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## Low temperature CL investigation of BN1 vibronic structure in c-BN

R. Cossio<sup>a</sup>, F. Fizzotti<sup>a</sup>, E. Vittone<sup>a</sup>, A. Lo Giudice<sup>a</sup>, C. Manfredotti<sup>a,\*</sup>, S. Nistor<sup>b</sup>

<sup>a</sup> *Experimental Physics Department and Center of Excellence NIS, University of Torino, Italy*

<sup>b</sup> *National Institute for Material Physics, Bucharest, Romania*

### Abstract

A full vibronic spectrum has been measured for the first time by LNT Cathodoluminescence in HPHT c-BN amber-coloured microcrystalline samples. The related BN1 centre at 3.293 eV seems not created by electron irradiation in this case and the accurately determined phonon energy ( $141 \pm 3$  meV) could be related to LO phonon at *X* point in Brillouin Zone (BZ) of c-BN, as determined by CL results obtained at indirect gap. Consequently, BN1 centre has not the full cubic symmetry of c-BN, as being due to N interstitials. The interpretation of the results is possibly twofold: either we are observing a vibronic spectrum with ZPL at BN1 centre, together with other two centres called PF-1 and PF-2 at 3.573 and at 3.412 eV, respectively, or, since all the 6 or 7 observed peaks are exactly equally spaced, the whole vibronic spectrum is related to a ZPL line at 3.573 eV. This new interpretation seems to be in better agreement with the general theory of colour centres.

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*Keywords:* c-BN; Cathodoluminescence; Vibronic structure; Defect centres

### 1. Introduction

Cubic boron nitride (c-BN) is a wide band gap semiconductor still in an early stage of development with respect to diamond, but with the advantage of being the stable phase at room temperature and of being easily doped both p and n type, a fact that opens the way to several kinds of possible devices. More than 25 different centres have been discovered until now not only in HPHT (High Pressure High Temperature), but also in CVD deposited c-BN: many of them are created by irradiation and their importance is based both on the possibility of future production of ion implanted devices and also on the likely use of c-BN devices in a radiation hard environment.

The major difference with respect to diamond is related to the existence of off-stoichiometry and to the binary nature of c-BN, with the consequence of a larger variety of native defects, and to the polar nature of the B–N bond (25% ionic in character), which gives rise to polar longitudinal optical phonons (LO) strongly interacting with incident or emitted light. The investigations on these centers are carried out by PhotoLuminescence (PL), by CathodoLuminescence (CL) and by IonoLuminescence (IL or IBIL, Ion Beam Induced Luminescence) [1–5]. Also Raman

spectrum of c-BN has been extensively investigated [6–9]. Centres have been reported from 1.55 up to 4.05 eV, being generally the radiation-induced centres such as RC1, RC2, RC3, etc., much more intense than “natural” centres such as PF1 and PF2, for instance [1]. One of the more recently reported centre, indicated as BN1, was found in electron irradiated samples (230–300 keV, about  $10^{20}$  e/cm<sup>2</sup>), with a ZPL (Zero Phonon Line) placed at 376.4 nm (3.293 eV) and with some phonon (LO, TO) replicas at the anti-Stokes side [1]. Because of its similarity with the 3.188 eV centre in electron irradiated diamond, attributed to interstitial nitrogen, and also because calculations [8,9] indicate a lower formation energy for N<sub>i</sub> with respect to B<sub>i</sub>, it was concluded that this centre was created only during electron irradiation. Raman spectra quote very consistently a LO phonon line at 1305 cm<sup>-1</sup> (161.5 meV) and a TO line at 1054.7 cm<sup>-1</sup> (130.5 meV) [7] and these values are in close agreement with phonon replicas reported previously at 7 K under 325 nm excitation, from which a LO energy between 159.7 and 163 meV can be evaluated from the quoted PL spectrum. The authors report that below 200 keV only very weak BN1 luminescence was observed under UV illumination, which completely disappeared after irradiation at 150 keV. CL seems to be a more powerful method with respect to excitation mode, which does not follow specific selection rules and can fill up any radiative recombination centre. In fact [10] by CL some phonon-assisted free-exciton luminescence lines were

\* Corresponding author.

E-mail address: manfredotti@to.infn.it (C. Manfredotti).

64 discovered quite recently at 83 K below the indirect band gap of c-  
 65 BN (6.25 eV) and were attributed to  $LO_x$ ,  $LA_x$ ,  $TO_x$  and  $TA_x$   
 66 phonons with energies of 138, 124, 104 and 88 meV, respectively,  
 67 at  $X$  point in BZ instead of  $\Gamma$  point, to which first order Raman  
 68 measurements refer.

## 69 2. Experimental

70 Two free-standing c-BN samples, CBN6 and CBN7, in the  
 71 form of sintered microcrystalline powders in platelets of  
 72 comparable dimensions (1.2 mm thick, 8.4 mm in radius), were  
 73 investigated. The grains had typical dimensions of some tens of  
 74 microns (10–40). The powders were produced by HPHT method  
 75 by using  $Ca_3N_2 + LiF$  as precursors and were amber coloured.

76 Secondary electron (SE) and BSE (BackScattered Electrons)  
 77 images were obtained by means of a Cambridge S360 Scanning  
 78 Electron Microscope which, for CL measurements, was  
 79 equipped with an Oxford Mono-CL2 apparatus together with a  
 80 MMR Technologies cold stage as a sample holder.

81 Together with CL and SEM maps, some other maps were  
 82 obtained by recording directly EDS X-ray characteristic spectra  
 83 in an energy region between Be and Si, in order to avoid in any  
 84 case to include materials different from c-BN. In CL measure-  
 85 ments, probe current was typically 5 nA over an investigated area  
 86 of  $5 \times 5 \mu m$ ; the temperature was varied between 86 and 300 K.

## 87 3. Results and discussion

88 Fig. 1 is a topographic secondary electrons SEM image of  
 89 the sample CBN7 under study which has been mixed with an  
 90 EDS map in which the different characteristic X-rays are  
 91 selected in energy between 0.1 keV (deep red) and 1.9 keV  
 92 (deep blue). The selected regions for CL measurements,  
 93 labelled as D, E and F for this sample, are in the centre of the  
 94 grains and do not include regions of different colour, which can  
 95 include different elements. CL spectra as obtained at 297 K on

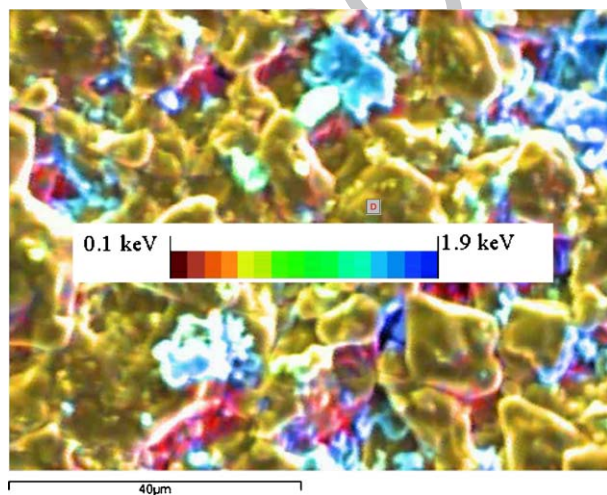


Fig. 1. Mixing of secondary electrons SEM signal and false colour characteristic X-ray maps: the colour scale is from deep red (X-ray energy 0.1 keV) to deep blue (X-ray energy 1.9 keV). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

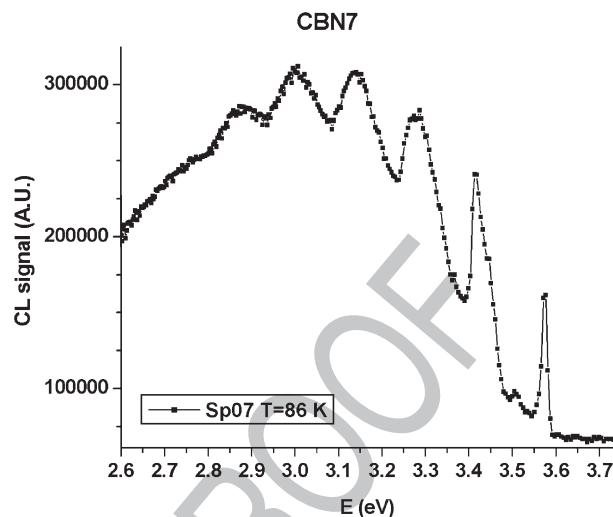


Fig. 2. High energy side of CL spectrum at grain D obtained at 86 K together with the indication of peak positions.

different grains do not show any clear structure and are 96  
 dominated by a broad band centred at about 3 eV. At lower 97  
 temperature peaks are clearly seen at the short wavelength side, 98  
 with increasing intensities. Other small peaks in the long 99  
 wavelength region, at 1.76, 1.71 and 1.63 eV, could be related 100  
 to the centres called GC1 and GC2 [1], probably due to vacancies. 101  
 PF1 and PF2 centres, probably related to Frenkel pairs (donor- 102  
 acceptor  $V_N - B_i$ ), are the first two at the left-hand side. No 103  
 evidence of RC centres is appearing in this and in other spectra: 104  
 since these centres should grow in the same way as BN1 as a 105  
 function of irradiation dose, it is quite hard in our case to 106  
 attribute the ZPL, which is found exactly at 3.293 eV (the 107  
 details will be presented afterwards) and the whole vibronic 108  
 structure which we are observing to a radiation induced defect 109  
 strongly coupled with LO phonons. 110

Fig. 2 shows quite clearly the high energy side of CL 111  
 spectrum with 6 equally spaced peaks: it is evident that the peak 112  
 at 3.573 eV is much narrower than the other ones, with the 113  
 exception of the nearby peak. This is even more evident in Fig. 3, 114

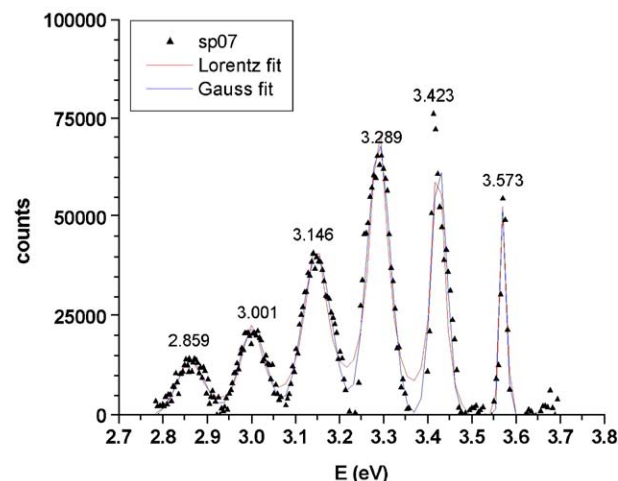


Fig. 3. Peaks observed in this figure after a “subtraction” of the fitted wide band for a better visibility.

115 where a “subtraction” of the fitted wide band at about 3 eV has  
 116 been carried out just in order to carry out the fit. It can be  
 117 observed that both the gaussian and the Lorentz fit are in good  
 118 agreement with experimental data. The narrow line at 3.573 eV,  
 119 fitted with a Lorentz line, displays a FWHM of about 10 meV  
 120 including the contribution of the monochromator.

121 A full quantitative view of the results is presented in Table 1,  
 122 where all the found peaks in six positions of the two samples are  
 123 reported together with the mean values, the differences in  
 124 energy between nearby peaks and finally the average value of  
 125 the difference itself.

126 In our view, the best interpretation of the results is to attribute  
 127 the entire spectrum, which is of course vibronic in nature, to a  
 128 ZPL at 3.573 eV. In effect, some phonon replicas have been  
 129 seen in c-BN by PL at low temperature and related to a BN1  
 130 centre at 3.293 eV and, moreover, by looking at Table 1, a  
 131 variation of the energy difference can be observed with respect  
 132 to the other peaks (even if the average distance between the first  
 133 two peaks and the second two peaks is just equal to the average  
 134 distance). However, the “narrow” line at 3.573 eV is much more  
 135 justified as ZPL than the line at about 3.293 eV, which is a factor  
 136 2 or 3 wider. But there are other evidences: first of all, the  
 137 FWHM of the whole band is about 0.83 eV: taking into account  
 138 a phonon energy of 0.141 eV, this gives a Huang–Rhys factor  $S$   
 139 of 6.25. As a general rule, since the ratio between nearby peaks  
 140 is given by  $f/S$ , where  $f$  is the order of the peak, we should  
 141 observe a maximum of the vibronic spectrum around  $f=S$ ,  
 142 which is what we roughly see in the quoted data and in other  
 143 ones obtained on different grains and on the second sample.  
 144 Finally, we observe luminescence. If we attribute the first two  
 145 peaks to PF1 and PF2, we are left with a Huang–Rhys factor  $S$   
 146 of about 4, while a value of 6 seems to be just the threshold  
 147 above which radiative recombination is possible.

148 The question that remains now is: why the LO phonon  
 149 energy, which has been derived from our data and which is so  
 150 well defined, does not coincide exactly with LO phonon energy  
 151 as derived by Raman data, which is 161.5 meV? The answer is  
 152 that this energy coincide viceversa very well with  $LO_x$  phonon  
 153 energy as obtained by edge CL together with a second order  
 154 Raman measurement [10,11]: 140.7 meV with a SD of 2.7 meV.  
 155 The interpretation now could be quite straightforward, remem-  
 156 bering similar effects observed at former times of III–V  
 157 compounds proposed for LEDs and assuming here that also in  
 158 this case we are in presence of a neutral centre not substitutional  
 159 but interstitial: this centre, with ZPL at 3.293 eV if due to N  
 160 interstitials or with ZPL at 3.573 if due to B interstitials, as  
 161 indicated above, has to be referred to the minimum of  
 162 conduction band at  $X$  point in BZ of c-BN. N interstitials are  
 163 not numerous in B rich c-BN and must be created by irradiation,  
 164 even if they could be similar to native defects in nature. By PL it  
 165 is possible to charge these centre by UV light or by 325 nm laser  
 166 line [1] only if these centres are very point-like, with a  
 167 wavefunction extending from  $X$  to  $G$  point and the radiative  
 168 recombination is dominated by the LO phonon at the same  $\Gamma$   
 169 point (161.5 meV). Viceversa, by CL, these centres at 3.293 or at  
 170 3.573 eV are directly filled with much more efficiency and there  
 171 is no need to create them by electron irradiation. In fact it seems

Table 1

Peaks positions (in eV) as measured in different positions or grains in two samples, together with the mean values and standard deviations, the differences (in eV) between peaks positions and the average value of phonon energy

Peak	CBN6			CBN7			Mean	SD	Diff.
	Grain	Grain	Grain	Grain	Grain	Grain			
	A	B	C	D	E	F			
1	2.720	2.722	2.721				2.721	0.001	
2	2.868	2.866	2.856	2.868	2.863		2.864	0.005	0.143
3	3.006	3.009	3.001	3.006	3.004	3.024	3.008	0.008	0.144
4	3.147	3.145	3.143	3.145	3.148	3.149	3.146	0.002	0.137
5	3.294	3.289	3.292	3.293	3.294	3.294	3.293	0.002	0.140
6	3.425	3.424	3.423	3.425	3.424	3.425	3.424	0.001	0.141
7	3.574	3.573	3.574	3.574	3.572	3.574	3.573	0.001	0.139
							Average		0.141
							SD		0.003

impossible [1] to generate these centres at 30 keV, since they can  
 hardly created below just 200 keV. The radiative recombination,  
 in this case, should occur with the assistance of  $LO_x$  phonons, as  
 in the case of indirect transitions at band edge [10,11].

#### 4. Conclusions

A rich vibronic structure with a proposed ZPL at 3.573 eV  
 has been observed at LNT by CL on HPHT amber coloured, not  
 intentionally doped, c-BN samples. Up to seven replicas have  
 been observed for the first time with a very good reproducibility  
 among different microcrystals. There is a strong evidence that  
 ZPL is at 3.573 eV and not at 3.293 eV as previously reported  
 [1]: as a consequence, the centre PF2 should be the first phonon  
 replica of PF1, now identified as ZPL, and BN1 should be the  
 second phonon replica. The phonon energy,  $141 \pm 3$  meV, is  
 coincident with LO phonon energy attributed to  $X$  point of BZ  
 of c-BN and obtained by CL at indirect gap. The consequence of  
 this coincidence is the proposed connection of the involved  
 centre with conduction band minimum at  $X$  point. BN1 centre  
 could be quite likely present particularly in undoped or not B  
 rich c-BN samples, but it needs to be generated by high energy  
 (more than 200 keV) electrons in B rich samples, in which PF1  
 centre ( $V_N-B_i$ ) is more visible.

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