STRUCTURAL AND DIELECRTIC PROPERTIES OF $Zn_{1-x-y}Cd_xLi_yO$ SOLID SOLUTION

M. KAMRUZZAMAN[1*], M. K. R. KHAN[2], M. M. RAHMAN[2], M. SHAHJAHAN[2], M. A. S. KARAL[1]

[1]*Department of Physics, Bangladesh University of Engineering and Technology Dhaka-1000, Bangladesh*

[2]*Department of Physics, University of Rajshahi, Rajshahi-6205, Bangladesh*

ABSTRACT

$Zn_{1-x-y}Cd_xLi_yO$ (x=0.30 and y=0.05, 0.10, 0.15, 0.20) have been prepared by solid state reaction method. The prepared samples have been characterized by structural and dielectric measurements. X-ray diffraction (XRD) patterns show a good crystalline nature having double crystal structure and indicates the phase mixing of the constituent components. The hexagonal phase corresponding to ZnO and cubic phase to CdO is well defined and the lattice parameters are consistent with the published values (Grant in Aid report 1987). The estimated lattice parameters, bond length and crystallite size are quite consistent corresponding to the hexagonal ZnO and cubic CdO which suggests the formation of super lattice structure of the system. Crystallite size at different crystallographic planes analyzed from XRD for both ZnO and CdO lie between (15-50) nm. The variation of the dielectric constant of the samples with frequency is systematic and the dielectric constant increases with the increase of Li in the solution.

INTRODUCTION

Electronic materials are extremely important type of materials for advanced science and technology. Microelectronic devices have made possible, by new products of electronic materials such as communication satellites, advanced computers, hand-held calculators, digital watches etc. ZnO and CdO have high transparency in the visible and near infrared region of the electromagnetic spectrum and show n-type conductivity, mainly due to oxygen deficiency and lattice defects. With a band gap ranging 2.2-2.7 eV[(1)], CdO has a direct band gap of 2.3 eV[(2)] and presents the advantage of a low resistivity with respect to the high values obtained for ZnO, but this exhibits a higher transparency, having a band gap of ~3.2 eV.

Obviously, it is difficult to obtain a high transmission coefficient in the visible region and conductivity qualities simultaneously[(3)], however, a ternary compound which combines these properties in a controlled way may allow the optimization of the window layer. Since ZnO shows ultra-violet excitonic emission at room temperature, therefore it has attracted enormous interests for its potential opto-electronic applications Light Emitting Diode (LED) and Laser Diode (LD) in ultra-violet or blue spectral[(4-6)]. It is also used in solar cell and transducer. ZnO is of hexagonal wurtzite-type structure and an excitonic binding energy of ~60 meV, much larger than ~25 meV, which permits the efficient excitonic stimulated ultra-violet emission even at room temperature[(7-8)].To achieve applicable ZnO sample-based opto-electronic devices, there have been considerable experimental investigations focused on the preparation of p-type ZnO sample and its band gap engineering by impurity doping and various alloying methods[(9-10)].

To date, a various means of oxide alloying with ZnO samples in thin film form have been investigated but to our knowledge there are no such reports in bulk form. Considering immense application of ZnO in fabrication of devices mentioned above, our aim is to prepare highly conducting ZnO bulk samples by solid state reaction method. Motivated with these facts, we are investigating the effect of Cd (x=0.30) and Li (y=0.05, 0.10, 0.15 and 0.20) doped ZnO samples by studying structural and dielectric properties.

EXPERIMENTAL

The materials used in the preparation of the samples with analytical grade were ZnO, $CdCo_3$ and Li_2Co_3. All the materials were procured from local market. Thus $Zn_{1-x-y}Cd_xLi_yO$ (x=0.30; and y=0.05, 0.10, 0.15, 0.20) were prepared by solid state reaction method.

* Author for Correspondence : mkzaman_phybuet@yahoo.com

XRD patterns of the samples were taken using an X-ray diffractometer at the Department of Electrical and Electronic Engineering, Toyohashi University of Technology, Japan, to check the status and homogeneity. The lattice parameters of the samples were calculated by Hess-Lipson method.

(i) Lattice parameters calculation by Hess-Lipson method:

The interplanar spacing d_{hkl} for the hexagonal system with diffraction angle θ is given as

$$\frac{1}{d_{hki}} = \left[\frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{1^2}{c^2}\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, the wavelength (λ) of X-ray was used 1.5405 Å [CuK_a line]

$$\frac{4\sin^2\theta_{hki}}{\lambda^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{1^2}{c^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$\therefore \quad \sin^2\theta_{hkl} = XA + l^2C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where, $X = h^2 + hk + k^2$ …… (4)

$A = \lambda^2/3a^2$ …… (5)

$C = \lambda^2/4c^2$ …… (6)

and

$$\sin^2\theta_{100} = A \qquad \sin^2\theta_{010} = A \qquad \sin^2\theta_{001} = C$$

$$\sin^2\theta_{200} = 4A \qquad \sin^2\theta_{020} = 4A \qquad \sin^2\theta_{002} = 4C \qquad \ldots\ldots\ldots (7)$$

$$\sin^2\theta_{300} = 9A \qquad \sin^2\theta_{030} = 9A \qquad \sin^2\theta_{003} = 9C$$

$$\sin^2\theta_{110} = 3A \qquad \sin^2\theta_{220} = 12A \qquad \sin^2\theta_{330} = 27A \text{ and so on.}$$

Using relation (7) in equations (5) and (6), we have calculated lattice parameters a and c for hexagonal phase.

The interplanar spacing d_{hkl} for the cubic system with diffraction angle θ is given as

$$\frac{1}{d_{hki}} = \left[\left(\frac{h^2 + k^2 + l^2}{a^2}\right)\right]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\therefore \quad \sin^2\theta_{hkl} = \lambda^2/4a^2\,(h^2+k^2+l^2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Again, using relation (7) in equation (9), we have also calculated lattice parameter, a for cubic phase.

The Zn-O bond length has been calculated by the relation[11].

$$\sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2}$$

where, $u = a^2/3c^2 + 0.25$, u is the positional parameter of hexagonal structure. The d_{hkl} values of the $Zn_{1-x-y}Cd_xLi_yO$ are shown in the Tables 1-4.

(ii) Calculation of crystallite size:

The XRD patterns clearly indicate that the samples are of crystalline type, the reflection line profiles were subjected to calculate crystal or grain size perpendicular to the different crystallographic planes. The crystallite size, x, of the samples were determined quantitatively using the formula[12].

$$x = \frac{k\lambda}{B\cos\theta}$$

where, λ is the wavelength of the incident X-ray beam κ is a constant equal to unity and θ is Bragg angle. In general, B is full width at half-maximum (FWHM) of a diffraction peak expressed in radians.

(iii) Calculation of dielectric constant:

The dielectric constants were calculated from the capacitance, measured at room temperature by Precision Impedance Analyzer, Model, Agilen 429 A (40 Hz-110 MHz) using the relation

$$\varepsilon = \frac{C' d}{\varepsilon_0 A}$$

where, C is the capacitance, d is the thickness, A is the area of the sample and ε_0 is the permitivity of the free space.

RESULTS AND DISCUSSION

The XRD patterns for $Zn_{1-x-y}Cd_xLi_yO$ are shown in Fig.1

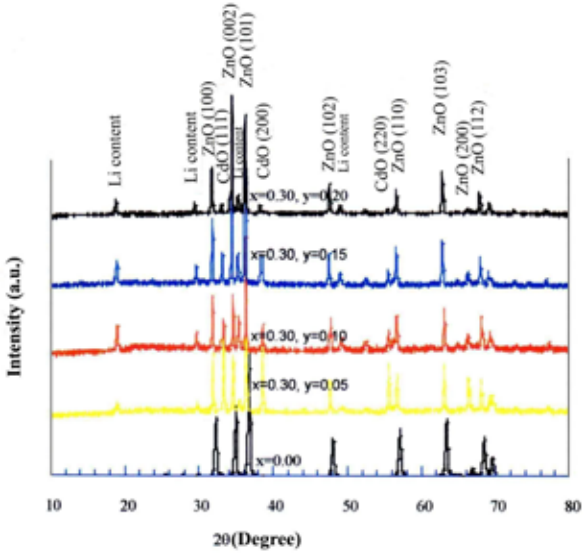

Fig. 1. XRD pattern for $Zn_{1-x-y}Cd_xLi_yO$

It is seen that all samples are very good crystalline in nature and preferently oriented. The different peak positions oriented in the different crystallographic planes of synthesized samples are tabulated in Tables 1-4. The diffraction pattern was collected for 2q values in the scattering range (10-80) degree for $Zn_{1-x-y}Cd_xLi_yO$. For pure ZnO, diffraction peaks identified as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0) and (1 1 2) planes. There are three distinct peaks at around angles (2θ values) 33.26°, 38.58° and 55.54°, correspond to planes (1 1 1), (2 0 0) and (2 2 0) appeared in addition to the ZnO peaks. Analyzing the peak positions of the spectrogram with standard JCPDS cards both for ZnO and CdO, it is clear that the spectrogram is the combination of two crystal structures-one for hexagonal ZnO and other for cubic CdO. Considering these two structures, the lattice parameters were found consistent with reported values for both structures. The lattice parameters, bond length, crystal volume and a/c ratio for ZnO are tabulated in Table 5. The reference values of lattice parameters, a and c for ZnO from JCPDS cards are, a = 3.24982 Å, c = 5.20661 Å. The lattice parameters determined in this study for cubic CdO is 5.359 for (2 0 0) plane. There are also four extra peaks found at around 20°, 30°, 35^0 and 50° for Li content phase. The intensity of these extra peaks increases with the increase of Li in the solution.

Table1.
The d_{hkl} values of $Zn_{1-x-y}Cd_xLi_yO$ (x=0.30, y=0.05)

Peak No.	2θ (degre)	d_{hkl} (Å) expt.	d_{hkl} (Å) (from JCPDS)	**Intensity (%) expt**	Standard Miller indice (hkl)	**Possible phase**	Crystallite size, ξ (nm)
1	18.80	4.7160	-	**22**	-	**Li content**	27
2	29.58	3.015	-	**15**	-	**Li content**	39
3	31.79	2.8124	2.8140	**49**	1 0 0	**ZnO**	44

4	33.12	2.7024	2.7120	**65**	1 1 1	**CdO**	44
5	34.44	2.601	2.6030	**46**	0 0 2	**ZnO**	47
6	36.27	2.4776	2.4759	**100**	1 0 1	**ZnO**	42
7	38.40	2.3421	2.3490	**58**	2 0 0	**CdO**	35
8	47.53	1.9113	1.9111	**28**	1 0 2	**ZnO**	35
9	55.42	1.6564	1.6610	**40**	2 2 0	**CdO**	34
10	56.56	1.6257	1.6247	**31**	1 1 0	**ZnO**	33
11	62.82	1.4779	1.4772	**38**	1 0 3	**ZnO**	32
12	66.04	1.413	1.4072	**28**	2 0 0	**ZnO**	25
13	68.88	1.3619	1.3782	**32**	1 1 2	**ZnO**	33

Table 2.
The d_{hkl} values of $Zn_{1-x-y}Cd_xLi_yO$ (x=0.30, y=0.10)

Peak No.	2θ (degree)	d_{hkl} (Å) expt	d_{hkl} (Å) (from JCPDS)	**Intensity (%) expt**	Standard Miller indices (hkl)	**Possible phase**	Crystallite size, ξ (nm)
1	18.80	4.7160	-	**22**	-	**Li content**	28
2	29.51	3.018	-	**15**	-	**Li content**	39
3	31.74	2.8167	2.8120	**49**	1 0 0	**ZnO**	42
4	33.08	2.6496	2.6600	**29**	0 0 2	**ZnO**	49
5	35.24	2.5445	-	**30**	-	**Li content**	35
6	36.22	2.4777	2.4759	**100**	1 0 1	**ZnO**	44
7	38.36	2.3444	2.3490	**25**	2 0 0	**CdO**	38
8	47.48	1.9132	1.9111	**29**	1 0 2	**ZnO**	46
9	49.00	1.8573	-	**11**	-	**Li content**	23
10	55.40	1.6570	1.6610	**17**	2 2 0	**CdO**	38
11	56.52	1.6268	1.6247	**30**	1 1 0	**ZnO**	33

12	62.77	1.4790	1.4771	37	1 0 3	ZnO	30
13	67.86	1.3799	1.3782	29	1 1 2	ZnO	33

Table 3. The d_{hkl} values of $Zn_{1-x-y}Cd_xLi_yO$ (x=0.30, y=0.15)

Peak No.	2θ (degree)	d_{hkl} (Å) expt	d_{hkl} (Å) (from JCPD)	Intensity (%) expt	Standard Miller indices(hkl)	Possibe phase	Crystallite size, ξ (nm)
1	18.80	4.7196	-	19	-	Li content	26
2	29.56	3.019	-	15	-	Li content	30
3	31.80	2.8115	2.8140	52	1 0 0	ZnO	38
4	33.16	2.6992	2.7120	25	1 1 1	CdO	42
5	34.48	2.5989	2.6030	72	0 0 2	ZnO	44
6	35.31	2.539	-	25		Li content	32
7	36.30	2.4726	2.4759	100	1 0 1	ZnO	38
8	38.45	2.3392	2.3490	23	2 0 0	CdO	40
9	47.56	1.9102	1.9111	39	1 0 2	ZnO	35
10	49.12	1.8531	–	23	- -	Li content	2928
11	55.47	1.6570	1.6610	12	2 2 0	CdO	3339
12	56.47	1.6254	1.6247	30	1 1 0	ZnO	3344
13	62.72	1.4829	1.4160	27	2 0 0	ZnO	5032
14	67.92	1.3788	1.3782	20	1 1 2	ZnO	26
5	36.20	2.4792	2.4759	85	1 0 1	ZnO	40
6	38.40	2.3421	2.3490	7	2 0 0	CdO	42
9	47.47	1.9136	1.9111	27	1 0 2	ZnO	29
10	56.49	1.6276	1.6247	20	1 1 0	ZnO	26
11	62.76	1.4792	1.4771	37	1 0 3	ZnO	20
12	66.04	1.413	1.4072	28	2 0 0	ZnO	25

Table 4. The d_{hkl} values of $Zn_{1-x-y}Cd_xLi_yO$ (x=0.30 y=0.20)

13	68.88	1.3619	1.3782	18	1 1 2	**ZnO**	28

Table 5.

Lattice constants, bond length and a/c ratio of $Zn_{1-x-y}Cd_xLi_yO$ estimated from XRD

$Zn_{1-x-y}Cd_xLi_yO$	Lattice constant of ZnO (Å)		Bond length (Å)	Bond length (Å) for ZnO[11]	Volume of ZnO ($Å^3$)	a/c ratio
	a	c				
x=0.0, y=0.0	3.1950	5.2240	1.877	1.877	46.152	0.6111
x=0.30, y=0.05	3.2447	5.202	1.9762	1.9778	47.507	0.6242
x=0.30, y=0.10	3.2524	5.2992	1.9902		48.544	0.6137
x=0.30, y=0.15	3.2464	5.1978	1.9753		47.439	0.6245
x=0.30, y=0.20	3.2539	5.208	1.9796		47.752	0.6247

We have calculated crystallite size for ZnO and CdO in different crystallographic planes and tabulated in Tables 6 and 7. The values obtained are consistent with the estimated values[13].

Table 6.

Crystallite size of ZnO at different (hkl) planes for $Zn_{1-x-y}Cd_xLi_yO$

Table.7

Crystallite size of CdO at different (hkl) planes for $Zn_{1-x-y}Cd_xLi_yO$

x and y (x=0.30)	Crystallite size (nm) for different (hkl) planes							
	(1 0 0)	(0 0 2)	(1 0 1)	(1 0 2)	(1 1 0)	(1 0 3)	(2 0 0)	(1 1 2)
y=0.05	44	46	42	35	33	32	25	26
y=0.10	42	49	44	46	33	30	-	33
y=0.15	38	44	38	35	33	-	25	26
y=0.20	40	44	40	29	26	21	42	28

x and y (x=0.30)	Crystallite size (nm) for different (hkl) planes		
	(1 1 1)	(2 0 0)	(2 2 0)
y=0.05			
y=0.10	42	38	38
y=0.15	42	40	33
y=0.20	42	42	32

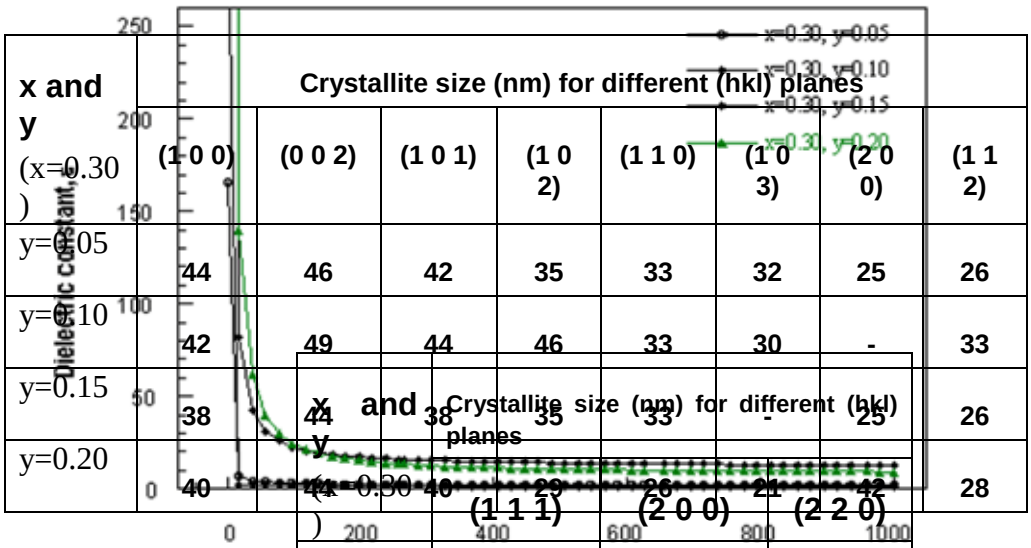

Fig. 2. Variation of dielectric constant with frequency for $Zn_{1-x-y}Cd_xLi_yO$

CONCLUSIONS

From the XRD analysis, it is clear that there exists hexagonal ZnO and cubic CdO phase in the $Zn_{1-x-y}Cd_xLi_yO$. The estimated lattice parameters, bond length and crystallite size are quite consistent corresponding to the hexagonal ZnO and cubic CdO crystals which suggests the formation of super lattice structure of the system. The variation of the dielectric constant of the samples with frequency is systematic and also the dielectric constant increases with the increase of Li in the solution.

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REFERENCES

1. K. L. CHOPRA AND S. RANYAN DAS, Thin Film Solar Cells, Plenum Press, New York, 1993.
2. C. SRAVANI, K. T. R. REDDY AND P. J. REDDY, Influence of oxygen partial pressure on the physical behaviour of CdO films prepared by activated reactive evaporation, *Mater. Lett*. **15,** 356-358, 1993.
3. K. L.CHOPRA, S. MAJOR AND D.K. PANDYA, Transparent conductors--A status review, *Thin Solid Films*, **102,** 1-46, 1983.
4. D. M. BAGNALL, Y. F. CHEN, Z. ZHU, T. TAO, S. KOYAMA, M. Y. SHEN AND T. GOTO, Optically pumped lasing of ZnO at room temperature, *Appl. Phys. Lett*. **70,** 2230, 1997.
5. Z. K. TANG, G. K. L. WONG, P. YU, M. KAWASAKI, A. OHTOMO, H. KOINUMA AND Y. SEGAWA, Room-temperature Ultraviolet Laser Emission from Self-assembled ZnO Microcrystalline Thin Films, *Appl. Phys. Lett*. **72,** 3270-3272, 1998.
6. P. ZU, Z. K. TANG, G. K. L. WONG, M. KAWASAKI, A. OHTOMO, H.KOINUMA AND Y. SEGAWA, Ultraviolet spontaneous and stimulate emission from ZnO microcrystalline thin films at room temperature, *Solid State Commun*. **103,** 459-463, 1997.
7. J. NARAYAN, K. DOVIDENKO, A. K. SHARMA AND S. OKTYABRSKY, Defects and interfaces in epitaxial ZnO/alpha-Al_2O_3, *J. Appl. Phys*. **84,** 2597**,** 1998.
8. M. KAWASAKI, A. OTTOMAN, I. OHKUBO, H. KOINUMA, Z.K. TANG, P. YU, G. K. L. WONG, B. P. ZHANG AND Y. SEGAWA, Excitonic Ultraviolet Laser Emission at Room Temperature from Naturally Cavity in ZnO Nano-crystal *Thin Films, Matter. Sci. Eng*. **B 56,** 249-245, 1998.
9. **Y.YANTA, S.B. ZHANG AND S. T. PANTELIDES, Control of Doping by Impurity Chemical Potentials: Predictions for *p*-Type ZnO, *Phys. Rev. Lett*.** 86, **5723-5726, 2001.**
10. A. OHTOMO, M. 0KAWASAKI, T. KOIDA, K. MASUBUCHI, H. KOINUMA, Y.YOSHIDA AND Y. SEGAWA, $Mg_xZn_{1-x}O$ as a II-VI wide gap semiconductor alloy, *Appl. Phys. Lett*. **72,** 2466-2464, 1998.
11. J. ALBERTSSON, S. C. ABRAHAMS AND A. KVICK, Atomic displacement, anharmonic thermal vibration, expansivity and pyroelectric coefficient thermal dependences in ZnO, *Acta Cryst*, **B 45,** 34-40,1989.
12. B. D. CULLITY, Elements of X-ray diffraction, Addision-Wesley Publishing Co. Inc, 262, 1967.
13. M. K. R. KHAN, M. M. RAHMAN AND I. TANAKA, Preparation, structural and electrical properties of $Zn_{1-x}Li_xO$ solid solution, *The Nucleus*, **39(3-4),** 149-154, 2002.