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Chemical identification of luminescence due to Sn and Sb in ZnO

J. Cullen,¹ D. Byrne,¹ K. Johnston,^{2,3} E. McGlynn,¹ and M. O. Henry¹

¹*School of Physical Sciences, National Centre for Plasma Science and Technology, Dublin City University, Glasnevin, Dublin 9, Ireland*

²*PH Department, ISOLDE/CERN, 1211 Geneva 23, Switzerland*

³*Technische Physik, Universität des Saarlandes, Building E2.6, P.O. Box 151150, 66041 Saarbrücken, Germany*

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We show that the I_{10} line in ZnO photoluminescence is associated with Sn impurities. The evidence comes from material implanted with radioactive ^{117}Ag , which decays through ^{117}Cd and ^{117}In to stable ^{117}Sn , and ^{121}Ag , which decays through the same chain to stable ^{121}Sb . Supporting evidence is provided by ZnO:Sn prepared by the in-diffusion of stable Sn. Furthermore, the I_2 and I_9 lines are shown conclusively to be due to In, confirming earlier identifications in the literature. We also observe shallow bound exciton emission at 3.3643(3) eV due to Sb impurities produced at the end of the decay chain of ^{121}Ag . © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4807288>]

The low temperature band edge photoluminescence (PL) of ZnO is characterised by a series of sharp lines commonly referred to as the I-lines. Although first reported decades ago and known to be due to recombination of excitons at impurity centres, progress on unambiguously associating these I-lines with particular chemical impurities was initially slow. At present, however, the majority of the I-lines have been identified with either neutral or positively charged donor bound exciton (DBX) recombination usually designated by D^0X and D^+X , respectively. Meyer *et al.*¹ give a general review on excitons in ZnO; more recent and comprehensive reviews of ZnO research generally are provided by McCluskey and Jokela² and Klingshirn.³ The situation at present is that the group III donor impurities Al, Ga, and In on Zn sites account for six of the I-lines: Al/Al⁺ produce I_6/I_0 , Ga/Ga⁺ produce I_8/I_1 , and In/In⁺ produce I_9/I_2 . In addition to these, the I_4 line has been associated with hydrogen,⁴ but there remain several lines in the I-line sequence that have yet to be identified conclusively with a particular impurity or defect. Among these are I_5 and I_7 and the sequence I_{10} , I_{11} , and I_{12} .

Building on our earlier studies using implantation of radioactive Zn, Ga, and As isotopes,^{5,6} we devised PL experiments using radioactive Ag that allow us to investigate several types of impurity in their radioactive decay sequences. The isotope ^{117}Ag (half-life $\tau_{1/2}$ of 72.8 s) decays through Cd ($\tau_{1/2}$ of 2.49 h) and In ($\tau_{1/2}$ of 43.2 m) to stable Sn. The short half-life of ^{117}Ag means that, when annealing prior to making PL measurements, the implanted impurities have largely transformed to ^{117}Cd and ^{117}Sn , with a small population of ^{117}In also present. Accordingly, three types of impurity can be examined—*isoelectronic* Cd_{Zn}, *single donor* In_{Zn}, and *double donor* Sn_{Zn}—provided the recoil energies are sufficiently low not to displace the daughter atom. For ^{117}Cd and ^{117}In , the average recoil energies are ~ 14 eV and ~ 6 eV, respectively, below displacement energies of Zn or O atoms which fall in the range of 18.5–57 eV,^{7,8} so this condition should be satisfied. We also studied ^{121}Ag which decays through the same chain as ^{117}Ag except that it terminates in stable ^{121}Sb . For this isotope, with ^{121}Ag , ^{121}Cd , ^{121}In , and

^{121}Sn half-lives of 0.78 s, 13.5 s, 23.1 s, and 27.06 h, respectively, only ^{121}Sn and ^{121}Sb are present at the time of the PL measurements. In this way, we addressed a sequence of impurities from groups II, III, IV, and V using the two radioactive isotopes, one stopping at group IV (Sn), the other at group V (Sb), and we supplemented this study with a ZnO:Sn sample prepared by thermal diffusion of stable Sn. The main findings that we report are that the I_{10} line is associated with the group IV impurity Sn and that Sb impurities give rise to shallow bound exciton luminescence at 3.3643(3) eV. We also confirm earlier identifications of I_9 and I_2 with D^0X and D^+X recombination, respectively, due to In_{Zn}.

The starting material was hydrothermally grown c-plane single crystal ZnO obtained from Tokyo Denpa. The concentration of Sn in the starting material was below the supplier's detection limit of 0.1 wt.-ppm. For the radioactivity experiments, radioactive ^{117}Ag and ^{121}Ag were implanted at the On-Line Isotope Mass Separator facility (ISOLDE) in the European Organisation for Nuclear Research (CERN), with nominal ion doses of $5 \times 10^{12} \text{ cm}^{-2}$ at an ion beam energy of 60 keV. The implanted samples were annealed in air at 830 °C for 20 min to remove implantation damage. The samples were cooled to ~ 3 K over a period of 2 h for PL measurements. During PL measurements, the laser remained positioned on the same part of the sample and the temperature was maintained at ~ 3 K (to eliminate possible impurity diffusion and/or complexing effects) for a total of at least five half-lives of the final decay stage. To complement the radioactivity experiments, a ZnO:Sn sample was prepared using a chemical ion exchange reaction followed by thermal diffusion, a method previously used to dope ZnO with Cu.⁹ Single crystal ZnO was soaked in an aqueous tin(II)chloride solution (10 mg/ml) for 120 s, rinsed with deionised water, and dried under a nitrogen flow. The sample was annealed at 700 °C in air for 3 h to facilitate diffusion of Sn. A second sample of stable ZnO:Sn was provided at the end of the decay of the ZnO: ^{117}Ag sample. Although the radioactive decay recoil energies were not expected to be significant, as noted above, nevertheless, the sample was annealed a second

time at 750 °C for 30 min in air and the PL of implanted and un-implanted parts of the sample was compared. Details of the spectroscopic and cryogenic equipment are given elsewhere.^{5,6}

The I-lines of interest in this study are I₂, I₉, and I₁₀, none of which appears in the spectrum of the starting material, which is dominated by the I₄, I₅, and I₆ lines. The PL data obtained for the various samples studied are now described.

We first consider the case of ¹¹⁷Ag implantation. Representative spectra for three time delays after annealing are shown in Figs. 1(a) and 1(b) for ¹¹⁷Ag implanted ZnO. The main changes over 18 h are the decrease in intensity of the I₉ line (Fig. 1(a)) and the I₂ line (Fig. 1(b)). The integrated intensities for I₉ and I₂ normalized to that of the DD₁ line at 3.333 eV are shown in Fig. 1(c) together with the calculated relative populations of Cd, In, and Sn due to decay of the implanted ¹¹⁷Ag. The excellent agreement between the I₂ and I₉ intensities and the ¹¹⁷In population proves that these lines are due to In, confirming a result previously obtained for the case of I₉ only by Muller *et al.*,¹⁰ using radioactive ¹¹¹In. The data reported here provide definitive chemical proof of the association of I₂ with In also, copper-fastening the identification of I₂ with D⁺X recombination at In donors.¹¹ (Clearly, the I₉ and I₂ intensities also fit the Cd population but we discount this given the strength of prior evidence linking them to In).

It is clear from Fig. 1(c) that the ¹¹⁷Sn population increases by a factor of ~2 during the PL measurements, yet there is no evidence of any PL close to the I-lines growing in intensity. This indicates that the isolated substitutional impurity Sn_{Zn}, produced by the decay of ¹¹⁷In_{Zn}, does not produce radiatively efficient shallow bound exciton emission. Similarly, no features could be seen down to ~2 eV that could be assigned

to stable Sn_{Zn} formed at the end of the decay. For completeness, we illustrate the unchanging I₁₀ line intensity in Fig. 1(c) where we normalized the intensity to the populations of both Cd and Sn at the point when their populations are equal. Since data of this nature are clearer for the case of a decaying isotope, exemplified by I₉ and I₂ above, we repeated the measurement using another isotope that includes radioactive Sn in its decay chain.

We now consider the case of ¹²¹Ag implantation. The very short half-life values for the atom in its Ag, In, and Cd forms means that, at the annealing stage, the sample was essentially ZnO:¹²¹Sn. The recoil in the ¹²¹Sn → ¹²¹Sb decay step is <10 eV, below the displacement energy of a Zn or O atom^{7,8} so the final product should be Sb_{Zn} assuming that Sn impurities occupy Zn sites. As noted above, the sample was kept at ~3 K for the duration of the PL measurements to eliminate possible impurity diffusion and/or complexing issues.

Representative spectra recorded during the ¹²¹Sn decay are shown in Figure 2. While I₆ dominates the luminescence, spectra recorded at high gain show a weak I₁₀ line (Fig. 2(a)). The line clearly weakens further as Sn impurities decay to Sb. Additionally, a line at 3.3643(3) eV is evident in Fig. 2(b) which grows from a very low initial intensity. Quantitative data for the intensities of these lines, normalized to that of the first LO phonon replica of I₆, over the course of the ¹²¹Sn to ¹²¹Sb decay are plotted in Fig. 2(c). The change in the I₁₀ intensity fits a single exponential decay with an effective half-life of 26 ± 2 h, while the growth of the line at 3.3643 eV fits a single exponential also based on an effective half-life of 26.5 ± 0.7 h. These values are both very close to the known ¹²¹Sn half-life of 27.06 h, providing strong evidence that I₁₀ is due to Sn and that the 3.3643(3) eV emission is due to Sb.

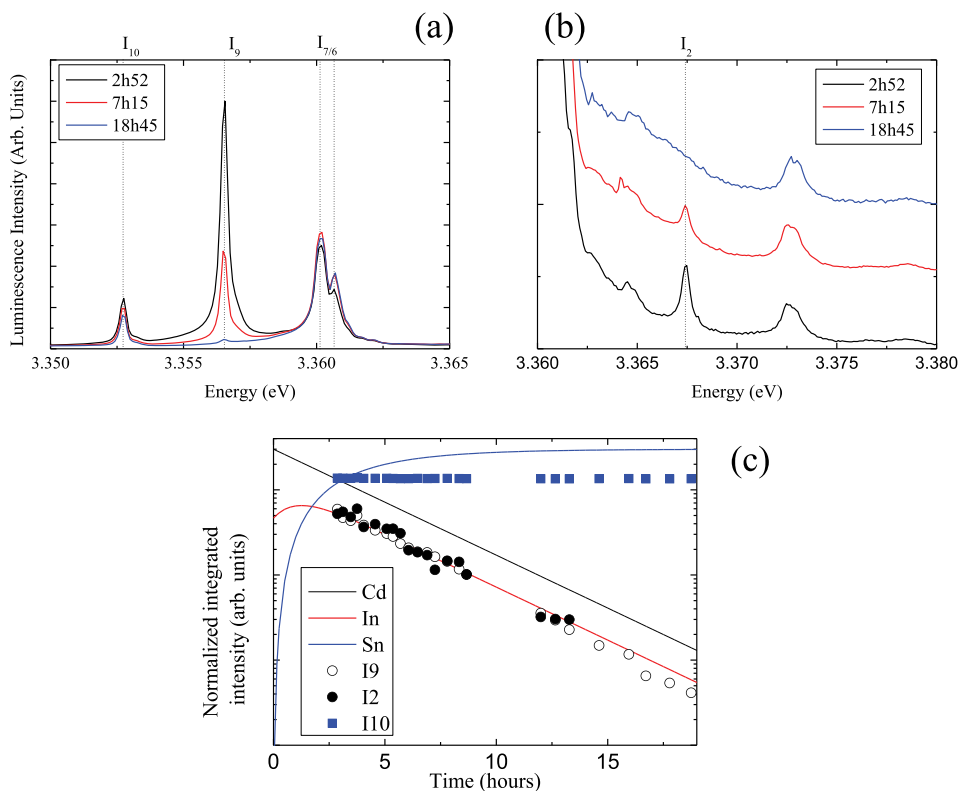


FIG. 1. PL spectra of ¹¹⁷Ag implanted ZnO at various times after annealing: (a) the I₉ line region and (b) the I₂ line region. In (c), the normalized intensities of the I₉ and I₂ lines are fitted to the population of ¹¹⁷In and the steady intensity of I₁₀ is also indicated.

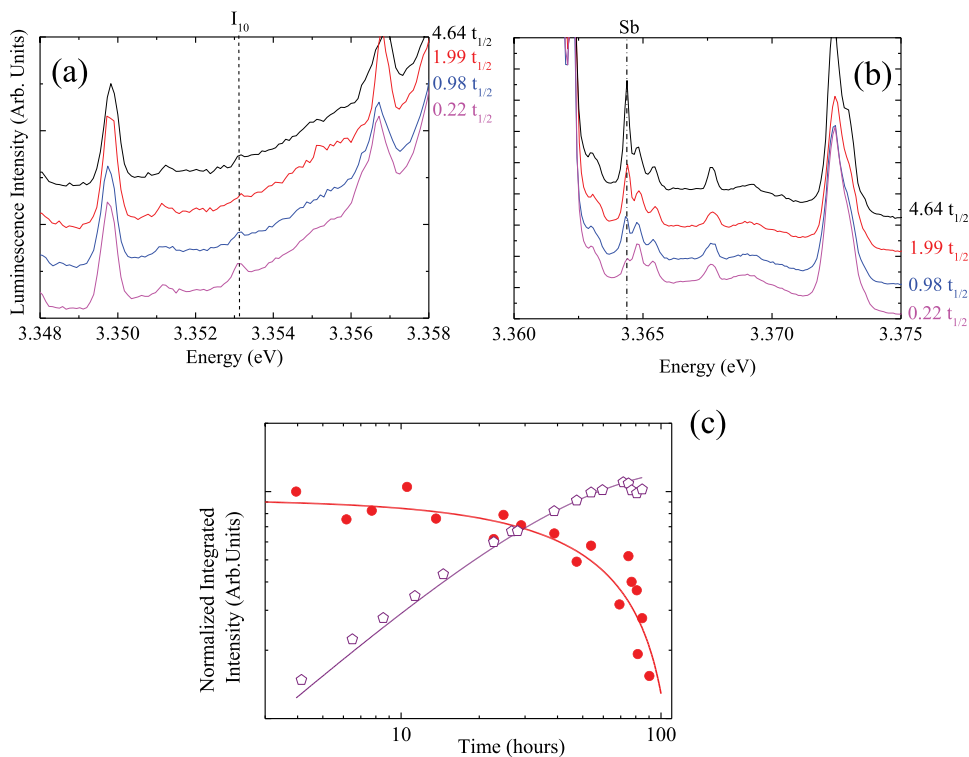


FIG. 2. PL spectra of ^{121}Ag implanted ZnO at various times after annealing: (a) the I_{10} line region and (b) the region above the I_6 line where a PL line at 3.3643 eV is observed. In part (c), the normalized intensities of the I_{10} line and the 3.3643 eV line are fitted to a single exponential decay (closed circles) and growth (open circles), respectively, demonstrating their correlation with the ^{121}Sn and ^{121}Sb populations.

For further confirmation of the involvement of Sn in the I_{10} line, we prepared a ZnO:Sn sample using the ion exchange and diffusion process described above.⁹ The PL data in Fig. 3 show a comparison between (a) the unimplanted part of a sample, (b) the Sn-implanted part of a sample, and (c) the Sn-doped sample. There is strong I_{10} line emission from the implanted region of the sample and none from the un-implanted region of the sample, while the sample with Sn doping by diffusion also clearly shows I_{10} emission. These findings add to the weight of evidence that I_{10} involves Sn.

We now consider the implications of the results described above for the properties of the four impurities In, Cd, Sn, and Sb in ZnO.

For the cases of ZnO:In and ZnO:Cd, the excellent agreement shown in Fig. 1(c) between the intensity changes of the I_9 and I_2 lines and the changing population of ^{117}In produced by the decay of radioactive ^{117}Cd , establishes beyond any doubt that these two lines are associated with In impurities, as is already widely accepted in the literature, and as has been proven conclusively for the case of the I_9 line.¹⁰ Therefore, for ZnO:In, our results provide definitive corroboration of these earlier identifications. It is important to note that the I_9 and I_2 luminescence we have observed is produced by In atoms being created from the decay of ^{117}Cd , and not from those ^{117}In atoms that existed at the time of annealing. If the emission were due to the latter, the I_9 and I_2 intensities would decrease with the half-life of ^{117}In which is only 43.2 min, instead of the much longer decay time we observe which is determined by the 2.49 h half-life of the mother isotope, ^{117}Cd .

Considering the data from the perspective of ZnO:Cd, since the In_{Zn} were created from the decay of Cd_{Zn} , the spectra might be expected to show emission associated with Cd_{Zn} if such emission exists. However, the PL spectra of the band

edge region in Figure 2 do not show any feature that can be associated with (isoelectronic) Cd_{Zn} centers. Thus, we conclude that ZnO:Cd, unlike ZnO:Hg,¹² does not produce radiatively efficient isoelectronic bound exciton emission. This difference between Cd and Hg defects may be a consequence of the larger Hg impurity creating sufficient strain to bind an exciton in contrast to the smaller Cd impurity. The importance of strain effects for exciton binding is discussed by Allen.¹³ We note finally regarding ZnO:Cd that the intensity of the weak band observed in the region of 2.85 eV by Muller *et al.*¹⁰ for the case of $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ decay would be below the detection limit of the CCD-based spectrometer system used in this study.

For the case of ZnO:Sn, there are several aspects to be considered. First, the data for ^{121}Ag decaying through Sn and on to Sb provide clear evidence linking I_{10} to Sn impurities. This is corroborated by the data from the chemical indiffusion of stable Sn and by the observation of a strong I_{10} line only in the region of the ZnO: ^{117}Sn sample that contains stable ^{117}Sn . If I_{10} is due to Sn, then the fact that the line intensity did not change for the ZnO: ^{117}Sn sample as the population of ^{117}Sn increased by a factor of approximately two requires an explanation. This can be explained if the center producing I_{10} requires the participation of some other impurity or defect in addition to Sn rather than being a simple isolated Sn_{Zn} impurity. In this scenario, the I_{10} center is created in all samples containing Sn during the high temperature annealing stage by interactions of some other participant(s) with Sn_{Zn} impurities. For the case of the ^{121}Ag implanted sample, which has completely decayed to radioactive ^{121}Sn by the time of annealing, the PL intensity will decrease as the ^{121}Sn decays to ^{121}Sb . However, for the ^{117}Ag implanted sample, the initial I_{10} intensity is determined by the amount of stable ^{117}Sn in the sample at the time of annealing. Thereafter, with the sample held at liquid helium

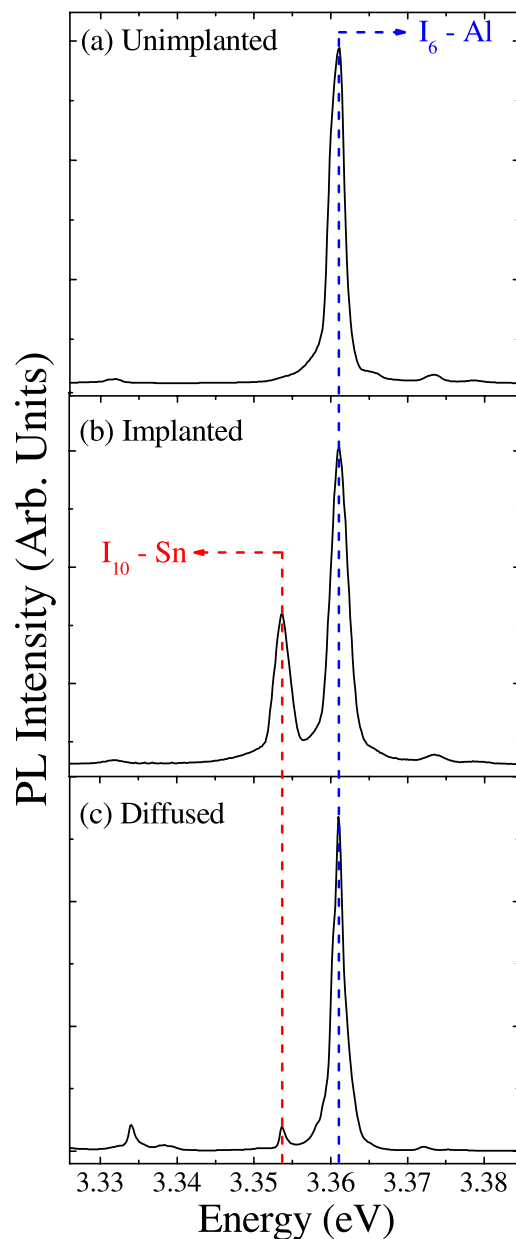


FIG. 3. Part (a) shows the PL spectrum of the un-implanted region of a ZnO: ^{117}Sn sample produced long after the decay of the implanted radioactive ^{117}Ag , while part (b) shows the spectrum from the implanted region. In part (c), the spectrum of ZnO:Sn prepared by chemical in-diffusion is shown.

temperatures, the creation of more stable ^{117}Sn from ^{117}In will not result in an increase in the I_{10} intensity because the necessary association of other participants with the newly created ^{117}Sn cannot occur at low temperatures. Accordingly, no change in the I_{10} intensity should occur, consistent with our experimental observations. For the ZnO:Sn sample prepared by thermal diffusion, the 3 h annealing process at 700°C allows the production of a defect involving the complexing of Sn_{Zn} with another impurity to take place.

Regarding the detailed nature of the I_{10} center, it has been reported that I_{10} is due to D^0X recombination,¹ so we now consider how such a center involving Sn could be produced. As a group IV impurity on the Zn site, Sn_{Zn} would be expected to act as a double donor, analogous to the other

group IV impurities Si and Ge.^{14,15} The compensating effect of deep acceptors produces sizeable concentrations of ionized donors in n-type material and the same process in ZnO:Sn would result in Sn_{Zn} double donor impurities being partially compensated by acceptors, thereby causing them to act as single donors. We also note that the intensity of I_{10} was found by others¹ to be very substantially increased by co-doping with Li, a deep acceptor. Therefore, we propose that the I_{10} line is produced by a defect complex involving Sn_{Zn} and an associated acceptor impurity, most likely Li_{Zn} since Li is a common impurity in hydrothermally grown ZnO.

Finally, for the case of ZnO:Sb, the data in Fig. 3 provide unequivocal evidence for the involvement of Sb in the PL emission at 3.3643 eV. It is customary to attribute PL in this region to either D^0X or D^+X recombination, but recent studies have shown that other types of center also produce bound exciton recombination emission in this region, including isoelectronic centres.^{16,17} At this stage, we do not have sufficient data to speculate further as to the nature of the 3.3643 eV Sb-related emission. Our identification of the emission at 3.3643 eV with Sb_{Zn} impurities is fully consistent with the very recent report of Senthil Kumar *et al.*, who identify a feature at exactly the same energy in Sb-doped ZnO nanowires with D^0X emission at Sb defects; we only became aware of this report at the time of submission of the present work.¹⁸

In conclusion, our data unambiguously confirm the identifications of I_9 and I_2 with In_{Zn} impurities in ZnO. In addition, our results show that the isoelectronic impurity Cd_{Zn} , unlike its counterpart Hg_{Zn} , does not produce radiatively efficient isoelectronic bound exciton emission in ZnO. We have also shown compelling evidence from both radioactive isotope implantation and chemical doping and diffusion that the I_{10} line is associated with Sn. The possibility that the I_{10} binding centers are defect complexes involving partially compensated Sn double donors is suggested, with Li_{Zn} proposed as the most likely candidate. Finally, we identify a PL line at 3.3643(3) eV with Sb_{Zn} impurities.

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