Understanding the Temperature Dependence of the Gap in Bulk and Nanocrystalline Hybrid Perovskites

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The popular use of hydrostatic pressure in optical studies of materials is partly due to the fact that a lattice-constant variation by a few percent has a large impact on the electronic band structure and thus on the optical properties. For hybrid organic/inorganic lead halide perovskites the use of optical spectroscopy techniques like photoluminescence (PL), combining experiments as a function of temperature and pressure, has led, for instance, to a deeper understanding of the atypical temperature dependence of their fundamental gap [1]. For the archetypal perovskite $MAPbI_3$ (MA stands for methylammonium) it is shown that the variation of the gap with temperature is due to an almost equal footing of thermal expansion and electron-phonon interaction effects [2]. This result seems to possess general validity, holding also for the tetragonal or cubic phases, stable at ambient conditions, of most halide perovskite counterparts. As an example, recent results obtained for MA rich $FA_xMA_{1-x}PbI_3$ solid solutions, where FA stands for formamidinium, will be presented [3]. Finally, evidence of a size-dependent enhancement of the electron-phonon contribution to the temperature-induced renormalization of the gap in $MAPbI_3$ nanocrystals (NCs) will be provided [4]. Interestingly, it is found that as the NC size decreases, the electron-phonon contribution gains in importance, gradually increasing from ca. 50% as in bulk to about 75% for NCs of a few nanometers in diameter. In all these cases, the outcome from high-pressure PL experiments was crucial for the quantitative assessment of the weight of the electron-phonon interaction relative to thermal expansion, as far as the temperature dependence of the fundamental gap of hybrid perovskites is concerned.

References

[1] A. Francisco-López et al., J. Phys. Chem. C, **122** (2018) 22073-22082.
[2] A. Francisco-López et al., J. Phys. Chem. Lett., **10** (2019) 2971-2977.
[3] A. Francisco-López et al., J. Phys. Chem. C, **124** (2020) 3448-3458.
[4] A. Rubino et al., J. Phys. Chem. Lett., **12** (2021) 569-575.

Figures

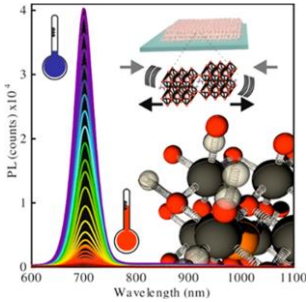

Figure 1: Temperature dependence of the photoluminescence in $MAPbI_3$ nanocrystals.