Structural and Optical Studies of Ni-doped ZnO

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Abstract: An investigation of structural and optical properties of Ni doped ZnO nanoparticles, prepared by modified sol-gel process at different annealing temperature. X-ray diffraction study reveals that there is no secondary phase formation and confirmed about its space group $P6_3mc$. Rietveld refinement of X-ray data shows decrease in c/a ratio of ZnO with Ni doping. Optical bandgap decreases with Ni doping for both the temperature and decrease most with higher temperature from ~ 3.21eV to ~ 3.18 eV. Ni doping cause formation of Urbach tails which increases with Ni doping and thereby reduces the bandgap.

INTRODUCTION

ZnO, a prominent and popular transition metal oxide has a wide band gap (3.37 eV) and large exciton binding energy of 60 meV[1]. It is a promising material for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region. Moreover, due to its good conducting properties, ZnO has also been investigated as a transparent conducting and piezoelectric material for use as electrodes, catalysts and sensors[1]. Changes in optical, electrical, and magnetic properties may occur when dopants are added to a wide band gap semiconductor. Thus, doping a certain element into ZnO may be used to optimize optical, electrical, and magnetic properties[2].

Ni is an important dopant in ZnO and has been discussed in literature as probable dilute magnetic semiconductor. However, contradictory results provide an unclear scenario. Ni^{2+} (ionic radius ~0.69Å) is of same valence state and similar size as Zn^{2+} (~0.74 Å) [2]. Hence, Ni^{2+}may replace Zn^{2+} with ease in the ZnO lattice. Here we report for structural and optical investigation of Ni doped ZnO using modified sol-gel synthesis. Decreases in Optical bandgap for Ni doped samples annealed at different temperature 450°C & 600°C were observed. It shows wide band gap change from ~3.18 to ~3.22eV.

EXPERIMENTAL

Ni doped ZnO of chemical formula $Zn_{1-x}Ni_xO$ (x=0, 0.01, 0.03) (hereafter called Z0, ZN1 and ZN3 respectively) powders, were synthesized usingmodified sol-gel method. ZnO (Alfa Aesar, purity 99.99%) powder was dissolved in appropriate amount of diluted HNO_3 (Alfa Aesar, purity 99.99%). Stoichiometric solutions of nickel nitrate for nickel precursor was prepared in different beakers. Dopant solutions was mixed with parent solutions separately for different concentration of nickel (x= 0.01, 0.03). The resultant solution was stirred for ~3h at room temperature.A mixture of ethylene glycol and citric acid 1:1 molar ratio was added and followed by vigorous stirringat ~70°C temperature on a hot plate[3]. A gel was formed after considerably amount of time as a result of slow evaporation of the solvent.Cations get attached to polymer chains formed from the monomers of citric acid and glycerol. The gels were later burnt in open air inside a fume hood[3]. The burnt powderswere ground carefully.For decarburization and denitrification,powders were heated at 450 °C for 6 h.Powder x-ray diffraction was performed using a Bruker D2

PhaserX-ray Diffractometer to confirm the phase purity and structure of the sample. The optical reflectance was collected by UV-VIS-NIR Shimadzu (UV-3600).

RESULTS AND DISCUSSION

Structural properties of the samples were investigated using XRD at room temperature as shown in Fig. 1[a, b].This reveals a hexagonal wurtzitestructure (space group $P6_3mc$) of ZnO. No impurity peaks is observed of Ni and its oxides except minor peak of zinc blend.

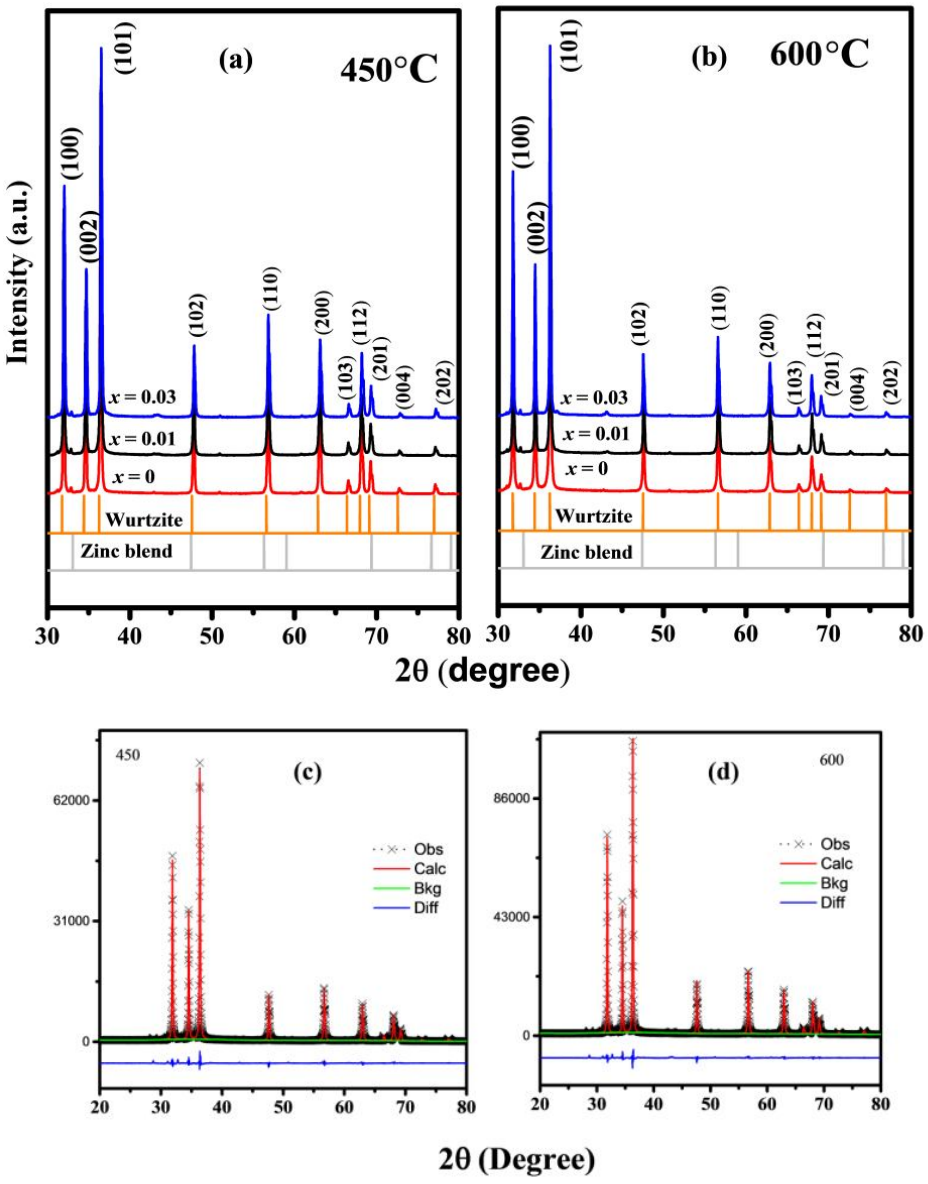

Figure 1: (a), (b) XRD pattern of ZnO and Ni doped ZnO **for x= 0.01, 0.03** annealed at 450°C & 600°C

(c), (d) Rietveld fitting using GSAS software samples annealed at 450°C & 600°C

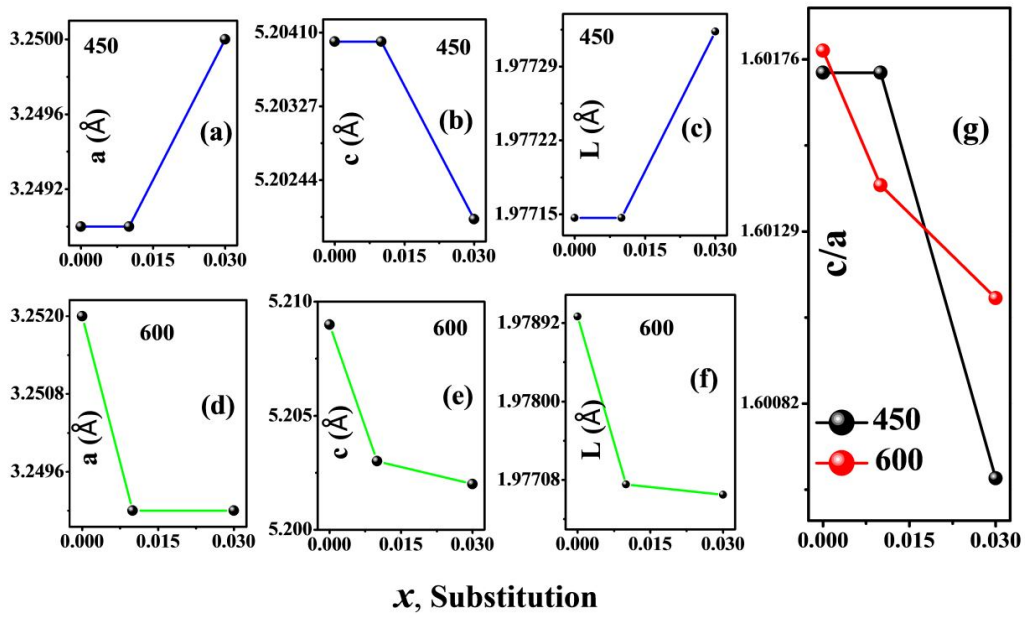

Figure 2: (a), (b), (d) and **(e)** obtained Lattice parameters a and c using GSAS software at 450°C & 600°C respectively

(c), (f), (g) bond lengths and c/a ratio at 450°C & 600°C respectively

Lattice parameters were estimated using GSAS software by Rietveld refinement as shown in Fig.2 [a, b, d, and e].Lattice parameter a (Å) increasesand c (Å) decreases while negligible change in bond length observed for 450°Cannealed samples. Whereas samples annealed at 600°Cshow decrease in lattice parameter a and c while bond lengthsdecreases from 1.978 (Å) to 1.977 (Å) withNi doping asshown in Fig.2 [f].

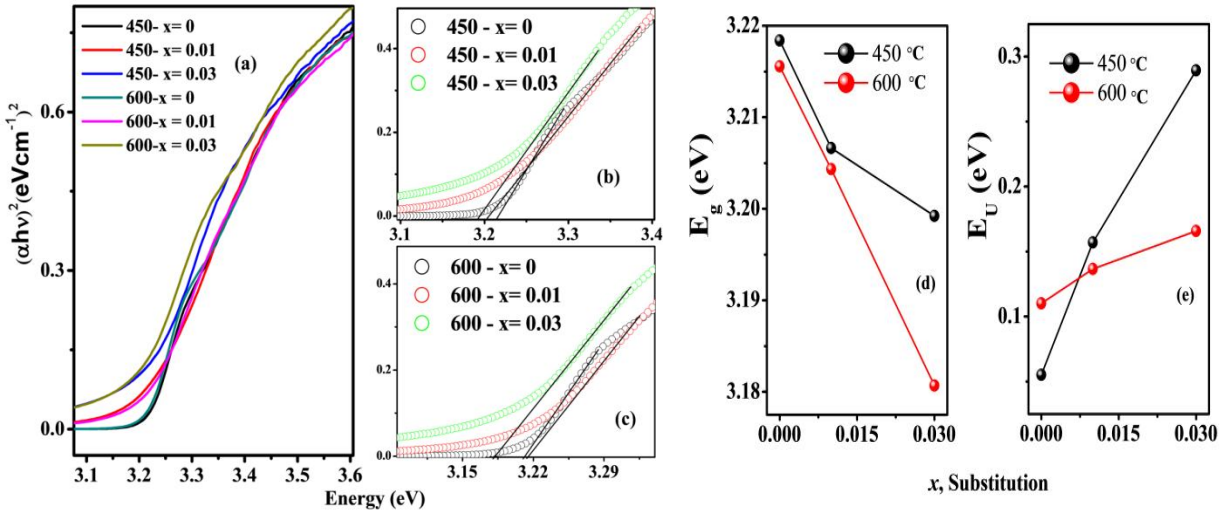

Figure 3: KubelkaMunk plot **(a)** x=0, 0.01 & x=0.03 at 450 and 600 annealed temperature and **(b), (c)** Optical energy bandgap estimation using Tauc plot relation respectively**(d),(e)** bandgap and urbach energy Vs x, substitution

From reflectance data bandgap is estimated using Tauc relation, $(\alpha h\nu)1/n=\beta(h\nu - Eg)$, where, α is absorption constant, β is band tailing parameter, Egis energy of the optical band gap and n is power factor of transition mode[4].The band gap values were obtained by extrapolating the linear part of the curve obtained between $(\alpha h\nu)^2$ and

$h\nu^5$(Fig. 3 (a, b and c)). Bandgap decreases with Ni doping and decreases most at 600°C. The decrease in the band gap may be due to the sp-d exchange interactions between the band electrons and the localized d electrons of the substituted divalent ions i.e. indication of strong exchange interaction present between d electron of Ni, and the s and p electrons of host matrix. Ni^{2+} ions exist in an octahedral crystal field in the divalent valency state without changing the Wurtzite crystal structure of ZnO[6,7].Urbach energy estimated using relation$\alpha(h\nu)= \alpha_0.\exp(h\nu/E_U)^5$. It increases from ~55 meVto ~300 meV for 450°C and ~110 meV to ~150 meV. This increase in E_U may be due to formation of defect states which result in reduction of bandgap.

CONCLUSION

Ni doped ZnO nanoparticles were successfully synthesized using the modified sol-gel method. XRD confirms successful incorporation of Ni ions inZnO lattice.Rietveld refinement shows that with Ni doping lattice parameter 'a' decreases and 'c' increases for 450°c annealed samples whereas both the lattice parameter 'a' and 'c' decreases for 600 annealed samples. Bond length increases for 450 °C annealedsamples but decreases for 600°C annealed samples. Bandgap decreases with Ni doping for both the annealing temperature and decreases most with 600°C annealed samples. Increase in Urbach energy confirms band formation between valance band and conduction band which cause reduction of bandgap. We can conclude there are more possibilities of energy splitting, reduction in bond length and increase in bond angle respectively for higher annealed samples. The wide band gap observed for both annealed samples reveals that the obtained Ni-doped ZnO samples are promising candidate materials to fabricate nanoscale optoelectronic devices. The decreasing Bandgap also shows it can be used a good photocatalytic material.

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