contribution so far, reporting a simple fabrication and detailed structural analysis of Ti doped ZnO nanocomposites. It is expected that the reported results for Ti doped ZnO nanocomposites will provide significant information for future nanotechnological applications, spintronic devices in particular.

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Figure captions:

Figure 1: XRD patterns of Ti doped ZnO nanocomposite samples with different doping concentrations. Reference data of TiO₂ in anatase and rutile form and ZnO are also given for comparison.

Figure 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.

Figure 3: Normalized (a) Zn K edge and (b) Ti K edge XANES spectra of Ti doped ZnO nanocomposite samples with different doping concentrations.

Figure 4: (a) Experimental Zn K edge EXAFS spectra in k-space and (b) corresponding FT functions in real space for Ti doped ZnO nanocomposite samples with different doping concentrations.

Figure 5: (a) Experimental Ti K edge EXAFS spectra in k-space and (b) corresponding FT functions in real space for Ti doped ZnO nanocomposite samples with different doping concentrations.

Figure 6: Best fit of FT function for Ti doped ZnO nanocomposite sample with 10% Ti doping concentration. Inset shows experimental Zn K edge EXAFS spectrum of the same sample with Artemis fit.

Figure 7: Best fit of FT function for Ti doped ZnO nanocomposite sample with 10% Ti doping concentration. Inset shows experimental Ti K edge EXAFS spectrum of the same sample with Artemis fit.

Table captions:

Table 1: Rietveld refinement results for microstructural parameters of Ti doped ZnO nanocomposite samples with different doping concentrations.

Table 2: Results of local atomic structure parameters for Ti doped ZnO nanocomposite samples with different doping concentrations obtained from fitting of experimental EXAFS data at Zn and Ti K edge (N: coordination number, R: interatomic distance, and σ^2 : Debye-Waller factor).

Table 1: Rietveld refinement results for microstructural parameters of Ti doped ZnO nanocomposite samples with different doping concentrations.

Doping concentration	Crystallite size (nm)	Microstrain ($\text{lin}^{-2}\text{m}^4$)	Lattice parameters (Å)		2θ (degree) (101)
			<i>a</i>	<i>c</i>	
x = 0	22.3	0.0025	3.252	5.214	36.2458
x = 0.03	13.6	0.0137	3.257	5.246	36.0476
x = 0.05	10.5	0.0178	3.258	5.252	36.0028
x = 0.1	9.1	0.0193	3.257	5.249	35.7104

Table 2: Results of local atomic structure parameters for Ti doped ZnO nanocomposite samples with different doping concentrations obtained from fitting of experimental EXAFS data at Zn and Ti K edge (N: coordination number, R: interatomic distance, and σ^2 : Debye-Waller factor).

<i>Shell</i>	<i>x = 0.03</i>			<i>x = 0.05</i>			<i>x = 0.1</i>		
	N	R (Å)	σ^2 [Å ²]	N	R (Å)	σ^2 [Å ²]	N	R (Å)	σ^2 [Å ²]
Zn-O	4.02 ± 0.01 0.02	1.98 ± 0.01	0.007 ±	3.75 ± 0.01	1.99 ± 0.02	0.006 ± 0.01	3.63 ± 0.01 0.01	1.98 ± 0.01	0.006 ±
Zn-Ti	1.1 ± 0.01 0.01	2.88 ± 0.01	0.017 ±	1.45 ± 0.02	3.22 ± 0.01	0.023 ± 0.01	1.55 ± 0.01 0.02	3.11 ± 0.01	0.013 ±
Zn-Zn	11.2 ± 0.01 0.01	3.11 ± 0.01	0.004 ±	10.3 ± 0.01	3.33 ± 0.01	0.016 ± 0.03	9.1 ± 0.01 0.01	3.32 ± 0.01	0.012 ±
Ti-O	3.98 ± 0.01 0.02	1.92 ± 0.01	0.012 ±	3.8 ± 0.02	1.95 ± 0.01	0.013 ± 0.01	3.72 ± 0.01 0.01	1.94 ± 0.01	0.022 ±
Ti-Zn	11.1 ± 0.02 0.01	3.25 ± 0.01	0.019 ±	9.8 ± 0.01	3.25 ± 0.01	0.044 ± 0.02	8.8 ± 0.01 0.01	3.27 ± 0.01	0.029 ±
Ti-Ti	1.03 ± 0.01 0.01	3.22 ± 0.01	0.001 ±	1.5 ± 0.02	3.2 ± 0.01	0.002 ± 0.01	1.61 ± 0.01 0.01	3.21 ± 0.01	0.002 ±
<i>ZnO (x = 0)</i>									
	N		R (Å)		σ^2 [Å ²]				
Zn-O	4.1 ± 0.02		1.97 ± 0.01		0.005 ± 0.01				
Zn-Zn	11.1 ± 0.01		3.22 ± 0.01		0.009 ± 0.01				

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7