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Precise Determination of Optical Band Gap in Cr-Doped Semiconductor Nanowires

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Abstract:

Pristine and chromium-doped ZnO nanowires were prepared following the traditional co-precipitation method. X-ray diffraction data identified a pure wurtzite hexagonal crystal structure characteristic for ZnO, irrespective of the doping level. The particle size, as deduced from Williamson–Hall plots, was found to be 45-55 nm for all samples. Scanning electron microscopy revealed a clear nanowires morphology for the pure and doped samples, while elemental analysis ensured the successful Cr-doping. Distinct spectroscopic signatures of Cr-doping were revealed from a detailed deconvolution process applied to optical spectra of doped samples, where Cr³⁺ optical transitions were unambiguously identified at ~420 and ~665 nm. Particularly relevant, is the spectral decomposition here performed for the superimposed absorption edge (~385 nm) and Cr³⁺ optical resonance at ~420 nm, allowing to claim practically doping-independent optical band gap behavior in the present doping regime. This is further supported by identifying the characteristic ZnO near edge photoluminescence peak (~ 392 nm) which maintains fixed wavelength after Cr-doping. These findings contrast earlier studies on Cr-doped semiconductor nanoparticles and glass systems where the optical band gap has been largely underestimated. We attribute the inconsistency band gap values reported in literature for Cr-doped semiconductors to the proximity of Cr optical transitions to the semiconductor absorption edge.

Keywords: Semiconductor nanoparticles; Optical band gap; Optical absorption spectroscopy; Transition metals; Diluted magnetic semiconductors; Elemental analysis

Graphical Abstract:

Introduction:

SEMICONDUCTOR nanoparticles are essential building blocks in diverse applications spanning biology, chemistry, and physics, as they offer a high degree of control over the material properties through fine manipulation of nanoparticles with on-demand size, morphology, and chemical composition ^[1-6]. Such a remarkable advance has been facilitated by the rapidly progressing nanofabrication tools, including liquid and vapor phase methods as effective and costless “*bottom-up*” routes ^[7-10]. A valuable textbook example of the size-property interplay can be found in, *e.g.*, semiconductor quantum dots, where quantum confinement was found to tune the optical band gap over the entire visible ^[11-13] and infrared spectral regimes ^[14-16]. The actual size of the semiconducting energy gap with their possible modulation through nanotechnology is enormously important as it defines their possible integration in a wide range of technologically relevant applications. For instance, ZnO and TiO₂ with their characteristic wide band gap (~ 3.3 eV) and large exciton binding energy are highly suitable for transparent electronics ^[17,18], photovoltaic devices ^[19,20], and ultraviolet light emission and laser diodes ^[21,22]. Additional means of band gap engineering rely on slight modification of the chemical composition through doping or alloying ^[23,24]. In such diluted doping/alloying regime, some basic characteristics of the host material are barely affected, while emerging hybrid properties inherited by the dopant come into play. Diluted magnetic semiconductors are such examples, where traces of transition metal (TM) dopant can induce room temperature (RT) ferromagnetism in the otherwise nonmagnetic material ^[25,28].

Nanoparticles made of such diluted magnetic semiconductors offer wider platform to explore altogether the size, morphology, and chemical composition effects on materials. Although the variation of the semiconducting band gap with the nanoparticle size/shape is well established for pure materials ^[29-32], this remains controversial for TM-doped semiconductors, since largely inconsistent values are reported in literature for the same explored systems. For instance, different band gaps ranging from ~300 meV to ~1.5 eV smaller than the pristine values were reported for Cr-doped TiO₂ and ZnO nanocrystals in spite of the similarly low doping level involved ^[33,40]. Notice that such large modulation in gap size, with minimal doping, can be seriously misleading, since variations within this order can potentially shift the operation platform for devices from ultraviolet to infrared spectral ranges. Similar gap size discrepancies can be found in other gapped systems, such as glasses, when doped with TMs. The band gap in Cr-doped borate glasses, for example, was reported to be ~1.3 eV smaller than the typical value for borate glasses ^[41,42], while recent studies claim barely affected (± 0.2 eV) band gap due doping ^[43,44]. In fact, on theoretical bases, one should not expect large band structure variations (except for energy shifts) or gap size modulation for doping level as diluted as dopants per more than six-unit cells ^[45,46].

Here we address the origin of this rather recurrence and controversial optical band gap size, by utilizing the co-precipitation method to synthesis pristine and Cr-doped ZnO nanoparticles that exhibit practically identical crystalline structures and morphologies as inferred from X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Discrete Cr³⁺ optical transitions were identified by performing spectral decomposition of the optical absorption spectra for doped samples. We estimated the typical ZnO band gap energy (3.2 ± 0.15 eV) for all samples irrespective of the doping. By performing such a detailed deconvolution process, complemented by photoluminescence measurement, and through a simple thought-experiment we state that the proximity of Cr³⁺ optical transition, here located at ~2.95 eV, to the absorption edge appears to be at the origin of the largely underestimated band gap values reported in some earlier literature.

Experimental methods:

PURE and chromium-doped [Cr_x Zn_(1-x) O] samples ($x = 1\%$, 3% , 5% , and 7%) were prepared by utilizing the conventional co-precipitation method. The following commercial grade (LOBA Chemie) chemical reagents were used: Zinc acetate dehydrate [Zn(CH₃COO)₂·H₂O, purity 98%], Chromium(III) chloride hexahydrate [CrCl₃·6H₂O, 93% purity], and Sodium hydroxide [NaOH, purity 93%]. 21.95 g and 16.0 g of Zinc acetate and NaOH, respectively, were separately dissolved each in 100 ml distilled water and magnetically stirred at room temperature (RT) until homogenous solutions are obtained. For the Cr-doped samples, the respective amount of CrCl₃·6H₂O [0.26645 g (1%), 0.79935 g (3%), 1.33225 g (5%), and 1.86515 g (6%)] are added at the expense of Zinc acetate. Droplets of NaOH solution was slowly added to the solutions containing Zn and/or Cr kept under continuous stirring for three hours at RT. The product precipitates are then filtered

out, washed thoroughly with ethanol and distilled water to eliminate chemical residuals, and eventually oven dried at 70 °C for 3-4 hours. All powder samples were softly annealed to 400 °C for 24 hours to ensure good crystallinity of the formed nanoparticles.

The crystalline structure and nanoparticle size were examined from XRD measurements on the powder samples. PANalytical X'pert Pro-type X-ray diffractometer operating with $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) was used. The 2θ diffraction scans were collected with 0.02° angular step. The morphology and chemical compositions of the selected samples were determined using scanning electron microscopy (SEM, Quanta FEG 250-type 20 KV) equipped with energy dispersive X-ray (EDX) utility. The powder sample was mounted on the sample holder and coated with Au as a conducting metal. The UV-Vis optical reflectance, expressed here conveniently as apparent absorption, spectra were acquired using JASCO V-650 spectrophotometer in the 200-1100 nm range, on powders of the samples pressed into thin disks. The Photoluminescence spectra were recorded using Shimadzu Europe - RF-5301 Spectrometer with excitation wavelength of 340 nm. The fitting of XRD data and deconvolution process performed on the optical absorption spectra were utilized using Igor Pro software (WaveMetrics, Inc.). All experiments were performed at RT under ambient conditions.

Results and Discussions:

Figure 1A depicts the XRD diffraction patterns of the pure and all Cr-doped ZnO samples. All samples exhibit well defined diffraction peaks characteristic for the crystalline wurtzite hexagonal ZnO single phase [47]. The position of the predominant diffraction peaks labeled (100), (002), (101), (102), and (110) agrees well with the standard values reported in the JCPDS 00-036-1451 card [48]. The representative color plot of the diffraction data (Fig. 1A, bottom) revealed homogenous peak intensity and practically the same peak width and position for all samples, irrespective of the doping level. In order to quantify minor changes, particularly, in the peak width, the spectra were fitted with a set of Lorentzian peaks convoluted with a Gaussian broadening to account for the instrumental resolution.

Figure 1: (A) XRD patterns for pure and Cr-doped ZnO nanoparticles. The lower panel is a color scale plot for the same data on top. (B) The deconvolution process for the XRD spectrum of 3% Cr-doped ZnO sample. The pink and black spectra are the experimental data and overall fitting. The dashed green and red curves are the background and fitting residuals. (C) The Williamson-Hall plot for the pristine and Cr-doped ZnO samples

A representative example of such fitting process is presented in Fig. 1B exclusively for the 3% Cr-doped sample. The resulting fitted peaks are shown in blue, while the overall fitting curve (black) clearly coincides with the experimental data (pink), with only marginal residuals (red). The same procedure is applied to all samples and the peak position, intensity, and width are obtained. In order to estimate the crystalline sizes (D), we substitute the obtained peak position (θ) and the full width at half maximum (β_{hkl}), in radian, for each diffraction peak (hkl) into the Williamson-Hall equation [49-50];

$$\beta_{hkl} \cos(\theta) = K\lambda/D + 4\epsilon \sin(\theta), \quad (1)$$

where $K = 0.94$ is the shape factor, λ is the wavelength of X-ray Cu $K\alpha$ radiation, and ϵ is the micro-strain.

In Fig. 1C we present the Williamson-Hall, i.e., $\beta_{hkl} \cos(\theta)$ vs. $\sin(\theta)$ plots for all samples. All data points fall within the yellow shaded region indicating a similar average particle size and lattice strain for the samples. The particle size as determined from the intercept with y-axis was found to be $D = 50 \pm 5$ nm, while the micro-strain was $\varepsilon = 0.0051$ as obtained from the slope of Williamson-Hall plot. The present analysis, therefore, revealed practically no effects on the pristine ZnO atomic structure, lattice strain, or the particle size.

In order to shed the light into the morphology of these nanoparticles and, most importantly, to ensure the successful Cr-doping we present, in Fig. 2, SEM images (A-B) and EDX spectra (C-D) for the pure and 7% Cr-doped ZnO samples. Both the pure (A) and Cr-doped (B) samples revealed micrometer long nanowires morphology commonly reported for ZnO nanostructures^[51-52]. The chemical compositions of the two selected samples are obtained from the EDX spectra presented in (C-D). The EDX spectrum for the pristine ZnO sample (C) consists of the characteristic Zn and O peaks^[33,37]. The blue peak close to 2.2 KeV is resulting from Au coating required for the measurement. The atomic percentage of Zn and O are tabulated at the figure insets, and clearly corresponds to pure and highly stoichiometric ($\sim 1:1$) ZnO phase. Likewise, the EDX spectrum of the 7% Cr-doped sample (D) features the Zn and O characteristic peaks, in addition to specific signals (green peaks) stemming from Cr dopant^[33,37]. The atomic percentage of Cr was 3.85 %, i.e., 45 % lower than the nominal doping level for this sample (7%), suggesting a limited Cr incorporation ability within the ZnO lattice when performed through this conventional co-precipitation synthesis method. However, such a doping level is considered reasonably high when compared to the maximum 4.65 % Cr-doped ZnO produced by the more aggressive microwave assisted synthesis^[37]. Interestingly, the $\sim 1:1$ Zn:O stoichiometry of pristine ZnO is here maintained after Cr doping ($\{\text{Zn}+\text{Cr}\}:\text{O}$) which is certainly advantageous and clearly contrasts the nonstoichiometric ($\sim 1:3$) Cr-doped ZnO produced by efficient microwave assisted methods^[37].

Therefore, this gentle and homogenous doping process allows to maintain fixed stoichiometry, similar lattice constant, and eventually similar average nanoparticle size for the pure and Cr-doped samples as revealed from their typical EDX and XRD data in Fig. 1-2. With such a one-to-one structural and morphological correspondence between pure and doped samples, we can proceed by investigating the effect that Cr-doping has on the optical properties of ZnO, being the main concern of this manuscript.

Figure 2: (A-B) SEM images for the pure (A) and 7% Cr-doped (B) ZnO nanowires. (C-D) Elemental microanalysis of EDX spectra for the samples presented in (A-B), respectively. The atomic percentages of the elemental composition for each sample are tabulated in the insets of (C-D).

Figure 3A presents the optical absorption spectra for all samples. The pure sample (black) is characterized by a sharp absorption edge centered at ~ 385 nm (black arrow) corresponding to a band gap energy of ~ 3.22 eV. This value coincides with the optical band gap reported for bulk ZnO [53]. From a qualitative view into Fig. 1A it appears that all Cr doped samples undergo a red shift compared to pure ZnO sample. However, a closer inspection revealed the presence of Cr features indicated by the red arrows. In particular, Cr feature close to the band gap which appears as a weak shoulder renders the estimation of band gap energy rather difficult. In order to disentangle those “discrete” Cr specific transitions from the bulk ZnO “continuum” we performed a detailed deconvolution process to the optical spectra. Figure 2B depicts the optical spectrum of the nominal 7% Cr-doped samples (blue) and the corresponding peaks (light blue) and edge (dotted black) decomposition. The overall fitting of the spectrum (red) matches perfectly the experimental data. The optical band gap size determined from the center of the band edge resulting from this deconvolution process (dotted black) was ~ 3.24 eV, i.e. practically identical to pure ZnO sample. This finding allows us to revisit some earlier studies where the optical band gap of Cr-doped ZnO and TiO₂ was largely underestimated [33-35,54,55]. In fact, similar ambiguous determination of the optical band gap for other systems doped with Cr, such as borate glasses, is often found in literature [41,42].

Figure 3: (A) Optical absorption spectra for the pure and Cr-doped samples. The black and red arrows point to the position of the absorption edge and Cr transitions, respectively. (B) Deconvolution process applied to the 7% Cr-doped sample. The red and blue curves stand for the overall fitting and experimental data, while the dashed black edge and light-blue peaks are the resulting absorption edge and Cr transitions, respectively. (C) The deconvoluted optical transitions of Cr^{3+} for all Cr-doped samples. (D) The optical absorption spectra presented in (A) after normalization to the pure ZnO spectrum.

In Fig. 3C we separate the discrete optical transitions characteristic for Cr after detailed deconvolution process applied to all samples. Two clear peaks were found at ~420 and ~665 nm, which are brought by $d-d$ transitions of Cr^{3+} and are commonly assigned to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ transitions, respectively ^[43]. The systematic increase in the intensity of these bands reflects the different amount of Cr-doping within each sample. Notice, from Fig. 3A, that Cr^{3+} peak at ~665 nm can be readily recognized without the deconvolution process, while the band at ~420 nm is largely screened by the absorption edge. Since the optical band gap was found to be doping-independent (within ± 0.15 eV), it should be possible to unmask this near edge Cr^{3+} transition by normalization to the featureless absorption spectrum of the pristine ZnO (black spectrum in Fig. 3A). These absorption-edge-normalized spectra are presented in Fig. 3D, for all Cr-doped samples, where the strong Cr^{3+} optical transitions (at ~420 nm) are now clearly recognized.

Figure 4: (A-B) Optical absorption spectra for Cr-doped ZnO (A) and TiO₂ (B) nanoparticles as extracted from Ref. [54] and Ref. [34], respectively. The red and black arrows point to different choices of the position of the absorption edge, while green arrow refers to Cr transitions. The black, light-blue, and red curves are the result from the deconvolution process applied to the blue spectra. (C) Literature survey of the band gap variation with Cr concentration for ZnO, TiO₂, and glasses compared to the present system.

In order to highlight the presence of near-edge Cr³⁺ transition in some earlier studies and to re-estimate the band gap accordingly, we present in Fig. 4(A-B) the optical spectra extracted from Ref. [54] and Ref. [34] for Cr-doped ZnO and TiO₂ nanoparticles, respectively. The data points (blue) contain a clear shoulder (green arrow) close to 440 nm resulting from Cr³⁺ transition, which was not taken into account in Ref. [54,34]. Therefore, the band edges according to Ref. [54,34] were assigned to the position of the blue arrows, leading to band gap values of 2.5 eV and 2.94 eV, respectively. After the here performed deconvolution of these spectra the estimated band gaps were found to be ~3.13 eV and ~3.41 eV for ZnO and TiO₂, respectively, consistent with the present study. Additional examples from literature for Cr-doped systems and their underestimated band gap values due to Cr³⁺ transitions are depicted in Fig. 4C.

Figure 5: Photoluminescence spectra for selected samples; pure (black), 1% Cr-doped (red), and 5% Cr-doped (green) ZnO. The black arrow points to the position of the near-edge emission from ZnO. The excitation wavelength is 340 nm.

Information regarding the size of the optical band gap can be inferred from the emission measurements. Figure 5 depicts the typical photoluminescence spectra of the pure ZnO and two selected Cr-doped (1% and 5%) samples measured at room temperature. The features above 400 nm belong to various zinc or oxygen lattice defect states within the ZnO band gap ^[56-58]. In particular, the broad spectral feature at ~470 nm corresponds to a deep level emission from either oxygen vacancies or interstitial Zn ions within the ZnO lattice. Importantly, the narrow UV emission at ~392 nm (see black arrow), which corresponds to the near-band excitonic transition or band-to-band recombination, has fixed wavelength for the pure and Cr-doped samples, rather likely indicating unperturbed band structure at the bottom (top) of the valence (conduction) band, i.e., fixed band gap energy.

We stress that the estimation of the optical band gap for a semiconductor or insulating material, should be carefully examined in the presence of dopants with near-edge optical transitions, otherwise the analysis and interpretation of such highly featured optical absorption spectra would be largely mistaken. In Fig. 5 we highlight the importance of this issue and possible misleading interpretations of relatively simple doped semiconductor system. Figure 6(A-C) presents schematic representation of the band structure characteristic for direct semiconductors (A), the corresponding simulated absorption spectrum (B), and the often used Tauc's plot (C) applied to the data in (B). The optical band gap can be estimated either from the inflection point of the absorption edge (black dot in B) or from the intercept of the green line in (C) with $h\nu$ axis at $(\alpha h\nu)^2 = 0$ (black dot in C). The two approaches yield practically (within ± 0.1 eV) identical gap size for this

pristine semiconductor or insulating systems. Unlike valence and conduction bands (VB and CB) continuum in solids, individual ions/atoms offer discrete electronic structures as sketched in (D) that, when optically active, contribute well-defined peaks in the optical absorption spectra (E). Here T1 and T2 refer to simulated optically allowed transitions with similar (T1) and smaller (T2) energies than the band gap of the material in (A-C).

In Fig. 6(F) we sketch the electronic structure of the system in (A) when doped with the ions in (C) assuming no change of the properties for the doped system. The positioning of the atomic levels with respect to VB and CB is arbitrary, since optical features are decided by the energy separation indicated by arrows. Within this non-interacting regime, the optical absorption of the doped system (G) is simply the sum of the spectra in (B) and (E). Notice how a qualitative inspection into Fig. 1(G) can lead to several misleading conclusions. For instance, the gap size as determined from the inflection point (black dot) should be ~ 0.3 eV smaller than the gap in (A), which is obviously not the case. Additionally, the T1 transition is completely screened, while the peak resulting from T2 (black dot at ~ 520 nm) is barely recognized. In fact, the gap size can be even largely underestimated (by more than 1.0 eV) if Tauc's plot is employed, which is often the case. Fig. 5(H) presents the Tauc's plot for the spectrum in (G). Following the pink line, the optical band gap is found to be ~ 1.7 eV, which is ~ 1.5 eV smaller than the actual gap size. In fact, another linear part of the plot, the green line, indicates the presence of a second artificial gap of size ~ 2.2 eV. Indeed, this ambiguity is brought by the shape of T2 transition in (G) which resembles more a second absorption edge, as if the spectrum belongs to an indirect semiconductor as sketch in (I).

The above analysis of the thought-experiment given in Fig. 6, allows us to draw several important findings. First, the optical band gap size can be very easily and largely underestimated for doped semiconductors with near edge optical transitions. Under such circumstances it is often preferred to minimize uncertainties by extracting the band gap size from the inflection point of the absorption edge, when applicable, rather than Tauc's graphs. Secondly, the spectral decomposition, here performed through the deconvolution process, is compulsory in such cases, provided that reminiscence near-edge shoulders are distinguishable. For example, the band gap as determined from Tauc's plot for Cr-doped glasses ^[41,42] was found to be ~ 1.0 eV smaller than the actual size obtained from proper deconvolution ^[43,44]. Similar uncertainties and recurrence underestimated gap size were found for ZnO and TiO₂ nanoparticles doped with Cr for the same reason. It should be noted that such a shift of ~ 1.0 eV in the gap size is considerably huge, and can potentially influence the performance of devices by easily pushing the system from, e.g., visible to Infrared spectral regime. In the same manner, if the optical transitions brought by the dopant occur to the high energy side of the absorption edge, an overestimation of the gap could similarly be determined.

Figure 6: (A) Schematic representation of the band structure of semiconductors and insulators, where VB and CB refer to the valence and conduction bands, respectively, and the red double arrow sets the gap size. (B) Simulated absorption edge characteristic for materials in (A). (C-D) Sketch for level structure of optically active dopant (C) highlighting two possible transitions, T1 and T2, and the corresponding simulated absorption spectra (D). (E) The resulting summation of the spectra presented in (B) and (D).

Overall, it appears that an accurate estimation of the gap size for doped systems with overlapping discrete transitions and continuum energy spectrum is highly challenging and demands detailed/accurate spectral decomposition. In this context, low temperature optical measurements could help resolving features by enlarging the lifetime of optical transitions, thereby shrinking the peak width. In the limit where indicative shoulders from near-edge transitions are still completely screened, the determination of the actual band gap size from absorption spectra is formidable task ^[59,60]. Alternative techniques include scanning tunneling and electron energy loss spectroscopies, as well as a combination of valence-band and inverse photoemission spectroscopies which are perhaps more appealing in this context, since the relative cross section of bulk and dopant transitions could be effectively tuned at synchrotron facilities ^[61-64].

Conclusion:

Pure and chromium-doped ZnO nanowires were successfully prepared following a conventional co-precipitation method. All samples exhibit wurtzite hexagonal crystal structure, similar nanoparticle size (45-50 nm), and nanowire morphology as deduced from complementary XRD, SEM, and EDX measurements. A detailed analysis of the optical absorption spectra allowed to disentangle the discrete Cr³⁺ optical transitions located at ~420 and ~665 nm from the absorption edge centered at ~385 nm. With such spectral decomposition process, and the fixed wavelength of the UV photoluminescence peak with doping, we realized an almost doping-independent optical band gap behavior, contrasting the largely underestimated band gap reported for Cr-doped semiconductors and glasses in earlier literature.

Declarations:

- o **Ethics approval and consent to participate:** Not applicable
- o **Consent for publication:** Not applicable
- o **Availability of data and materials:** Not applicable

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- o **Research involving Human Participants and/or Animals:** Not applicable
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