Anisotropic excitons in cast-capping 2D perovskites with vertical and horizontal orientations

Le Khanh Linh[1,*], Le Si Dang[1], Nguyen Tran Thuat[2], Joël Cibert[1], David Ferrand[1]

[1]Univ. Grenoble Alpes, CNRS, Institut Néel, Grenoble, France
[2]VNU University of Science, Hanoi, Vietnam

Two-dimensional halide perovskites have emerged as promising semiconductors for optoelectronic applications due to their exceptional light emission properties and ease of fabrication. The near-band-edge optical properties arise from optically allowed transitions of triplet bright excitons, which are split into doublet in-plane and singlet out-of-plane excitons in a 2D structure. In this study, we investigate the excitonic properties of the 2D perovskite phenylethylammonium lead iodide (PEAPI) in the Ruddlesden-Popper phase. High-quality crystalline samples are grown on Si/SiO_2 substrates using the cast-capping method. We successfully obtain microcrystals up to 100 micrometers wide, with the *c*-axis oriented either in-plane (Fig. 1a) or out-of-plane (Fig. 1b), and thicknesses ranging from a few hundred nanometers to several micrometers. The samples are characterized using polarization-dependent micro-photoluminescence (PL) and micro-reflectivity (R) at 6K (Fig.1c). The PL spectra feature a main excitonic peak around 2337 meV, accompanied by Stokes and anti-Stokes sidebands, consistent with previous literature [1,2]. The presence of both crystal orientations enables a detailed characterization of the anisotropy and fine-structure splitting of exciton resonances. In crystals with the *c*-axis in-plane, we observe strongly linearly polarized exciton resonances (Fig. 1c and polar plot in Fig. 1a), with a larger oscillator strength perpendicular to the c-axis and a fine-structure splitting of approximately 3 meV between the (X, Y) and Z exciton lines. In contrast, in crystals with the *c*-axis out-of-plane, excitonic resonances appear nearly isotropic (polar plot in Fig. 1b), with a fine-structure splitting of about 1 meV between the X and Y exciton lines. By modeling and fitting the reflectivity spectra, we determine the oscillator strengths of the various exciton lines. We find an oscillator strength ratio of about 20 between the (X, Y) and Z exciton lines. The ability to grow high-quality 2D PEAPI thin layers with both vertical and horizontal crystalline orientations holds great promise for further optical studies and potential applications.

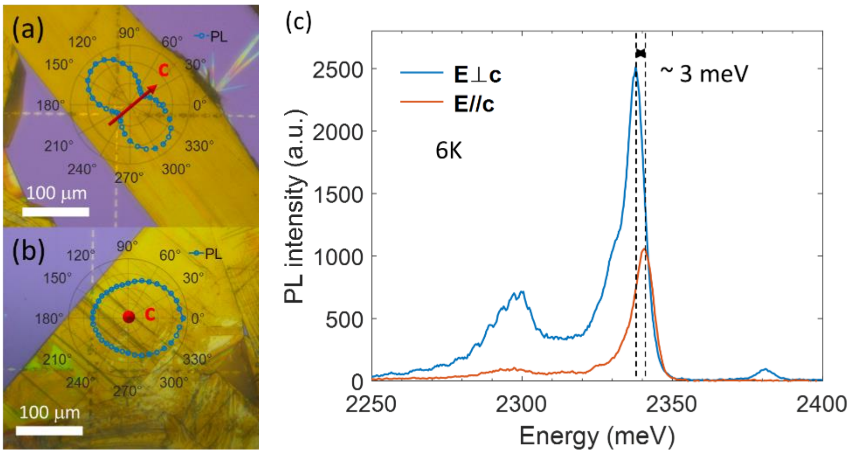

Figure 1: (ab) Optical images of PEAPI crystals with *c*-axis in plane (a) and out of plane (b). The photoluminescence polar plots (intensity versus linear polarization angle) reveal the exciton oscillator strength anisotropy. (c) Polarized photoluminescence spectra of PEAPI crystals having the *c*-axis in-plane

Acknowledgements

This work is supported by the MSCA Cofund QuanG (Grant Number: 101081458) funded by the European Union.

References

[1] K. Posmyk *et al.*, *J. Phys. Chem. Lett.*, **13**, 4463 (2022); K. Posmyk *et al.*, *Nanomaterials* **13**, 1119 (2023); K. Posmyk *et al., Advanced Optical Materials*, **12**, 2300877 (2024).
[2] T. Do *et al., Nano Lett.*, **20**, 5141 (2020).

*Email: linh-khanh.le@neel.cnrs.fr