**Structure, phase transition and impedance of Zn1-xLixO(**$0.10\leq x\leq 0.70)$ **ceramic**

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**Abstract**

Structural transformations of Li-doped Zn1-xLixO($0.10\leq x\leq 0.70)$ which was synthesized by solid state reaction was investigated. XRD carried out on powder specimens of the samples show that they are polycrystalline in nature with a hexagonal wurtzite structure having minor impurities. The result indicates the maximum limit of substitution of Zn atoms by Li is at x= 0.4. The lattice parameter a reduced from 3.01 to 2.99 Å while c reduced from 5.21 to 5.19 Å. Whereas the Zn-O bond length reduced from 1.88 to 1.87Å for the undoped, to x=0.60 for the doped, respectively. The c/a ratio is 1.73 and is almost constant for all samples. The grain size of the (100) peak of the undoped ZnO is 41.73 nm and that of x= 0.10 is 41.76 nm. For x= 0.2 to 0.70, the grain size is 41.72 nm indicating that the grain size is almost independent of doping. The SEM results indicate a variation of grain size from 2.18 to 5.15 µm for the undoped ZnO to x= 0.50, which shows increase in grain size and reduction in grain boundaries as doping increases. The results show that x = 0.50 has the highest grain size, highest transition temperature and the marks the solubility limit. DTA results indicate the structural phase transition temperature of the doped ZnO ranged from ~371 to ~409 K and increased as the amount of Li increases. A single arc is observed in all the impedance plots of the ZnO together with the presence of a relaxation process which is non Debye. The impedance data show reduced resistance with increase in lithium content. A general increase in dielectric constant with increase in lithium content is observed.

***Keywords****:* ZnO; phase transition; structure; impedance; microstructure.

1. **Introduction**

There has been renewed interest in research on ZnO films as transparent conducting coating materials due to their low cost and resistivity, high transparency in the visible region and high light trapping properties (Bilgin, 2009). It exhibits properties such as piezoelectricity, strong photoluminescence, high electron mobility, thermal conductivity and a wide and direct band gap (Salama, 2009; Janotti and Vande walle, 2009).

ZnO is an intrinsic semiconductor with band gap of 3.2 eV at room temperature and crystallizes in the hexagonal wurtzite lattice with space group *Pb3mc* (Bilgin, 2009; Singh *et al*, 2007). It is generally n-type due to native defects created during its preparation which have been attributed to excess zinc in the interstitial position or oxygen vacancy or both (Bilgin, 2009). Doping ions larger in size than Zn ions substitutes for Zn sites and may result in the dopants being inserted between Zn and oxygen ions because of the small size of the ion (Jeong *et al*, 2007). ZnO has been doped with several dopants including Li. Discrepancies in results have been obtained on several of its physical properties when different dopants are used and even when in its pristine form. These have been reported on dielectric anomaly, ferroelectric transition and phase transition temperatures, to mention but a few. Theoretical calculations show that group I elements are better dopants than those of group V in terms of acceptor levels where energies could be up to 0.09 eV in the case of Li-substituting Zn, which is the shallowest level amongst energy levels of acceptor dopants reported (Salama, 2009). On the other hand, experimentally, 30% of the Zn sites have been found to be occupied by Li in single crystals of ZnO, but the substitution is easily followed by the formation of interstitial Li which are most likely to be shallow donors causing p-type doping to be limited by the formation of interstitial Li complex.

Concerns have been raised on phase transition which some workers (Du *et al*, 2005) claimed there is no evidence for it at atmospheric pressure, rather, the existence of Li-induced structural disorder and a high temperature phase transition. Further, dielectric, ferroelectric hysteresis loop and specific heat anomalies have been reported in Li-doped ZnO thin films and ceramics. But some workers (Sing *et al*, 2007) reported studies of ferroelectric properties and the effect of Li+ and mg2+ dopants in ZnO bulk samples in which the ferroelectric transition temperature was reported at 330 K for Zn1-xLixO, at x = 0.15. On the other hand, ellipsometric investigations of phase transition of Zn0.8Li0.2O failed to confirm the ferroelectric phase transition.

In the current work, the solubility limit, structural phase transition temperatures and impedance and dielectric properties of Zn1-xLixO (0.10$\leq x\geq $ 0.70, 0.0 being pristine sample) have been studied in order to elucidate some of the above problems.

1. **Experimental**

Analytical grade ZnO (99.99%), Li2CO3 (99.99%), ethanol (99.7%), Toluene mixed with polyvinyl chloride and distilled water were used for the preparation of Zn1-xLixO (0.10$\leq x\geq $ 0.70) by solid state reaction. Stoichiometric amounts of the powders were thoroughly mixed and ground and 10 ml of ethanol was added to aid homogeneity. The mixture was placed in a platinum crucible in an RHF 1600 carbolite England furnace for calcination at 1073 K for 8 hours in air atmosphere. The obtained white powder was thoroughly ground using an agate mortar and pestle and further pressed into disc pellets of 19 mm in diameter and 4 mm thickness with three drops of toluene mixed with polyvinyl chloride as binder. A pressure of 137,900 kN/m2 was used. The prepared pellets were sintered at 1473 K for 10 hours in air atmosphere and furnace-cooled.

Phase identification and crystalline properties of the samples were studied using X-ray diffraction (Pan Analytical, X’pert Pro) in reflection-transmission mode using Cu K$α$ radiation at 1.54060 Å at 30 kV and 10 mA in the 2$θ$ range 10$°\leq 2θ\geq 100°$ with scan time 29.85 s and scan step size of 0.064$°$ in continuous scan mode. Using a Phenom World Scanning electron microscope (SEM) at 15 kV the microstructure was determined at different magnifications on specimens of sintered samples. Specimens were also characterised using Differential Thermal Analysis (DTA) (NETZSCH DTA 404 PC) in the temperature range 300 to 573 K at a heating rate of 20 K/min to determine the structural phase transformations.DTA is a thermoanalytic technique in which a material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference. The differential temperature is then plotted against time, or temperature (known as DTA curve, or thermogram). Changes in the sample could either be exothermic or endothermic and can be detected relative to the inert reference. The DTA curve thus provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation.

 Impedance data were collected for eight samples for the real$(Z^{'})$ and imaginary ($Z^{''})$ parts versus frequency f. The data were collected for all the samples at 23$℃$ and 46 % relative humidity. Measurements were also carried out on the specimens of the samples as a function of temperature for x=0.0,0.1,0.2 and 0.3 at temperatures 50, 100, 150 and 200o C, each using AC fields of 50 mV or 10 mV and an equilibration time of 15 minutes. 100 nm Au sputter and Ag electrode (air-dry) paste (cured at 80oC for ten minutes) were used. Measurements were carried out using an Ametek Modular impedance analyser. The geometric density of the sample was 43% (density of ZnO = 5.606 g/cm3).

1. **Results and discussion**

Figure 1 shows the result of the X-ray diffraction pattern for x= 0.0 to 0.7, including the reference pattern. It matches the reference ICSD, 1997 crystal pattern which indicates the synthesised compounds are crystalline and hexagonal in structure with minor impurity peaks as observed by other workers (Du *et al*, 2005; Khan *et al*, 2003a). The peaks lie between 20$°$ and 30$°$ (x = 0.5) and between 10$°$ and 20$°$ and at 43$°$ 2θ, respectively, for x = 0.60 and 0.70.



Figure 1. X-ray diffraction pattern for x= 0.0 to 0.7 compared to the reference pattern

The result suggests the solubility limit of Li in ZnO is up to x = 0.4 and thus contrasts with that reported by other workers (Khan *et al*, 2003b). As the amount of lithium increased the angle at which 2θ begins reduces indicating that more interstitial sites become occupied in agreement with earlier works (Khan *et al*, 2003a; Polarz *et al*, 2009). Slight shifts in peak positions to lower and higher angles as a function of doping concentration have been reported (Ardyanian and Sedigh, 20014) and attributed to various factors such as competition between tensile and compressive stress in the lattice structure, the substitution of Zn atoms by Li atoms and to the presence of Li atoms at the interstitial sites (Zeng *et al*, 2005).

These have been reported to lead to lattice distortion (Wang *et al*, 2003) and changes in ferroelectric properties (Kim *et al*, 2011). Systematic shifts in peak positions to higher values with increase in Li content were not observed contrary to what has been reported (Jeong *et al*, 2007). The slight decrease in peak intensity is apparent in some compositions and has been attributed to the reduction of atomic mass as a result of the substitution of Li atoms (ionic radii, 0.68 Å) at the lattice sites of Zn2+ atoms (ionic radii, 0.74 Å) (Bilgin, 2009; Ardyanian and Sedigh, 2014). Also the relative intensity of the (101) peak is the same for all the samples at 100% intensity and may be related to the preferred orientation (Khan *et al*, 2003a). The determined lattice parameters of the Li-doped ZnO are slightly different from those of the pristine sample and are in agreement with the result of other workers (Onodera *et al*, 1997) who attributed it to the substitution by Li atoms which results in a slight difference in their c/a ratios. This shows that ZnO is still hexagonal though with slight distortions (Khan *et al*, 2003a). Reductions also occur in the Zn-O bond length and further confirm the substitution of Zn by Li. The crystallite sizes are virtually the same for all samples, irrespective of level of doping (Khan *et al*, 2003a).

The result of microstructural characterisation is shown in figure 2(a-h) at a magnification of$ ×10,000$. The undoped ZnO has a close packed morphology with average grain size of 2.18$ μm$, whereas this is absent in the doped samples where agglomeration of the grains is observed in some regions in x = 0.20 to 0.60. Porous domains are also visible in all the samples and have been reported (Soukiassian *et al*, 2011) to be due to the segregation of insoluble Li atoms at the grain boundaries (Ardyanian and Sedigh, 2014).



Figure 2(a-h). Microstructure of sample at a magnification of$ ×10,000$ at different dopant levels.

The shape of the grains changes from hexagonal to cylindrical as the doping increased and the average grain size for the Li-doped samples also increased in the order 1.90, 2.63, 4.35, 4.70, 5.15 and 2.40$ μm$, respectively, x = 0.50 having the largest grain size.

There are no phase transformations observed below 300 K in ZnO (doped/undoped) as shown in the representative DTA plot in figure 3 for x= 0.0.



Figure 3. Representative DTA plot of x= 0.0 show no phase transformations below 300 K in ZnO (doped/undoped).

This is in accordance with reported results (Wang *et a*l, 2003). The plot of undoped ZnO show anomaly which corresponds to a phase transition at a temperature of 375 K with steep and narrow peaks which are indicative of a sharp first order structural phase transformation. For the Li-doped ZnO the transition temperatures increase (figure 4) with increase in Li doping in accordance with the result obtained by some workers (Wang *et al*, 2003).



Figure 4.The of Li-doped ZnO shows increase in transition temperatures as the doping increases.

This contradicts the work reported on Li0.3Zn0.7O and pure ZnO in which they found no phase transformation from 373 to 423 K. From 408 to 377 K there is a decrease in transition temperature for x = 0.5 and 0.6 with subsequent increase to 379 K in x = 0.70. The peaks of the DTA plots of doped ZnO samples are broader than those of the undoped ZnO. There is almost first order phase transition in the doped ZnO which is attributed to Li atoms occupying off-centred positions where the order-disorder characteristics relating to transitional shifts of Zn and O sublattices have effect on the phase transition (Wang *et al*, 2003) causing dielectric anomalies. The sample with the highest transition temperature is x = 0.6 while the one with the highest grain size (when compared with the SEM results) is x=0.5.

Impedance measurements were carried out at room temperature for all the samples and at selected temperatures 50, 100, 150 and 200oC, for x= 0.0 to 0.4. Figure 5 shows the composite impedance plot of x=0.0 taken at the selected temperatures and plotted using *ZVIEW* program.



Figure 5.Composite impedance plot of x= 0.0 taken at selected temperatures and plotted using *ZVIEW* program.

 It can be seen that the curvature of the impedance curves increases with increase in temperature indicating a reduction of resistance. The curve at 200oC has the greatest curvature. Figure 6(a and b) is a plot of impedance (real and imaginary) versus frequency for representatives x= 0.0 and 0.3 at temperature of 200oC obtained using the software *ZSim*.



1. (b)

Figure 6. (a) Plot of impedance (real and imaginary) versus frequency for representatives x= 0.0 and (b) x=0.3 at temperature of 200oC obtained using the software *ZSim*.

The square legends (in red) represent the real values of measured (Msd) impedance ($Z^{'})$ while the blue triangles represent the imaginary part$(Z^{''})$. The plots show relaxation behaviour and the frequencies shift from lower to higher values with increase in lithium content at the same temperature. A broad relaxation peak which indicates a distribution in relaxation times, with the difference between the peaks of the $Z^{'},Z^{''}$ vs frequency being about two decades of frequency, exhibits non-Debye character ..Non Debye behaviour is due to the absence of a single relaxation time and can be determined from the plot of $z^{'}$ vs log f in which the width at half height is greater than 1.14 decades of frequency and also suggests departure from ideal Debye behaviour (Ahmadu *et al*, 2011).

Figure 7(a-c) are representative plots of impedance for x=0.0, 0.2 and 0.3 at temperature of 200oC fitted to the same circuit model. The numbers on the curves indicate the frequencies, the green squares the fit and the red squares the measured values of impedance. It is clear that the impedance curve of x= 0.0 (figure 7a) is a single semicircle similar to that of x = 0.2(figure 7b) which though is not a complete semicircle but shows it is single arc and has lower impedance value due to its higher Li content. All the samples have single arcs without separation between grain and grain boundaries (the frequency increases in an anticlockwise direction).The single arc result has been reported (Zhou *et al*, 2004) and references therein, where it was attributed to the conduction processes through the grain and grain boundary having the same time constants; and to the fact that the model used has resistive grain boundaries and conducting grain cores (Zhou *et al*, 2004).



Figure 7. (a-c) are representative plots of impedance for x = 0.0, 0.2 and 0.3 at temperature of 200oC fitted to the same circuit model.

The intersection of the arc with both impedance axes is at zero. The circuit model used for the fitting is shown in figure 8, where Q represents constant phase element, R resistance, C capacitance and L inductance. Four iterations were used to obtain the fit with chi square value of 1.23.$10^{-3}$ (figure 7a).



Figure 8. Circuit model used for the fitting with the various circuit elements, where Q represents constant phase element, R resistance, C capacitance and L inductance.

Thirteen parameters were used for the fitting (which is not perfect) with ten having relative standard error greater than 10%. In figure 7b the number of iterations is six and the same thirteen parameters (eleven have relative standard error greater than 10%) were needed for the fit, the chi square values being 3.11.$10^{-3}$. Figure 7c shows a similar plot fitted to the same circuit model described above but at lower temperature of 150oC (x = 0.2) in which only four iterations were used and the chi square value is much smaller at 1.02.$10^{-2}$.Visual inspection shows an almost perfect fit but fitting parameters indicate there are still some mismatches. Figure 9 is a composite plot of the permittivity (dielectric constant) plotted at different frequencies for all the samples at room temperature.



Figure 9. Composite plot of permittivity (dielectric constant) at different frequencies for all samples at room temperature.

The patterns show the characteristic dispersion of dielectric constant with increase in frequency. The dielectric constant falls with increase in frequency and decreases much faster for x= 0.0, 0.3, 0.4 and 0.7, becoming almost independent of temperature at high frequencies, particularly for x= 0.2 which has a value of ~7. Polarisation in dielectrics has been attributed to many factors, such as space charge effects, dipole orientation, electronic, among others. The high values of the dielectric constant at low frequencies could be attributed to space charge effects resulting from charge accumulation because of dc conductivity. However, at high frequencies interfacial polarisation increases hence the saturation or constant value of dielectric constant. Also the dipoles can no longer follow the field fast enough and therefore tend towards static values at all temperatures (Ahmadu *et al*, 2011). A maximum value of dielectric constant has been reported (Khan *et al*, 2003b) for all frequencies at the same concentration of x=0.2, on the contrary and has been attributed to lattice mismatch between Zn and Li ions. Further work is required to explain this behaviour. Also, around 150 kHz, small wiggles in the dielectric constant are clearly seen in all the samples at room temperature and may be related to structural transformation that may have occurred. Some workers (Onodera *et al*, 1997) have reported dielectric anomaly at 330 K for Li–doped ZnO at x$>0.1(Khan et al, 2003b)$, and a similar report of a dielectric phase transition has been found between the ferroelectric and paraelectric phase at 330 K for Li–doped system for x= 0.15(Singh *et al*, 2007).Since the temperature is in the vicinity of room temperature, it could be responsible for the behaviour. Similarly, other workers have reported small peaks around 15-35oC in the dielectric constant in Li-doped samples measured in air atmosphere (Soukiassian *et al*, 2011). Further work such as dc electrical conductivity and Raman spectroscopy studies carried out at this frequency may be helpful. There is generally an increase in dielectric constant with increase in Li content with the highest dielectric constant obtained for x= 0.0 and 0.7 being ~28.0.The value of dielectric constant for pristine x=0.0 reported to be ~ 9(Jeong *et al*, 2007) is high and could be due to the presence of water vapour in the atmosphere (Soukiassian *et al*, 2011) which has been found to increase the dielectric constant at room temperature, given the relative humidity reported at the experimental condition.

1. **Conclusion**

ZnO was prepared by solid state reaction and phase analyses of the samples show that they are polycrystalline and majorly of single phase with hexagonal structure. The lattice parameters were found to reduce (a and c) with the c/a ratio almost constant for all samples, which is an indication that the crystal structure did not change but suffers some slight distortion. The crystallite size appears to be independent of doping level with solubility limit at x=0.4 but the grain size increased with increase in Li content. Agglomeration was observed in some of the samples’ microstructure. Phase transition analyses show that all Li-doped samples have no phase change near room temperature and the transition temperatures generally increase up to a maximum with increase in Li doping before decreasing at certain levels of Li doping. At 375 K a phase transformation was observed for undoped ZnO which increased as Li concentration increased with the highest temperature being ~ 409 K for x = 0.6. Impedance results show a general increase in dielectric constant with increase in Li doping while the impedance curves characterized by single arcs which show relaxation behaviour that is non Debye. .Further work is required in order to resolve issues like the dielectric anomaly at ~150Hz and the very low dielectric constant of x=0.2 .This implies that Li-doped ZnO still has some peculiarities.

**References**

Bilgin, V.(2009) “Preparation and characterization of ultrasonically sprayed zinc oxide thin

 films doped with lithium”. *Journal of electronic mater*, 88, 1969 – 1978.

Salama, A. H.(2009). “Electrical properties of Li doped p-type ZnO ceramics”. *J. Mat. Sci. Technol*, 25.

Janotti, A. and Van de Walle.(2009). “Fundamentals of zinc oxide as a semiconductor. *Rep. prog.*

 *Phys*, 72, 126501.

Singh, D.S., Nagaraju, J.and Krupanidhi, S.B.(2007).”Dielectric anolay of Li doped zinc oxide thin films grown by sol-gel route”. *Journal of Appl. Phys. A* 88, 421-424.

Jeong, S.H., Park, B.N., Lee, S. –B., Boo, J. –H.(2007). Study on the doping effect of Li doped ZnO film, *Journal of thin solid films*, 516, 5586-5589.

Du, Y.L.., Deng, Y., Zhang, M.S.(2005).”Investigation of Li –induced structural disorder and phase transition in zinc oxide by Raman spectroscopy”. *Solid state communications journal*, 137, 78-81.

Khan, M.K.R., Rahman, M.M. and Tanaka, I.(2003a).”Preparation, Structural and Electrical

 Properties of Zn1-xLixO solid solution”. *The Nucleus*, 39,149-154.

Khan, M.K.R., Rahman, M., Mia, S.J. and Shahajahan, M.(2003b).“Anomalous resistive

Transition and frequency dependent dielectric constant of ZnMO[M=Li(Mg, Ba]system”. *Indian* *Journal of pure & applied physics*, 41, 211-216.

Polarz, S., Orlov, A., Hoffmann, A., Wagner, M.R., Rauch, C., Kirste, R., Lehmann, M.(2009). *“*A systematic study on ZnO materials containing group I metals (Li, Na, K)-synthesis from organometallic precursors, characterisation and properties”. *Chem. Matter,* 21, 3889-3897.

Ardyanian, M. and Sedigh, N.(2014). “Heavy lithium doped thin films prepared by spray pyrolysis method”. *Bulletin of materials science*, 37, 1309-1314.

Zeng, Y., Ye, Z. Z., Xu, Z.Z., Chen, W.Z., Li, L. I., Zhu, D.Y. , and Hu, Y.L.(2005). “Realization of p-type ZnO films via monodoping of Li acceptor”. *Journal of crystal growth*, 283 (1) 180.

Wang, X.S., Wu, Z.C., Webb, J.F., Liu, Z.G.(2003).”Ferroelectric and dielectric properties of Li-doped ZnO films prepared by pulsed laser deposition”. *Appl. Phys. A*, **77**, 561- 565.

Kim, J.S., Lee, H.J., Seog, H.J. and Kim, W.(2011).“Dielectric and Electrical properties of ZnO films”. *Journal of Korean Physical Society,* 58,640-644.

# Onodera, A., Tamaki, N., Jin, K. and Yamashita, H.(1997). “Ferroelectric Properties in

# Piezoelectric Semiconductor Zn1-*x*M*x*O (M=Li, Mg)”.*Jpn. J. Appl. Phys*., 6, 6008.

Soukiassian, A., Tganstsev, A. and Seller, N.(2010).“Anomalous dielectric peak in Mg and Li

doped ZnO ceramics and thin films”. *Applied Physics Letters*, 07**,** 192903.

Ahmadu, U., Salkus, T., Musa, A. O., Isah, K.U.(2011). “Electrical and Dielectric Characterization

 of Na0.5Li0.5Zr2(PO4)3”.*Open Journal of Physical Chemistry*, 1**,** 94-

103**.**

# Z. Zhou Z., K. Kato K., T. Tomaki T., M. Yoshino M., H. Yukawa H., M. Morinaga M. and Morita K.(2004).”Effects of dopants and hydrogen on the electrical conductivity of ZnO”. *Journal*

#  *of the European Ceramic Society*, 24,139-146.