Excitons in bulk black phosphorus evidenced by photoluminescence at low temperature

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Atomic layers of Black Phosphorus (BP) present unique opto-electronic properties dominated by a direct tunable bandgap in a wide spectral range from visible to mid-infrared [1]. In this work, we investigate the infrared photoluminescence of BP single crystals at very low temperature [2]. Near-band-edge recombinations are observed at 2 K, including dominant excitonic transitions at 0.276 eV and a weaker one at 0.278 eV (Figure 1). The free-exciton binding energy is calculated with an anisotropic Wannier-Mott model and found equal to 9.1 meV. On the contrary, the PL intensity quenching of the 0.276 eV peak at high temperature is found with a much smaller activation energy, attributed to the localization of free excitons on a shallow impurity. This analysis leads us to attribute respectively the 0.276 eV and 0.278 eV PL lines to bound excitons (I°X) and free excitons (X) in BP. As a result, the value of bulk BP electronic bandgap is refined to 0.287 eV at 2K, to serve as reference for future work on thin BP layers.

REFERENCES

[1] Ling, X., Wang, H., Huang, S., Xia, F. & Dresselhaus, M. S. The renaissance of black phosphorus. *Proc Natl Acad Sci USA* **112**, 4523–4530 (2015).
[2] Carré E. *et al.* - https://arxiv.org/abs/2010.15449

FIGURES

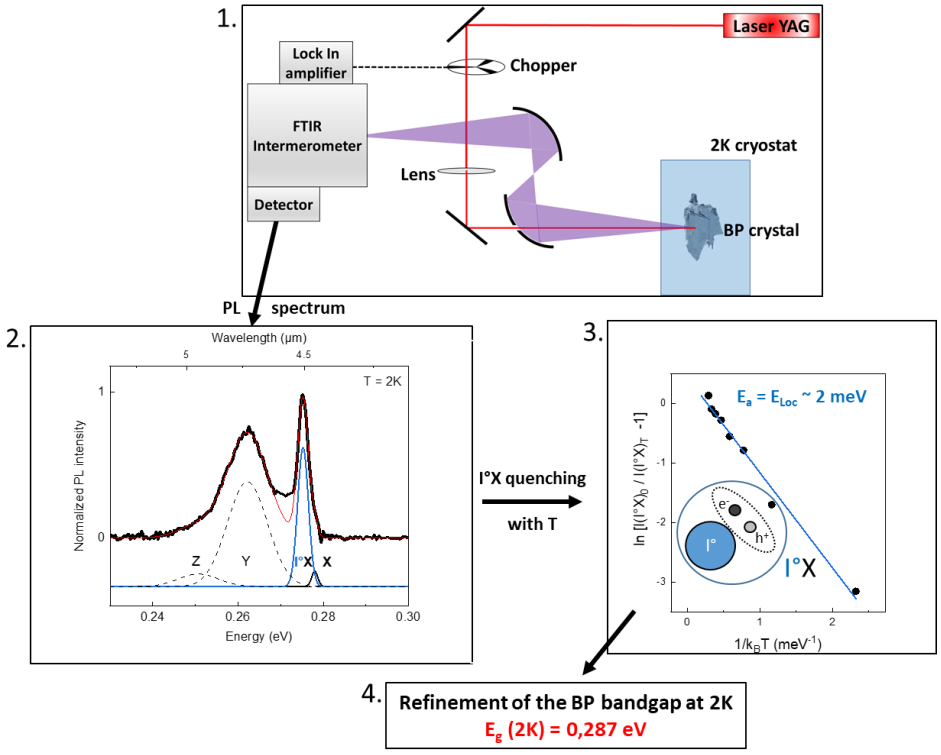

Figure 1: *1.* MacroPL setup. *2.* PL spectrum of BP crystal at 2 K. *3.* Quenching of I°X intensity with temperature.