

Intrinsic Raman signatures of pristine hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ and its multiple stages of structure transformation

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Abstract — By performing spatially resolved Raman and photoluminescence spectroscopy with different illumination conditions, we have achieved a unified understanding towards the spectroscopy signatures of the organic-inorganic hybrid perovskite, transforming from the pristine state ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) to fully degraded state (i.e., PbI_2), for samples with varying crystalline domain size from mesoscopic scale to macroscopic size, synthesized by three different techniques.

Index Terms — perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, pristine Raman spectrum, transformation stages.

I. INTRODUCTION

The rapid progress in the device performance of MAPbI_3 based solar cell devices has led to explosive research on the material optical property.[1] Unfortunately, some optical characterization work has been done in a rush without paying sufficient attention to the extreme structural instability, thus, yielded results of extrinsic to the material. For example, there is a large discrepancy among the reported Raman spectroscopy results for MaPbI_3 . [2-7] In this work, we reveal the Raman signatures of the pristine state and multiple characteristic transformation states toward PbI_2 . The information is of importance to the fundamental understanding of this unique group of hybrid material, and provides an easy indicator to the material degradation and guidance to various applications involving different levels of light-matter interaction.

II. EXPERIMENTAL DETAILS

Three types of samples were used in this work: (1) polycrystalline films synthesized by SKKU group of polycrystalline domains of typical ~ 500 nm in size (referred to as SKKU-p); (2) small domain polycrystalline films by NREL group (NREL-p); and (3) macroscopic size ($\sim \text{mm} - \text{cm}$) single crystalline samples by SNU group (SNU-c). Samples were received vacuum packed, and stored in a continuously pumped chamber. The optical properties of the hybrid perovskite are very sensitive to the measurement conditions. In this work, excitation densities varying from about $170 \text{ W} - 50 \text{ kW/cm}^2$ were used, allowing careful examination of the possible heating and photo-degradation effects. The lowest excitation density is significantly lower than the lowest level in the previous reports. Data were taken using either a $100\times$ ($\text{NA} = 0.9$) or $50\times\text{L}$ ($\text{NA} = 0.5$, long working distance) microscope lens on a Horiba LabRam HR800 confocal Raman microscope with a 1200g/mm grating, using a 532 and 441.6 nm laser with a full power of ~ 18 and ~ 13 mW, respectively, measured when exiting the microscope lens. Built in D1 – D4 neutral density (ND) filters were used to approximately attenuate laser power by 1 – 4 order. To minimize or examine heating and/or photo-degradation effect, a mechanical shutter was employed to block the laser beam in a Raman measurement: (1) when the CCD detector was not actively taking data; and (2) periodically during a long data collection cycle. All measurements were performed at room temperature with continued low N_2 flow to slow down the sample degradation (no significant change for a few hours).

III. RESULTS AND DISCUSSIONS

Fig. 1 compares Raman and photoluminescence (PL) spectra of a few SKKU samples. Fig. 1(a) and (b) include 5 representative Raman spectra from 5 samples using the 532 nm laser, where SKKU-p-1 to SKKU-p-4 were measured on a single spatial spot under ND filter (D)/total acquisition time (TAT)/continued data collection time (CT)/interruption time (IT) = $D4_{100x}/800s/0.5s/0.5s$ (except for SKKU-p-3 under $D4_{50xL}$), and SKKU-p-5 was measured under the same excitation level of SKKU-p-1 but only for 1s/spatial-point and averaging over 2420 total spatial points in an interval of $5\ \mu\text{m}$ ($D4_{100x}/1s/1s$). The SKKU-p-5 measurement was to minimize any potential accumulative effect of the large total illumination time in the other cases. Exposed to air for different lengths of time, these samples represent different stages of spontaneous or natural degradation. The degradation is manifested in the evolution of two major spectral features: (1) in the vicinity of $100\ \text{cm}^{-1}$, from no visible feature above a smooth background in SKKU-p-1, to emergence of a small “bump” in SKKU-p-2, to two resolvable peaks in SKKU-p-3, and finally to multiple well-developed sharp peaks in SKKU-p-4 that has almost fully converted back to PbI_2 ; (2) a broad band $\sim 550\ \text{cm}^{-1}$ with a valley at $\sim 900\ \text{cm}^{-1}$ exhibits a systematic intensity reduction till completely vanishes from SKKU-p-1 to SKKU-p-4. This broad band was absent in the previous reports. Clearly, the spectra of SKKU-p-1 and SKKU-p-5 are the two most closest to each other, which confirms that the spectrum of SKKU-p-1 can indeed represent that of a pristine sample. Comparing SKKU-p-1 and SKKU-p-4, the Raman cross sections near $100\ \text{cm}^{-1}$ are at least a factor of 15 difference between PbI_2 and MAPbI_3 . Fig. 1(c) compares the PL spectra of the same samples measured from the same spot as that for the respective Raman spectrum (taken before the Raman measurement) using the 442 nm laser under $D4_{100x}/1s/1s$ ($D4_{50xL}/1s/1s$ for SKKU-p-3) in order to examine the PL emission not only near the band gap of the hybrid but also that of PbI_2 . With increasing level of degradation, the hybrid related PL peak exhibits major peak intensity reduction, for over four orders in magnitude from SKKU-p-1 to SKKU-p-4, accompanying with blue shift in peak position, from $\sim 769\ \text{nm}$ near the hybrid bandgap,[8] in SKKU-p-1 to $\sim 743\ \text{nm}$ in SKKU-p-4 (only visible under 532nm excitation). Additionally, a weak PL peak at $\sim 514\ \text{nm}$ close to the bandgap of PbI_2 ,[9] appeared in the most degraded sample SKKU-p-4 but absent in the other samples. The Raman spectrum of SKKU-p-3 or SKKU-p-4 resembles the spectra for the hybrid material reported in the literature,[2-5] and that of SKKU-p-4 is also nearly the same as those reported for PbI_2 . [10] Above results suggest that the Raman spectrum of SKKU-p-1 or SKKU-p-5 can be taken as that of a pristine MAPbI_3 : no visible peak near $100\ \text{cm}^{-1}$ but with a broad band at $\sim 550\ \text{cm}^{-1}$.

Fig. 1(d) compares Raman spectra of the most pristine sample SKKU-p-1 measured under three conditions consecutively: $D4_{100x}/800s/0.5s/0.5s$, $D3_{100x}/400s/0.5s/0.5s$, and $D2_{100x}/100s/0.5s/0.5s$. For this type of sample, the combination of $D4_{100x}/800s/0.5s/0.5s$ appears to be a safe condition that does not result in visible change in the overall

shape of the Raman spectrum, although maybe some intensity reduction of the $550\ \text{cm}^{-1}$ peak. Under the other two conditions, two peaks are resolved at ~ 96 and ~ 111 or ~ 93 and $\sim 110\ \text{cm}^{-1}$, which are in fact similar to the another group of spectra in the previous reports.[6, 7] We note that in the Raman spectrum, despite the change near $100\ \text{cm}^{-1}$, the $\sim 550\ \text{cm}^{-1}$ band remained after the two higher level measurements; also in the PL spectrum (not shown), the hybrid bandgap emission remained, and no emission near the PbI_2 band gap was observed. This situation represents a subtle structural change of the hybrid without significant conversion back to PbI_2 .

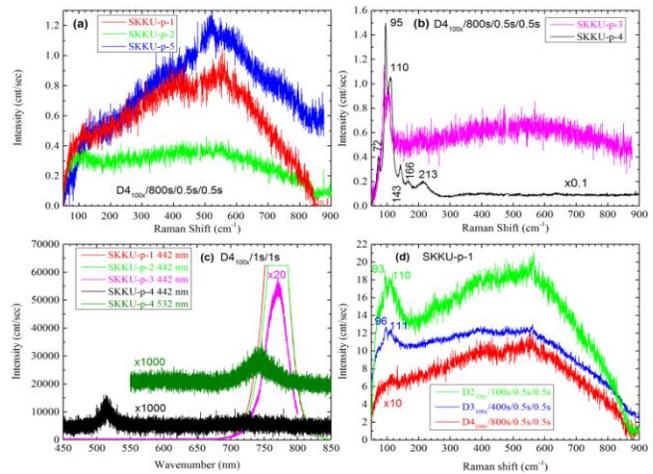


Fig. 1. Raman and PL spectra of SKKU samples at different stages of structure transformation. (a) & (b) Representative Raman spectra at different stages of structure transformation from MaPbI_3 to PbI_2 measured at $D4$. (c) PL spectra measured at $D4$ from the same location as in (a) & (b). (d) Raman excitation density dependence of the most pristine sample SKKU-p-1.

Raman of a NREL-p sample are shown in Fig. 2. Fig. 2(a) compares two spectra taken under the same D/TAT but with different CT/IT combinations. Clearly, the shorter interruption ($0.5s/0.5s$) yielded a more apparent $100\ \text{cm}^{-1}$ feature. Although $D4_{100x}/800s/0.5s/0.5s$ was found to be “safe” for SKKU-p-1, one should be alerted that the “safe” condition depends on the sample condition. Possibly due to the lower thermal conductivity and/or the difference in surface effect, it seems that the small domains are more sensitive to the illumination than the large ones. Clearly in Fig. 2(b), the $\sim 100\ \text{cm}^{-1}$ feature becomes more and more apparent with increasing excitation density. Although there was no individually resolved peaks near $100\ \text{cm}^{-1}$, these results are qualitatively consistent with those from the SKKU-p-1 sample. We note that in the NREL-p sample, even under $D4_{100x}/800s/1s/4s$, the $\sim 550\ \text{cm}^{-1}$ band is not as prominent as in SKKU-p-1, rather comparable to that in SKKU-p-2, which might suggest that the sample was slightly degraded, possibly because the further reduced polycrystalline domain size in this sample made it even less stable. This observation might explain why the previous reports also did not show the $\sim 550\ \text{cm}^{-1}$ band.[2-5]

The single crystal sample SNU-c results are given in Fig. 3. Fig. 3(a) contrasts two D4_{50xL}/1600s/0.5s/0.5s Raman spectra taken between one D2_{50xL}/200s/10s/0.2s measurement. While the D2 spectrum shows a visible $\sim 100\text{ cm}^{-1}$ peak, the two D4 spectra are nearly the same, indicating that the D2_{50xL}/100s/0.5s/0.5s illumination did not cause irreversible change. However, in Fig. 3(b), one D2_{50xL}/800s/20s/0.2s was followed by another D2_{50xL}/100s/0.5s/0.5s measurement, in the repeated D4 spectrum the 100 cm^{-1} peak now becomes somewhat visible, indicating that the longer D2 illumination did induce some structural change. Besides, comparison of D2 spectra in Fig. 3(a) and Fig. 3(b) suggested that longer D2

spectroscopy studies reflected partially degraded structures of different degrees.

ACKNOWLEDGEMENT

The work at UNC-Charlotte was partially supported with funds from Y.Z.'s Bissell Distinguished Professorship; at SKKU by the National Research Foundation of Korea (NRF) grants funded by the Ministry of Science, ICT & Future Planning (MSIP) of Korea; at NREL by the hybrid perovskite solar cell program of the National Center for Photovoltaics funded by the U.S. DOE/EERE; at SNU by the National University Research Fund, the Changjiang Scholar and Innovative Research Team, the Overseas Talent Recruitment Project, and the Chinese National 1000-talent-plan program; at the Molecular Foundry by the Office of Science, US DOE/BESS.

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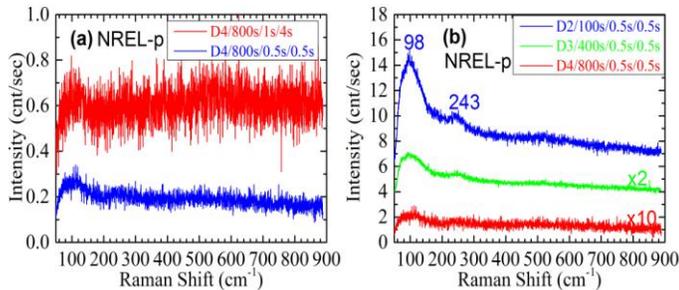


Fig. 2. Raman and PL spectra of NREL-p samples measured at different conditions. (a) D4 Raman spectra measured with different interruptions. (b) Raman spectra measured under different excitation density D4-D2.

illumination has resulted in more prominent $\sim 100\text{ cm}^{-1}$ peak, much reduced $\sim 550\text{ cm}^{-1}$ band, and appearance of a broad peak near 250 cm^{-1} . In fact, the D2 spectra in Fig. 3(b) are similar to that in Fig. 2(b) for the NREL-p sample. The results of this single crystal sample again confirm the conclusion about the intrinsic Raman spectrum of the material derived from the polycrystalline samples.

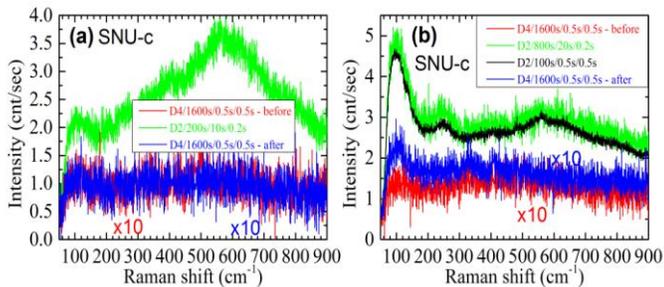


Fig. 3. Low excitation density (D4) Raman spectra of SNU-c samples measured before and after different higher excitation density measurements.

IV. SUMMARY

To sum up, by applying diligent controls in the measurement conditions, we have been able to reveal the intrinsic spectroscopy signatures of the pristine samples, and shown that much of the previously reported Raman

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