Optical Characterization of Hybrid Organic-Inorganic 2D Perovskites

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Introduction

Solar cells made with 3D hybrid organic-inorganic perovskites (HOIPs) have reached efficiencies above 20% in just a few years but they show low device stability. Replacing the 3D HOIPs with its two dimensional counterpart results in a more stable perovskite based solar cell, though with a lower efficiency. Previously, we found that the organic cations play an important role in 3D perovkskite $MAPbI_3$ in extending its charge recombination lifetime and thus improving its solar cell performance. To investigate if similar effect occurs in 2D perovskite structures, we performed temperature dependent PL, TRPL, and Raman measurements for the 2D HOIP structure series $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n=1, 2; BA = $C_4H_9NH_3$,; MA = CH_3NH_3). We used PL and Raman spectra to identify the phase transition temperatures of the 2D perovskite. The observed large PL lifetime change at the phase transition supports a similar screening role played by the organic cations in 2D perovskite in extending its PL lifetime.

2D Perovskite Structure

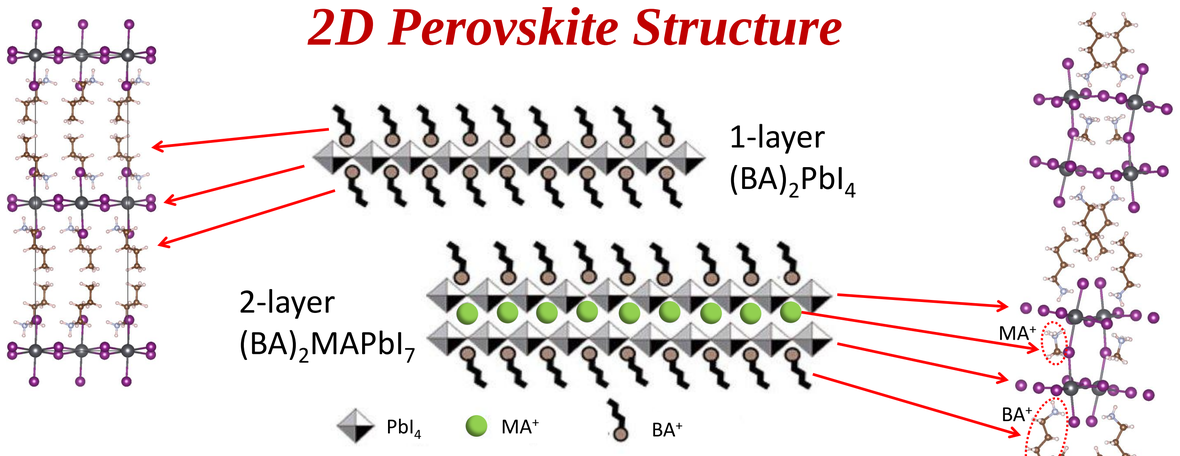

Fig.1 Structure of 1- and 2- layer (n=1,2) 2D perovskite $(BA)_2PbI_4$ and $(BA)_2MAPbI_7$. As n → ∞ , the structure becomes 3D perovskite $MAPbI_3$.

Temperature Dependent Photoluminescence

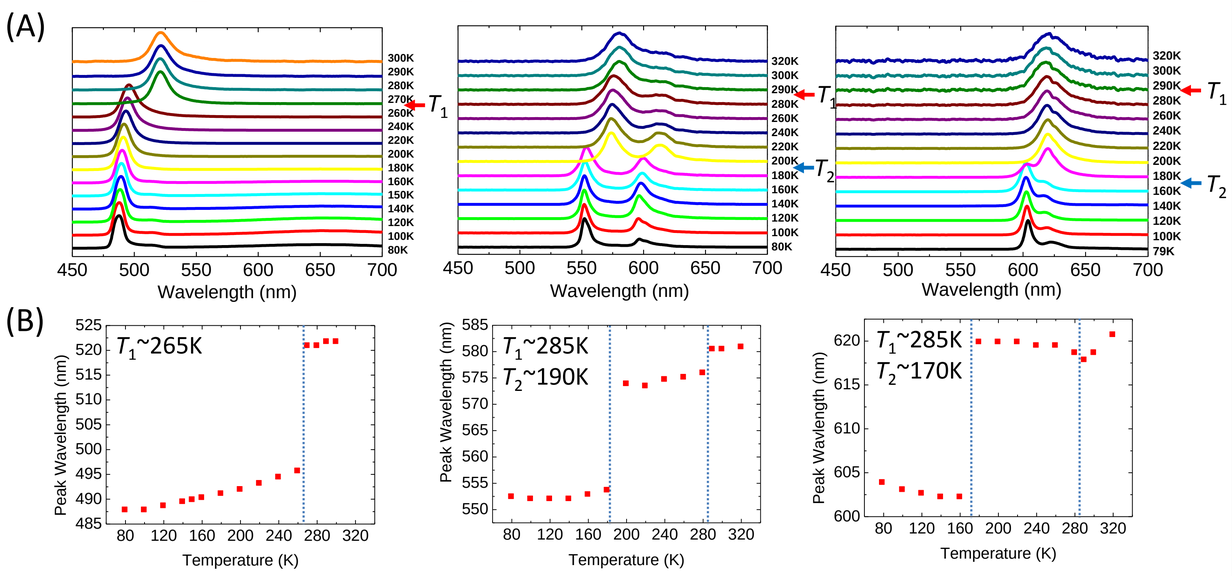

Fig. 2 (*A*) shows normalized temperature dependent PL spectra for the n=1,2,3 sample (*B*) shows the position of the PL peak as a function of temperature. The vertical dotted lines in (*B*) and the red and blue arrows in (*A*) mark the phase transition temperatures T_1 and T_2.

Temperature Dependent TRPL

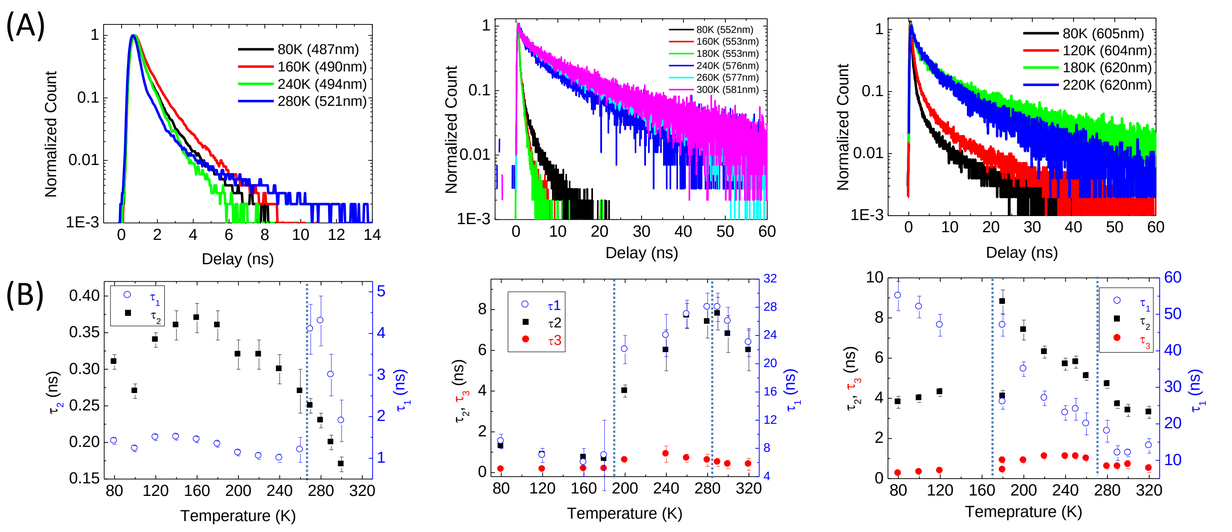

Fig. 3 (A) Normalized time-resolved photoluminescence (TRPL) histogram of the three samples for selected temperatures near their phase transition temperatures (B) Fitted lifetime for the TRPL at various temperature and phases. For n=2 and 3 we observed a lifetime jump similar to previously observed orthorhombic – tetragonal transition at 170K for $MAPbI_3$. The vertical dotted lines in (B) mark the phase transition temperatures shown by the photoluminescence.

Temperature Dependent Raman Spectroscopy

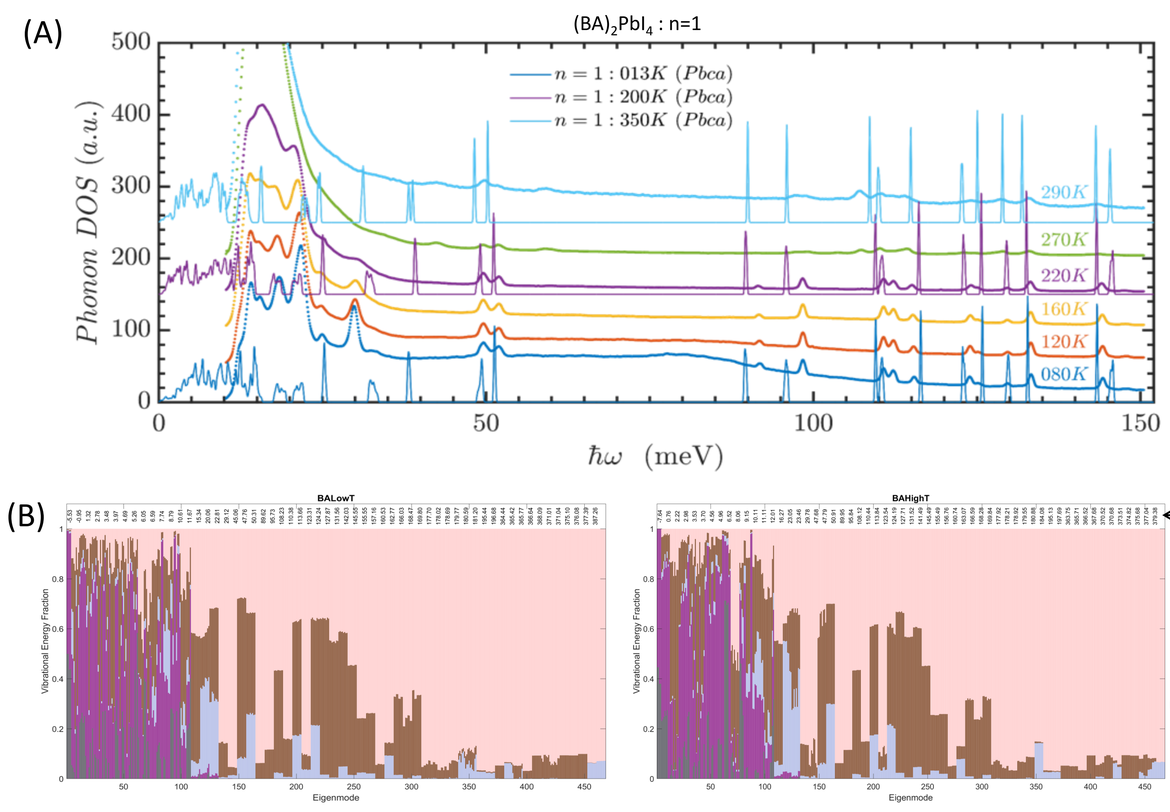

Fig. 4 (A) Temperature dependent Raman spectra for the 1-layer 2D perovskite $(BA)_2PbI_4$. Also shown are the calculations of phonon density of states for two low T phase temperatures 13K, 200K and one high T phase temperature 350K. Phonons are calculated using VASP package and Phonopy software. (B) Vibrational energy distribution of the phonon modes for the low and high temperature case. The colors refers to different atoms as shown on the right. The distribution show that of the vibration modes above ~16 meV are associated with the organic molecule BA^+.

1- and 2-layer Raman Spectrum Comparison

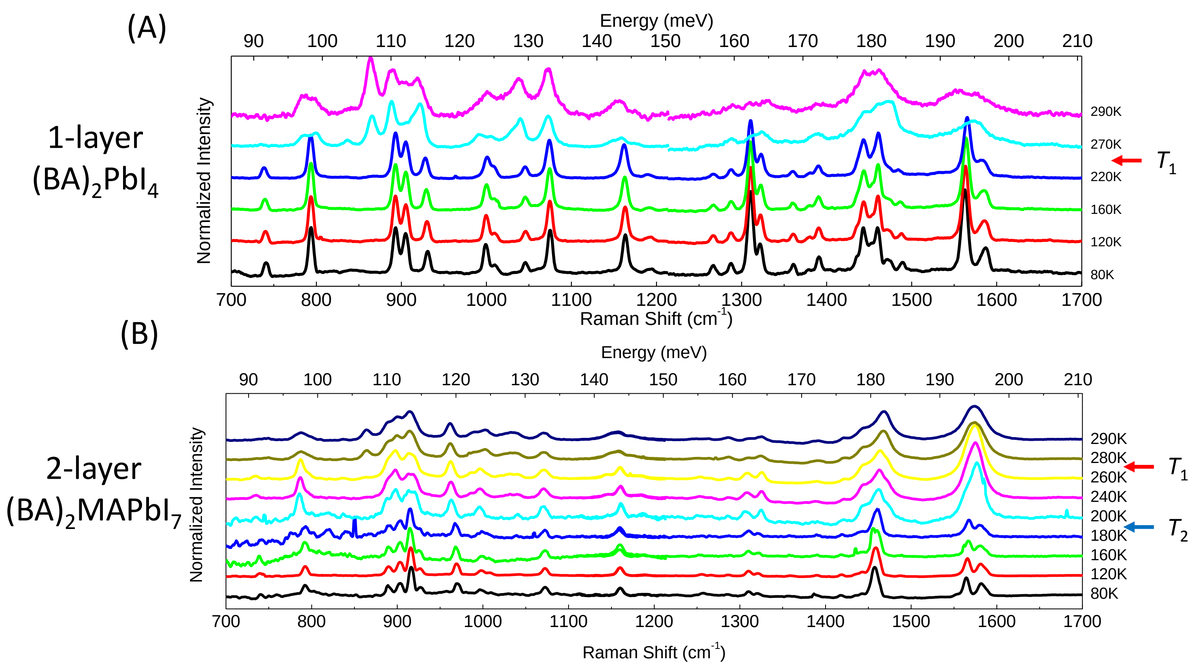

Fig. 5 Temperature dependent Raman spectra for (A) 1-layer $(BA)_2PbI_4$ and (B) 2-layer $(BA)_2MAPbI_7$ normalized to peak feature within the spectral range shown. One layer structure $(BA)_2PbI_4$ shows clear qualitative change at ~270K (red arrows), similar to T_1 of PL measurement, corresponding to the phase transition between the low T and high T phase. For 2-layer $(BA)_2MAPbI_7$, there is an additional transition between 180K and 200K (blue arrows) that can be associated with the orthorhombic to tetragonal transition of 3D perovskite $MAPbI_3$.

Conclusion

- Temperature dependent PL and Raman measurements show phase transition temperatures for the three 2D perovskite samples.
- 2- and 3-layer sample containing MA^+ have a transition at ~165K-185K similar to 3D perovskite $MAPbI_3$ and show similar lifetime increase to the orthorhombic-tetragonal transition of $MAPbI_3$.
- This lifetime increase suggests the screening of charge carriers by rotation of organic cations is important in 2D perovskite as in 3D perovskite.

Acknowledgement

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