

Optical properties of 3D hybrid organic perovskites monocrystals

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Since 2012, the 3D hybrid organic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ causes an incredible enthusiasm due to its application as absorbant material in solar cells, achieving efficiency as large as 21% [1]. It is now well established that this hybrid perovskite is a semiconductor whose band structure can be calculated using solid state physics methods such as DFT or tight-binding calculations [2]. At this date, the origin of their remarkable performances is still quite unknown, so fundamental studies about the photophysics of these compounds are quite necessary.

Until now, the fundamental studies are usually performed on spin-coated hybrid organic perovskite thin layers [3,4]. These thin layers are highly polycrystalline (fig. 1a) and the quality of the layers depend strongly on the synthesis conditions and on the substrates. As a consequence, the studies show a great variability of the electronic properties as a function of the morphology of the polycrystalline thin layers, since the optical properties are dominated by the defects at low temperature. In particular, the size of the crystallites, varying between several 100 nanometers to several micrometers, has a great impact on the gap energy, the lifetimes and the excitonic properties [5,6].

In this context, the recent possibility to synthesize 3D hybrid organic perovskite monocrystals having millimetric sizes (fig 1b) allows to study the intrinsic properties of the material. We report here the emission and absorption properties of 3D hybrid organic perovskites at low temperature around the orthorhombic-tetragonal phase transition. We observe a hysteresis cycle related to the phase transition in these monocrystals and we show that the emission is dominated by the free excitons from time-resolved photoluminescence experiments. In particular, an important narrowing of the excitonic emission line as a function of temperature is observed in the orthorhombic phase, in contrast with previous studies [4,7].

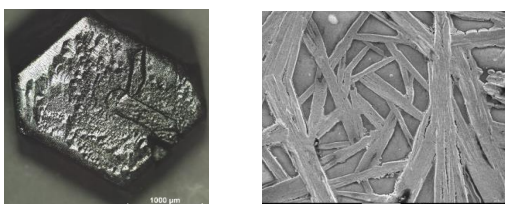


FIG 1: Microscopic image of a millimetric monocrystal (left) and MEB image of a thin layers (right) of $\text{CH}_3\text{NH}_3\text{PbI}_3$

[1] NREL (National Renewable Energy Laboratory) chart : http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

[2] J. Even et al, *J. Phys. Chem.* **2015**, *C119 (19)*, 10161–10177. DOI: 10.1021/acs.jpcc.5b00695

[3] Y. Yamada et al, *JACS* **2015**, *137 (33)*, 10456–10459.

[4] C. Wehrenfennig et al, *APL Mater.* **2014**, *2*, 81513.

[5] H.-H. Fang et al, *Adv. Funct. Mater.* **2015**, *25 (16)*, 2378–2385.

[6] V. D’Innocenzo et al, *JACS* **2014**, *136 (51)*, 17730–17733.

[7] G. Grancini et al, *J. Phys. Chem. Lett.* **2014**, *5 (21)*, 3836–3842.

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