Self-trapped excitons with unusually large Huang-Rhys factor in halide double perovskite semiconductor $Cs_2AgInCl_6$

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In the search for stable and non-toxic alternatives to single perovskites, lead-free halide double perovskite semiconductors have emerged as a promising class of optoelectronic materials having a common chemical formula $A_2MM'X_6$ with potential applications in photovoltaics and lighting technology [1]. Here, A is a monovalent cation, M and M' are a monovalent and a trivalent metal ion, respectively, and X is a halide ion. These materials possess a soft polar lattice with strong electron-phonon coupling, which favors the formation of self-trapped excitons, leading to broad photoluminescence (PL) spectra. The strength of this coupling is estimated with a dimensionless number called Huang-Rhys factor [2].

Temperature-dependent PL spectra of $Cs_2AgInCl_6$ single crystals under 375 nm excitation show a bright, broad emission centered around 500 nm at temperatures below 150 K. However, above 180 K, the emission shifts to a significantly broader and much less intense peak around 600 nm [Figure 1(a)]. Polarized Raman scattering studies confirm that no global structural phase transition is involved.

Further investigations using temperature- and excitation-power-dependent PL studies indicate that these emissions originate from two distinct excitonic populations, with the 600 nm peak appearing above 90 K. Time-resolved spectral evolution reveals that the 500 nm emission dominates at earlier times, while the 600 nm emission becomes more prominent at later times.

Regular and time-resolved temperature-dependent broadening analysis confirms that the 500 nm peak corresponds to a previously identified self-trapped exciton emission, characterized by a large Huang-Rhys factor (S) of 38 [2]. In contrast, the 600 nm peak exhibits an exceptionally large S value of approximately 400 [Figure 1(c)]. Thermal expansion studies [Figure 1(d)] suggest that, although no phase transition occurs, the unusually strong electron-phonon coupling arises from lattice dynamics.

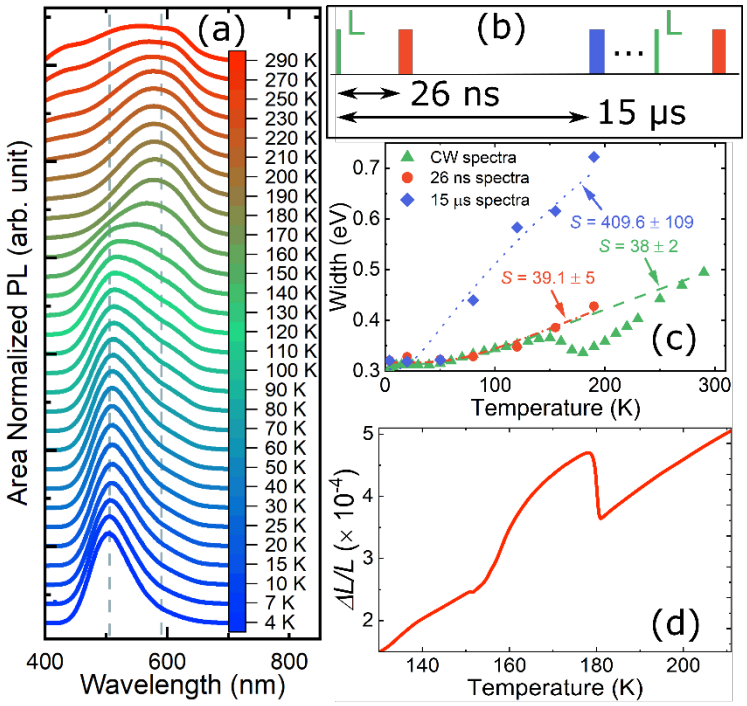

Figure 1: (a) Temperature-dependent evolution of the PL spectra of $Cs_2AgInCl_6$ single crystals under continuous-wave (CW) excitation at 375 nm. (b) Schematic representation of the protocol used to acquire time-resolved PL spectra. The thin green rectangle labeled 'L' represents a 2 ps laser pulse. A charge-coupled device (CCD) camera is exposed for a set duration at varying time delays relative to the laser pulse. This cycle is repeated to accumulate and record PL spectra. (c) Temperature-dependent broadening, $\Gamma(T)$, of the PL spectra, used to estimate the Huang-Rhys factor (S) by fitting with the equation $\Gamma(T) = 2.36\sqrt{S}\,\hbar\omega\,coth\left(\frac{\hbar\omega}{2k_BT}\right)$. The green triangles correspond to the PL widths from the spectra in (a), while the red circles and blue diamonds represent the widths of time-resolved PL spectra recorded at 26 ns and 15 µs after the laser pulse, respectively. The solid lines indicate fits to the equation. (d) Thermal expansion behavior of $Cs_2AgInCl_6$ single crystals.

References

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