

# Unambiguous identification of the role of a single Cu atom in the ZnO structured green band

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High quality and purity single crystal ZnO doped with <sup>63</sup>Cu, <sup>65</sup>Cu, equal isotopic concentrations, and with natural Cu using a wet chemical atomic substitution reaction and anneal were studied using low temperature optical spectroscopy. Our data on the zero phonon line of the structured green band in ZnO confirm unambiguously the involvement of a single Cu atom in this defect emission. These data allow us to confirm the main features of the assignment proposed by Dingle in 1969 and to comment further on the defect structure.

## Introduction:

The structured green band (SGB) emission in ZnO is one of the most well-known and studied deep level emission centres in ZnO, a material of considerable promise for a range of optoelectronic and other technology areas.<sup>1</sup> SGB emission in ZnO is a classic example of a deep level emission, showing a strong electron-phonon coupling effect, with a sharp zero phonon line (ZPL) region and a strong sideband with clear “steps” at multiples of the ZnO LO phonon energy (~ 72 meV). The SGB has been reported since the 1950’s, and the work of Dingle, from the late 1960’s and early 1970’s has been one of the defining contributions in the field.<sup>2-5</sup>

The main work of Dingle led to the proposal that the SGB arises from a transition at a single substitutional Cu<sup>2+</sup> atom on the Zn site in the ZnO lattice, with the Cu acting as a neutral deep acceptor. The ground state of the transition corresponds to a tightly bound hole at a level just below the ZnO conduction band with the excited state of the hole at ~ 450 meV above the valence band.<sup>5</sup> The involvement of a Cu<sup>2+</sup> atoms in this transition arises from three pieces of strong, but circumstantial, evidence. Firstly the Zeeman data yield an anisotropic g-factor for the ground state of the hole which closely matches that found for the known Cu<sup>2+</sup> IR absorption transition at ~ 717 meV.<sup>6</sup> Secondly, the ZPL region shows two sharp and non-thermalising lines with an intensity ratio close to the known <sup>63</sup>Cu / <sup>65</sup>Cu natural isotope distribution ratio. Finally, the emission is generally only seen in crystals with some degree of Cu impurity. In the years following Dingle’s work, a large literature on the SGB topic has appeared, with occasional suggestions of other origins for the defect, but with the majority view agreeing with the Dingle interpretation. A detailed discussion of this history is given in some more recent reviews.<sup>7-8</sup> It is also worth noting that both the intensity ratio and the anisotropic g-factor have been the subject of some varying reports (including from Dingle himself for the g-factor results) in earlier years, but again the more recent and majority of reports are convergent with Dingle’s main work.<sup>3-4, 9</sup>

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It is however important to note that the key experiment (i.e. the production of Cu samples with isotopic enrichment of either  $^{63}\text{Cu}$  or  $^{65}\text{Cu}$  concentration) to control the relative intensities of the elements of the ZPL doublet has never, to the best of our knowledge, been reported. This is despite the availability of such data (at least in part) for the 717 meV IR transition.<sup>6</sup> In Dingle's main work, attempts at producing such samples were alluded to, but these attempts failed, due to strain broadening of the ZPL doublet. The absence of this critical experimental data means that the association of the SGB to a single substitutional  $\text{Cu}^{2+}$  atom is not as yet unambiguously proven.

Proof of the involvement of Cu in the SGB is important from both a technological and scientific viewpoint. From a technological perspective, the definitive identification of chemical elements responsible for photoluminescence (PL) emissions provides an important route to monitoring/controlling the impurity and defect concentration in a material. This is especially important for PL emissions in the UV and visible regions which might be utilised for applications in photonic devices such as displays and lighting, and when the impurity elements in question are transition metals (TM) which might be applicable as dopants for e.g. dilute magnetic semiconductors (DMS). From the scientific viewpoint, studies of the SGB have involved a wide variety of topics, such as the theory of intermediately bound excitons and the nature of the isotope shift in the ground and excited states.<sup>10-13</sup> Proof of the involvement of Cu in the SGB emission would provide a clear experimental underpinning of the assumptions behind such studies.

In the present work we report the results of doping single crystal ZnO with various Cu isotopes and subsequent optical spectroscopic studies at low temperatures which definitively confirm the involvement of a single Cu atom in the SGB emission. In combination with uniaxial stress (e.g. in reference 2) and other data in the literature this allows us to confirm the main features of the Dingle assignment and comment further on the defect structure and likely factors affecting the defect production.

## **Experimental:**

The ZnO single crystal samples used, purchased from the Toyko Denpa company, were (0001) oriented samples, polished on both the O- and Zn-terminated faces. Details of the sample properties are given in reference 14. In particular the background Cu impurity concentration of these samples is very low ( $\sim 1 \times 10^{15} \text{ cm}^{-3}$ , according to the manufacturers). The samples were doped with Cu isotopes using a wet chemical atomic substitution reaction and subsequent anneal.  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  isotopes in the form of small metal flakes (with isotopic enrichments of 99.8% and 99.2%, respectively) were obtained from Isoflex. Flakes of  $\sim 15$  mg were partially dissolved in 80  $\mu\text{l}$  of hydrogen peroxide and 40  $\mu\text{l}$  of acetic acid to produce copper acetate solutions. These solutions were allowed to react for several hours before being diluted to 20 ml with DI- $\text{H}_2\text{O}$ . Only a small fraction of the Cu isotope flakes dissolved. For the majority of measurements ZnO single crystals were soaked in these solutions for 40 seconds before being removed, rinsed with ethanol and dried under a gentle nitrogen stream. Whilst submerged in the Cu isotope solution the  $\text{Cu}^{2+}$  undergoes a displacement reaction with the Zn to deposit  $\text{CuO}$ .<sup>15</sup> The samples were then annealed for 16 hours at 700°C in atmospheric conditions. Some samples underwent an additional anneal, at 900°C for 10 minutes, also in atmospheric conditions to thermally activate the sample. Natural isotope distributions for PL measurements were prepared by thermal activation of the residual Cu in the as-received samples, using the short 10 minute 900°C anneal only. (We refer to this residual Cu as intrinsic hereafter, to distinguish it from externally introduced Cu in other samples). Other natural isotope distribution doped samples for absorption measurements were prepared in a similar manner from commercially available copper nitrate,

the nature of the counter ion (acetate or nitrate) being unimportant. For some absorption spectroscopy measurements on the co-doped sample (equal concentrations of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ ) and the sample with natural isotopic distribution the soaking step was carried out for twice as long (80 seconds), followed by the  $700^\circ\text{C}$  anneal, and the soaking and annealing step was repeated one further time in an attempt to increase the doping level.

Samples were prepared from solutions of  $^{63}\text{Cu}$ ,  $^{65}\text{Cu}$ , equal concentrations of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  (co-doped and labelled  $^{63+65}\text{Cu}$ ) and with the natural isotopic distribution, (labelled  $^{\text{nat}}\text{Cu}$  hereafter). The process appears to proceed most effectively on the Zn-terminated basal plane, where the displacement reaction is effective due to the availability of surface Zn atoms and does not appear to work on the O-terminated basal plane, with surface O atoms.

Samples doped with different isotopes were then studied using both PL and absorption spectroscopies. PL spectroscopy was performed using a HeCd laser operating at 325 nm as an excitation source (output  $\sim 20$  mW focussed on the sample surface). Data were obtained at a temperature of 20 K, with samples cooled using a Janis CCS-500 closed-cycle cryostat and the emission was spectrally analyzed with a Bomem DA8 FT spectrometer fitted with a Hamamatsu R1913 PM-tube. The resolution of the presented spectra is  $\sim 0.07$  meV. The SGB ZPL emission was separated from the bandedge and broadband emission using an Omega Optical 3RD notch filter centred at 435 nm in conjunction with an Omega Optical 606HSP visible bandpass filter. The SGB broadband emission was filtered using just the 606HSP filter. Band edge measurements were made using a BG25 Schott glass filter. All the PL spectra shown are from the Zn-terminated face.

Infrared absorption spectra were recorded with a Bomem DA3.01 Fourier transform spectrometer equipped with a global light source, a CaF<sub>2</sub> beamsplitter and a liquid-nitrogen-cooled InSb detector. The spectral resolution was  $0.25\text{ cm}^{-1}$ . The samples under study were mounted in a He exchange gas cryostat equipped with ZnSe windows. The IR absorption measurements were performed at 6–7 K.

## Results and Discussion:

Figure 1(a) shows the PL spectra for samples annealed at  $700^\circ\text{C}$  for 16 hours and the thermally activated intrinsically doped sample annealed at  $900^\circ\text{C}$  for 10 minutes, over a broad spectral range. The SGB is clearly visible in all samples. Figure 1(b) show the ZPL region of the SGB with the  $^{63}\text{Cu}$  sample showing a single emission line at 2.8591 eV, the  $^{65}\text{Cu}$  sample showing a single emission line at 2.8590 eV, the sample with equal isotope concentrations showing the two features with roughly equal intensities and the thermally activated sample with natural Cu isotopic concentrations showing the familiar doublet with an intensity ratio of roughly 7:3 ( $^{63}\text{Cu}$ :  $^{65}\text{Cu}$ ). These data conclusively show that the origin of the SGB involves a single Cu atom, consistent with Dingle's assignment.

The rather small linewidths and separations mean that some caution is required in this discussion. Small strains due to sample cleavage or mounting, as well as due to annealing, can occur which shift the spectral features and we have noticed such effects in certain samples. Figure 1(c) shows the near bandedge (NBE) region of the same samples shown in figures 1(a) and 1(b), where multiple donor bound exciton features (the I lines) are present, and specifically shows the  $I_8$  region (3.3598 eV) line region.<sup>7-8</sup> The shifts in the peak energy of the  $I_8$  line are in all cases less than 0.03 meV, of a similar order of magnitude to, but clearly less than, both the linewidths of the components of the SGB ZPL doublet ( $\sim 0.11$  meV) and the separation of the doublet components ( $\sim 0.11$  meV), which confirms the conclusions of the previous paragraph.

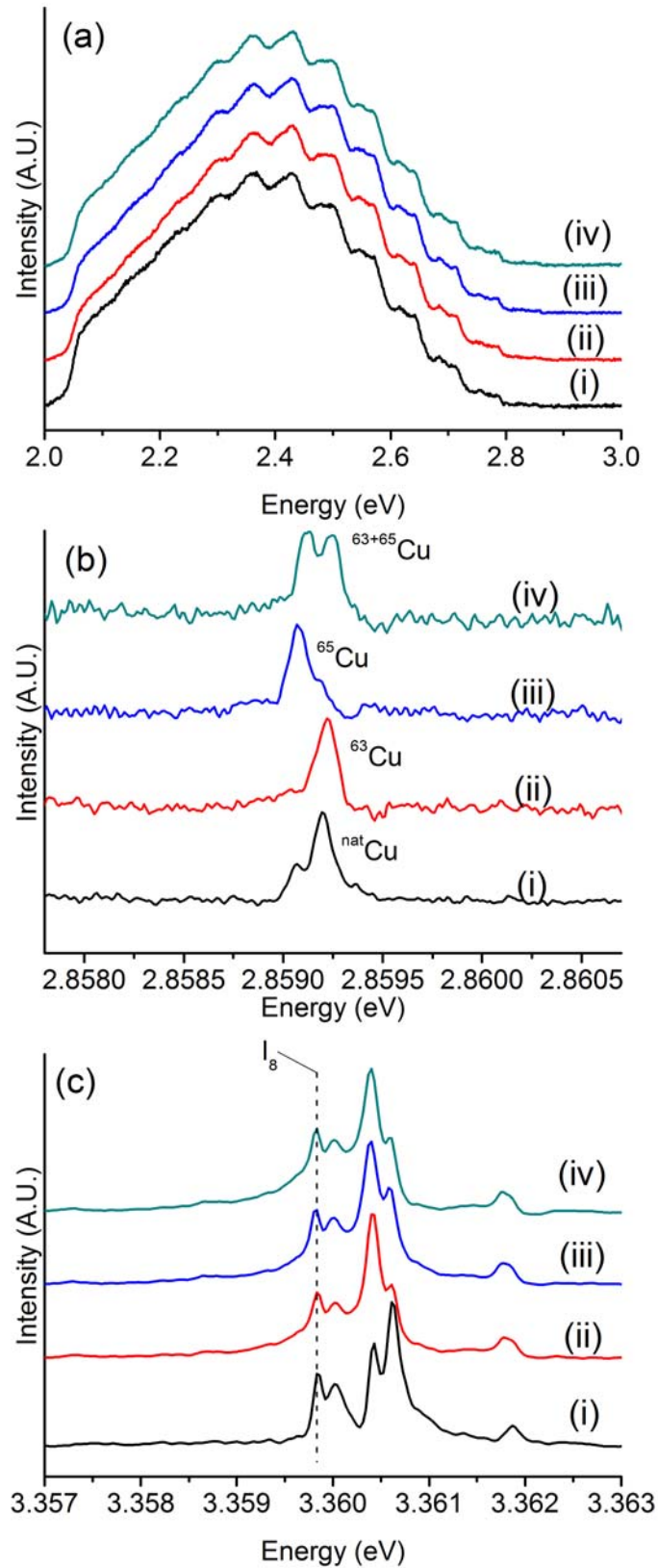


Figure 1: Low temperature PL spectra for (i)  $^{nat}\text{Cu}$  doped, (ii)  $^{63}\text{Cu}$  doped, (iii)  $^{65}\text{Cu}$  doped and (iv)  $^{63+65}\text{Cu}$  co-doped samples. (a) shows a broad spectral range in the visible region, (b) shows the zero phonon region of the SGB and (c) shows the near band edge region. The spectra have been normalised and off-set for ease of comparison

To the best of our knowledge this is the first report of such a full set of isotope enrichment data for the SGB. There are practical difficulties associated with the collection of PL data in such samples. A great deal of ZnO material contains Cu as an unintentional dopant in varying concentrations and probably in a range of different charge states, on different lattice sites and also in complexes with other Cu atoms and perhaps also with native defects and impurities.<sup>16-21</sup> Reports in the literature indicate that some fraction of this intrinsic Cu may be activated by annealing at high temperatures ( $\sim 900$  °C), rendering the defect configuration responsible for the SGB optically active.<sup>16</sup> The authors of reference 16 specifically attribute this activation to a change in Cu charge state from  $\text{Cu}^{1+}$  to  $\text{Cu}^{2+}$ . We note in this regard that the sample which showed the best SGB ZPL signal to noise behaviour in our measurements was actually one heated treated at  $\sim 900$  °C with no deliberately introduced Cu, consistent with the reports of intrinsic Cu activation. In a number of cases PL data were also taken using samples prepared similarly to those shown in figure 1 which were then further annealed at  $900^\circ\text{C}$  for 10 minutes (data not shown). Small changes were observed in the ZPL region of the SGB after this  $900^\circ\text{C}$  anneal which were in all cases again consistent with an activation of the intrinsic Cu. Thus, in order to observe isotopic effects in PL it is necessary to dope the sample with isotopically enriched Cu so that the externally introduced Cu concentration becomes the dominant contribution to the SGB emission in the region being probed (typically some hundreds of nm or less for PL excited by above bandgap radiation; the penetration depth of the 325 nm HeCd laser is  $< 100$  nm) and the samples prepared at  $700^\circ\text{C}$  satisfy this requirement.

In order to see the isotopic enrichment effects in PL it is thus necessary to (i) use crystals with a background Cu concentration as low as possible and (ii) to ensure that the isotopically enriched Cu introduced is the dominant optically active Cu species (compared to any background Cu concentration) in the near surface region probed by PL. Thus the surface doping technique used here is effective for our PL measurements. These considerations are however complicated by the fact that the PL emission intensity of the SGB (unlike the IR absorption feature) appears to be self-limiting (and even self-quenching) in ZnO; a greater Cu concentration serves to quench the overall luminescence yield, even as the relative intensity of the SGB grows, which means that increases in Cu concentration beyond a critical level yield no increase in the SGB intensity or improvement in signal to noise ratio, and can lead to decreases in these quantities, as reported previously.<sup>17-18</sup> We again point as evidence for this to the result mentioned above that the sample which showed the best SGB ZPL signal to noise behaviour was one heated treated at  $\sim 900$  °C with no deliberately introduced Cu.

IR absorption measurements (data not shown) for ZnO samples doped with  $^{63}\text{Cu}$ ,  $^{65}\text{Cu}$ ,  $^{63+65}\text{Cu}$  and with  $^{\text{nat}}\text{Cu}$  were attempted in the spectral region of the  $\text{Cu}^{2+}$  absorption around 717 meV. In all cases only very weak or no absorption signals were seen even though PL emission was observed in the 2.859 eV region for the same samples. In no sample is clear evidence found of isotopic enrichment effects in the 717 meV region. For absorption measurements, where the entirety of the crystal bulk is probed, the contribution of a surface-doped layer and the background Cu impurities to the  $\text{Cu}^{2+}$  absorption may be at or below the detection limit of our spectrometer system.

Figure 2 shows PL spectra at the same resolution from two co-doped samples, one using the normal doping conditions for PL and the other using the “double” doping procedure used for some absorption measurements on co-doped samples. There is a clear broadening of the combined ZPL components for the latter sample (from  $\sim 0.23$  meV to 0.31 meV) and while the two ZPL components are resolvable in the former, they are not in the latter. The use of very high quality crystalline starting material and a relatively gentle doping procedure (e.g. where Cu is introduced by substitution onto the Zn lattice sites directly before annealing) and quite low doping levels all appear important for observing and resolving the details of such

spectra. From the range of experiments we have conducted we conclude that if these conditions are not fulfilled the details of the SGB ZPL (i.e. the doublet structure) is generally not resolvable. The result of all these issues is that preparing samples which show discernable and resolvable SGB ZPL features in PL is very challenging. We speculate that these issues may be responsible for the absence of such Cu isotope enrichment data in the literature before now, although the experiment has been tried.<sup>4</sup>

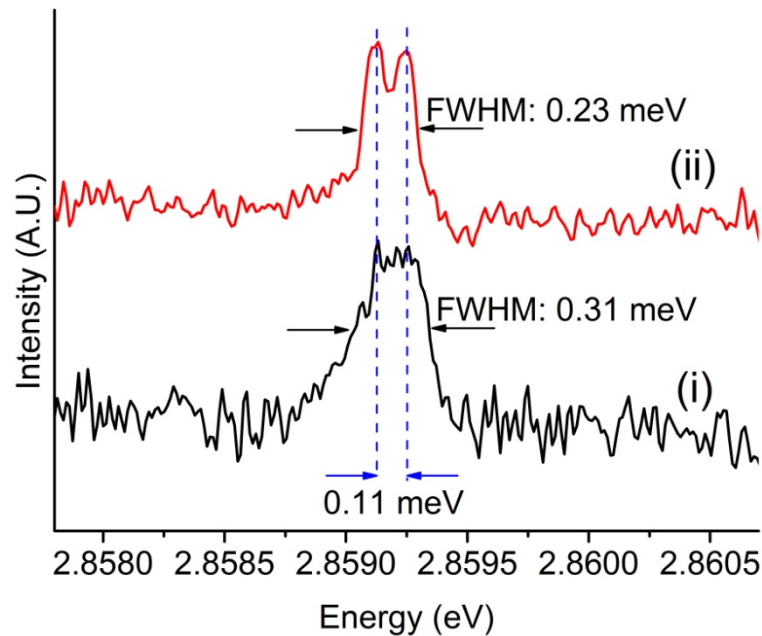


Figure 2: Low temperature PL spectra showing zero phonon region for (i)  $^{63}\text{Cu}/^{65}\text{Cu}$  heavier co-doped sample for absorption measurements (ii)  $^{63}\text{Cu}/^{65}\text{Cu}$  co-doped sample for PL measurements. (Spectra have been normalised and off-set for ease of comparison).

These data, together with the existing data on the anisotropic g-factor and uniaxial stress data confirming the trigonal symmetry of the defect all support Dingle's more detailed assignment of the SGB emission as arising from a transition at a single substitutional  $\text{Cu}^{2+}$  atom on the Zn site ( $\text{Cu}_{\text{Zn}}$ ) in the ZnO lattice.<sup>2, 4</sup> The uniaxial stress data and trigonal symmetry assignment are fully consistent with the role of an isolated single substitutional  $\text{Cu}^{2+}$ , however it must be noted that (a) a complex of a single  $\text{Cu}_{\text{Zn}}$  atom with other defects located along the  $c$ -axis would also be consistent with the data (e.g. a  $\text{Cu}_{\text{Zn}} - \text{V}_{\text{O}}$  or  $\text{Cu}_{\text{Zn}} - \text{V}_{\text{Zn}}$  complex) and (b) a complex of a single Cu atom with a larger number of defects or impurities arranged around the  $c$ -axis to produce a defect with overall trigonal symmetry could also reproduce the data. The latter case is generally regarded as less likely due to the necessity for a larger complex to form, but recent data from Si has shown that such large complexes may indeed form quite readily in some semiconductors.<sup>22</sup>

While the exact defect structure remains unknown our studies, and other reports in the literature, suggest that the defect chemistry of Cu in ZnO is quite complicated and that Cu may exist in ZnO in a variety of charge states, lattice sites and complexes with other defects and impurities.<sup>16-21</sup> For example, we have grown ZnO nanorods using a carbothermal reduction-based vapour phase transport (VPT) process and have doped the deposited material by introducing Cu into the source powder prior to VPT growth by a modified Pechini process. Directly after growth there is only a very weak SGB emission. However, after a high temperature anneal at  $900^{\circ}\text{C}$  for 10 minutes in atmospheric conditions, the SGB dominates

the emission spectrum. We speculate that this is possibly due to  $\text{Cu}_{\text{Zn}}$  in the unannealed material being in a  $\text{Cu}^+$  charge state after VPT growth (due to Zn vapour reducing  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  during VPT growth) which is oxidised during the anneal, consistent with reports in the literature.<sup>16</sup> Based on this hypothesis, our surface doping technique by contrast introduces the Cu into the ZnO lattice in the  $\text{Cu}^{2+}$  charge state directly and thus should require only a lower temperature  $700^\circ\text{C}$  anneal to prepare the sample, rather than the higher  $900^\circ\text{C}$  anneal needed to alter the charge state of the intrinsic Cu from  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ , and also this treatment ought not activate the intrinsic Cu to a significant extent (for the anneal times used in this work), both predictions which are consistent with our results. Finally we note that the Cu charge state in any particular defect configuration is ultimately dependent on the Fermi level position, and hence the doping due to other defects and impurities in the sample also. Annealing steps which affect these other defects and impurities for example, and thus the Fermi level, will affect the Cu charge state and, based on the hypothesis above, the SGB emission. Thus even for the relatively simple hypothesis that the main determinant of the SGB emission is the  $\text{Cu}_{\text{Zn}}$  charge state, the range of possible factors which can affect this state means that a rather complex behaviour may be expected for the SGB emissions from different samples grown by different techniques and with different thermal and/or doping histories, especially when the self-limiting/self-quenching nature of the SGB is taken into account. Further work is therefore needed to fully understand the details of the behaviour of Cu in ZnO.

Our data, in combination with previous work, show that Dingle's assignment of the SGB emission as arising from a transition at a single Cu atom is correct, and that the Cu atom most likely substitutes for Zn and is in a  $\text{Cu}^{2+}$  charge state. These results provide a definitive experimental underpinning of other studies of the ZnO SGB based on the involvement of Cu following Dingle, including the theory of intermediately bound excitons and the nature of the isotope shift in the ground and excited states.<sup>10-13</sup>

## Conclusions:

We have doped high purity (0001) oriented ZnO single crystals with  $^{63}\text{Cu}$ ,  $^{65}\text{Cu}$ ,  $^{63+65}\text{Cu}$  and with  $^{\text{nat}}\text{Cu}$  using a wet chemical atomic substitution reaction and anneal. Low temperature PL measurements on the ZPL region around 2.859 eV show unambiguously that the SGB emission involves a single Cu atom, consistent with Dingle's assignment. The use of high quality and purity single crystalline starting material and a gentle doping technique which introduces relatively little crystal damage and low Cu concentrations appear necessary to observe the effects reported here.

The more detailed aspects of the conventional assignment of the SGB to a single substitutional  $\text{Cu}^{2+}$  atom on the Zn site are fully consistent with our data and other data (uniaxial stress and Zeeman) in the literature, although we note that the defect chemistry of Cu in ZnO is potentially quite complicated, involving different charge states, different lattice sites and complexes. Our studies suggest that the production of the SGB emission may well be affected by some or all of these phenomena, to different extents in different samples, and is also significantly hampered by the self-limiting/self-quenching nature of the SGB PL intensity in Cu-doped ZnO. Further experimental work which could provide information on the linkage between the local crystal/defect structure and the PL emission, including theoretical/computational studies and compositional depth profiling of the dopant species would help clarify these issues, as well as studies of the defect chemistry using techniques such as photoemission and near edge x-ray absorption fine structure spectroscopy.

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