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# Study and Characterization of Li and Co, Co-Doped ZnO Micro Structures

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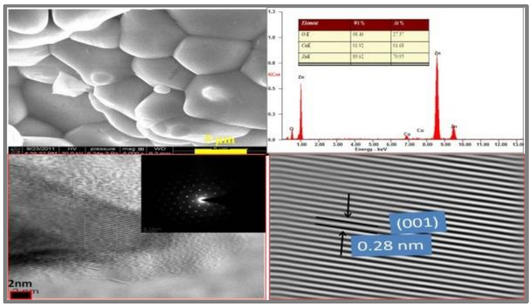
## ABSTRACT

*We report on the structural and morphological study of Li and Co codoped ZnO powder by solid state reaction route. X-ray diffraction studies show Li and Co codoped ZnO powder sample is phase pure and is in hexagonal wurtzite structure. Transmission electron microscopy and selected area electron diffraction (TEM and SAED) also confirms the wurtzite structure of Li and Co codoped ZnO powder sample.*

### Graphical Abstract



### Highlights:

- Li and Co codoped ZnO powder samples are synthesized by solid state reaction method.
- XRD patterns reveal that the ZnO powder samples crystallize in hexagonal wurtzite structure.
- Shift in the peak position of high intense peak of Li, Co codoped ZnO powder indicates the substitution of Li and Co in ZnO.
- Scanning Electron Microscope (SEM) images reveals that Li, Co codoped ZnO powder has a spherical structured particle.
- HRTEM and SAED studies of Li, Co codoped ZnO powder sample revealed phase pure and is in wurtzite crystal structure

**Keywords:** ZnO, Codoping, p-type ZnO, XRD, HRTEM, SEM, EDS, SAED, DMS

## INTRODUCTION

ZnO is one of II-IV group semiconductors and it is one of the most important material candidates for ultraviolet light emitting diodes and laser diodes because of its direct wide band gap ~ 3.37 eV and relatively large exciton binding energy (~ 60 meV) compared to GaN (25 meV) and ZnSe (22 meV) at room temperature [1]. The exciton binding energy (60 meV) is more than room temperature thermal energy (~25 meV) [2]. This means that the excitons can survive even at and above room temperature and can ensure an efficient emission at room temperature. Other favorable aspects of ZnO include low power threshold for optical pumping, radiation hardness and chemical stability leading to many opportunities for wet chemical etching. Together, these properties of ZnO make it an ideal candidate for a variety of devices ranging from sensors through to ultra-violet laser diodes and nanotechnology-based devices such as displays. In addition to this the band gap of ZnO can be tuned easily from 2.7 eV to 7.0 eV by alloying with MgO and CdO [3]. However, the fabrication of these devices still suffers from the lack of stable *p*-type ZnO **[**4]. The quest for stable *p*-type ZnO is a challenging one because the electronic and optical properties of ZnO are very sensitive to minute concentrations of dopants, impurities, and to microscopic perturbations of the lattice [5].

ZnO is a natural n-type semiconductor because of its native defects such as oxygen vacancies and zinc interstitials [6]. Hence the growth of *p*-ZnO is a highly challenging problem. All possible p-type dopants, such as, group-V elements [N, P, As, Sb], group-I and IB elements [Li, Na, K, Ag, Cu], have been tried to realize p-type conduction [7] and UV-electroluminescence in ZnO. Nitrogen substitution at the oxygen site in ZnO appears to be promising for p-type conduction and many groups have reported room temperature electroluminescence from N doped ZnO based homo junctions. P, As and Sb also seem to be good *p*-type dopants [8]. Among group I elements, theoretically, Li possesses shallow acceptor levels [9]. However, no electroluminescence is achieved from Li substituted ZnO based homo junctions. In contrary to theoretical prediction, it was observed experimentally that Li doping in ZnO increases the resistivity drastically to several orders and makes it insulating. This is because Li being a small ion can easily occupy the interstitial positions rather than the substitutional sites[10]. Thus, stabilizing Li in the ZnO lattice as an acceptor dopant and the growth of low resistive and, stable p-type ZnO still remains a challenging problem [11]. Donor-acceptor codoping method is believed to be promising, because it will enhance the acceptor solubility limit and raise the acceptor in to a shallow level [**4, 10]**. Recently Shubra *et.al.*, has reported a dramatic decrease in the bulk resistivity of Ni doped ZnO. This was attributed to the impurity d-band splitting of Ni ion in the tetrahedral crystal field of ZnO[12]. Recent experimental and theoretical reports show that incorporation of Li in transition metal (TM) ion doped ZnO will stabilize the ferromagnetic ordering thereby increase the Curie temperature[13-16]. However, sufficiently less interest is shown to see what happens to the stability of p-type conduction when a TM ion is incorporated in Li doped ZnO lattice. Recently E. S. Kumar *et. al*., has succeeded in achieving the stable and low resistive *p*-type conduction in ZnO by codoping with Li and Ni [**9, 13, 17]**.So in this we present the initial studies of the synthesis of Li and Co codoped ZnO powder by solid state reaction method. X-ray diffraction studies show that Li, Co codoped ZnO powder has phase pure and is in hexagonal wurtzite structure. High resolution transmission electron microscopy (HRTEM) studies show Li, Co coded ZnO powder is in wurtzite structure and EDS studies revealed around ~1.7 At% of Co is incorporated in Li, Co codoped ZnO powder samples.

## MATERIALS AND METHODS

**Synthesis of Li, Co codoped ZnO targets:** 2 mol % Li and 2 mol % Co codoped ZnO targets were prepared using conventional solid-state reaction method. ZnO, $Li_2CO_3$ and $Co_3O_4$ were used as starting materials for synthesising the Li and Co codoped ZnO targets. The initial materials were weighed, mixed in appropriate amounts and ground for 1h then calcinated at 1000°C for 12 h. the calcinated material was ground for 1h and made in the form of disc shaped pellet with a diameter of 12mm and sintered at 1000°C for 12 h. This sintered pellet was used as a target material for the growth of thin films using pulsed laser deposition (PLD). The morphological analysis was carried out using field emission scanning electron microscopy (FESEM, FEI, Inspect F). Transmission Electron microscopy (TEM) and High Resolution TEM (HRTEM) images, and selected area electron diffraction patterns (SAED) were recorded on an FEI Tecnai TF-20 twin operating at 200 kV. Structural properties were investigated using X-ray diffraction (XRD) using Panalytical XRD unit in θ-2θ mode.

## RESULTS AND DISCUSSION

**X-ray diffraction (XRD) of Li and Co codoped ZnO powder:** Figure 1 shows XRD of 2 mol% Li and 2 mol % Co codoped ZnO powder (Li, Co: ZnO) and undoped ZnO powder.

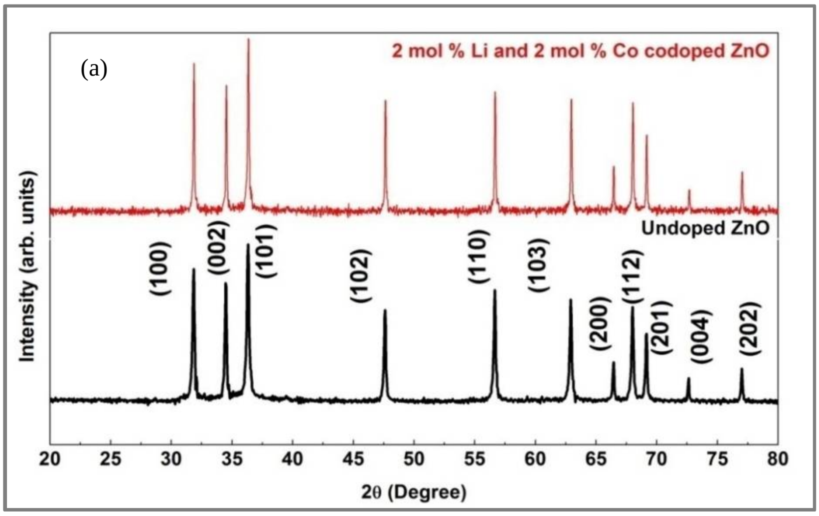


**Figure 1(a).** XRD patterns of Li,Co: ZnO powder and undoped ZnO powder.

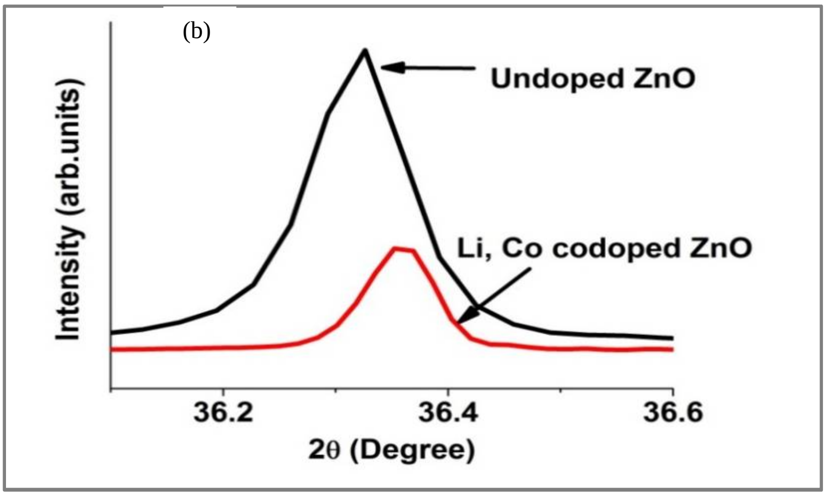


**Figure 1(b).** Magnified view of (101) peak of both undoped ZnO and codoped ZnO.

The XRD patterns of Li, Co: ZnO match with that of bulk undoped ZnO. XRD analysis reveals that Li, Co: ZnO crystallizes in a hexagonal wurtzite structure. Peaks corresponding to LiO, metallic Co and CoO were not observed in the XRD pattern of Li, Co: ZnO. In addition to this, high intensity peak (101) position of Li, Co: ZnO material was shifted towards higher angle side. This shift may be due to decrease in the d- spacing due to the difference in the ionic radii of $Li^+$ ( 0.60Å), and $Co^{2+}$ ( 0.72Å) which are smaller than the ionic radius (0.74Å) of $Zn^{2+}$[18].This clearly suggests that Li and Co have been substituted at the Zn site without segregation.

**FESEM images of undoped ZnO powder and Li and Co codoped ZnO powder:** Figure 2a and b shows a comparison of FESEM images of undoped ZnO powder and Li and Co codoped ZnO powder under identical conditions. Doping of Li and Co in ZnO resulted in a dramatic change in morphology of ZnO powders. As shown in Fig. 1a, undoped ZnO powder shows a spherical particle and their approximate size 100 nm. However, doping of Li and Co in ZnO changes the morphology from nanostructures to micron sized particles as shown in fig 2b. Increase in the particle size may result of doping and agglomeration. It is well known that doping has a strong influence on the morphology of the ZnO nanostructures.

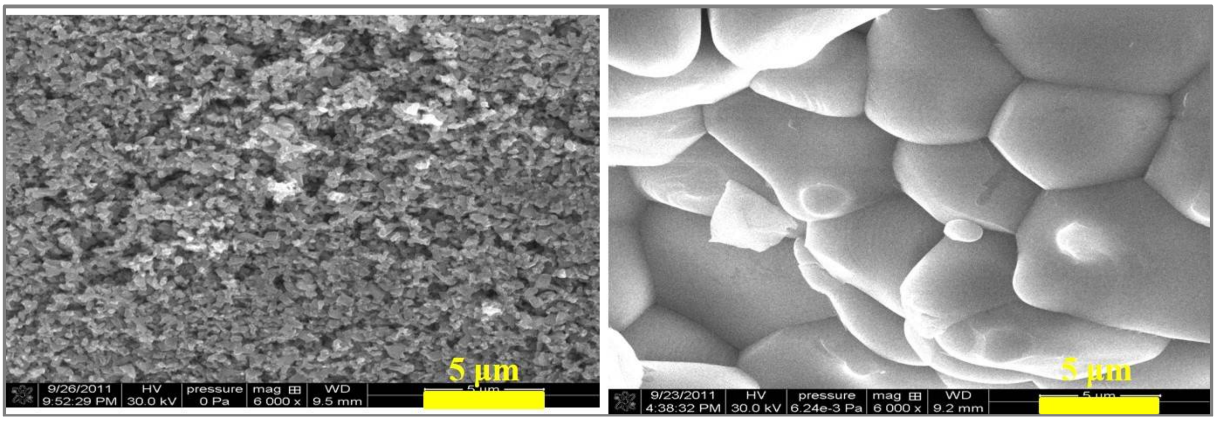


**Figure 2**. FESEM images of (a) undoped ZnO powder and (b) Li and Co codoped ZnO powder.

**Energy Dispersive x-ray spectroscopy (EDS) of Li, Co: ZnO powder:** Figure 3 shows the EDS spectrum of Li, Co: ZnO powder. The EDS spectrum shows that only the expected elements are present in the as prepared material. Elemental weights of Zn, O and Co in Li, Co: ZnO are found to be 70.95 *At* %, 27.37 *At* % and 1.68 *At* % respectively. Li could not be detected by EDS spectrum as it cannot produce x-rays.

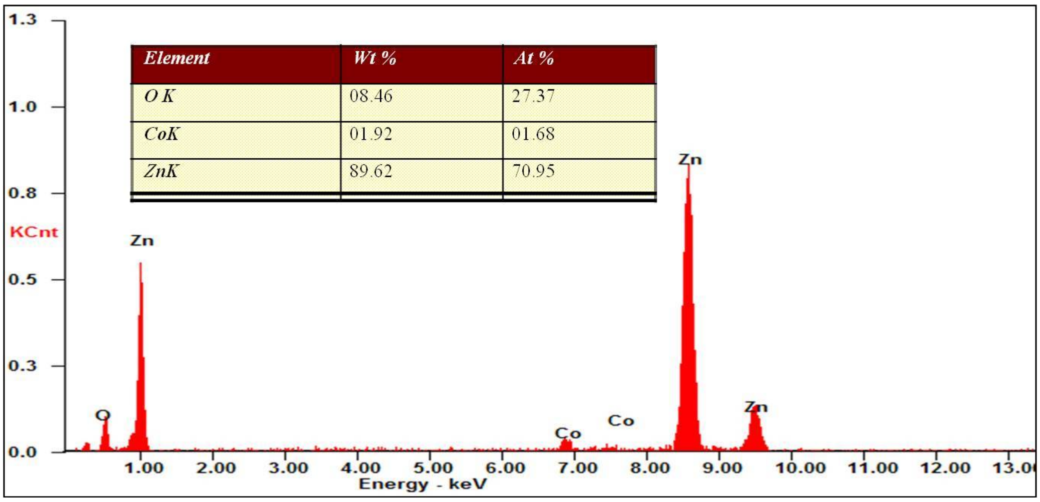

| *Element* | *Wt %* | *At %* |
|---|---|---|
| *O K* | 08.46 | 27.37 |
| *CoK* | 01.92 | 01.68 |
| *ZnK* | 89.62 | 70.95 |

**Figure 3.** EDS spectrum of Li, Co: ZnO powder and inset shows the elemental composition of Li, Co: ZnO.

**Transmission electron microscopy (TEM) studies on Li, Co codoped ZnO powder:** Figure 4(a) The TEM image of Li, Co: ZnO powder, (b) Lattice fringes of Li, Co: ZnO powder and inset of fig 4 (a) is the selected area electron diffraction (SAED) pattern of Li, Co: ZnO powder. From TEM image, the d-spacing of the crystal plane was found to be 0.28 nm, which corresponds to the d- spacing of (001) plane of ZnO [19] hence it is clear that there was no secondary phase and no metallic Co clusters, present in the material. The Selected area electron diffraction pattern (SAED) of Li, Co: ZnO as shown inset of figure 4(a) shows a highly crystalline nature of the as prepared Li, Co: ZnO powder.

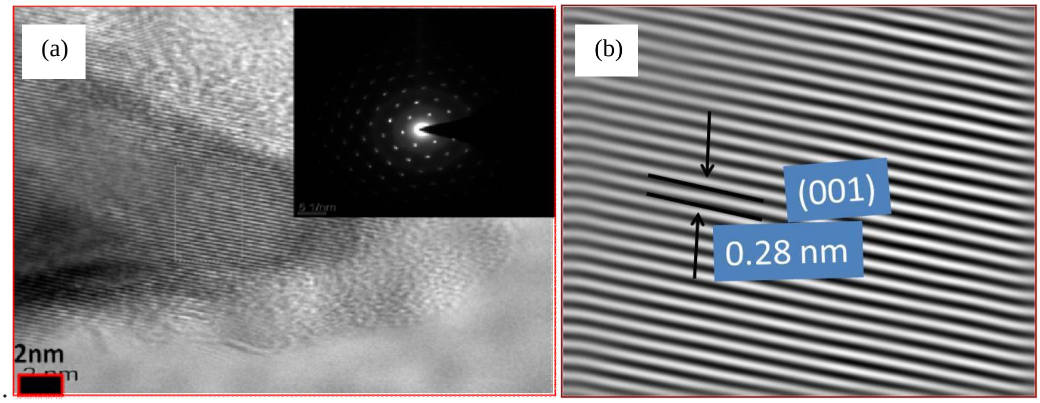


**Figure 4.** Shows the TEM image of Li, Co: ZnO powder.

## APPLICATION

Li, and Co codoped ZnO powder samples can be find potential applications of dilute magnetic semiconductors as both Li and Co are doped ZnO. Doping of Li and Co in ZnO produces room temperature ferromagnetism. Also Li and Co cooping in ZnO can also contribute whole conduction in ZnO and acts a p-type semiconductor. Producing p-type ZnO is a challenging task and Li, Co codoped ZnO will find a potential application the field of optoelectronics to produce intense UV light emission diodes.

## CONCLUSION

Li and Co codoped ZnO powder samples were successfully synthesized by solid state method. X-ray diffraction, HRTEM and SAED studies of Li, Co codoped ZnO powder sample revealed phase pure and is in wurtzite crystal structure. Morphological studies shows a spherical structures and EDS studies shows 2 wt% of cobalt in Li, Co codoped ZnO powder samples.

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