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Letter

Enhanced Third Harmonic Generation in Lead Bromide Perovskites with Ruddlesden–Popper Planar Faults

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ABSTRACT: Lead halide perovskites provide a test bed for exploring nonlinear optical properties. Although the underlying centrosymmetric crystal structure of 3D lead halide perovskites precludes the phenomenon of second harmonic generation, the third and higherorder harmonic generation are allowed. In this work, we probe the third harmonic generation (THG) from CsPbBr₃ nanocrystals (NCs) and compare it to the THG from CsPbBr₃ NCs with Ruddlesden-Popper planar faults (RP-CsPbBr₃), formed via postsynthetic fusion-growth. The THG from CsPbBr₃ NCs is negligible compared with that of RP-CsPbBr₃ NCs within a wide range of femtosecond excitation wavelengths. We further compare the THG from a thin film of RP-CsPbBr₃ with that of a single crystal of methylammonium lead bromide (MAPbBr₃). The THG efficiency of RP-CsPbBr₃ is found to be three times greater than that of MAPbBr₃. An effective third-order susceptibility of the order of 10^{-18} m²V⁻² is obtained for a RP-CsPbBr₃ film, opening up the prospect of inorganic halide perovskite NCs with planar defects for a range of nonlinear optical applications.



here has been an unprecedented development in metal halide perovskite-based optoelectronics in the past decade. Metal halide perovskites share the general formula ABX₃, in which A, B, and X are occupied by monovalent cations, bivalent metal cations, and halide anions, respectively. In hybrid organic-metal halide perovskites (OHPs), the A cation is typically methylammonium (MA) or formamidinium (FA), and the B cation is Pb or Sn. In all-inorganic metal halide perovskites (IHPs), Cs is a common A-site cation. Tunable, narrow emission, and high photoluminescence quantum yield (PLQY) of halide perovskite quantum dots make them promising candidates for next-generation displays. Along with exploring the linear optical properties of IHPs and OHPs, there has been a significant interest in deciphering the nonlinear optical (NLO) properties for photonic applications.² These include two- and multiphoton absorption processes³⁻⁹ and third- and higher harmonic generation from OHPs.¹⁰⁻¹³ Because most 3D OHP and IHP systems have a centrosymmetric crystal structure, second harmonic generation (SHG) is not allowed. However, surface effects may break inversion symmetry due to which SHG has been observed in MAPbI₃ (I4/mcm space group).¹⁴ Other strategies for observing SHG include tuning the van der Waals interaction in 2D lead halide perovskite¹⁵ and synthesis of chiral lead halide perovskite nanowires.¹⁶ Third harmonic generation, on the other hand, does not depend upon the crystal symmetry and allows a comparison of NLO properties between different materials.

2D hybrid organic-inorganic Ruddlesden-Popper (RP) halide perovskites, based on inorganic layers sandwiched between organic dielectric spacers, have been leading contenders in optoelectronics because of their strong excitonic effects and quantum confinement. Nanosheets exfoliated from such 2D RP single crystals yield large third-order susceptibility $(\chi^{(3)})$ of ~10⁻¹⁷ m²/V² with conversion efficiencies much greater than that of other 2D materials.¹⁰ The synthesis of CsPbBr3 nanocrystals (NCs) with RP faults has opened the prospect of exploring NLO properties in 3D halide perovskites, which are easily solution processable. The RP faults in these NCs are introduced during a postsynthetic fusion growth process, where the lateral size of the NCs may be as large as 90 nm compared to the ~8 nm lateral dimension for non-RP CsPbBr₃ NCs.¹⁷ The RP faults in CsPbBr₃ NCs appear when a CsBr bilayer is incorporated between the CsPbBr₃ domains, where the adjacent layers are shifted with respect to each other by half a unit cell. Density functional theory predicts the absence of any deep-level defects associated with these RP faults, but they result in band offsets which may favorably impact charge transport and exciton recombination processes.¹⁸ In fact, the presence of RP faults in CsPbBr₃ NCs enhances the photoluminescence (PL) quantum yield and improves the stability.¹⁷ Under 1 GPa of hydrostatic pressure,

Received: February 19, 2021 Accepted: April 13, 2021 Published: April 22, 2021





Figure 1. (a) Single-photon and multiphoton normalized PL from MAPbBr₃ single crystal. The inset shows an image of the sample that was mounted on a glass slide. (b) Normalized THG spectra from MAPbBr₃ by varying the incident wavelength from 1120 to 1450 nm. (c) THG integrated intensity versus incident power at excitation wavelength of 1280 nm. The red line shows a power-law dependence fit to the experimental data. The inset shows the THG spectra for varying incident power.

the PL intensity from RP-CsPbBr₃ NCs is seen to further increase. 19

Inverse temperature crystallization (ITC),²⁰ which has opened up a rapid growth method for defect-free single crystals of MAPbX₃ (X = Br⁻, I⁻, or Cl⁻), has been instrumental for several fundamental NLO studies. In particular, two-photon absorption (TPA) from MAPbBr₃ for application in nonlinear optics has been heavily explored.^{3,6} MAPbBr₃ metasurfaces show an efficient three-photon luminescence process which has been utilized in color nanoimprinting and optical encoding.¹² The PL spectrum of the MAPbBr₃ single crystal is characterized by at least two excitonic peaks with varying binding energies.^{21,22} Spatial variation in the photocarrier distribution in MAPbBr3 crystals with different excitation wavelengths (above band gap versus near IR) results in differences in the emission spectrum;^{23,24} the two-photon PL process shows only the low-energy excitonic peak. As we shall see here, the multiphoton process also shows a similar behavior.

In this work, we obtain the third-harmonic generation (THG) spectrum from a 350 \pm 20 nm film of CsPbBr₃ NCs with RP faults (RP-CsPbBr₃) by varying the incident wavelength from 1120 to 1450 nm with a 100 fs pulse duration. An identical film of CsPbBr3 with no RP faults shows negligible THG. The THG from RP-CsPbBr₃ is enhanced when the incident wavelength varies between 1200 and 1300 nm. At 1280 nm, the RP-CsPbBr₃ film yields a THG efficiency of 6×10^{-6} . We further compare the results with THG from a single crystal of MAPbBr₃. The overall THG efficiency in MAPbBr₃ (for a 0.5 mm thick crystal) is found to be 2×10^{-6} and 1×10^{-6} at excitation wavelengths of 1280 and 1200 nm, respectively. Our results indicate that RP-CsPbBr₃, with the advantages of postfusion synthesis and 3D structural stability, provide an excellent platform for exploring nonlinear optical properties.

The RP-CsPbBr₃ NCs were prepared as outlined in ref 17, where the RP faults are introduced by a postsynthesis process using diethyl zinc. The structural, morphological, and optical properties of the CsPbBr₃ NCs are provided in the Supporting Information. The colloidal RP-CsPbBr₃ solution was drop-coated on an Al slide with a film thickness of \sim 350 ± 20 nm, as determined with a profilometer. A similar film was formed from the colloidal non-RP CsPbBr₃ solution on an Al slide. Because glass has a strong THG, it cannot be used as a substrate. The Al substrate used here was nonreflecting and rough, which contributes to the uncertainty in the thickness

 $(\pm 20 \text{ nm})$ of the film. For ellipsometry measurements, glass was used as the substrate. The synthesis of MAPbBr₃ single crystals was carried out using the ITC method.²⁰ The THG signal was measured in a reflection geometry (see the Supporting Information). The excitation wavelength 1120-1400 nm (100 fs) was obtained from an optical parametric amplifier (TOPAS). The calibration of the CCD and the spectrometer were achieved by a CW diode laser with emission at 400 nm. The diode laser has an identical path compared to the THG. Using the same slit width and known integration times, the CCD counts were correlated with the power of the diode laser, which was measured at the entrance of the spectrometer. For both MAPbBr3 and RP-CsPbBr3 samples, the THG signal (measured using the spectrometer/CCD) could thus be converted into output power. The incident power was measured in front of the sample. The ratio of the output to input power gives an estimate of the THG efficiency.

Prior to measuring the THG from the CsPbBr₃ films, we measured the THG from a single crystal of MAPbBr₃. This sample was chosen mainly for two reasons: first, the optical constants are well-known,²⁵ allowing an independent estimate of $\chi^{(3)}$ for a perovksite sample; second, this sample provides a basis of comparison of the THG efficiency between a single crystal and thin films of CsPbBr₃. Figure 1a shows the singlephoton PL (measured using a 400 nm CW laser diode) and multiphoton PL from MAPbBr₃ single crystal for wavelengths varying between 1120 and 1380 nm. The PL spectrum shows two excitonic peaks at 540 and 570 nm. The multiphoton emission shows only the low-energy peak. Recent investigations from MAPbI₃ show that the origin of the high-energy PL peak is mainly from the surface and the low-energy PL peak, which is subjected to self-absorption effects, is from the bulk.²⁶ Because of the high excitation intensity in a multiphoton process, the laser beam is focused in the bulk of the sample, and thus, only the low-energy peak is observable. The multiphoton PL and the THG intensities were maximized by changing the z-axis (perpendicular to the sample surface). The normalized THG spectra from MAPbBr3 are shown in Figure 1b. For this sample, the highest THG intensity is observed when the excitation wavelength is at 1280 nm. A power dependence measurement at this wavelength confirms the third power of the THG versus incident power. By calibrating the optical power in the setup and the responsivity of the monochromator and detector with a diode laser and neutral density filters, the THG efficiency at 1280 nm is found

to be 2 \times 10⁻⁶. A similar power dependence at 1200 nm excitation yields a THG efficiency of 1 \times 10⁻⁶.

Detailed structural studies show that under ambient conditions, MAPbBr₃ adopts a cubic symmetry (space group: $Pm\overline{3}m$) with a lattice constant of ~5.9 (see the Supporting Information). Considering the isotropic nature of the crystal, we estimate $\chi^{(3)}$ for the MAPbBr₃ single crystal from the known refractive indices and using the conditions for the reflection geometry^{27,28} (details are provided in the Supporting Information). Given that the THG efficiency (I_3/I_1) of MAPbBr₃ is 2×10^{-6} at 1280 nm, we obtain $|\chi^{(3)}| = 1.3 \times 10^{-20} \text{ m}^2/\text{V}^2$. This value is reasonable, especially if we compare $\chi^{(3)}$ values of other semiconducting cryastals: cadmium sulfide with a refractive index of 2.34 has $\chi^{(3)}=9.8 \times 10^{-20} \text{ m}^2/\text{V}^2$, and zinc selenide with a refractive index of 2.7 has $\chi^{(3)} = 6.2 \times 10^{-20} \text{ m}^2/\text{V}^2^{2.8}$

The THG from the CsPbBr₃ films was measured with the same geometry as the MAPbBr₃ single crystal. Figure 2



Figure 2. Comparison of the THG spectrum from RP-PbBr₃ and non-RP CsPbBr₃ films measured at an incident wavelength of 1200 nm. The inset shows the power dependence of the 390 nm peak for the non-RP sample. The overall intensity does not scale as what is expected from THG.

compares the THG spectra of RP-CsPbBr3 and non-RP CsPbBr₃ films of similar film thicknesses (~350 nm) with the fundamental wavelength at 1200 nm. Unlike MAPbBr₃, which is a single crystal, the CsPbBr₃ NCs have stabilizing ligands to prevent agglomeration. The ligands are stripped in RP-CsPbBr₃ during the formation of the RP faults and growth of the NCs, which enhances the presence of surface states.¹⁷ The presence of surface states in CsPbBr₃ may drive the THG process into a nonparametric process, resulting in a slight shift of the THG energy.²⁸ The non-RP sample shows a negligible signal near 400 nm compared to the RP sample. A wavelength dependence of the incident beam does not show the expected shift in the THG in non-RP CsPbBr₃. There is some nonlinear response when the incident beam is at 1200 nm, but it is not THG, which is also reflected in the power dependence of the intensity. For the non-RP sample (inset), the power dependence does not scale as the third power of intensity. Therefore, we focus on the RP-CsPbBr₃ film for the THG analysis.

Figure 3a shows a representative high-resolution TEM image of RP-CsPbBr₃. The RP fault planes are marked by white arrows, and a close-up image of an RP fault is shown on the right. We note that that RP NCs grow with time in colloids because of the loss of stabilizing surfactants in the fusion process (see the Supporting Information); the average size of the NCs while the films were formed was ~25 nm. Detailed characterization and analysis of the RP faults are provided in



Figure 3. (a) High-resolution TEM image of RP-CsPbBr₃ NCs. The white arrows denote the RP fault plane. A close-up image of an RP fault and the luminescence from the colloidal solution are shown on the right. (b) Single-photon PL from a thin film of RP-CsPbBr₃. The inset shows an optical image of the PL and an atomic structure of CsPbBr₃. The Cs⁺ ions are shown in green, and the octahedral cage with gray and brown spheres depict Pb²⁺ and Br⁻ ions, respectively. (c) Normalized THG spectra from RP-CsPbBr₃ by varying the incident wavelength from 1120 to 1450 nm. (d) THG integrated intensity versus incident power at excitation wavelength of 1280 nm. The red line shows a power-law dependence fit to the experimental data. The inset shows the THG spectra for varying incident power.

refs 17 and 18. The PL properties of RP-CsPbBr₃ were shown to be enhanced and more stable compared to non-RP CsPbBr₃.¹⁷ A slight bathochromic shift in the PL is observed (Figure 3b) because it is from a thin film compared to the colloidal solution in ref 17. The inset of Figure 3b shows an optical image of the PL. The normalized THG spectra from the RP-CsPbBr₃ thin film are shown in Figure 3c. The THG intensity is maximum when the incident wavelength ranges between 1200 and 1300 nm. The power dependence of the THG spectrum measured at an excitation wavelength of 1280 nm is shown in Figure 3d. The THG efficiency at this wavelength was found to be 6×10^{-6} , approximately three times higher than that of MAPbBr₃.

Although spectroscopic ellipsometry measurements were performed on a spin-coated film of RP-CsPbBr₃ (grown on glass), because of the high THG from the glass substrate itself, this film (with an approximate thickness of 100 nm) could not be used for the THG measurements. Instead, for the THG measurements, the RP-CsPbBr₃ film was dropcasted on a roughened Al substrate, as stated earlier. We use the complex refractive index determined from ellipsometry (see the Supporting Information) to estimate the $\chi^{(3)}$ value for RP-CsPbBr₃. Using Maxwell's nonlinear equation, as shown by Youngblood et al.,²⁹ the intensity of the THG signal (I_3) from a thin film may be expressed as

$$I_{3} = \frac{9\omega^{2}}{16|\tilde{n}_{3\omega}||\tilde{n}_{\omega}|^{3}\epsilon_{0}^{2}c^{4}}I_{1}^{3}|\chi^{(3)}|^{2}\left(\frac{e^{-2\alpha t} - 2\cos(\Delta kt)e^{-\alpha t} + 1}{\alpha^{2} + \Delta k^{2}}\right)e^{-2\alpha t}$$
(1)

where t is the thickness of the sample; \tilde{n}_{ω} and $\tilde{n}_{3\omega}$ are the complex refractive indices at the fundamental and third harmonic frequencies, and α is the absorption coefficient at the THG wavelength. The phase mismatch condition, Δk_{i} ,

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Figure 4. THG images from MAPbBr₃ single crystal and films of RP-CsPbBr₃ and non-RP CsPbBr₃. The excitation source was 1200 nm. The horizontal yellow line depicts the region over which the plot profile was measured in each case.

between the fundamental and the third harmonic generated wave for backward propagation is given by $6\pi(n_1 + n_3)/\lambda_1$, where λ_1 is the wavelength of the fundamental. The incident intensity (I_1) was estimated to be 1.2×10^{16} W/m² from the incident laser power, the repetition rate and pulse width of the laser, and from the focal length and aperture of the focusing lens. As mentioned above, the THG efficiency (I_3/I_1) of the RP-CsPbBr₃ film was found to be 6×10^{-6} at 1280 nm. Using the thickness of the RP-CsPbBr₃ film as 350 ± 20 nm, from eq 1, we estimate $\chi^{(3)}$ in the range of 0.85×10^{-18} to 1.20×10^{-18} m²/V². This range is similar to what has been estimated for thick exfoliated 2D RP perovskite crystals.¹⁰

We have further imaged the THG emission using an excitation wavelength of 1200 nm from the three samples using a microscope objective (50x) and a CMOS camera. The THG images are shown in Figure 4 and give a snapshot of how the intensities compare from the three samples. The incident power and acquisition times (5 s) were similar in all cases. A plot profile for a 300 pixel line, chosen at the same location for each image, is included. The non-RP CsPbBr₃ sample shows no THG for this acquisition time and has only a uniform background illumination. The THG image from the RP-CsPbBr₃ film is brighter than that from MAPbBr₃.

The enhancement of THG in RP-CsPbBr₃ originates from the size of the NCs and the quantum confinement effect due to the RP faults. Compared to non-RP CsPbBr₃, where the lateral dimension is ~8 nm, the lateral dimension of RP-CsPbBr₃ NCs in this work is ~25 nm. We note that the RP-CsPbBr₃ NCs may have some amount of 2D structure, but the overall structure is still cuboid. This was discussed in detail in ref 17. Despite the rather large size increase in RP-NCs, the PL shows a relatively small red-shift compared to non-RP NCs, which we believe is due to the RP-induced quantum confinement effect.

The RP-CsPbBr₃ film as well as the MAPbBr₃ crystal shows an enhancement in THG around 1280 nm, indicating some resonance contributions to the nonlinear susceptibility tensor. In this limit there are two contributions to the susceptibility: one- and two-photon resonant terms. The one-photon term is always negative as long as the frequency is smaller than any resonance frequency of the material system. The two-photon term, which is usually positive, is directly related to the linear polarizability of the system. Further, the linear polarizability of the system in the excited state is larger than in the ground state, and thus intense optical fields result in a contribution to $\chi^{(3)}$ which is positive.²⁸ The size of the NCs in RP-CsPbBr₃ is expected to result in a large linear polarizability and thus a higher contribution to $\chi^{(3)}.$

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Third-order susceptibilities as large as $10^{-16}-10^{-17}$ m²/V² have been observed in π -conjugated semiconductors and C₆₀ because of the response of delocalized π electrons.^{30–32} More recently, 2D layered materials such as transition metal dichalcogenides and graphene have been investigated for their nonlinear optical properties.³³ Monolayer graphene and MoS₂ show $\chi^{(3)}$ values of the order of 10^{-19} m²/V².³⁴ Dirac semimetal thin films of Cd₃As₂ have shown a $\chi^{(3)}$ value of 2.3 × 10^{-19} m²/V², slightly higher than that of graphene and MoS₂.³⁵

In summary, we demonstrate that CsPbBr₃ NCs with the inclusion of RP faults have strong nonlinear optical properties. The THG efficiency from a thin film of RP-CsPbBr₃ is found to be at least three times greater than that of a single crystal of MAPbBr₃. The value of $\chi^{(3)}$ for a 350 ± 20 nm thin film of RP-CsPbBr₃ was estimated in the range of 0.85×10^{-18} to 1.2 $\times 10^{-18}$ m²/V². The high $\chi^{(3)}$ value observed in RP-CsPbBr₃ NCs is attributed to a strong excitonic effect due to quantum confinement. The RP faults act as natural built-in quantum wells within the perovskite domains, enhancing the excitonic binding energy and thus boosting the transition dipole moment. This is different from 2D perovskites where alternating organic and inorganic perovskite layers form multiquantum well architectures. The ease of solutionprocessed perovskite films opens up a new direction for exploring nonlinear optical properties and their application in photonics.

METHODS

Detailed synthesis procedure for CsPbBr₃ nanocrystals (NCs) were provided in ref 17. Briefly, Cs-oleate was injected into a mixture, containing PbBr₂, oleic acid, oleylamine, and octadecene, under N₂ atmosphere at 185 °C. Immediately after injection the mixture was cooled with an ice–water bath. Nanocrystals were collected by centrifugation at 4000 rpm for 12 min. Ruddlesden–Popper planar faults were formed in CsPbBr₃ nanocrystals by introducing diethyl zinc in the glovebox under Ar atmosphere at room temperature. The experimental THG setup and other experimental conditions are discussed in detail in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00555.

Synthesis and experimental procedures; optical absorption, photoluminescence, TEM, X-ray diffraction, estimation of χ^3 for MAPbBr₃, and spectroscopic ellipsometry results (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the support of this work through the National Science Foundation under Grant Nos. DMR-1807263 and ECCS-1827846. We thank Randy Burns and Sorb Yesudhas for the growth of the MAPbBr₃ crystals.

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