In the present decade, ZnO has been widely studied in sight of optoelectronic applications. However the main barrier to overcome in order to industrialize ZnO optoelectronic compounds is to engineer the doping properties and especially the $p$-doping one. In this context, the possibility for some features of the low-temperature excitonic luminescence to be the optical signature of the $p$ doping is a major issue.

In order to study the origin of excitonic bands in ZnO we have made a systematic study of three kinds of ZnO samples which are structured at different scales: a single crystal (macroscale - MC), a microcrystalline powder (mesoscale - Pd), and an assembly of ZnO nanoparticles (nanoscale - Nps) which are controlled in stoichiometry, and crystallinity and deposited in ultrahigh vacuum (UHV). The nanoparticles being made from the microcrystalline powder by a hyperquenching process[1], we expect to find embedded in them the same impurities as in the microcrystalline powder if they are present in the latter. This enables us to discriminate the influence of impurities from pure size effects, and among the latter the role of the surface states. The emission of these samples is compared to the one of a ZnO single crystal, which is characterized by its long-range crystalline order. The temperature dependence of the time-resolved luminescence of these samples was studied under UV-VUV excitation at SUPERLUMI (beamline I, DORIS) and was compared with data measured under multiphoton 800 nm) and VUV (20-50 eV) excitation of 1 KHz Ti-Sapphire laser.

In this report, we present the results related to 3.31 eV emission band [2]. This band has been seen in a lot of intentionally p doped ZnO samples and it has been tempting to attribute it to the optical signature of $p$ doping. Since the energy of the 3.31 eV band (A-band , fig.1) is close to the one expected for the optical phonon replica of the free exciton (FX, fig.1), this band has been first interpreted in this way. On the other hand, the 3.31 eV band can be related to the presence of acceptor impurities (hence the name “A band” for acceptor band) through different radiative
mechanisms like a donor acceptor pair, a free to bound transition or an exciton bound to a defect. The appearance of this band in various kinds of nanostructured samples as dots \[3,4\] or nanorods \[5\] has conducted some authors to interpret this feature as a surface defects contribution.

At low temperature (10K), the DX-band (donor bound exciton) dominates the emission spectra of NPs and MC (fig.1), the 3.31 eV band is only present in the microcrystal spectra, in the form a symmetric Gaussian contribution (simulation by dashed black line, fig.1, panels left and middle) and absent in the single crystal and nanoparticles spectra. This shows that increasing the surface/volume ratio does not imply a monotonic increase in the 3.31 eV emission yield. It demonstrates that small ZnO nanoparticles free of this emission can be synthesized, even though two distinct reasons for can be argued (absence of radiative surface defects or quenching of these by non radiative defects). For these two samples, an asymmetric band appears at 80K and grows bigger as the temperature increases, revealing the presence of the 1LO-FX replica.

In order to confirm this statement, we have modelled the line shapes of both the 3.31 eV band and its 1LO replica \[2\] by the modified Permogorov model based on an exciton gas at thermodynamic equilibrium that includes the homogeneous broadening due to acoustic phonons \[6-8\]. Figure 1 (right panel) demonstrates the improved accuracy in the 3.30 eV region when the Permogorov law is modified by taking into account the interaction of the free exciton with the acoustic phonon. The modelling, which can easily be extended to other semiconductors, reproduces very accurately the experimental spectra, confirming the assignment of the 3.31 eV band to a phonon replica in these samples. On the other hand, for the microcrystalline sample, the presence of the 3.31 eV band at low temperature points out to an alternate origin, namely a defect state. Since the nanoparticles are made from the ablation of the pellet via a hyper-quenching, the possibility of an impurity to be the origin of the 3.31 eV emission is unlikely in our experiment. Instead, following previous works from the literature, we propose that the corresponding defect could rather be of crystalline origin. The temperature variation of its transition energy suggests a free to bound transition emission and gives an activation energy of 122 meV.

In summary, we emphasize that both the defect hypothesis and the 1LO-FX replica that have been controversially evoked in the literature to explain the origin of the 3.31 eV band in ZnO are concomitantly valid. The growth process, leading to the creation of extended staking faults is also to be stressed. Eventually, the use of the 3.31 eV band in order to assess p-doping in ZnO must be invoked with great caution.

References