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Phonon Coupling with Excitons and Free Carriers in Formamidinium Lead Bromide Perovskite Nanocrystals

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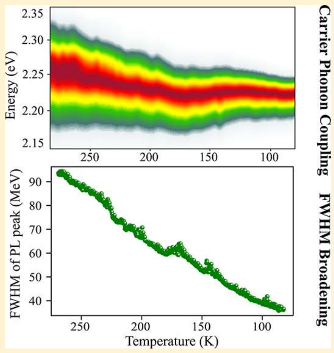
ABSTRACT: Organometal halide perovskites in the form of nanocrystals (NCs) have attracted enormous attention due to their unique optoelectronic and photoluminescence (PL) properties. Here, we examine the phase composition and the temperature dependence of emission line width broadening in formamidinium lead bromide ($FAPbBr_3$) perovskite nanocrystals (NCs) for light-emitting applications and identify different charge-carrier scattering mechanisms. Our results show most of the emission is from the orthorhombic phase. The PL line width broadening at high temperature is dominated by the Fröhlich interaction between the free charge carriers and the optical phonons. At low temperatures, the peak of the PL spectrum exhibits a continuous red shift indicating an increase of excitons contribution at lower temperatures, and concurrently the line width also narrows down due to the inhibition of the optical phonons. From the temperature-dependent measurements, the coupling strength of both the charge phonon interaction and the exciton phonon interaction have been determined. The obtained results indicate that the charge phonon coupling strengths are higher compared to the exciton phonon coupling.



Hybrid lead halide perovskites are one of the most promising emerging semiconductor materials for the development of low cost optoelectronic devices.[1−6] After the intense research activity following their first implementation as thin film solar cells,[7] the power conversion efficiency (PCEs) of the perovskites have increased to more than 20%.[2,8,9] This rapid progress is attributed to the excellent optoelectronic properties of the perovskites, like high absorption coefficients across the visible spectrum,[10] direct band to band recombination,[11,12] low exciton binding energies, long recombination lifetime, and high diffusion length.[3,13−17] Moreover, the perovskites are also appropriate for the realization of highly sensitive photodetector at visible, ultraviolet, and X-ray wavelength regions.[18] The direct band gap of the perovskites makes them even excellent emitters with promising photo- and electroluminescence yields and tunable optical gain at visible region. Excellent coherent light emitting properties from amplified spontaneous emission by optical pumping has also been observed.[12,19] Among the different halide perovskites, the formamidinium-based NCs show excellent optical properties with PL quantum yield above 70% and low lasing threshold ($<7.5\ \mu J\ cm^{-2}$). These crystals also have significantly higher chemical durability compared to the Cs based counterparts.[20] The emission from formamidinium lead halide ($FAPbX_3$) NCs, PL can be tuned over a wide range (470−550 nm). Recently it has been introduced as an alternative to methylammonium lead halide ($MAPbX_3$) perovskite because of high thermal stability and low band gap energy.[20] Furthermore, $FAPbX_3$ has been shown to be thermally more stable compared to $MAPbX_3$.[21,22]

Generally, perovskite NCs show a high PL yield compared to their bulk counterparts because of the formation of bright excitons that result from strong spin−orbit coupling in the conduction band in combination with Rashba effect[23] and increased exciton binding energy. The large exciton binding energy in perovskite NCs result from the strain-induced lattice compression and enhanced localization of s^2 electron density of Pb^{2+}.[24] High PL yield is essential for light emitting diodes (LED).[25] Similarly, the spectral line width is an important factor in the LEDs and the lasers. Thus, it is important to understand the mechanisms that contribute to the broadening of the line widths in the NCs. Previous studies on the bulk and the 2D perovskite films have shown a significant influence of the phonons on the PL spectra.[5,26−33]

In 2D material, the line width broadening is mainly due to exciton phonon coupling.[34] While in the bulk material, the broadening is mostly governed by the interaction between the phonons and the free charge carriers.[28,33,35] In addition, at low temperatures (<100 K) the broadening has been attributed to the acoustic phonon scattering and at high temperatures to the optical phonon scattering.[28,34] The NCs, on the other hand, show distinct behavior than their bulk counterparts due to high

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