

Structural Properties of $Zn_{1-x}Li_xO$ ($0.10 \leq x \leq 0.70$)

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ABSTRACT: The phase composition and structural transformations of Li-doped Zinc oxide, $Zn_{1-x}Li_xO$ ($0.10 \leq x \leq 0.70$) which was synthesised by solid state reaction technique was investigated. The sample was calcinated at 1073 K for 10 hours after which the pelletised samples were sintered at 1473 K for 10 hours to get homogenous samples. XRD carried out on the samples showed that the samples are crystalline in nature and of single phase with a hexagonal structure. The SEM characterisation showed that the grain size varies from 2.18 to 4.35 μm for the undoped ZnO to $x = 0.50$ samples, showing increase in the grain size and reduction in grain boundaries as doping increases.

Keywords: Structural, crystallite, Grain

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I. INTRODUCTION

Zinc Oxide is an inorganic compound with the formula ZnO. ZnO is a white powder that is insoluble in water, which is widely used as an additive in numerous material and products including plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, batteries, ferrites, fire retardants and first aid tapes, [2]. It occurs naturally as the mineral Zincate which usually contains manganese and other impurities that confer a yellow to red colour, [3]. This colour change is caused by a small loss of oxygen to the environment at high temperatures to form the non-stoichiometric $Zn_{1+x}O$, that is at 1073 K, where $x=0.00007$, [6].

The Crystallite size was determined quantitatively using Debye Scherrer's formular;

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

Where β is the full width at half maximum (FWHM) of the diffraction peak expressed in radians, θ is the Bragg diffraction angle of the XRD peak, λ is the wavelength of the X-ray radiation used which is 1.54060 Å and D is the crystallite size in nanometers.

Zinc Oxide crystallises in two main forms hexagonal wurtzite and cubic zincblende, [1]. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilised by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral, the most characteristic geometry for Zn(II), [4]. In addition to the wurtzite and zincblende polymorphs, ZnO can be crystallised in the rocksalt motif form at relatively high pressures, [5]. The Hexagonal and zincblende polymorphs have no inversion symmetry (reflection of a crystal relative to any given point does not transform it into itself).

II. EXPERIMENT

Solid state reaction technique in which polycrystalline solids were prepared from a mixture of solid starting materials and heated at high temperature was used for the synthesis of the compound. The compounds (ZnO and Li_2CO_3) were synthesised for the following compositions. ZnO, $Zn_{0.9}Li_{0.10}$, $Zn_{0.8}Li_{0.20}$, $Zn_{0.7}Li_{0.30}$, $Zn_{0.6}Li_{0.40}$, $Zn_{0.5}Li_{0.50}$, $Zn_{0.4}Li_{0.60}$, $Zn_{0.3}Li_{0.70}$

Synthesis of Li – Doped ZnO

All chemicals used (ZnO and Li_2CO_3) in the synthesis were of analytical grade. The synthesis was carried out by solid state reaction technique. After the compositions have been weighted out using an analytical balance, they were placed in a petri dish and were mixed thoroughly using a spatula. 10mls of ethanol ($\text{C}_2\text{H}_5\text{OH}$) was added to the mixture to aid homogeneity. The paste formed was mixed thoroughly, during the process of grinding and mixing, the ethanol liquid gradually volatilised and evaporated completely. The mixture was placed in a platinum crucible placed in an RHF 1600 Carbolite England Furnace for Calcination at 1073 K for 10 hours. The obtained white powder were thoroughly grounded using an Agate Mortar and Pestle and then pressed into circular pellets of 19 mm in diameter and thickness of 4 mm using three (3) drops of toluene ($\text{C}_6\text{H}_5\text{CH}_3$) mixed with Polyvinyl Chloride (PVC) as the binder and applying pressure of about 20,000 pounds per square inch. The prepared pellets were then sintered at a temperature of 1473 K for 11 hours and furnace cooled in order to obtain a crystalline phase.

III. MEASUREMENTS/RESULTS

Table 1.1: Computed crystallite size, D of $\text{Zn}_{1-x}\text{Li}_x\text{O}$ crystals ($x = 0.00$ to 0.70) with respective hkl values.

hkl	ZnO (nm)	Zn _{0.9} Li _{0.1} O (nm)	Zn _{0.8} Li _{0.2} O (nm)	Zn _{0.7} Li _{0.3} O (nm)	Zn _{0.6} Li _{0.4} O (nm)	Zn _{0.5} Li _{0.5} O (nm)	Zn _{0.4} Li _{0.6} O (nm)	Zn _{0.3} Li _{0.7} O (nm)
100	41.733	41.761	41.719	41.719	41.719	41.719	41.719	41.719
002	42.021	31.540	42.071	42.000	31.540	42.000	42.071	63.000
101	42.235	42.285	42.285	42.213	31.700	42.213	42.285	42.213
102	43.845	32.956	32.913	43.845	32.913	43.845	32.222	34.175
110	34.175	34.222	34.222	34.175	34.175	34.175	34.222	34.175
103	28.254	35.337	28.254	35.287	35.287	28.254	23.536	35.287
200	35.948	36.000	28.775	47.977	35.948	35.948	47.977	35.948
112	29.043	36.367	29.077	36.314	29.043	36.314	29.077	36.314
201	36.543	29.282	29.247	48.727	29.247	29.247	24.387	29.594
004	24.923	12.486	24.948	24.923	12.462	24.923	29.914	10.880
202	38.441	38.512	25.667	38.441	25.640	51.228	30.800	25.640

The crystallite grain size, D measured in nanometer (nm) is 41.73 nm for $x = 0.00$ and 41.76 nm for $x = 0.10$. For $x = 0.20$ to 0.70 is the same (41.72 nm) irrespective of doping concentrations at hkl value 100. This implies that the crystallite size is almost independent of doping concentrations (as shown in Table 1.1) since all the samples were prepared under identical conditions.

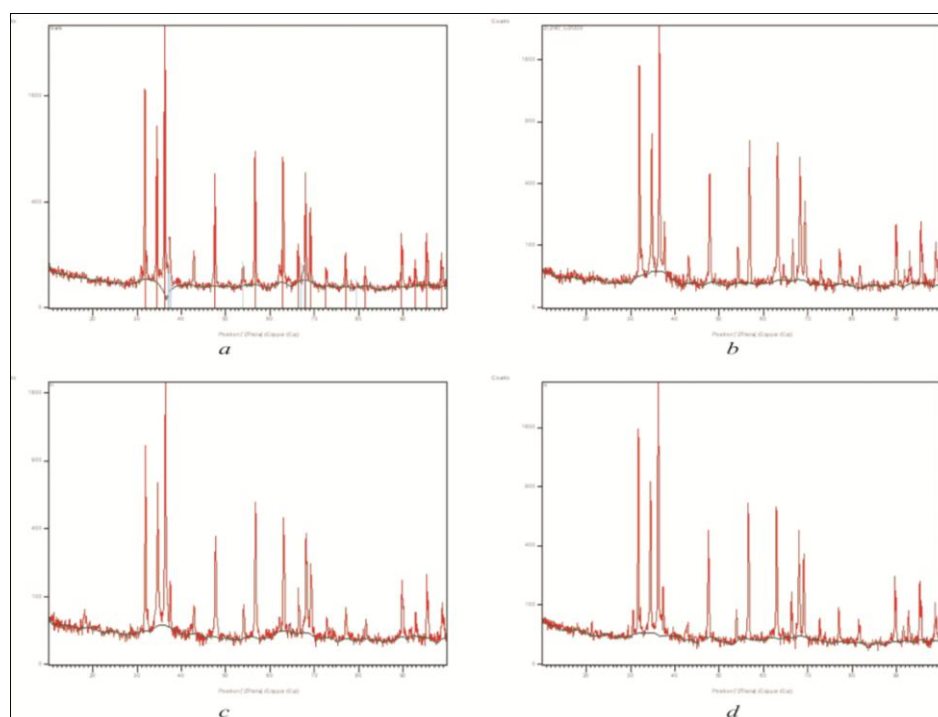


Figure 1.1: XRD Diffraction Pattern of $\text{Zn}_{1-x}\text{Li}_x\text{O}$ ($x = 0.00$ to 0.30) samples at diffraction angular range of $10^\circ \leq 2\theta \leq 100^\circ$, (a) undoped ZnO ($x = 0.00$) (b) $x = 0.10$ (c) $x = 0.20$ (d) $x = 0.30$

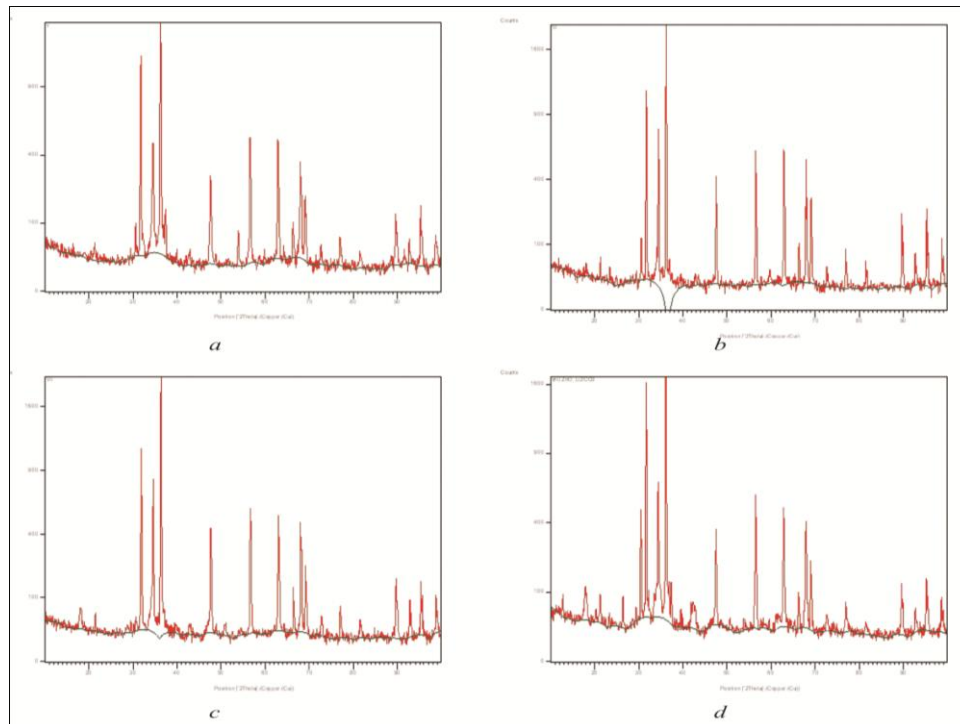


Figure 1.2: XRD Diffraction Pattern of $Zn_{1-x}Li_xO$ ($x = 0.40$ to 0.70) samples at diffraction angular range of $10^\circ \leq 2\theta \leq 100^\circ$, (a) $x = 0.40$ (b) $x = 0.50$ (c) $x = 0.60$ (d) $x = 0.70$

The diffraction Pattern in figure 1.1 and figure 1.2. The X-ray diffraction patterns clearly indicate that the samples are hexagonal and crystalline in nature. There are other few peaks in the XRD pattern lying between 20° to 30° 2θ - scan for $x = 0.50$. There are peaks in the XRD patterns lying between 10° to 20° 2θ - scan and at around 42° and 43° 2θ - scan for $x = 0.60$ and $x = 0.70$. These indicate that Li is soluble in ZnO up to $x = 0.40$, that is the maximum the lattice substitution have reached. Li atoms were substituted up to $x = 0.70$, as the amount of Li atoms substituting the Zn atoms increases, more peaks were established in the diffraction pattern and the angle at which the 2θ - scan begins reduces indicating that more interstitial sites become occupied. There are small diffraction peaks around 34° and 54° 2θ - scan whose match were not found. It was also found that the peak position slightly shifted to lower and higher angles alternatively as a function of doping concentrations. This implies a competition between tensile and compressive stress in the lattice structure that may be caused by the substitution of Zn atoms by Li atoms, and also by the presence of Li atoms at the interstitial sites as the amount of Li concentration increases. Figure 1.3 shows the Scanning Electron Microscope (SEM) images of undoped and Li-doped ZnO for $x = 0.00$ to 0.30 scanned at a magnification of $10000\times$

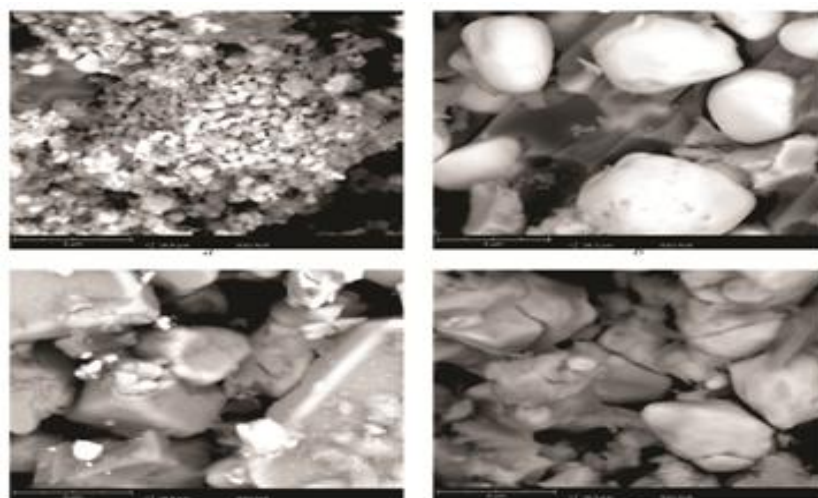


Figure 1.3: SEM Images of $Zn_{1-x}Li_xO$ ($x = 0.00$ to 0.30) samples at magnification of $10000\times$ (a) undoped ZnO ($x = 0.00$) (b) $x = 0.10$ (c) $x = 0.20$ (d) $x = 0.30$

It was observed that the undoped ZnO has a closed packed morphology with an average grain size of 2.18 μm determined from the lateral SEM image. There is absence of closed packed morphology in the Li-doped ZnO samples, but there exist agglomeration of small grains in some regions in the $x=0.10$ to 0.30 samples which may be due to segregation of insoluble Li atoms at the grain boundaries. The shape of the grains changes from hexagonal to cylindrical as doping increases. The grain size varies from 2.18 to 4.35 μm because the size of the large clusters increases as the amount of Li concentration increases. The average grain size of the $x=0.10$ to 0.30 Li-doped ZnO samples are 1.90 μm , 2.63 μm , 4.35 μm , respectively. The increase in grain size decreases the grain boundaries due to increase in crystallinity and orientation.

The XRD characterisation shows that the samples are crystalline in nature and of single phase with hexagonal structure. The maximum in lattice substitution of Zn by Li was at $x=0.40$. As the amount of Li atoms substituting the Zn atoms increases more interstitial sites becomes occupied. The computed crystallite size is almost the same irrespective of doping concentrations. The SEM characterisation showed that there is agglomeration of smaller grains resulting in larger grains in the doped samples. The increase in grain size decreases the grain boundaries due to increase in crystallinity and orientation in agreement with the XRD result.

III. RECOMMENDATION

Based on the discussions of the results of the structural properties of the undoped ZnO and the Li-doped ZnO. The structural distortion and transformation implies different microscopic property variation in each of the dopant concentration. As the doping concentration increases, the grain size and crystallinity of the samples increases. All these variations suggest that these properties will not be the same for all the material. So there is need for further research to pinpoint how the phase composition and structural transformations effects on the bulk material and property such as conductivity of this synthesised material, Thus, it is recommended that, Impedance Spectroscopy (IS) characterisation should be carried out on the samples to determine the electrical properties (conductivity, impedance and dielectric) which are its major properties that are used for various application such as rechargeable lithium ion battery, for capacitors, thermistors, electro-optic materials for data storage application and light display.

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