

Supporting Information

Behavior of Methylammonium Dipoles in MAPbX_3 ($X = \text{Br}$ and I)

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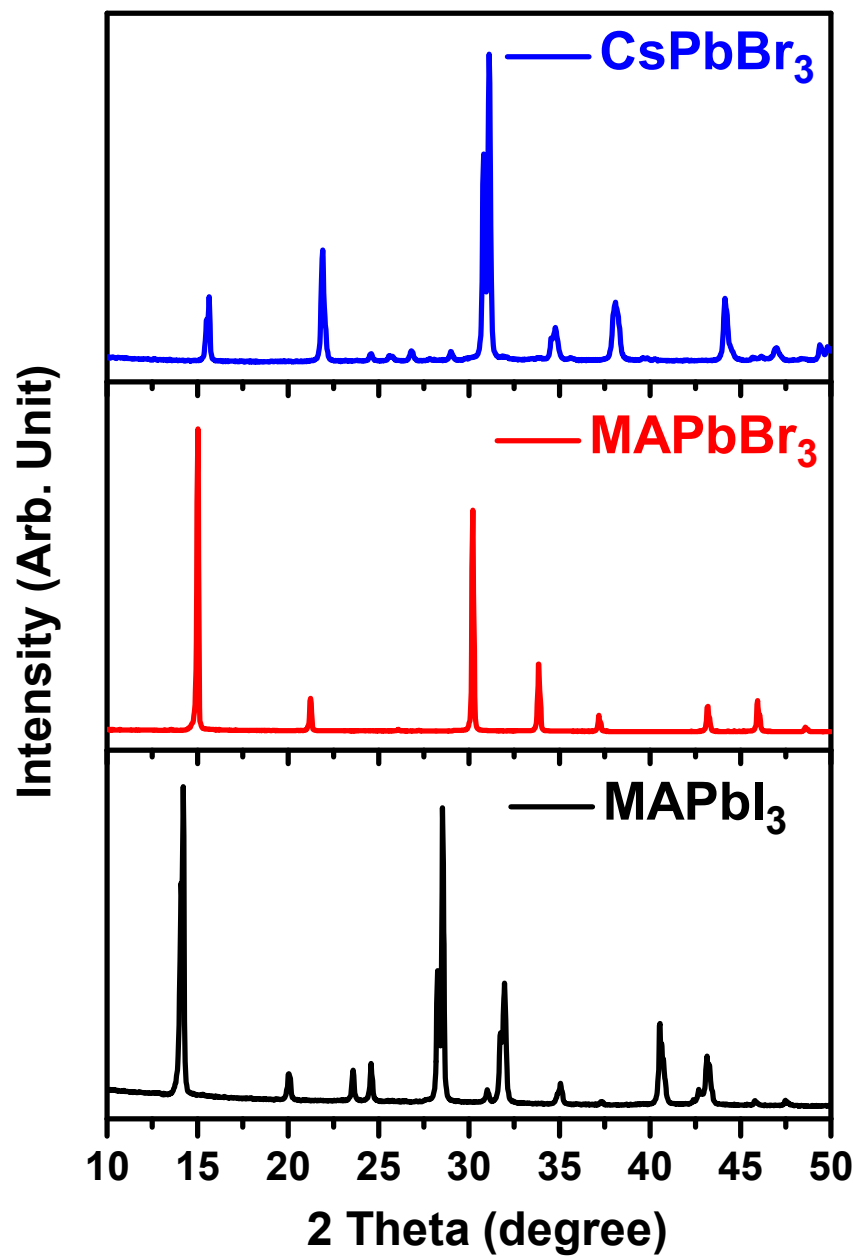


Figure S1: Powder XRD patterns of CsPbBr₃, MAPbBr₃ and MAPbI₃ shown in the range of 2 theta from 10° to 50°.

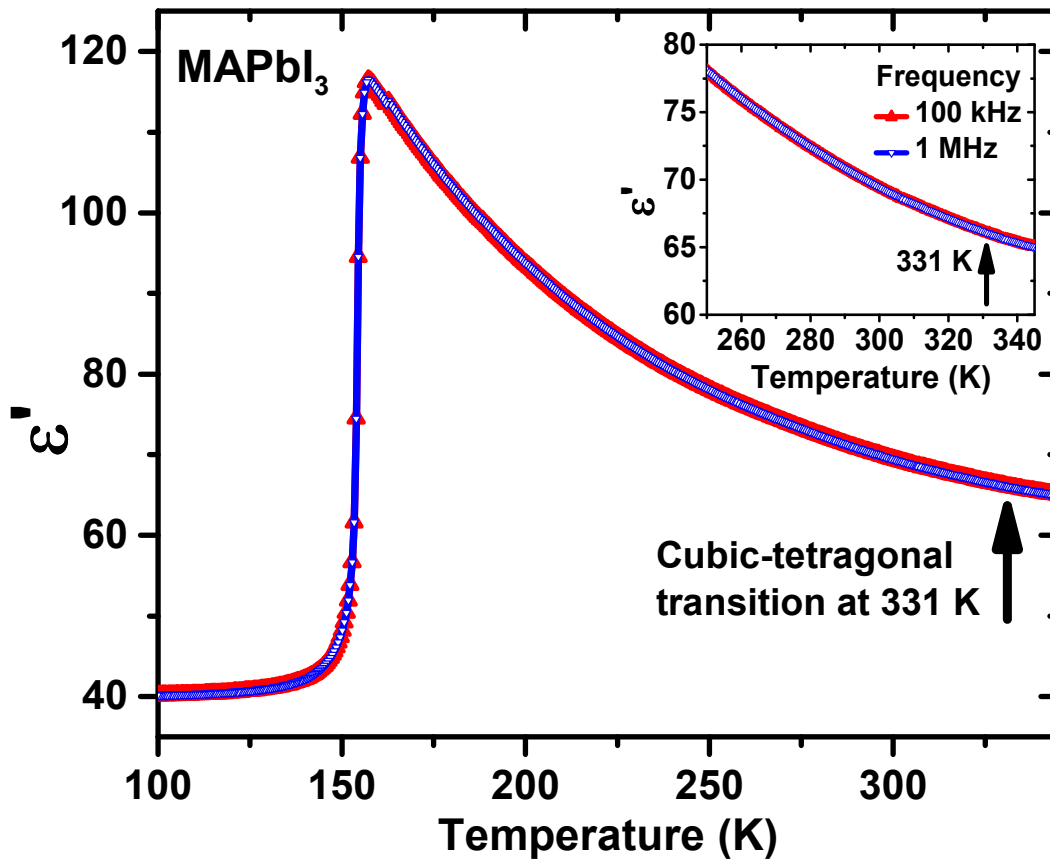


Figure S2: Dielectric constant as a function of temperature measured on MAPbI_3 showing the smooth behavior of dielectric constant across the tetragonal to cubic transition at 331 K. The inset shows an expanded view of the same in the relevant temperature range.

Analysis of spectra for calculating upper limit of SHG efficiency:

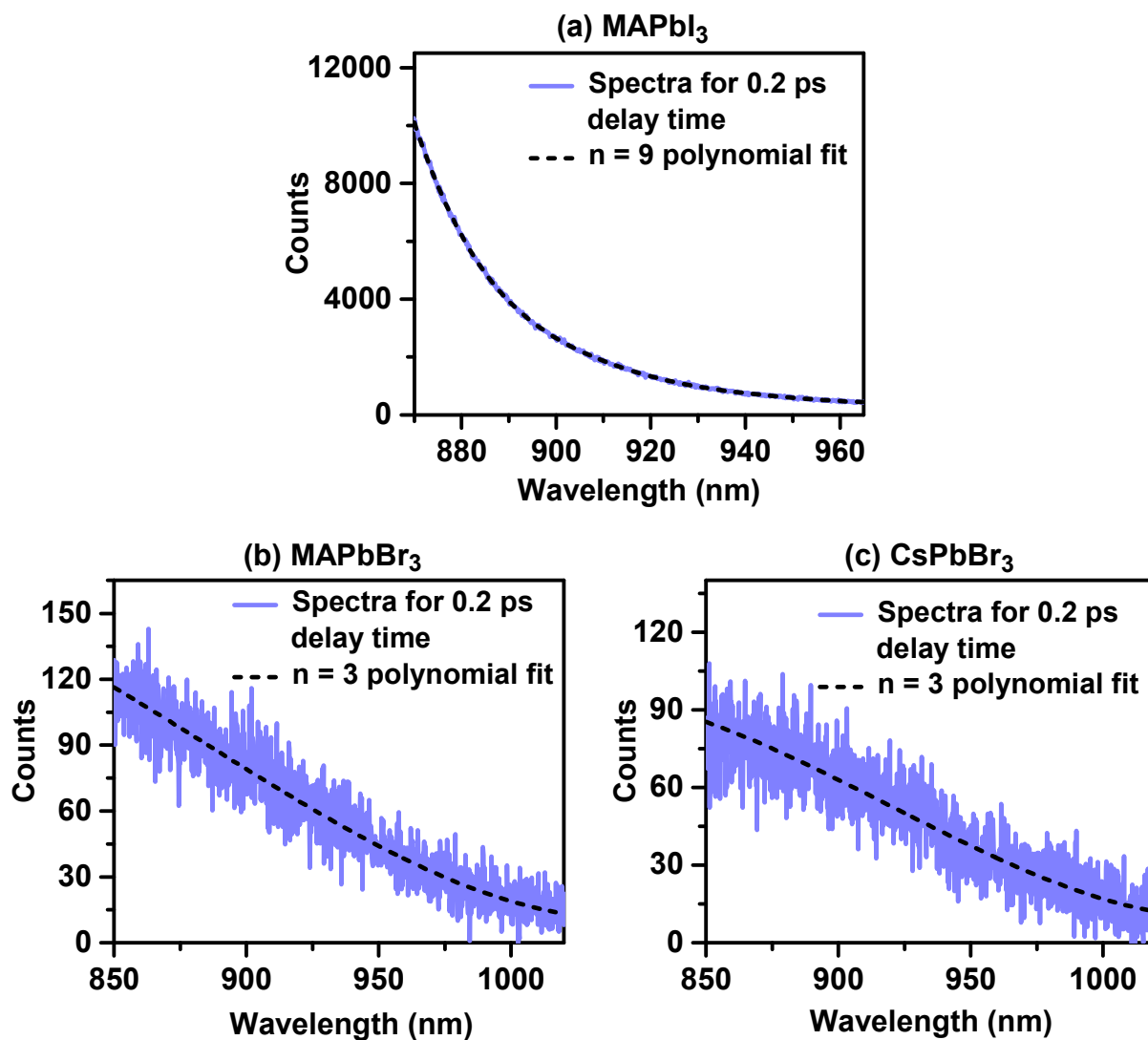


Figure S3: (a) Polynomial fit to tail of PL spectra of MAPb₃ (b) Polynomial fit to background of MAPbBr₃ spectra (c) Polynomial fit to background of CsPbBr₃ spectra. A typical spectrum at a delay time mentioned is shown for each sample.

The residual of polynomial fit is fitted with Gaussian of width 21 nm (corresponding to the source) and peak position 915 nm (as obtained from SHG of urea). These fits are shown in Figure S4.

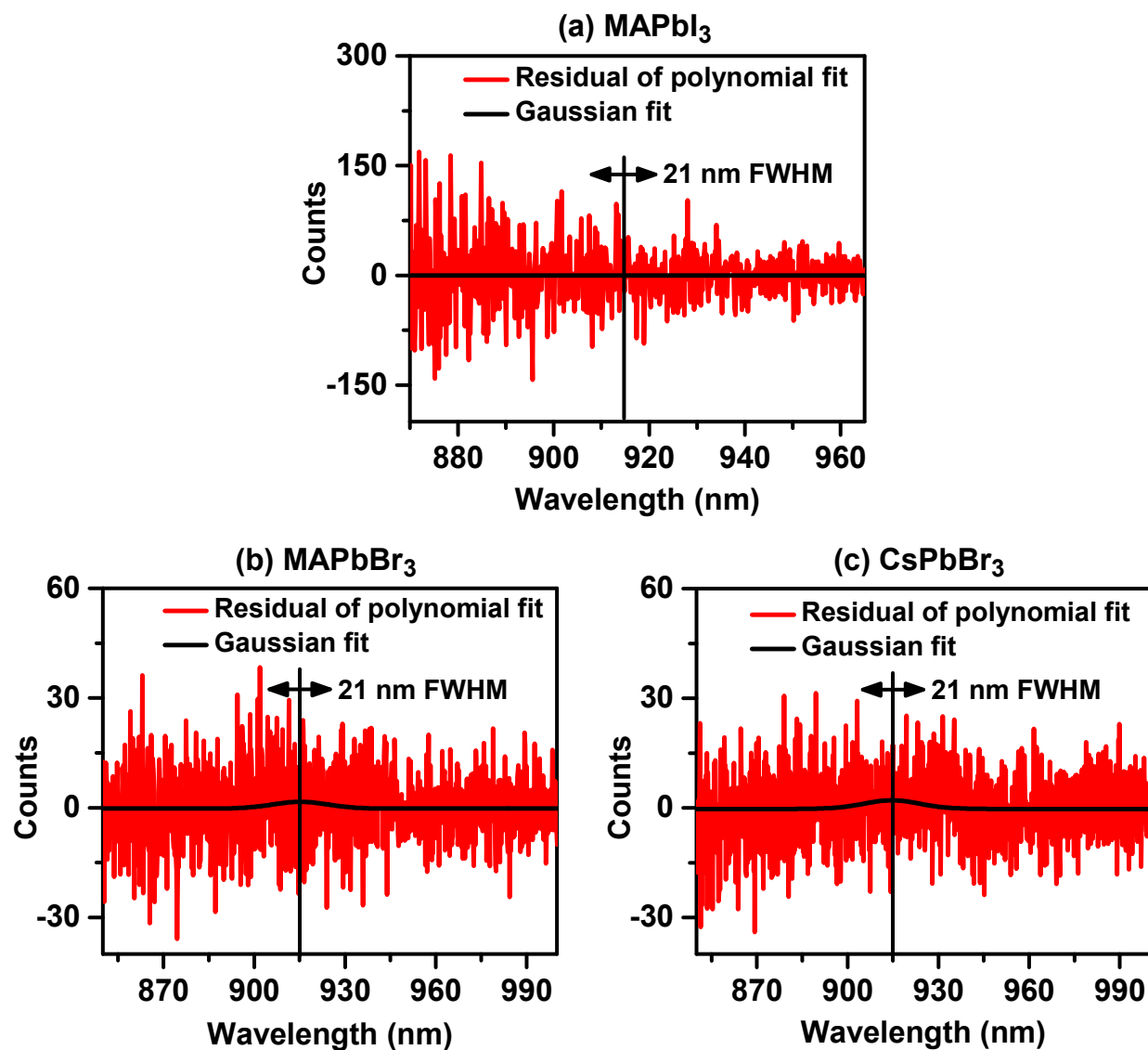


Figure S4: Gaussian fit at 915 nm of FWHM 21 nm, to get the SHG intensity from the residual of polynomial fit of the spectra for (a) MAPbI₃ (b) MAPbBr₃ and (c) CsPbBr₃.

Spectra for all delay times overlapped and a similar analysis is carried out for each of them. The ratio of the area of Gaussian obtained by this fit to the area of Gaussian obtained from spectra of urea is calculated. This is the relative SHG efficiency plotted in Figure 4 in the main text.

The measurement and analysis is carried out for CsPbBr₃ also, even though it is centrosymmetric, in order to show the comparison with MAPbBr₃. It can be seen that similar SHG efficiency ratio with respect to urea are obtained for both, which suggests that there is no detectable SHG and the small signal at 915 nm is limited by the sensitivity of the detector.