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Micro-Raman Studies of Li Doped and Undoped ZnO Needle Crystals

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1. Introduction

The interest in ZnO structures has increased drastically in recent years as it is a wide band gap (3.4 eV) II-VI compound semiconductor, with a stable wurtzite structure with lattice spacing $a = 0.325$ and $c = 0.521$ nm. A prominent feature of ZnO is its large exciton binding energy (~ 60 meV) at room temperature which results in extreme stability of exciton [Khan,2005]. ZnO has been used as transparent conductors in solar cells, UV light emitters, as components in high power electronics and gas and chemical sensors. ZnO nanostructure has attracted attention for possible applications in optoelectronic and spintronic devices, such as high-emitting and laser diodes with polarized output, spin based memory and logic [Vladimir,2006].

The topic of p-doping is especially difficult and undoped ZnO exhibits n-type conductivity, and resists being doped p-type. This technological issue pulls up the use of ZnO for optoelectronics. p-type ZnO can be hypothetically achieved by doping with either Group-I or Group-V elements. Doping with Group-I elements is possibly more effective than doping with Group-V elements because of more shallow acceptors [Yamamoto,1999]. It was observed that doping with Group-I elements increases donor concentration. This is attributed to tendency of Group-I dopants to occupy the interstitial sites, partly due to their small atomic radii [Park,2002]. The Group-V elements have low solubility in ZnO due to the mismatch in ionic radii. Several works on p-type ZnO doping have been made and however the results are not reproducible or questionable [Look,2002, Look,2004].

It is believed that large difference in ionic radii between the host Zn (0.74\AA) and the dopant Li (0.60\AA) is very important for the appearance of Ferroelectricity in Li-doped ZnO. The electrical resistivity due to carriers can be improved by the introduction of Li ions [Wang,2003]. The interstice impurity may result in lattice distortion. Therefore the resistivity of the ZnO sample will increase. If the annealing temperature is high, the oxygen vacancy increases which produces more electrons and hence the resistivity of Li-doped ZnO decreases [Min-Rui,2005].

Raman spectroscopy is a non destructive characterization method of choice for many recent studies of the vibrational properties of ZnO nanostructures [Khan,2005, Vladimir,2006, Harish Kumar,2007]. In the present work we have carried out a comprehensive Micro-Raman scattering study of the phonons in Li doped and undoped ZnO needle crystals have been grown using flux growth to ensure good quality and an effective incorporation of the

dopant ions. Flux growth offers the convenience of operating under relatively low temperatures and also it is helpful to obtain crystals with more control on the stoichiometric properties, annealed at 800°C for 1 hour to enhance oxygen vacancy.

2. Experimental

Raman spectra were measured from Li doped and undoped ZnO needle crystals using a Dilor XY double spectrometer under 514.5nm excitation from an Ar⁺ laser. The samples were placed on a glass plate and the laser beam was focused onto the sample using a 50X objective lens. Before the spectra were recorded the instrument was calibrated using the Raman line of Si wafer. The total power of laser excitation at the sample was about 1.05mw.

3. Results and discussion

ZnO is a semiconductor with wurtzite crystal structure, having the space group c_{6v}^4 with two formula unit primitive cell, where all atoms occupy C_{3v} sites [Roth,1967]. The optical phonons at the Γ point of the Brillouin zone belong to the following irreducible representation.

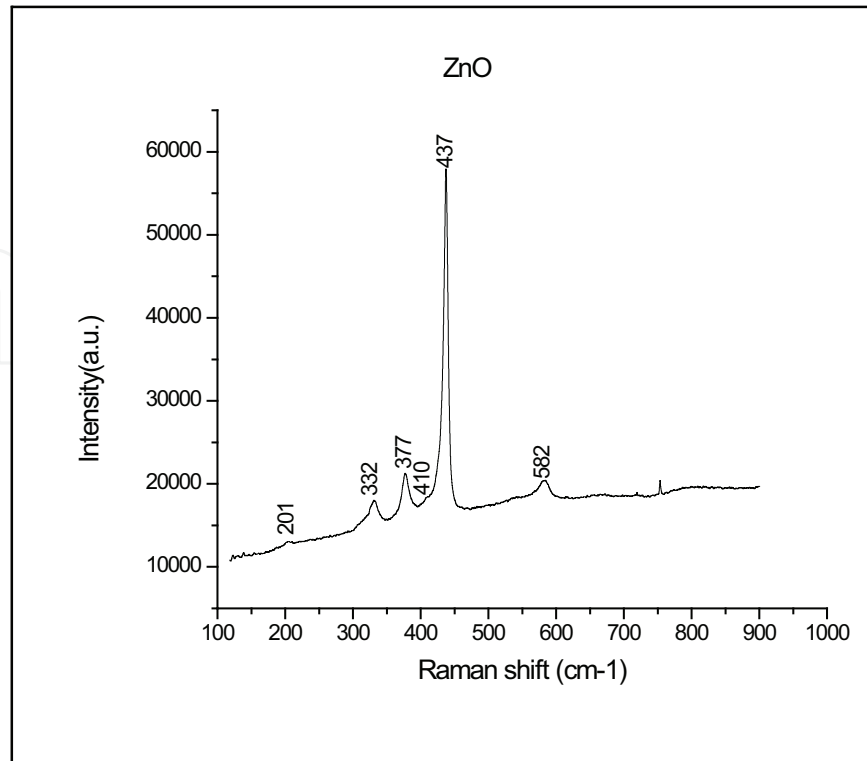
$$\Gamma_{\text{opt}} = 1A_1 + 2B_1 + 1E_1 + 2E_2 .$$

Both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active. The two non polar E_2 modes having two wavenumbers, E_2 (high) is associated with oxygen atoms and E_2 (low) is associated with Zn sublattice. Both are Raman active only. The B_1 modes are infrared and Raman inactive that is they are silent modes [Khan,2005, Bundesmann,2003].

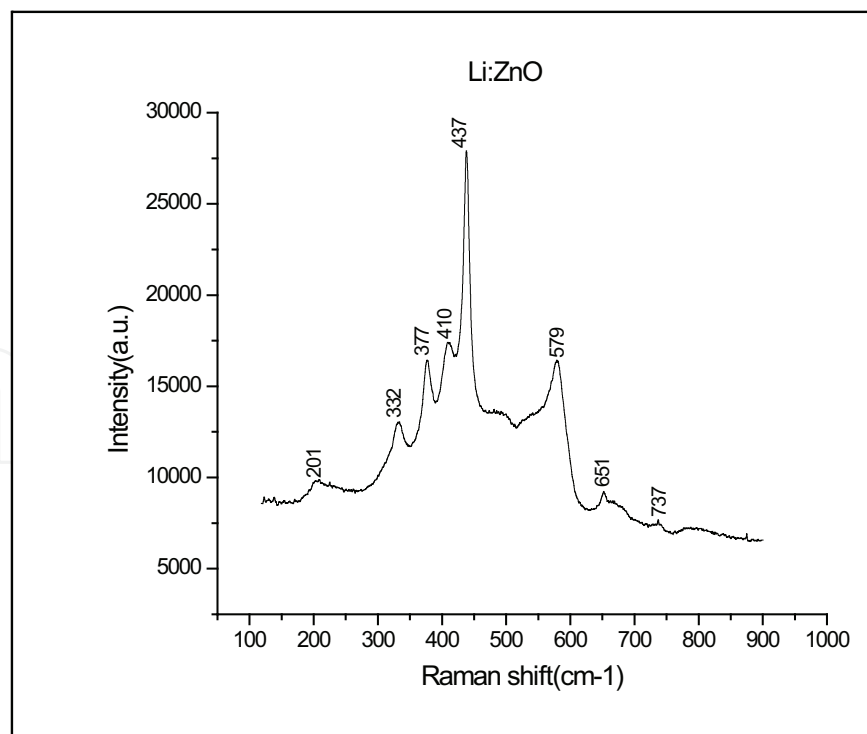
The measured micro-Raman spectra at an arbitrary point of needle ZnO crystal and Li doped needle crystal are shown in Figs. 1(a) and 1(b) respectively.

The wavenumbers of the Raman active phonon modes reported previously for bulk and needles crystals are presented in Table1. [Khan,2005, Tatjana,2007].

Comparison of Fig1 (a) with Table 1, shows that four fundamental and two second-order modes are observed. The only Raman active non polar E_2 (high) mode associated with oxygen atom vibration appears at 437 cm^{-1} with appreciable intensity and E_2 (low) associated with the heavy Zn sublattice is absent [Khan,2005, Alim,2005]. This fact explains that the low-frequency E_2 mode does not resonate at E_o . The vibration of the Zn sublattice does not modulate valence-band states of ZnO which compose almost exclusively of oxygen 2p wave functions [Calleja,1977]. 377 cm^{-1} corresponds to A_1 (TO) and E_1 (TO) mode at 410 cm^{-1} is not predominant in the spectra due to the chosen scattering geometry. A weak E_1 (TO) band at 410 cm^{-1} will appear in the spectrum of the sample consisting of tripods which are not c-axis orientated and may be ascribed to the contribution of the polarization due to crystals mixed orientation [Gupta,2006]. Thus the presence of a very weak band at 410 cm^{-1} corresponding to E_1 (TO) mode indicates that ZnO needle crystals have not grown preferably c-axis perpendicular to the substrate [Tatjana,2007]. A weak peak is observed at 582 cm^{-1} . This band may be due to A_1 (LO) or E_1 (LO) mode (see Table 1). It is reported E_1 (LO) can occur at 584 cm^{-1} as this mode is related to the defects such as oxygen vacancy or interstitial zinc in zinc oxides [Zhang,2006, Zhao,2006]. This is the reason for the appearance of a weak band at 582 cm^{-1} in our case. The A_1 (LO) mode is not observed shows the absence of resonance of exciting phonon energy with that of electronic interband transition with in the ZnO particle [Rajalakshmi ,2000].



(a)



(b)

Fig. 1. (a) and (b) Micro-Raman spectra of ZnO and Li: ZnO needle crystal.

| First Order | | Second Order |
|-----------------------|-----------------------------------|-----------------------------------|
| Optical Phonon | wavenumber (cm ⁻¹) | wavenumber (cm ⁻¹) |
| E ₂ (low) | 102 | 208 |
| A ₁ (TO) | 379 | 334 |
| E ₁ (TO) | 410 | 540-670 |
| E ₂ (high) | 439 | 986 |
| A ₁ (LO) | 574 | 1050 |
| E ₁ (LO) | 591 | 1084-1149 |

Table 1. Wavenumber and symmetry of the fundamental and second-order optical modes in ZnO.

The peaks at about 201 and 332cm⁻¹ are attributed to the second-order Raman spectra arising from zone boundary phonons. [Khan,2005, Tatjana,2007].The peak at 201cm⁻¹ corresponds to the wavenumber of 2E₂ (101cm⁻¹) at Γ . The peak at 332cm⁻¹ should be ascribed to two phonons from the K-M- Σ around 160cm⁻¹[Calleja ,1977].These processes presumably occur for phonon wave vectors considerably removed from the center of the Brillouin zone. Without the knowledge of critical points and selection rules for various points in the zone, appropriate interpretation cannot be made [Tatjana,2007, Nusimovici,1965].

On comparison of Micro-Raman spectra of Li doped ZnO Fig.1 (b) with that of Fig.1 (a), it is noticed that in the case of undoped ZnO the intensity has been decreased. When Li atoms are introduced there will be a change in the electronic bonding force between the nearest two atoms. This in turn will influence the Raman peak positions and line profile. Moreover a drastic phonon anomaly feature was not observed in our case. Hence it suggests that the electronic effects are predominant than the ionic instability [Ehleeaul, 2002].

The E₂ mode at 437cm⁻¹ of Li doped ZnO does not show the Li-dependence [Ehleeaul ,2002] as it is associated with oxygen atom vibration[Khan, 2005, Alim ,2005].The second order mode at 201cm⁻¹ occurring due to oxygen vacancies is pronounced. The peaks at 332 and 377cm⁻¹ are same in both cases. The peak at 410cm⁻¹ E₁ (TO) mode is much intense than undoped crystal. This feature is expected where in the crystals are not grown preferably in c-axis perpendicular to the substrate. This is an evidence of the growth conditions imposed on the system. [Tatjana,2007]. The E₁ (LO) mode is highly intense and broad but shifted to a lower wavenumber side (579cm⁻¹) confirms the point defect density. E₁ (LO) mode is associated with lattice defects, such as oxygen vacancies and zinc interstitials E₁ (LO) mode increases after annealing, so it is possible that defect level such as oxygen vacancies was increased [Tak,2006]. The From fig.1 (b) the origin of two new peaks at 651 and 737cm⁻¹ is not well understood. These peaks could be associated with multiphonon processes [Tatjana, 2007] or unlisted weak plasma lines [Rajalakshmi,2000].

In the present work the micro-Raman spectra was recorded at three different positions (center, tip and wall) of the doped and undoped ZnO needle crystals. The plots are given in Fig.2 (a) and 2(b)

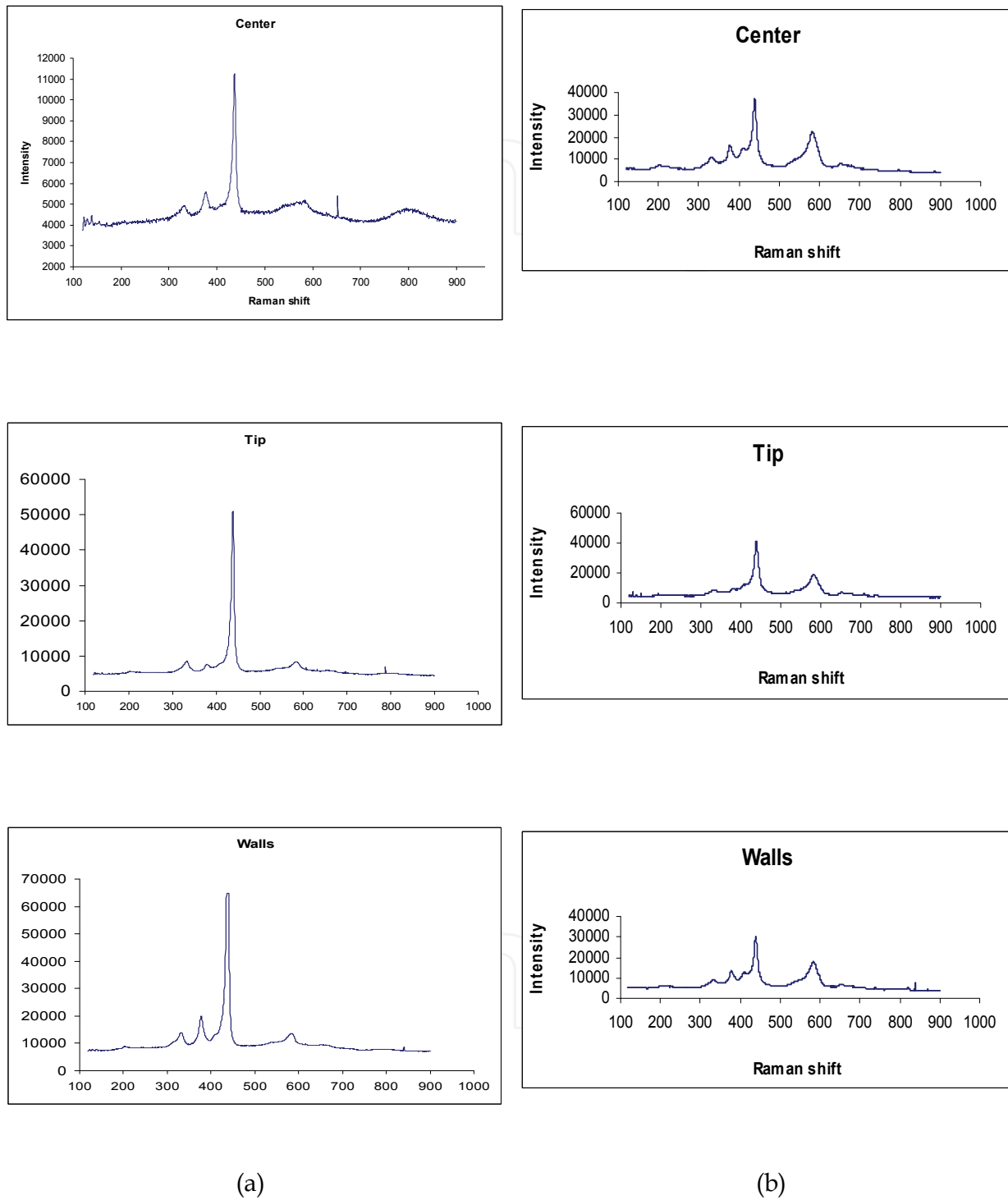


Fig. 2. (a) and (b) are plots of micro-Raman spectra of ZnO and Li: ZnO at different position To study the quality of the crystal the strongest Raman active peak at 437cm^{-1} was intensity normalized and a Gaussian fit was applied to get the area and width under each curve for different regions given in fig. 3(a) and 3(b).

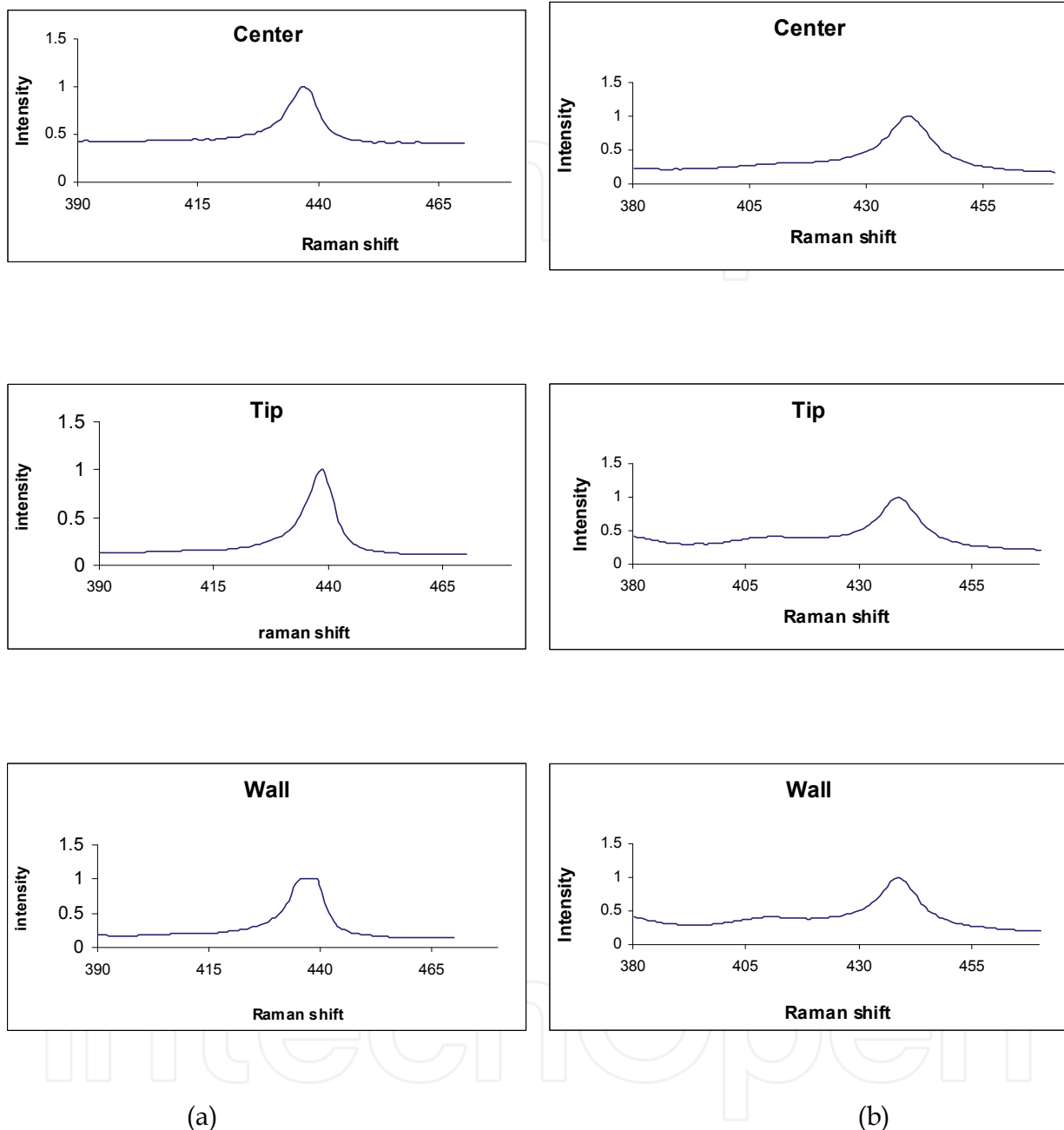


Fig. 3. (a) and (b). Intensity normalized ZnO and Li: ZnO peaks at various positions.

Line width and grain size are inversely proportional to each other [Harish Kumar,2007, Zhang, 2006]. When width decreases grain size increases, a good crystallinity is expected. Similarly area under the peak also shows the same feature as a sharp peak will be observed for a regular degree of structural order. Table 2. presents area and width at center, tip and wall of ZnO and Li doped ZnO needle crystals. On comparison of doped and undoped ZnO needle crystals, it is found that tip of the crystal shows a good crystallinity and high degree of structural order.

| | ZnO needle crystal | | Li doped ZnO needle crystal | |
|--------|-------------------------|--------------------------|-----------------------------|--------------------------|
| | Area(cm ⁻²) | Width(cm ⁻¹) | Area(cm ⁻²) | Width(cm ⁻¹) |
| Center | 5.8 | 7.3 | 7.6 | 9.7 |
| Tip | 5.0 | 7.2 | 7.4 | 9.6 |
| Walls | 8.9 | 8.4 | 9.6 | 11.3 |

Table 2. Area and Width of doped and undoped needle crystal at different positions

4. Conclusions

We have made a careful Micro-Raman study on ZnO and Li doped ZnO annealed needle crystals. It was found that E₂ phonon mode of doped and undoped ZnO does not show any shift. But E₁ (TO) mode is predominant and two new less intense peaks have been observed in Li doped crystal. The shift in the E₁ (LO) mode to a lower wavenumber confirms that our material shows nano dimensional character. With the intensity normalized plots we can conclude that for both Li doped and undoped ZnO crystals the crystallinity is improving towards the tips of the needle crystals.

5. Reference

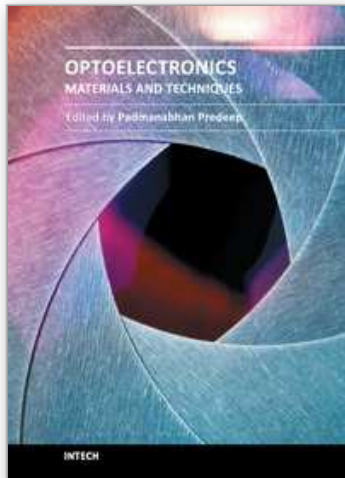
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Optoelectronics - Materials and Techniques

Edited by Prof. P. Predeep

ISBN 978-953-307-276-0

Hard cover, 484 pages

Publisher InTech

Published online 26, September, 2011

Published in print edition September, 2011

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How to reference

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R. Jothilakshmi (2011). Micro-Raman Studies of Li Doped and Undoped ZnO Needle Crystals, Optoelectronics - Materials and Techniques, Prof. P. Predeep (Ed.), ISBN: 978-953-307-276-0, InTech, Available from: <http://www.intechopen.com/books/optoelectronics-materials-and-techniques/micro-raman-studies-of-li-doped-and-undoped-zno-needle-crystals>

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