# Distinguishing Different Stackings in Layered Materials Via Luminescence Spectroscopy

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Despite its simple crystal structure, layered boron nitride features a surprisingly complex variety of phonon-assisted luminescence peaks[1, 2]. These spectral fine structures are due to the dynamical interaction between electronic excitations and lattice vibrations and can be seen as fingerprints of different structural phases. We present a combined experimental and theoretical study on ultraviolet-light emission in hexagonal and rhombohedral bulk boron nitride crystals, both indirect-gap materials. These two polytypes are similarly stable and are difficult to distinguish from a standard crystallographic point of view. Yet, accurate emission spectra of high-quality samples are measured via cathodoluminescence spectroscopy and display characteristic differences between the two polytypes. These differences are explained using a first-principles computational technique that takes into account radiative emission from "indirect" – finite-momentum – excitons mediated by the coupling to finite-momentum phonons[3].

Thanks to the excellent agreement between theory and experiment, we show that the differences in peak positions, number of peaks and relative intensities can be qualitatively and quantitatively explained, together with the identification of the finite-momentum exciton and phonon states involved. In particular, the crucial spectral difference comes from the coupling of excitons to out-of-plane lattice vibrations, which is permitted by the lower symmetry of the rhombohedral stacking but forbidden in the centrosymmetric hexagonal phase. Our results demonstrate that cathodoluminescence is a viable tool to characterise fundamentally similar BN polytypes, and more generally low-dimensional materials with indirect gaps. In addition, we unambiguously show the predictive capabilities of first-principles methodologies accounting for exciton-phonon interactions beyond the state of the art[4].

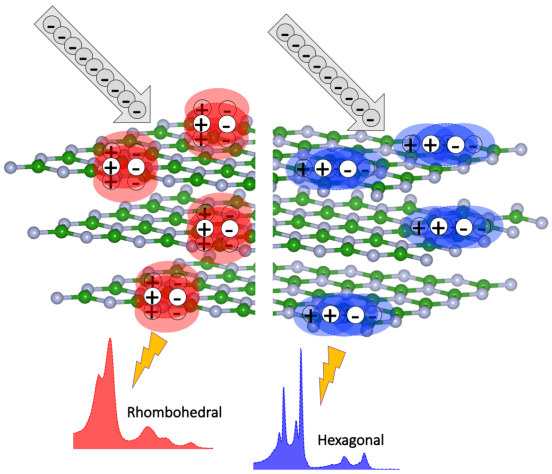


Fig. 1. Scheme of phonon-assisted luminescence in rhombohedral BN (rBN, left, red) and hexagonal BN (hBN, right, blue). The light-emitting recombination of excitons (electron-hole bound pairs) can be mediated by out-of-plane lattice vibrations only in rBN, resulting in a different emission spectrum with respect to the hBN case.

References

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