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Structural and optical properties of Co-doped ZnO nano-ampoules synthesized by co-precipitation method

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ABSTRACT

Pure ZnO and Co-doped ZnO ($Zn_{0.98}Co_{0.02}O$) nano-powder have been synthesized by co-precipitation method. Detailed XRD analysis shows that prepared nanocrystalline samples have single phase, wurtzite structure. Relative increment in (002) Bragg peak has been observed due to one dimensional growth in Co ions doped ZnO. The SAED pattern and TEM images confirm the single phase, wurtzite structure and nano-ampoule shape of Co-doped ZnO. In UV–vis measurements, the absorption edge is blue shifted with Co-doping in ZnO lattice. Tuned band gap of ZnO with Co-doping offers its potential application in solar cells.

1. Introduction

ZnO is a wide band gap energy (3.37 eV) semiconductor with high excitation binding energy (~60 meV) which is a promising material for transitional metal (TM) doping. TM doping in metal oxides assists in tuning their structural and optical properties. Numerous research groups have studied the effect of TM doping in ZnO [1–3]. Metal oxides (e.g. ZnO) with different morphologies have been synthesized via different physical deposition methods (like chemical/physical vapour deposition, pyrolysis, thermal reduction method) and wet chemical methods (like sol-gel, hydro-thermal, co-precipitation methods) [4–9]. Various research groups have been studied Co-doped ZnO nano-particles which were spherical in nano-structure nature [10–13]. One dimensional (1-D) structures of metal oxide are very effective in thin film solar cells due to large surface area and high electron scavenging rate [14]. Therefore, appropriate synthesis process is much required which must be low cost, facile, and room temperature solution processed bench-top technique. Among above mentioned techniques, co-precipitation technique provides a vital solution for this challenge. In present study, we have synthesized pure ZnO and 2% Co-doped ZnO nanocrystals by co-precipitation method. The structural, morphological and optical properties have been investigated. Co-doped ZnO with 1-D novel nano-ampoule structure can be promising semiconductor for application as a photo-anodic material in thin film solar cells.

2. Experimental section

Appropriate proportion of analytical grade metal nitrates [$Zn(NO_3)_2$ $6H_2O$ and $Co(NO_3)_2$ $6H_2O$] powders were thoroughly mixed to prepare an homogenous 0.11 M solution in 150 ml DI water (Sol A). Also, a 1 M homogenous solution of LiOH H_2O was prepared by dissolving it into DI water under continuous stirring (Sol B). The Sol B was added drop wise into Sol A (~20–25 drops per minutes) under vigorous stirring until pH ~ 7. It was then allowed to relax up to next three hours. The precipitate was separated by filtration and washed repeatedly with DI water, ethanol. Then, it was dried at 120 °C for 12 h in hot air oven. The obtained product were ground thoroughly and further annealed in air for 6 h at 200 °C followed by grinding to get $Zn_{1-x}Co_xO$ nanocrystals. The whole synthesis process was repeated without adding Co precursor for synthesis of pure ZnO nanocrystals.

The XRD patterns of $Zn_{1-x}Co_xO$ samples were recorded by X-ray diffractometer (D-8 Advance Bruker AXS) with Cu Kα radiation. TEM measurements were done with Technai G^2 S-Twin FEI. UV-vis spectra were recorded using UV-vis spectrometer (Perkin Elmer instrument, lamda 25, USA).

3. Result and discussions

3.1. XRD

XRD patterns of the prepared nanocrystals are shown in Fig. 1a. Observed Bragg peaks have been indexed using the standard JCPDS file for ZnO (JCPDS #36-1451). Bragg peaks corresponding to Co

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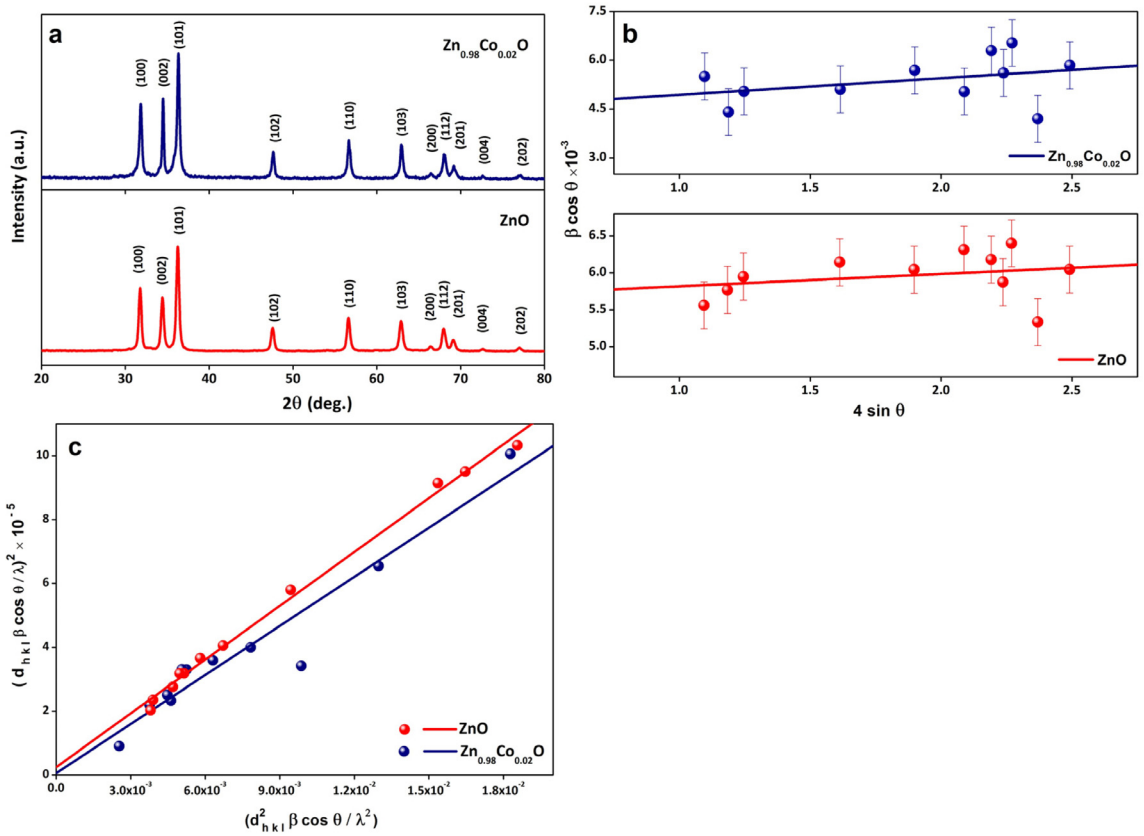

Fig. 1. (a) XRD patterns of $Zn_{1-x}Co_xO$ (x = 0, 0.02) nanocrystals. (b) Williamson-Hall plots of $Zn_{1-x}Co_xO$ (x = 0, 0.02) nanocrystals, (c) size-strain plots of $Zn_{1-x}Co_xO$ (x = 0, 0.02) nanocrystals.

cluster, secondary phase or any other impurity have not been detected within the sensitivity limit of XRD which suggests single phase, wurtzite structure of prepared samples.

Table 1 comprises the calculated value of lattice parameters, volume of unit cell, interplanar spacing (d values), c/a ratio, degree of distortion, bond length and bond angles. Analyzed XRD data reveal that lattice constants (*a*, *c*) decrease with Co ion doping concentration whereas values of u, *c/a*, and R remain almost constant with doping of Co ions in ZnO lattice. In tetrahedral arrangement, the ionic radii of Zn^{2+} and Co^{2+} are 0.60 and 0.58 Å, respectively.

Table 1
Analyzed values of lattice parameters, interplanar spacing, bond lengths, bond angles, density, volume of unit cell, size and strain for $Zn_{1-x}Co_xO$ samples.

Parameters	ZnO	$Zn_{0.98}Co_{0.02}O$
a (Å)	3.25042	3.24374
c (Å)	5.20376	5.19261
c/a	1.60095	1.60081
U	0.38005	0.38008
R	1.02002	1.02010
d (100)	2.81495	2.80916
d (002)	2.60295	2.59447
d (101)	2.47591	2.47077
"b" $d_{Zn\text{-}O}$ (Å)	1.97771	1.97359
"b_1"	1.97771	1.97359
α (O_a-Zn-O_b) (°)	108.39711	108.39251
β (O_b-Zn-O_b) (°)	110.52364	110.52806
V (Å^3)	47.61184	47.31464
Crystallite size (nm) (Scherrer formula)	23.30	27.48
Crystallite size (nm) (W-H plot)	24.53	31.30
Crystallite size (nm) (size-strain plot)	24.70	27.07
Strain (size-strain plot)	3.1506×10^{-3}	1.5914×10^{-3}
Strain (W-H plot)	1.6628×10^{-4}	0.6998×10^{-4}

[15] Decrease in *a* and *c* is attributed to smaller ionic radius of Co^{2+} than Zn^{2+}. Unit cell volume has been decreased with doping of Co ions due to decreased lattice constants. The d-values of (100), (002) and (101) planes decrease with doping of Co ions which is due to change in bond length and bond angles. The strain developed in lattice is responsible for change in interplanar spacing. In Co doped ZnO sample, the increased relative intensity of (002) peak in XRD pattern suggests the specific one dimensional growth of nanostructure.

Average crystallite size 'D' and lattice strain 'ε' were calculated from Debye-Scherrer's formula, Williamson-Hall (W-H) plot (Fig. 1b) and size-strain plot (Fig. 1c). The increase in crystallite size with Co ions doping can be attributed to slightly smaller ionic radius of Co^{2+} (0.58 Å) than Zn^{2+} (0.60 Å).

3.2. TEM

In TEM analysis, prepared nanostructures are 1-D in shape with smooth surfaces (Fig. 2). The average length of 1-D nanostructure is ~165 nm ranging from 75 nm to 205 nm. The average minimum width and maximum width of nanostructure are ~5–6 nm and ~25–32 nm, respectively.

The d-values calculated from indexed-SAED are in good agreement with d-values obtained from XRD analysis. SAED analysis shows polycrystalline nature and confirms the wurtzite structure of prepared sample.

3.3. UV–Vis measurements

Room temperature UV-Visible spectra were recorded by dispersing prepared samples in DI water and using DI water as