Synthesis of Mixed Ceramic $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ Nanofibers via $\text{Mg}^{2+}$ Doping Using Sol–Gel Electrospinning

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ABSTRACT: We report on the synthesis of tuned energy band gap $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ nanofibers (NFs) with different $\text{Mg}^{2+}$ content via the sol–gel electrospinning (ES) technique wherein the addition of the doping material affects not only the morphologies of as-spun ZnAc/PVA and MgAc/ZnAc/PVA nanofibers but also the crystal microstructure and optical properties of calcined ZnO and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ nanofibers. Following an appropriate aqueous solution preparation of magnesium acetate (MgAc) and zinc acetate (ZnAc) with poly(vinyl alcohol) (PVA), electrospinning is performed and then as-spun nanofibers are calcined in an air atmosphere at 600 °C for 3 h. As-spun and calcined nanofiber diameters and morphologies are evaluated with scanning (SEM) and transmission (TEM) electron microscopies, whereas crystalline microstructural interpretations of ZnO and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ are conducted with wide-angle X-ray diffraction spectra (XRD). Surface chemical composition and elemental evaluation of calcined nanofibers are examined with X-ray photoelectron spectroscopy (XPS), and optical properties and crystal defect analyses of the calcined nanofibers are conducted with photoluminescence spectra (PL). We observe a sharp reduction in fiber diameter upon calcination as a result of the removal of organic species from the fibers and conversion of ceramic precursors into ceramic nanofibers, and the appearance of a range of fiber morphologies from “bead in a string” to “sesame seed” coverage depending on fiber composition. Because $\text{Zn}^{2+}$ and $\text{Mg}^{2+}$ have similar ionicity and atomic radii, some $\text{Zn}^{2+}$ atoms are replaced by $\text{Mg}^{2+}$ atoms in the crystals, leading to a change in the properties of crystal lattices. The band gap energy of the calcined fibers increases significantly with addition of $\text{Mg}^{2+}$ along with an increase in the ultraviolet (UV) photoluminescence emission of the fibers.

1. INTRODUCTION

Nanomaterials such as nanofibers are of great interest in many applications, such as in energy storage, photoactive layers in solar cells, and biomedical engineering. ¹⁻⁴ A unique method to produce nanofibers is by electrospinning, where the resulting nonwoven nanofibers possess high surface-to-volume ratios, high porosity, and continuous morphology. Several different polymer systems have been electrospun, offering a vast number of options for materials and applications.⁵⁻⁷ The electrospinning process can be manipulated to control the fiber diameter, surface property, morphology, and porosity of the resulting nonwoven mat.

Ceramic electrospun nanofibers are promising candidates for various usage, from batteries to solar cells and catalysts. Sol–gel electrospinning is an efficient and functional ceramic nanofiber production technique that has been used to produce a variety of different materials. In this regard, two additional steps are applied to the conventional electrospinning process: sol–gel preparation and calcination process.⁸⁻¹³ After electrospinning, the ceramic precursor/polymer composite nanofiber mat is calcined at high temperatures in a gas atmosphere to remove organic residues and convert the ceramic precursor into the final ceramic nanofibers. The properties of these ceramic nanofibers, especially optical and electronic, are often related to the crystalline structure of the calcined ceramic fibers, which in turn are controlled by the calcination parameters, such as temperature, heating and cooling rates, and the amount and pressure of the applied gases in the calcination chamber.¹⁴,¹⁵ Photovoltaic devices are one application that can benefit from ceramic nanofibers. In particular, ceramic nanofibers can be used in dye-sensitized solar cells, where the scattered light could be absorbed multiple times with a nanofibrous structure, resulting in more exciton.¹⁶ The high surface areas of the electrospun mats may accommodate a greater concentration of dye molecules or quantum dots, which could result in more efficient electron transfer compared to traditional film-based technologies. Furthermore, the continuous structure of nanofibers may allow for effective electron transfer as a result of the direct conduction pathway of the photoelectrons along the fibers.

For example, titanium(IV) isopropoxide can be electrospun as a precursor and subsequently converted to titanium dioxide...
(TiO$_2$) nanofibers. Titanium dioxide has been widely established as a material in solar cells due to its wide band gap semiconducting property (around 3.2 eV for anatase and 3.0 eV for rutile morphologies) and absorption photon energy in the UV range. Zinc oxide (ZnO) is another material that has applications in solar cells and can be electrospun. Furthermore, the inherent material properties of ZnO can have significant effects on the performance of photovoltaics (PV); however, the crystal lattice defect of ZnO can negatively affect its electronic and optical properties. To overcome this problem and enhance material properties, a ZnO precursor has been processed with surfactants and doped with other materials that alter the band gap energy level of ZnO.\textsuperscript{1,18}

The band gap energy of ZnO (3.2 eV) can be further increased by doping ZnO with Mg\textsuperscript{2+} to produce mixed oxides, Mg$_x$Zn$_{1-x}$O.\textsuperscript{19} Since the atomic radii of Zn\textsuperscript{2+} (0.6 Å) and Mg\textsuperscript{2+} (0.57 Å) are similar, the substitution between these two atoms in the structure does not change the lattice constant of Mg$_x$Zn$_{1-x}$O significantly but causes a substantial change in optical and electronic properties of ZnO.\textsuperscript{20} In addition, the crystal defect structure of ZnO can be minimized by doping with Mg\textsuperscript{2+}.

However, fabrication of Mg$_x$Zn$_{1-x}$O is practically limited because of the demarcated solubility of MgO in ZnO. On the basis of the phase diagram of ZnO and MgO binary systems, the thermodynamic solid solubility of MgO in ZnO is less than 4% since the crystal structure of MgO (cubic, $a = 4.24$ Å) and ZnO (hexagonal wurtzite, $a = 3.24$ Å and $c = 5.20$ Å) are different.\textsuperscript{21,22} The production of an enlarged band gap in Mg$_x$Zn$_{1-x}$O with the replacement of Zn\textsuperscript{2+} species with Mg\textsuperscript{2+} has however been achieved by some groups using a variety of techniques including pulsed laser deposition (PLD), molecular-beam epitaxy (MBE), metalorganic vapor-phase epitaxy (MOVPE), magnetron sputtering, sol–gel, chemical vapor deposition, and electron beam evaporation.\textsuperscript{23–26} However, no attempts have been made to fabricate nanofibers of the mixed oxides taking advantage of the inherent benefits offered by the nanofibrous structures. In addition, existing studies mostly involve the use of complex processing strategies to develop the material.

In the present work, we report on a simple approach to develop tuned band gap Mg$_x$Zn$_{1-x}$O nanofibers with different Mg\textsuperscript{2+} content via sol–gel electrospinning by using ZnAc and MgAc as precursors. A systematic study of the effect of Mg\textsuperscript{2+} content on morphology, crystalline microstructure, and optical properties on Mg$_x$Zn$_{1-x}$O nanofibers are investigated by using various analytical techniques. The results from this investigation show that Mg$_x$Zn$_{1-x}$O nanofibers exhibit lower crystalline defect structures than ZnO nanofibers and enhanced optical properties, rendering them as promising nanostructured materials for potential use in optoelectronic devices.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials.

Zinc acetate (Zn(CH$_3$COO)$_2$·2H$_2$O), magnesium acetate (Mg(CH$_3$COO)$_2$), poly(vinyl alcohol) (PVA; 88% hydrolyzed with weight-average molecular weight 127 000 Da), and a nonionic surfactant (Triton X-100) were purchased from Sigma-Aldrich and used as received. Deionized water was used throughout the experiments. For preparation of ZnO nanofibers, a stock solution consisting of 14 wt % of aqueous zinc acetate/PVA (1:1) solution with addition of $4 \times 10^{-5}$ mol/dm$^3$ (respect to prepared stock solution) of Triton X-100 was prepared by magnetically stirring at 60 °C until a homogeneous solution was obtained. The same stock solution was used for the Mg$_x$Zn$_{1-x}$O nanofiber preparation, adding MgAc in the solutions at 15:100, 30:100, and 50:100 of MgAc:ZnAc ratio (weight) in the solutions for each sample separately. The stock solutions were stirred at ambient conditions for 2 h to get an appropriate viscous electrospinnable solution mixture.

#### 2.2. Electrospinning and Calcination.

Approximately 1 mL of each stock solution was loaded into a syringe fitted with a stainless steel needle (0.508 mm i.d.) and attached to a power supply (Gamma High Voltage Research, D-ES 30PN/M692). A flow rate of 0.5 mL/h, collector distance of 15 cm between the tip of the needle and the ground collector plate, and an applied voltage of 15 kV were used. The polymer jets were directed toward the grounded plate wrapped in aluminum foil and collected as a fibrous nonwoven mat. During the calcination process, in order to remove organic components from MgAc/ZnAc/PVA composite fibers and convert ceramic precursors into fully crystalline ceramic nanofibers, a Lindberg one zone furnace with a quartz tube (inner diameter of 45 mm, model S8114) was used. First the temperature was increased to 600 °C in an air atmosphere for each sample at a heating rate of 5 °C/min. Each sample was then maintained at this temperature for 3 h to remove all organic components from the fibers and to get well crystallized ZnO and Mg$_x$Zn$_{1-x}$O nanofibers.\textsuperscript{27}

#### 2.3. Solution Properties.

The solution parameters of each electrospinning stock solution were measured at ambient conditions; results are provided in Table 1. For the viscosity measurements, a TA Instruments AR-2000 rheometer with a 40 mm diameter, 2° cone and plate geometry was used. Electrical conductivities of the solutions were measured with a Fisher Scientific accuret Excel XL50 conductivity meter. Surface tensions of the solutions were determined using a pendant drop method using an automated contact angle goniometer (Rame-Hart Inc., Mountain Lakes, NJ) with DROPimage software for data collection and calculation. A 10 μL pendant drop of electrospinning solution was generated from a stainless-steel capillary into the DROPimage software for accurate surface tension measurement by the software.

#### 2.4. Nanofiber Characterization.

For morphology and diameter analyses of ZnO, Mg$_x$Zn$_{1-x}$O, ZnAc/PVA, and MgAc/ZnAc/PVA nanofibers, a field emission scanning electron microscope (FEI XL30 SEM-PEG) with acceleration voltage of 5 kV was used. For SEM imaging, the samples were coated with gold (Dentron Desk IV sputter coater) ~100 Å thick to reduce charging. For nanofiber diameter distribution determination, ImageJ software was used to measure at least 50 nanofibers from different regions of SEM images for each diameter.

### Table 1. Characteristics of Electrospinning Solution and Diameters of As-Spun and Calcined Nanofibers

<table>
<thead>
<tr>
<th>Mg(Ac) content (wt %)</th>
<th>Viscosity (Pa·s)</th>
<th>Surface tension (dyn/cm)</th>
<th>Conductivity (μs/cm)</th>
<th>diam$^a$ (nm)</th>
<th>diam$^b$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.61</td>
<td>31.23 ± 0.2</td>
<td>15.19</td>
<td>279 ± 95</td>
<td>116 ± 42</td>
</tr>
<tr>
<td>15</td>
<td>0.58</td>
<td>29.34 ± 0.2</td>
<td>17.54</td>
<td>231 ± 80</td>
<td>112 ± 34</td>
</tr>
<tr>
<td>30</td>
<td>0.63</td>
<td>29.40 ± 0.2</td>
<td>18.62</td>
<td>289 ± 88</td>
<td>165 ± 46</td>
</tr>
<tr>
<td>50</td>
<td>0.67</td>
<td>30.05 ± 0.2</td>
<td>21.05</td>
<td>299 ± 91</td>
<td>129 ± 42</td>
</tr>
</tbody>
</table>

$^a$Diameters of MgAc/ZnAc/PVA nanofibers (before calcination).

$^b$Diameters of Mg$_x$Zn$_{1-x}$O nanofibers (after calcination). All the diameter values are given as mean ± standard deviations (SD).
Excitation source, a He emission can be collected as both nanometer and photon energy. For precise characterization and analysis. Using the software, the PL measurements to be made at exactly the same position on the sample for between Raman and PL analysis without any need for adjustment. The photoluminescence measurements. The user has the ability to switch detector and an InGaAs Array detector, the latter being ideally suited were examined with a HORIBA Jobin Yvon LabRam/PL system. This luminescence spectra of the various nano energy. All XPS spectra were analyzed using CasaXPS software.

Analytical Axis Ultra XPS system installed at the Shared Materials were collected from 20° to 80° C/min in an air atmosphere.

The crystal structures of and Mg Zn1−xO and ZnO nanofibers were examined with wide-angle X-ray diffraction (XRD). For the XRD instrument, a Rigaku Smart Lab XRD customized Auto mount with a Cu Kα radiation source (λ = 1.54 Å) was used. Diffraction patterns were collected from 20° to 80° with a speed of 5°/min.

The XPS spectra of the calcined samples were collected on a Kratos Analytical Axis Ultra XPS system installed at the Shared Materials Instrumentation Facility (SMIF) of Duke University (Durham, NC). The calibration was conducted for a reference C 1s bonding energy at 285.2 eV, since the samples’ charges are caused to shift at bonding energy. All XPS spectra were analyzed using CasaXPS software.

Figure 1. SEM images of (A1) ZnAc/PVA, (B1) 15:100, (C1) 30:100, and (D1) 50:100 MgAc:ZnAc of MgAc/ZnAc/PVA composite nanofibers before calcination and (A2) ZnO, (B2) 15 wt % Mg2+ doped, (C2) 30 wt % Mg2+ doped, and (D2) 50 wt % Mg2+ doped MgZn1−xO nanofibers after calcination. (E2) High-magnification TEM lattice image of MgZn1−xO sample (30 wt % Mg2+ doped sample).

3. RESULTS AND DISCUSSION

3.1. Morphology Evaluation of MgZn1−xO and MgAc/ZnAc/PVA Nanofibers. Figure 1 shows SEM images of representative nanofibers, both prior to and after calcination. Electrospinning conditions (applied voltage, needle-to-collector distance, and solution flow rates) were kept constant during the preparation of all samples; the factors affecting the morphology and diameter of the as-spun nanofibers would thus be influenced by intrinsic features of the electrospinning solution such as viscosity, surface tension, and electrical conductivity,28−30 as reported in Table 1. We observe in all cases (Figure 1, A1, B1, C1, and D1) formation of bead-free fibers with mean diameter below 300 nm, albeit with a few flat fibers which may be attributed to wet fibers flattened on impact when deposited due to reduced solvent evaporation.31 The mean fiber diameter reduces from 279 to 231 nm (Figure 1, A1 and B1) upon addition of (15 wt %) MgAc to the ZnAc/PVA solution, possibly due to a combined effect of decreased viscosity, slightly reduced surface tension, and increased electrical conductivity (Table 1) as each of these effects can lead to a reduction in fiber diameter. Further increase in MgAc concentration (30 wt %) to the precursor solution leads to an increase in nanofiber diameter to 289 nm (Figure 1, C1). Since the surface tension remains unchanged in this case, and the slight increase in conductivity would result, if at all, in a decrease in fiber diameter, we can attribute the increase in fiber diameter to an increase in solution viscosity (Table 1). The nanofiber diameter remains essentially the same at a higher MgAc (50 wt %) doping (Table 1, Figure 1, D1). In this case, the solution viscosity, surface tension, and conductivity all increase wherein the effect of the first two to increase diameter is possibly negated by the effect of increased conductivity to decrease diameter. It is also interesting to note that increasing MgAc concentration in ZnAc/PVA nanofibers leads to a broader fiber diameter distribution. We have not probed this further as the primary focus in this study is the calcined nanofibers and their properties.

Figure 2 shows high-magnification SEM (left) and TEM (right) images of the nanofiber samples after calcination. Ceramic MgZn1−xO and ZnO nanofiber morphology and average fiber diameter after calcination depend on different parameters than as-spun MgAc/ZnAc/PVA and ZnAc/PVA.
nano-fibers, in particular on removal of organic species, chemical interactions among the precursors ZnAc and MgAC, and/or crystallization behavior of the different species. We find from Table 1 and Figures 1 and 2 (A3, B3, C3, and D3) that the average fiber diameter decreases in all samples upon calcination as a result of the removal of organic components from the fibers and conversion of ceramic precursors into ceramic nano-fibers. We observe a "bead-on-a-string" type nano-particulation (Figure 2, A2) in the Mg2+-free sample (ZnO sample). Combination of SEM, XRD, and XPS results suggest that all organic species are removed from the ZnAc/PVA sample, and only ZnO nano-fibers are obtained. However, the presence of MgAc in the precursor solution leads to the formation of Mg$_{x}$Zn$_{1-x}$O and some MgO in the calcined nano-fibers. The surface of the 30 wt % MgAc sample exhibits sesame seed-like structures as a result of the formation of MgO species in the fibers (Figure 2, C2). TEM studies of calcined ZnO and Mg$_{x}$Zn$_{1-x}$O nano-fibers were conducted to visualize crystal domains in nano-fibers (Figure 2, A3, B3, C3, and D3). We observe the biggest crystal domains in the 50 wt % Mg$_{2+}$ doped sample, whereas small crystals are formed in the 30 wt % Mg$_{2+}$ doped nano-fibers sample.

Average fiber diameter reduction ratios after calcination were calculated from the ratio of the average fiber diameters before and after calcination ($d_{BC}/d_{AC}$). On the basis of this approach, the average fiber diameter reductions of the fibers are approximately 2.4, 2.1, 1.8, and 2.3 for the 0, 15, 30, and 50 wt % Mg$_{2+}$ doped nano-fiber samples. The lowest reduction was observed in the 30 wt % sample. This can be explained by the crystal types and growth direction in the fibers. As measured and calculated from the XRD results, the lattice constants of the hexagonal wurtzite crystalline ZnO and Mg$_{x}$Zn$_{1-x}$O are similar and around ($a \approx 3.25$ Å and $c \approx 5.201$ Å), but the lattice constant of cubic crystalline MgO is ($a \approx 4.21$ Å). Crystal growth direction and packing through the fiber cross section affect the fiber diameter dramatically. The c-axis of wurtzite hexagonal crystal structures of Mg$_{x}$Zn$_{1-x}$O is perpendicular to the substrate surface, as reported by Dong et al. Since the c-axis is perpendicular to the fiber axes, the lattice constant of the hexagonal wurtzite c is bigger than the cubic a; maximum diameter reduction is seen in the 30 wt % sample as a result of the maximum formation of MgO phase in the fibers. Fiber roughness increases and fibers start to fall apart after calcination at high Mg$_{2+}$ content as is seen in the 50 wt % sample (Figure 2, D2). Figure 1 (E2) shows high-resolution TEM (HRTEM) of a 30 wt Mg$_{2+}$ doped Mg$_{x}$Zn$_{1-x}$O nano-fiber sample crystal lattice image and reveals that the lattice spacing is about 0.263 nm, which is consistent with previously measured d-spacing of Mg$_{0.23}$Zn$_{0.77}$O thin film as reported by Zhang et al.

Analysis of thermal behavior and weight loss of ZnAc/PVA precursor and MgAc/ZnAc/PVA composite nano-fibers with different magnesium acetate content were performed using TGA, and the results are given in Figure 3. The exothermic peaks where the slopes change show the continued...
decomposition and combustion removal of polymer (PVA) chains, magnesium acetate, and zinc acetate precursors. All of the decomposed organic components belonging to CH₃COO⁻ group of magnesium acetate and zinc acetate, and other volatiles during the decomposition of PVA (COₓ, H₂O, etc.) were removed from the fibers until reaching a stabilization temperature, after which point no weight loss is observed. It should be noted that the stabilization temperature is the minimum temperature that is needed to remove all organic residues and decompose magnesium acetate and zinc acetate into crystalline Mg₂Zn₁₋ₓO. This temperature is around 340 °C for the ZnAc/PVA sample and about 375–380 °C for the 15, 30, and 50 wt % MgAc/ZnAc/PVA samples (Figure 3). The slope of the ZnAc/PVA sample changes dramatically, and a sudden weight loss is observed around 327 °C. This likely corresponds to the oxidation and conversion of ZnAc to ZnO with removal of compositional residues. The residual weights of the samples were about 20 wt % for all samples; the weight loss corresponds to the amount of the final production of ZnO or Mg₂Zn₁₋ₓO nanofibers after removing all organic components from the fibers.

### 3.2. Crystal Structures of MgₓZn₁₋ₓO and ZnO Nanofibers

Schematic illustration of the crystal forms of MgO (cubic), ZnO (hexagonal), and MgₓZn₁₋ₓO (hexagonal) are shown in Figure 4. Crystal structure identification and phase evaluation of MgₓZn₁₋ₓO and ZnO with different Mg concentrations (15, 30, and 40 wt %) of nanofibers calcined at 600 °C was carried out at room temperature by XRD in the spectral range between 20° and 80°, and results are shown in Figure 5. For the samples before calcination, crystalline peaks are not observed since the samples are still in the amorphous state. On the other hand, with calcination of as-spun ZnAc/PVA and MgAc/ZnAc/PVA nanofibers, crystals start to form and transform, and peaks are detected at different 2θ degrees, depending on the crystal planes of the phases.

As seen in the X-ray spectral patterns in Figure 5, the electrospun ZnO nanofibers calcined at 600 °C have hexagonal wurtzite crystal structure and give the reflection peaks located at 2θ ≈ 31.72°, 34.44°, 36.2°, 47.48°, 56.6°, 62.88°, 66.28°, 67.84°, 68.92°, and 76.7°, corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) crystal planes. These hexagonal peaks were also detected in MgₓZn₁₋ₓO nanofibers with intensity changes and a slight diffraction angle shift. In addition to these peaks, two more peaks appear in the samples with addition of magnesium and are located about 2θ ≈ 42.5° and 2θ ≈ 61.9°, corresponding to cubic MgO planes of (200) and (220). The intensities of these peaks, located in the XRD spectra, first increase with the initial increase of Mg in the fibers and then decrease with increasing Mg concentration. We suggest that this results from crystal formation and transformation from cubic MgO phase to hexagonal wurtzite MgₓZn₁₋ₓO phase. Because the surface energy of the (002) crystal plane is low and causes formation of c-axis perpendicular to the fiber surfaces, the peak intensity of (100) orientation is much stronger than that of (002) crystal plane orientation in all samples except for the 15 wt % sample. Interestingly, the intensities of the cubic MgO planes of (200) and (220) are maximum in the 30 wt % sample, which indicates that the maximum percentage of transformation to hexagonal wurtzite MgₓZn₁₋ₓO occurs in the 30 wt % sample. Lattice parameters of the samples were calculated according to Bragg’s law, and the results (a ~ 3.25 Å and c ~ 5.2 Å, respectively) are quite similar to that reported before.

### 3.3. Elemental Analysis of MgₓZn₁₋ₓO and ZnO Nanofibers

We use XPS spectra to determine chemical and bonding composition of the surface of materials by measuring the bonding energy shift of the elements in the structure. Figure 6 shows typical XPS spectra of ZnO and MgₓZn₁₋ₓO nanofibers with different Mg²⁺ doping ratios, including Mg 2p, C 1s, O 1s, and Zn 2p, and Zn 3p peaks marked on the spectra, respectively. The characteristic of C, 1s peak at 285 eV, results from the contamination of hydrocarbons on the samples from the air environment since the sample is exposed to the atmosphere after calcination. The peak at 49.3 eV is attributed to Mg–O bonding, and other peaks on the spectra at around...
10, 49.3, 88, 140, 304, 475, 497, 531, 564, 586, 978, 1020, and 1043 eV correspond to Zn 3d, Mg 2p, Zn 3p, Zn 3s, Mg KLL, Zn LMM1, Zn LMMa, O 1s, Zn LMM3, Zn LMM2, O KLL, Zn 2p3/2, and Zn 2p1/2, respectively.36 The characteristic peak of Mg 2p3/2 around 49.3 eV represents the existence of MgO, and a positive shift of this peak can be associated with the formation of Mg$_{x}$Zn$_{1-x}$O phase.24,37 High-resolution scan of this peak is shown in right panel of Figure 6.

Figure 6. XPS spectra of (a) ZnO, (b) 15 wt % Mg$^{2+}$ doped, (c) 30 wt % Mg$^{2+}$ doped, and (d) 50 wt % Mg$^{2+}$ doped Mg$_{x}$Zn$_{1-x}$O nanofibers.

Figure 7 shows high-resolution XPS traces, including Gaussian deconvolution curves, for the O 1s region for three samples. The ZnO sample shows a peak at 529.8 assigned to Zn$^{2+}$O (attributed to O$^{2-}$ ions present in wurtzite the ZnO lattice) and a higher binding energy shoulder at 531.0 due to...

Figure 7. XPS spectra of (a) ZnO, (b) 15 wt % Mg$^{2+}$ doped, (c) 30 wt % Mg$^{2+}$ doped, and (d) 50 wt % Mg$^{2+}$ doped Mg$_{x}$Zn$_{1-x}$O nanofibers.

Figure 8. Photoluminescence spectra (PL) of calcined ZnO and Mg$_{x}$Zn$_{1-x}$O nanofibers with different Mg$^{2+}$ contents: (a) visible PL spectra and (b) UV PL spectra for ZnO, 15 wt % Mg$^{2+}$ doped, 30 wt % Mg$^{2+}$ doped, and 50 wt % Mg$^{2+}$ doped Mg$_{x}$Zn$_{1-x}$O nanofibers.

Figure 8. Photoluminescence spectra (PL) of calcined ZnO and Mg$_{x}$Zn$_{1-x}$O nanofibers with different Mg$^{2+}$ contents: (a) visible PL spectra and (b) UV PL spectra for ZnO, 15 wt % Mg$^{2+}$ doped, 30 wt % Mg$^{2+}$ doped, and 50 wt % Mg$^{2+}$ doped Mg$_{x}$Zn$_{1-x}$O nanofibers.
adventitious C–O and/or oxygen vacancies in the ZnO lattice. The sample with 15% Mg shows similar features, with a small shift in the metal–oxygen peak to higher binding energy, consistent with some Mg–O. The O 1s spectra for the 30 wt % MgO shows the O 3d peak shifted to lower binding energies and an increased intensity for the higher binding energy peak.

3.4. Photoluminescence (PL) Spectra of Electrospun Mg,Zn$_{1-x}$O Nanofibers. Photoluminescence measurements of the nanofibers were conducted at room temperature to determine the effect of Mg addition to ZnO nanofibers on the band gap and microstructural changes. In the photoluminescence (PL) spectra, emission peaks in the ZnO and Mg,Zn$_{1-x}$O nanofiber samples were found at one near band edge emission (NBE) (UV PL) and one green—yellow—red emission (visible PL).

Figure 8a shows the green—yellow—red emissions (visible PL) detected around 545 nm (2.27 eV) for the samples corresponding to radiative recombination of a hole with a singly ionized oxygen-vacancy defect. Since all samples show similar emission peaks around 2.27 eV, we surmise that similar defects are formed in ZnO and Mg,Zn$_{1-x}$O nanofiber samples and defect level changes due to Mg$^{2+}$ addition. The largest intensity of visible PL peaks is observed in the ZnO nanofiber sample, indicating more oxygen vacancy defects; the intensity reduces substantially with Mg$^{2+}$ incorporation because Mg$^{2+}$ helps to get enough oxygen into nanofibers during the calcination process. Therefore, the decrease of visible PL emission with Mg addition can be attributed to reduced oxygen vacancy level in the nanofibers.

The emission peaks in the UV PL spectra for the samples were recorded at 3.28 eV (for ZnO) and 3.39, 3.37, and 3.39 eV for the 15, 30, and 50 wt % of Mg$^{2+}$ doped samples, respectively (Figure 8b). Increasing Mg$^{2+}$ concentration in ZnO nanofiber samples leads to a fundamental band-to-band transition, which results in a strong blue emission with Mg addition can be attributed to reduced oxygen vacancy level in the nanofibers.

4. CONCLUSIONS

Different content of Mg$^{2+}$ doped Mg,Zn$_{1-x}$O nanofibers were synthesized via a sol–gel electrospinning technique. Magnesium acetate (MgAc) and zinc acetate (ZnAc) were used as ceramic precursors and poly(vinyl alcohol) (PVA) as polymer carrier in the electrospinning solutions. SEM images of the fibers before and after calcination show a dramatic reduction in nanofiber diameter as a result of degradation and removal of organic residues from the fibers and conversion of ceramic precursors into ceramic nanofibers. XRD and XPS results revealed that after calcination Mg,Zn$_{1-x}$O nanofibers with a small amount of MgO in the fibers were obtained with an initial addition of MgAc in the ZnAc/PVA nanofibers. With increasing MgAc addition, the amount of MgO phase increased, producing fibers with different crystal microstructures, a range of fiber morphologies from “bead in a string” to “sesame seed” appearances, and a concomitant change in optical properties. In particular, we observed an increase and shift in photoluminescence emission and an enhancement in the band gap energy which can have implication in the use of these materials in optoelectronics.

REFERENCE


