Effect of Co Doping on Microstructures and Dielectric Properties of ZnO

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**Complete List of Authors:**
Zhao, Ye; Changzhou University
Tong, Fan; Changzhou University
Wang, Mao Hua; Changzhou University

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**Keyword:** Co-doping, ZnO, Dielectric properties, Ceramics, Nanoparticles
Effect of Co Doping on Microstructures and Dielectric Properties of ZnO

Ye Zhao  Fan Tong  MaoHuaWang

Corresponding author: MaoHua Wang
School of Petrochemical Engineering, Changzhou University, Changzhou 213164; PR China
E-mail address: 627907188@qq.com

Author 1: Ye Zhao
School of Petrochemical Engineering, Changzhou University, Changzhou 213164; PR China
E-mail address: zhaoyezhaoye111@163.com

Author 2: Fan Tong
School of Petrochemical Engineering, Changzhou University, Changzhou 213164; PR China
E-mail address: 15261163512@163.com
Abstract.

Pure and Co-doped ZnO nanoparticles (2.5, 5, 7.5 and 10 at% Co) are synthesized by sol-gel method. The as-synthesized nanoparticles are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Field emission scanning electron microscopy (FE-SEM) analysis. The nanoparticles of 0, 2.5, 5at% Co doped ZnO exhibited hexagonal wurtzite structure and have no other phases. Moreover, The (101) diffraction peaks position of Co-doped ZnO shift toward smaller value of diffraction angle compared with pure ZnO powders. The results confirm that Co ions were well incorporated into ZnO crystal lattice. Simultaneously, Co doping also inhibited the growth of particles and the crystallite size decreased from 43.11 nm to 36.63 nm with the increase in doping concentration from 0 to 10at%. The values of the optical band gap $E_g$ of all Co-doped ZnO nanoparticles gradually decreased from 3.09eV to 2.66eV with Co content increasing. Particular, the dielectric constant of all Co-doped ZnO ceramics gradually increased from \(1.62 \times 10^3\) to \(20.52 \times 10^3\), and the dielectric loss decreased from 2.36 to 1.28 when Co content increased from 0 to 10at%.

**Keywords:** Co-doping; ZnO; Dielectric properties; Ceramics; Nanoparticles
1. Introduction

In the last decades nanostructured zinc oxide (ZnO) have gained a lot of attention due to their potential applications in different areas of science and technology\cite{1}. ZnO is a versatile semiconductor having a wide band gap of 3.37 eV and large exciton energy of 60 meV which crystallizes in hexagonal wurtzite structure. In addition, ZnO semiconductor has many advantages including the nontoxicity, suitability for doping, high thermal and chemical stability, etc\cite{2}. These characteristics make this material attractive for many applications, such as solar cells, optical coatings, photo catalysts, electrical devices and gas sensors\cite{3,4}.

In electronic industry semiconductor material with high dielectric constant has many applications\cite{5-8}. For instance, material with high dielectric constant and low loss are always very essential to be used in multilayer capacitor, memory devices and integrated circuits \cite{9}. ZnO is one of the potential candidates in the field of optoelectronics due to its high excitonic binding energy depending on the dielectric constant of the materials\cite{10}. It was found that doping with different impurity atoms is one of the best ways to modify various properties of host ZnO material\cite{11-14}. Recently doped-ZnO compounds became one of the most promising materials in the field of spintronics, especially Co-doped ZnO. In spite of that, very few studies on the dielectric constant of Co-doped ZnO have been reported. Ghosh et al. \cite{15} reported a research on dielectric properties of the Co-doped nanoparticles (up to at 2%Co) prepared by the phase reaction precursor method. They found that the dielectric constant was smaller than that for undoped-ZnO materials and decreased with increasing Co doping amount. ZnO nanostructures with different morphologies and dopants were obtained using different techniques such as co-precipitation, sol-gel, hydrothermal, solvothermal, emulsion and microemulsion methods etc\cite{16-21}. Among the various methods, sol-gel is one of the most important methods to prepare the nanoparticles. For sol-gel method, it has attracted much attention because of its relatively low equipment and processing cost, easily obtainable homogeneity of precursor\cite{22}. In this work, Co-doped ZnO nanoparticles were prepared by sol-gel method and their structure and dielectric properties were also investigated.

2. Experimental

Zinc acetate dihydrate (ZnAc₂·2H₂O), Cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O] and
Citric acid monohydrate \( (C_6H_8O_7\cdot H_2O) \) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene glycol and Ammonia solution were supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd. All reagents used were analytic grade and used without further purification.

A series of Co-doped ZnO samples with 0 at%, 2.5 at%, 5 at%, 7.5 at% and 10 at% were synthesized by the sol-gel method. During this synthesis procedure, citric acid was added to 100ml of distilled water to make its pH=1.5 at 50°C under stirring. Then 8.78 g ZnAc\(_2\cdot2H_2O\) and required amounts of Co(NO\(_3\))\(_2\cdot6H_2O\) were added to dissolve. When the solution became homogeneous 10 ml of ethylene glycol was added and a sol was formed. Next, the required amount of aqueous ammonia was added to solution drop wise, and the resulting suspension was continuously stirred for about 50 min. A pink colored gel was formed which was dried at 110°C for 12 h in an oven. Then, the precursors were further calcined at 500°C for 2 h and the products were obtained. After 2.5% PVA binder addition and drying, the obtained powders was thoroughly pulverized in an agate mortar and pressed at a pressure of 30 MPa into a disk of 1.2 mm thickness and 10.5 mm diameter. Then, the disks were sintered in static air at 1000°C for 2 h and then pure and Co-doped ZnO ceramics were obtained. The silver paste was used to coat both sides of the sintered disks, followed by firing at 550°C for 15 min to form electrodes for further dielectric performance measurement.

Samples were characterized by X-ray powder diffraction (XRD; Rigaku D/MAX-YA) using Cu K\(\alpha\) radiation (\(\lambda=0.154\) nm) at the scanning rate of 5°/min in a 2\(\theta\) range from 10° to 80°. The morphology and structure of the samples were characterized by field-emission scanning electron microscopy (FESEM, JEOL JSM-6360LA, Japan). Dielectric properties were measured using a LCR meter (AT821, China).

### 3. Result and discussion

Fig.1(a) shows the X-ray diffraction patterns of pure and Co-doped ZnO nanoparticles. All those diffraction peaks can be observed at about 31.759, 34.401, 36.240, 47.521, 56.579, 62.840 and 67.921 corresponding to (100), (002), (101), (102), (110), (103) and (112) respectively, which belong to a hexagonal wurtzite structure. It is found that up to 5 at% of Co doping, there were no extra peaks which implies that Co\(^{2+}\) ion perfectly replaced Zn\(^{2+}\) ion in
the crystal matrix. Further increase of Co\(^{2+}\) (≥ 7.5 at%), another peak located at 36.82 ° which is from peak of Co\(_3\)O\(_4\)\[^{[23]}\]. It’s shows that the content of Co\(^{2+}\) (≥ 7.5 at%) is beyond the solid solubility limit of Co\(^{2+}\) in ZnO, part of Co\(^{2+}\) ions did not enter the crystalline structure of ZnO and crystallized alone forming Co\(_3\)O\(_4\) grains as indicated in the XRD pattern of 7.5 at% and 10 at% doped powder \[^{[24]}\]. Fig.1(b) shows the magnified region of (101) peak, in which the diffraction angle of Co-doped ZnO nanoparticles with various concentration shifted to smaller angle side compared with pure ZnO nanoparticles. This shifting was due to the difference in ionic radii of Co\(^{2+}\) (r = 0.065Å) and Zn\(^{2+}\) (r = 0.074Å) which cause to the change of lattice parameters\[^{[25,26]}\]. Therefore, all of the above results provides conclusive evidence for the substitution of Co ions into the ZnO lattice. In addition, the full width half maximum (FWHM) of (101) peaks increased continuously with an increase of Co doping level, which means that the crystallize size decreases with the increase of Co content. The crystallite size for all the samples was calculated using Scherrer’s formula

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

(1)

where \(\lambda\) is the wavelength of X-ray radiation, \(\beta\) is the full width at half maximum (FWHM) of the peaks at the diffracting angle \(\theta\)\[^{[27]}\]. Volume of hexagonal close packed unit cell was calculated using formula,

\[
V = \frac{\sqrt{3}}{2}a^2c = 0.866a^2c
\]

(2)

The calculated crystallite size, lattice parameters a and c and unit cell volume of all samples were shown in Table 1. Fig.2 shows variation of crystallite size with the content of Co doped into ZnO nanostructure. It can be seen that the crystallize size decreased from 43.1098 to 36.6331 nm with increasing of Co concentration.

Fig. 1. X-ray diffraction patterns of Co doped ZnO powder.

Table 1 Variation of crystallite size, lattice parameters and unit cell volume with doping concentration.

Fig. 2. Variation of crystallite size for Co doped ZnO samples.
The characteristic peaks exhibited by FTIR spectra of pure and doped ZnO nanoparticles is shown in Fig. 3. The broad absorption peaks around 3432 cm\(^{-1}\) and 1637 cm\(^{-1}\) are attributed to normal polymeric O-H stretching vibration of H\(_2\)O in Co-Zn-O lattice \(^{[28]}\). The small absorption band at 2836 cm\(^{-1}\) is assigned to C-H bonding \(^{[29]}\). Another absorption band at 1384 cm\(^{-1}\) is attributed to H-O-H bending vibrating, which is assigned to a small amount of H\(_2\)O in the ZnO nanoparticles. The relatively broad bands at around 869 cm\(^{-1}\) are assigned to the vibrational frequencies due to the change in the microstructure due to the Co incorporation into ZnO lattice \(^{[30]}\). The stretching of the Zn-O bond corresponds to the frequency at 456 cm\(^{-1}\) for pure ZnO. This peak shifts to higher frequencies: 442 cm\(^{-1}\) for 2.5 at\% Co, 438 cm\(^{-1}\) for 5 at\% Co, 431 cm\(^{-1}\) for 7.5 at\% Co and 437 cm\(^{-1}\) for 10 at\% Co. It is worth noting that these results confirm a well-established theory of vibrational modes in mixed and doped crystals, mainly, that ion substitution should result in a downward shift of the transverse optical phonon mode \(^{[31]}\).

![Fig. 3. FTIR spectra of ZnO doped with different content of Co: 0%; 2.5%; 5%; 7.5%; 10%.](https://mc06.manuscriptcentral.com/cjc-pubs)

Fig. 3. FTIR spectra of ZnO doped with different content of Co: 0%; 2.5%; 5%; 7.5%; 10%.

Fig. 4 represents the FE-SEM and size distribution images of pure and Co-doped ZnO nanoparticles. From the images we can observe that the as-synthesized samples are consisted of many irregularly aggregated spheroid-like nanoparticles. The average particle size of all Co-doped ZnO nanoparticles gradually decreased from 100 nm to 50 nm when Co content increased from 0 to 10 at\%, confirming that Co doping restrained the growth of nanoparticles, which is consistent with the former XRD results.

![Fig. 4. FE-SEM images and size distribution images of (a)(b) pure ZnO; (c)(d) 2.5 at\%; (e)(f) 5 at\%; (g)(h) 7 at\%; and (i)(f) 10 at\% Co-doped ZnO.](https://mc06.manuscriptcentral.com/cjc-pubs)

Fig. 4. FE-SEM images and size distribution images of (a)(b) pure ZnO; (c)(d) 2.5 at\%; (e)(f) 5 at\%; (g)(h) 7 at\%; and (i)(f) 10 at\% Co-doped ZnO.

The UV-vis diffuse absorption spectra of pure and doped ZnO nanoparticles in the range of 200–800 nm are shown in Fig. 5(a). The onset of the absorption spectrum of pure ZnO appears at UV area which matches well with the intrinsic band-gap of ZnO. In addition, it can be seen that the absorption onset extended towards the higher wavelength for Co-doped ZnO samples, and it increases with the increasing Co doping concentration. Among all the samples, the largest red-shift can be found in 10 at\% Co-doped ZnO sample.

In order to calculate the band gap energies of pure and Co-doped ZnO, the plots of transformed Kubelka-Munk function versus photon energy are displayed in Fig. 5(b). The
band gap energy can be estimated by Beer-Lambert equation:

$$(\alpha hv)^2 = A(hv - Eg)$$

(3)

Where $\alpha$, $hv$ and $A$ are absorption coefficient, photon energy and a constant, respectively, and can be taken as the intercept of the linear part of Beer-Lambert equation at $(\alpha hv)^2 = 0$. The band gap of the Co-doped ZnO nanoparticles is observed to be 3.09-2.66 eV. The incorporation of Co is accompanied by a systematic low-energy shift of the band gap. Indicating that the Co doping can narrow the band gap of ZnO effectively.

Fig. 5. (a) Optical diffuse absorbance and (b) Optical band-gap $E_g$ calculated of pure and Co-doped ZnO nanoparticles.

Dielectric properties of nanomaterials depend on many factors such as temperature, frequency of the external applied electric field, chemical composition, grain structure, the sample preparation techniques etc. Dielectric loss ($\tan \delta$) represents a dissipated energy in a dielectric system. The dielectric constant ($\varepsilon$) was determined from the following equation:

$$\frac{14.4Cd}{D^2}$$

(4)

where $C$ is the capacitance, $d$ and $D$ are the thickness and diameter of the ceramic disc.

Fig.6 shows the temperature dependence of the dielectric constant and dielectric loss for pure and Co-doped ZnO ceramic samples at the frequency of 1kHz. The dielectric constant and dielectric loss increased continuously with increasing temperature, although the rate of these enhancements was not the same. From Fig.6 (a), it is obvious seen that the ceramic of Co-doped ZnO shows higher dielectric constant compared with the ceramic of pure ZnO. Furthermore, the 10at% co-doped ZnO ceramic exhibits the highest dielectric constant. Variation in dielectric loss with temperature at 1kHz for pure and Co-doped ZnO samples are shown in Fig.6 (b). It is also noticeable that dielectric loss is maximum when there is no Co-doping while it decreases when Co is incorporated into ZnO lattice. Thus, the dielectric constant of all Co-doped ZnO ceramics gradually increased from $1.62 \times 10^3$ to $20.52 \times 10^3$, and the dielectric loss decreased from 2.36 to 1.28 when Co content increased from 0 to 10at% at the temperature of 130 °C. The increase in dielectric properties is related to the density of the internal structure of ZnO. Oxygen vacancy and Zinc vacancy are the intrinsic defect of n-type ZnO, vacancies combined with small amounts of $Co^{3+}$ would stabilize the wurtzite structure of ZnO, which could reduce the number of vacancies. The increase of the
content of Co-doped ZnO nanoparticles enhances the internal densification of ZnO nanoparticles, resulting in the better dielectric properties.

Fig. 6. Temperature dependence of dielectric properties for pure and Co-doped ZnO ceramics after sintering at 1000°C: (a) dielectric constant, and (b) tan δ.

4. Conclusions

In summary, pure and Co-doped ZnO nanoparticles have been produced by sol-gel method. The nanoparticles of 0, 2.5, 5at% Co doped ZnO exhibited hexagonal wurtzite structure without any other impurities phases, confirming that Zn ions were well replaced by Co ions in the ZnO crystal lattice. However, secondary phase Co$_3$O$_4$ appeared when the dopant concentration up to 7.5at%. The calculated average crystalline size decreases from 43.11 nm to 36.63 nm when Co content increased from 0 to 10 at%. In addition, the values of the optical band-gap $E_g$ of all Co-doped ZnO nanoparticles gradually decreased from 3.09eV to 2.66eV with Co content increasing. A significant enhancement in dielectric constant resulted from the incorporation of Co ions in ZnO lattice while an opposite trend was observed for dielectric loss. The values of dielectric constant and dielectric loss were found to improve with the increasing temperature for all samples at the same frequency. Conclusively, the values of all Co-doped ZnO ceramics dielectric constant gradually increased from $1.62 \times 10^3$ to $20.52 \times 10^3$, and the dielectric loss decreased from 2.36 to 1.28 when Co content increased from 0 to 10at% at the frequency of 1kHz and the temperature of 130°C.

Acknowledgement:

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5. References


Table 1 Variation of crystallite size, lattice parameters and unit cell volume with doping concentration.

<table>
<thead>
<tr>
<th>Co concentration (wt.%)</th>
<th>FWHM</th>
<th>Crystallite size (nm)</th>
<th>Lattice a Parameter (Å) c</th>
<th>Unit cell volume (Å³)</th>
</tr>
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<tr>
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<td>3.2523</td>
<td>5.204</td>
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<tr>
<td>2.5</td>
<td>0.203</td>
<td>41.1963</td>
<td>3.2506</td>
<td>5.2096</td>
</tr>
<tr>
<td>5</td>
<td>0.204</td>
<td>40.9945</td>
<td>3.2512</td>
<td>5.2068</td>
</tr>
<tr>
<td>7.5</td>
<td>0.219</td>
<td>38.1845</td>
<td>3.2529</td>
<td>5.2096</td>
</tr>
<tr>
<td>10</td>
<td>0.273</td>
<td>36.6331</td>
<td>3.2506</td>
<td>5.2096</td>
</tr>
</tbody>
</table>
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