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Defects induced luminescence and tuning of bandgap energy narrowing in ZnO nanoparticles doped with Li ions


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I. INTRODUCTION

Zinc oxide (ZnO) exhibits an interesting combination of multifunctional properties, including optical transparency in the visible region, semiconducting, piezoelectric, and optoelectronic properties.\(^2,3\) ZnO exhibit wide direct bandgap (3.34 eV) and has a high exciton binding energy (60 meV) at room temperature,\(^3\) which makes it a promising material for devices.\(^2-5\) ZnO crystals are very rich in defects,\(^6\) native and dopant defects mostly exist within the bandgap and exhibit their luminescence at particular wavelength, which plays a key role in tuning the optical performance of devices.\(^7\) ZnO itself is an ideal ultra-violet emitter and can emit in the visible region when defects (i.e., dopants) are introduced.\(^8\) At room temperature, ZnO typically exhibits one sharp emission photoluminescence (PL) peak in the ultra-violet region due to the recombination of free exciton (FX), and possibly one or more peaks in the visible spectral range which are attributed to defect luminescence at different energy states.\(^5,9,10\) In addition to experimental studies of the defect emissions, theoretical studies of different defects\(^5,11,12\) and their formation energies\(^5,13,14\) have been determined. However, the origins of different defect emissions are still not fully understood, and different controversial hypotheses have been proposed to explain the different defect luminescence (violet, blue, green, yellow, and orange-red)\(^10\) at various energy levels.

Several studies have shown the relationship among defects in ZnO and the emissions in the visible region.\(^14,15\) For example, the blue, blue-green, green-yellow, and the red emissions have been assigned to interstitial zinc,\(^16\) Zn vacancy,\(^17\) oxygen vacancy,\(^15,18,19\) and oxygen interstitial\(^19,20\) respectively. Interestingly, ZnO shows a broad visible luminescence, which is linked to point defects in the structure.\(^9,21\) The green luminescence, or deep band emission (DBE), has also been studied extensively, but no consensus on its origin has emerged. Many groups have attributed the DBE to oxygen vacancies,\(^22,23\) oxygen antisite,\(^24\) Zn vacancy,\(^13,25\) interstitial zinc,\(^23\) as well as extrinsic impurities such as copper.\(^26\) However, Özgüür et al.\(^10\) suggested that the DBE may consist of bands having different origins but similar positions. The specific identification and nature of defects for luminescence in the visible region is difficult and challenging because of various types of defects are possibly exist in the ZnO nanostructures.\(^9,12\) Lithium (Li) related defects in ZnO typically lie in the bandgap such as substitutional Li (Li\(_{\text{Zn}}\)) and Zn vacancy (V\(_{\text{Zn}}\)) both act as shallow acceptors while interstitial Li (Li\(_i\)) behaves as donor defects and different complex defects, e.g., Li\(_{\text{Zn}}\)-Li\(_i\) and V\(_{\text{O}}\)-Li\(_i\) are possible at different energy levels within the bandgap.\(^21,27\)

From many fundamental optical properties of impurity-doped ZnO, particularly the variations in bandgap energy, which is about the crucial importance in fabricating devices, is still in need of detailed description. It is possible to tune the bandgap of ZnO by doping with suitable candidates. The correlation between the carriers (electrons/holes) and also with impurity doping ions gives rise to band edge shift, which causes the bandgap shrinkage.\(^28\) Different groups have demonstrated that the band tailing,\(^29\) Burstein–Moss,\(^30\) and band-gap renormalization effects,\(^31\) mechanisms are responsible for narrowing of the bandgap energy by doping of different elements in ZnO system. Particularly, to understand the variations in bandgap energy of the Li doped ZnO system, less attention has so far been paid and very few reports...
have been published. Bandgap energy decreased with increasing Li concentration in ZnO thin films due to substitutional Li defects.\textsuperscript{32} While Burstein-Moss shift has been observed in Li doped ZnO nanorods.\textsuperscript{32} There is however no report on the optical study of Li doped ZnO nanoparticles where finite size effects are also expected to play a significant role in the electronic and structural properties. Thus, a detailed and accurate test of the optical properties of these nanoparticles systems is needed.

In our previous report, we have demonstrated structural, electronic, and magnetic properties of Li doped ZnO nanoparticles.\textsuperscript{34} The present study specifically focuses on the optical response of the same nanoparticles. Detailed microstructural and morphological studies also have been presented here. In this paper, our aim is to investigate different defects via photoluminescence and to study their role in luminescence at different energy levels. We noticed that the bandgap energy of ZnO decreased due to doping of Li content. Finally, the bandgap narrowing energy has been discussed via band tailing effects due to the presence of defects (disorder) and carrier-impurity interactions.

II. EXPERIMENTAL DETAILS

The synthesis procedure of ZnO nanoparticles doped with Li [Zn\textsubscript{1−y}Li\textsubscript{y}O (y = 0.00, 0.02, 0.04, 0.06, 0.08, and 0.10)] has been reported earlier.\textsuperscript{34} Transmission electron microscopy (TEM) of FEI Company’s (Titan G260-300CT TEM)\textsuperscript{35} was used to analyze the samples by operating the microscope at 300 kV. Both selected area electron diffractions (SAEDs) and TEM Image-mode micrographs were recorded on a 4k × 4k CCD camera of Model US4000 from Gatan, Inc. Bright Field (BF) micrographs are acquired at around 70,000X as well as 500,000X for low resolution and high resolution TEM analysis, respectively. The samples were further analyzed with Electron Energy-Loss Spectroscopy (EELS) using Gatan Inc’s Tridiem\textsuperscript{TM} energy-filter. The EELS spectra were collected by keeping the energy of primary electrons to 300 keV and the dispersion to 0.5 eV per channel of energy-filter in EELS-mode.\textsuperscript{35} PL was excited with a He–Cd laser with 50 mW power and photon energy 3.81 eV (325 nm). The optical energy bandgap has been studied by diffused reflectance spectroscopy (DRS) on a Lambda-950 Perkin–Elmer spectrophotometer with integrating sphere attachment and Spectralon reflectance standards.

III. RESULTS AND ANALYSIS

A. Micro-structure and morphology

Low-magnification bright field transmission electron microscope (BF-TEM) micrographs were acquired for ZnO nanoparticles and are shown in Fig. 1(a). We noticed the agglomeration of nanoparticles as the samples are post annealed to improve the crystallinity. After the analysis of BF-TEM images, we found the size of ZnO nanoparticles was

![TEM images of ZnO nanoparticles](image-url)
in the range 10–50 nm (histogram shown inset of Fig. 1(a)). High resolution transmission electron microscope (HRTEM) image of ZnO sample has shown in Fig. 1(b). We found the homogeneous crystalline structure and no amorphous part was present. The fast Fourier transform (FFT) of the HRTEM micrograph is shown in Fig. 1(c). Hough Transforms (SAED) patterns were applied to the FFT to extract the \(d\)-spacing values as shown in Fig. 1(d). Low resolution BF-TEM micrographs of Zn\(_{0.98}\)Li\(_{0.02}\)O nanoparticles are shown in Fig. 2(a). Particles exhibited size distribution which was found to lie in the range, 15–70 nm (histogram shown inset of Fig. 2(a)). HRTEM micrograph (Fig. 2(b)), the FFT image of the HRTEM (Fig. 2(c)), and Hough transform (Fig. 2(d)) measurement was acquired for Zn\(_{0.98}\)Li\(_{0.02}\)O sample.

These \(d\)-values of above samples were extracted by SAED are in good agreement with the X-ray diffraction as we reported earlier.\(^{34}\) From the Hough transforms, we found that all \(d\)-values and planes correspond to ZnO crystalline structure (JCPDS file no. 36–1451). Hence, we observed the hexagonal (wurtzite) crystalline structure, which also confirmed the absence of any metallic or secondary phases in samples. It can be noticed that 2% Li doped ZnO sample has slightly larger \(d\)-spacing than ZnO sample. This observation suggests expansion of the unit cell which is due to the presence of more Li ions at interstitial sites for 2% Li doped sample. Decrease in lattice parameters is expected when Li substitutes Zn while the lattice parameter will increase when Li occupy interstitial sites.\(^{36}\) We reported that Li doped nanoparticles, expansion of lattice parameters at 2%, 8%, and 10% Li incorporation as Li occupy in interstitial sites (Li).\(^{34}\) In contrast, lattice parameters decrease for 4 and 6 at. % Li samples where Li substitutes Zn.\(^{34}\) Here, we can consistently observed increase in \(d\)-space for \(y = \) 0.02 and decrease in \(d\)-values for \(y = \) 0.04 using TEM technique as we extracted via XRD technique.

Energy dispersive spectroscopy (EDS) was acquired in TEM mode. We found that Li peak (signals) was not present in EDS spectra. Li was not detected via EDS. The reason is that the detector is often protected by a Beryllium window. Therefore, energy filtered transmission electron microscopy (EFTEM) measurements were carried out to detect and map Li in the samples. Using EFTEM mode, low resolution image of Zn\(_{0.98}\)Li\(_{0.02}\)O sample was attained as shown in Fig. 3(a). A Li map was acquired for Zn\(_{0.98}\)Li\(_{0.02}\)O sample (see Fig. 3(b)). This Li map revealed that Li was distributed uniformly and homogeneously into the ZnO crystal structure. These finds also confirmed the absence of precipitates or clusters. We observed the O-K edge and Zn-L\(_{2,3}\) edge in full scan range 400–1400 eV EELS spectrum for \(y = \) 0.02 sample shown Fig. 4. Li-K edge and Zn-M\(_{2,3}\) edge are clearly visible in lower scan range 50–180 eV spectra shown inset Fig. 4. No other element has been detected in EELS spectra. Microstructural analysis confirmed the crystalline structure and homogeneous distribution of Li (even in 2% Li doped sample).
B. Photoluminescence spectroscopy

The room temperature PL spectra in the range 800–350 nm are shown in Fig. 5 for the entire series (0.00 \( \leq y \leq 0.10 \)) of samples. The typical sharp UV and broad visible bands were observed. PL emission spectra of undoped and doped samples are similar in nature, but showing PL intensity variations with increasing of the Li concentration. Such PL intensity variation in nanostructures with change in dopant concentration can be understood via considering the formation of different defects. The UV peak is usually considered as the characteristic emission of ZnO and is attributed to the near band edge (NBE) exciton emission, which originates from free exciton (i.e., combination of electron and hole) luminescence and a broad visible band observed due to formation of native defects across the band gap of ZnO. UV and Visible bands in undoped and doped ZnO have multiple emission and frequently assigned to differentiate defects. UV emission (i.e., NBE) region \( \sim 350–450 \text{ nm} \) of some selected samples, e.g., \( y = 0, 0.06, \text{ and } 0.10 \) samples is enlarged for convenience and can be well fitted by two Gaussian line-shape peaks shown Figs. 6(a)–6(c), respectively. By fitting this sharp UV region, two transition energies are derived from the fitted components as \( 3.30 \pm 0.01 \text{ eV}(375 \pm 1.21 \text{ nm}) \) and \( 3.20 \pm 0.02 \text{ eV}(387.50 \pm 2.42 \text{ nm}) \), which are assigned to FX and donor–acceptor pairs (DAP) respectively for \( y = 0.00 \) sample. These values of energies are comparable with recent reported values. Deconvoluted peaks “a” and “b” shown in Figs. 6(a)–6(c) are therefore correlated by us as representing the FX and DAP luminescence. We found a decreasing change (towards lower energy) in the peak position of FX emission shown in Fig. 6(d). The FX peak is related to NBE emission that respond free exciton recombination through exciton-exciton collision process. We are suggesting that the NBE emission shifts towards lower energy due to carrier-impurity and carrier-phonon interactions (mechanism will be discussed in the Sec. IV), i.e., band tailing effects. Awan et al. vs
reported shifting of NBE towards lower energy in Li doped ZnO thin films. They suggested that Li serves as a defect mediator in ZnO by changing the relative concentrations of intrinsic defects. In contrast, broadening of the band-gap is reported (blue shifting of NBE emission) in Li doped nanorods. In their proposed mechanism, Li generated holes in the valence band shift the Fermi level to a lower position, thus widening (blue shift) the band gap. Srinivasan et al. found blue shifted NBE emission of higher energy due to the formation of Li at interstitial defects.

In literature, different types of defects are responsible for green, yellow, and orange-red emissions, but the natures of the defects for these luminescence have not been conclusively established. The most commonly observed green luminescence in ZnO is also the most controversial one, for which various hypotheses have been proposed. Yellow and orange-red emissions have been less controversial. It has been proposed that these two emissions may involve similar deep levels but different initial states (conduction band and shallow donors), and they were also found to exhibit different dependences on the excitation wavelength. The yellow emission is commonly attributed to oxygen interstitial defects, although some impurities such as Li may also play a role. In addition to this common hypothesis, the possible presence of Zn(OH)₂ at the surface was identified as a possible reason for the weak UV and the strong visible (broad yellow and green) emission. The orange-red emission centered at ~640–650 nm is also commonly attributed to the presence of excess oxygen in the samples, such as oxygen interstitial defects. Other hypotheses include surface dislocations and zinc interstitials are correlated with orange-red luminescence in ZnO.

We next turn to the broad visible band which has been decomposed into four different Gaussian peaks along the entire emission range shown in Figs. 7(a)–7(d) for 0, 0.02, 0.06, and 0.10 samples, respectively. Similarly deconvolution of the broad visible band for N and F co-doped ZnO:Li nanowires has been reported. Li and according to the literature, the binding energy of these deconvoluted peaks corresponds to different defects. The peak “c” located at 478 nm (2.59 eV) can be attributed to the electron transition from the shallow donor level of zinc interstitial and oxygen vacancies to the valence band. The peak “d” centered at 518 nm (2.39 eV) is attributed to the transition from the conduction band to VZn defect level. Peak “e” located at 542 nm (2.29 eV) is typically related...
to interstitial Oxygen defects. The yellow emission (550–650 nm) for undoped ZnO can be due to the Zn(OH)$_2$ or OH group. The peak “f” observed at 615 nm in our ZnO sample corresponds to yellow emission. The yellow luminescence in doped nanoparticles can be due to both Li$_{Zn}$ and Li$_i$ defects. The peak “f” observed at 574 ± 0.04 nm (2.16 ± 0.04 eV) in doped samples can correspond to the transition from donor levels (V$_{o}$, Zn$_{ni}$ and Li$_i$) in the crystal to Li$_{Zn}$ acceptor levels, releasing yellow luminescence. Pipat et al. have reported yellow luminescence in undoped ZnO due to OH ions and in doped ZnO nanorods due to Li ions. Rauch et al. observed experimentally that the deep Li$_{Zn}$ acceptor defect has been made responsible for yellow emission in Li doped ZnO nanocrystal. Borseth et al. experimentally demonstrated the luminescence at positions 2.53 eV, 2.35 eV, and 2.17 eV are assigned to V$_{Zn}$, V$_o$, and Li related defects, respectively. Meyer et al. observed that deep Li acceptor related photoemission at 2.05 eV and shallow acceptor Li related defects at 3.05 eV due to deep acceptor pair DAP recombination. Zhang et al. observed shallow V$_{Zn}$ at 2.07 and Li$_{Zn}$ at 3.0 eV using depth cathodoluminescence spectroscopy.

C. Diffused reflectance spectroscopy

Ultraviolet-Visible (UV-Vis) DRS technique was employed to measure the absorption edge for pelletized samples. The spectrum of diffuse reflectance signal is the ratio of the intensities of diffuse reflected light from the sample and from standard Spectralon ($R = I_{diffuse}/I_{standard}$). The DRS spectrum for a series of Zn$_{1-y}$Li$_y$O (0.00 ≤ $y$ ≤ 0.10) samples is shown in Fig. 8. All spectra were measured in the wavelength range of 250–800 nm at room temperature. We observed that reflectance was enhanced in the visible region of the reflectance spectra for doped samples as compared to undoped ZnO sample. The average diffuse reflectance is found to be almost in range between ~11–18 percent in the visible region for the entire series of samples. The absorption band edge shifts toward higher wavelength (lower energy) as a function of Li concentration.

The diffuse reflectance “R” of the samples can be analyzed using the Kubelka–Munk function $F(R)$ by the well known relation $F(R) = (1 - R)^2/2R$. The DRS spectra of
the entire series of samples after Tauc plot\textsuperscript{57} treatment have shown in Figs. 9(a)–9(f). The optical energy band-gap ($E_g$) of the samples was determined from the DRS spectra by plotting $[F(R)*h\nu]^2$ function versus energy\textsuperscript{58} and extrapolating the linear part of the curve to $[F(R)*h\nu]^2 = 0$. The intersection between the linear fit and photon energy axis gives the value of $E_g$. The optical direct band-gap for the entire series of samples was determined ranging from 3.26(±0.014) to 3.17(±0.018) eV. From the wavelength variation (red shift) in the absorption edges, the band gap can be seen to shift towards lower energies as a function of Li concentration as shown in Fig. 10. The detailed discussion of band-gap narrowing with increasing Li concentration is described below.

**IV. DISCUSSION**

The optical bandgap energy of a semiconductor is the minimum energy required to move an electron from its valence band (bound energy state) to conduction band (free energy state) where it can participate in conduction. From the point of view of applications, the energy gap of semiconductor is an essential parameter, which determines the current-voltage characteristic of a $p$-$n$ junction and also the energy of electroluminescent recombination radiation. A key issue in the development of materials is to produce semiconducting materials with high uniformity, small dimensions, and narrow bandgap energies, since bandgap narrowing allows low energy absorptions and excitations for effective operation of semiconductors under light irradiation.\textsuperscript{7,59} However, this aspect of narrow bandgap engineering is difficult to achieve, since most semiconductor would show an enlarged bandgap as dimensions reduce due to surface defects.\textsuperscript{60} The bandgap narrowing behavior is related to band tailing by impurity-introduced potential fluctuation,\textsuperscript{61} carrier–carrier and carrier–ion many-body interactions.\textsuperscript{62} The potential fluctuation introduced by the ionized impurities leads to the band tailing of the valence and conduction bands and contributes to the bandgap narrowing.\textsuperscript{61} The electron–electron, hole-hole, and carrier–impurity interactions could lead to the lowering of the conduction band and an upward shift of the valence band, which causes the band-gap narrowing.\textsuperscript{28,61–64} The band-gap narrowing due to Mott critical density is another way for the explanation of decreasing the band gap in semiconductors.\textsuperscript{65} For the $p$-type conduction,
the majority carriers are holes at the top of valence band; and for the n-type conduction, they are electrons at the bottom of the conduction band. When the carrier concentration in the conduction band exceeds a certain critical value (e.g., Mott critical density), the wave functions of donors begin to overlap, and the impurity band merges into the conduction band due to the spreading of the discrete donor levels in forbidden band. The Fermi energy level enters into the conduction band would cause a downward shift of the conduction band.

Generally speaking, absorption occurs when the incident photon energy is large enough to excite electrons across the energy gap between the valence and conduction bands. The band tail effect can be observed not only in the low energy region of absorption spectra but also in luminescence spectra, where band-to-impurity and band-to-band recombination processes dominate. The band tails in this Li doped ZnO system like other semiconductors caused by the disorder and carrier interactions in the material, structural disorder, impurities, and carrier concentration. It is noted that the absorption profile and luminescence spectra within the whole energy range can be reproduced by calculating the density of occupied states (DOS). Many efforts have been made to get an expression for DOS with the ionized impurity effects, which can produce potential fluctuations due to the Coulomb potentials and temperature effects. It is well known that the degree of disorder is associated with strain, dislocations, lattice imperfections, defects, as well as the effect of the grain surface. The evaluation of the disorder plays a significant role in studying polycrystalline materials. The increase of the disorder leads to the strong potential fluctuations, and therefore large the carrier–impurity and the carrier–phonon interactions.

The presence of impurities and defects in an otherwise perfect semiconductor perturb the band structure by introducing additional states within the bandgap in the form of tails of intrinsic bands thus affecting the physical properties of the system. Such band tailing is attributed to impurity band formation, point defects, structural disorder, excitonic transitions, or inhomogeneous strains in the system. The decrease of the bandgap with doping of Li as understood by us along the lines of Piet et al. In semiconductors when dopant impurities are inserted into the host lattice, the dopant ions can locally introduce a distinct level within in the bandgap. At high densities of dopants, these local levels can overlap to form a band. It has been shown that at sufficiently high p(n)-type doping concentrations, this impurity band can merge with the valance (conduction) band. The conduction carriers (electron/hole) together with the donor electrons form an interacting Fermi gas. The interactions of electrons both among themselves and with the positive impurity ions change the parabolic $E_n(k)$ relation of the non-interacting Fermi gas or equivalently the DOS of the unperturbed semiconductor considerably. These effects may be viewed as a rigid shift of the conduction band towards the valence band (bandgap narrowing) and a distortion of the DOS. In addition to this distortion, the fact that the impurities are randomly distributed in space causes the DOS to tail. In our Li doped nanoparticles, we attribute the bandgap narrowing to the combined effects of disorder and the formation of band tails as described in other p-type systems. Thus, we suggest that the narrowing of the bandgap occurs due to a structural disorder (defects), carrier-donor and carrier-acceptor impurity interactions, electron-phonon and hole-phonon interactions. At high Li doping concentrations, the impurity band merges with the valence band edge, and it becomes band tail states. The total bandgap energy shift is due to (a) the exchange energy for holes and electrons in the valence bad and conduction band, respectively, and (b) due to the interaction between impurity ions and charge carriers. It is obvious that the observed bandgap narrowing from DRS absorption and NBE emission from PL support each other. Present results could be crucial for future applications of ZnO based optoelectronic devices and to get further insight into the origin of narrowing bandgap effect in lighter elements doped ZnO nanoparticles.

V. SUMMARY AND CONCLUSIONS

We have studied the micro-structural and optical properties of Zn$_{1-y}$Li$_y$O (0 ≤ y ≤ 0.10) nanoparticles. Polycrystalline structure was confirmed from HRTEM analysis and compared with XRD results, and no diffraction patterns from secondary phases were detected. FFT and Hough transform micrographs confirmed the wurtzite structure of samples. The energy levels of different defects were investigated from the deconvolution of UV and broad band emissions are in good agreement with theoretical reports. We noted that PL data reflect the native and dopant related defects and the luminescence within the band gap of ZnO. The band gap narrowing was observed from NBE and DRS. An estimation of the band gap narrowing was obtained by considering various interactions among the carriers and ion cores and overall, the net effect of merging of the donor and conduction bands. This was explained by the shift of the band edges due to the existence of exchange and correlation energies among the impurity and hole-electron systems and also by the interaction between hole-hole and electron-electron systems. Finally, bandgap narrowing was explained via band tailing effect and it was concluded that these nanoparticles may find potential application in the novel spintronics and optical devices.

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