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Second harmonic generation in iodine quasi-2D halide perovskite crystals

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Abstract. Layered quasi-two-dimensional halide perovskites have attracted significant attention as exceptional materials for nonlinear optics and photonics applications due to their remarkable photophysical properties. The incorporation of quasi-2D spacer ligands into the halide perovskite framework induces alterations in the crystal structure and leads to changing its properties due to quantum confinement effects. Notably, certain crystal structures may exhibit a lack of center symmetry, facilitating the observation of second harmonic generation. Furthermore, the optical properties of halide perovskite crystals can vary dramatically based on the composition of the quasi-2D spacers. In this study, we investigate the second harmonic generation signal of two compositions: $\text{PEA}_2\text{MAPb}_2\text{I}_7$ and a novel methyl-substituted PEA derivative, $\text{MePEA}_2\text{MAPb}_2\text{I}_7$. Our results reveal distinct second-harmonic generation characteristics for both compositions and demonstrate enhanced stability in MePEA-based crystals. This work contributes to the understanding of the relationship between crystal composition and nonlinear optical behavior in quasi-2D perovskites, paving the way for future advancements in photonic applications.

Keywords: quasi-2D halide perovskites, second harmonic generation, photoluminescence, non-linear optics

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Конференционная статья

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Генерация второй гармоники в йодовых квазидвумерных галогенидных перовскитных кристаллах

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Аннотация. В данной работе исследуется генерация второй гармоники в квазидвумерных перовскитных йодовых кристаллах для получения стабильного сигнала во времени. Мы сравниваем различные квазидвумерные лиганды и изучаем их влияние на нелинейные эффекты в синтезированных кристаллах.

Ключевые слова: квазидвумерные галогенидные перовскиты, генерация второй гармоники, фотолюминесценция, нелинейная оптика

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Introduction

Quasi-two-dimensional (quasi-2D) halide perovskites are a unique class of materials characterized by the incorporation of organic spacer cations into the bulk halide perovskite framework [1]. An increasing number of research highlights the significant influence of the chemical composition of these organic spacers on the optical and structural properties of quasi-2D perovskite systems [2 – 4]. Notably, the choice of organic spacer can affect nonlinear optical phenomena, such as second harmonic generation (SHG). Since SHG requires the absence of an inversion center in the crystal structure, any modifications to the orientation or symmetry resulting from alterations to the spacer can substantially impact the efficiency of the nonlinear optical response.

Recent studies have demonstrated SHG in various iodine-based quasi-2D perovskite crystals, including those incorporating *n*-butylammonium (BA) [5], phenethylammonium (PEA) [2], and various chiral ligand-based structures [4]. However, the intensity and stability of SHG in these iodine-based crystals remain relatively low. In this work, we investigate SHG in a novel methyl-substituted PEA-based [6] single crystal, MePEA₂MAPb₂I₇, and compare its SHG characteristics with those of the more commonly studied PEA₂MAPb₂I₇ crystal.

Materials and Methods

MePEA₂MAPb₂I₇ and PEA₂MAPb₂I₇ solutions were synthesized using stoichiometric mixtures of 0.3 mmol PbI₂ (> 99.999 %) and 0.3 mmol MePEAI or PEA I (> 99.9 %) and 0.3 mmol MAI (> 99.9 %) in dimethyl sulfoxide. The solutions were prepared and stored in an inert atmosphere of a nitrogen-filled glove box. Each solution was deposited between two glass substrates that were pressed together and remained heated up to 60 °C for further crystal growth. Bright-field, dark-field and luminescent images of the structures were taken on an Axio Imager A2m optical microscope (Carl Zeiss SMT), optical pumping was performed using a 350 nm wavelength UV lamp. SHG spectra were measured on a Labram spectrometer with optical pumping by a TEMA femtosecond pulsed laser ($\lambda = 1045$ nm) and a frequency of 70 MHz through a NIR 50x (NA = 0.42) objective.

Results and Discussion

In this study, we investigate quasi-2D halide perovskite single crystals with the general formula L₂MA_(*n*-1)Pb_{*n*}I_(3*n*+1), where MA represents methylammonium, Pb denotes lead, I is an iodine, L is either PEA or MePEA ligand as the organic spacer, and *n* indicates the number of perovskite layers separated by these organic spacers from other perovskite layers [1]. Specifically, we focus on the quasi-2D perovskite phases with *n* = 2, namely PEA₂MAPb₂I₇ and MePEA₂MAPb₂I₇, which were synthesized from precursor solutions held between substrate glasses at a temperature of 60 °C.

For our experiments, we selected a series of perovskite crystals exhibiting similar photoluminescence (PL) spectra. Fig. 1, *a*, *b*, *c* shows the optical microscopy images of the crystals obtained in bright-field, fluorescence and dark-field modes, respectively, for MePEA₂MAPb₂I₇ (upper row) and PEA₂MAPb₂I₇ (lower row). The PL spectra for both compositions normalized

by the maximum of the most intense signal for MePEA are illustrated in Fig. 1, *d*, revealing a PL peak around 580 nm. This peak is consistent with the characteristics of the quasi-2D perovskite phase with $n = 2$, thereby confirming the composition of the synthesized crystals.

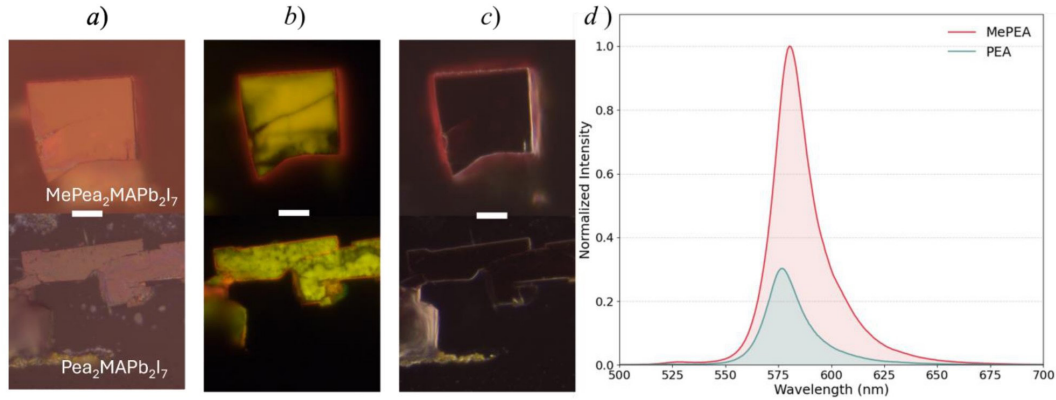


Fig.1. Bright-field (*a*), fluorescent (*b*) and dark-field (*c*) images of quasi-2D perovskite crystals with a scale bar of 10 microns, the upper row is MePEA₂MAPb₂I₇, the lower row is PEA₂MAPb₂I₇; PL spectra of PEA₂MAPb₂I₇ and MePEA₂MAPb₂I₇ crystals of the same phase group at the same pump fluence (*d*)

Upon excitation with a 1045 nm femtosecond laser, both samples exhibited SHG and two-photon photoluminescence (2PL). As is known, SHG is the second-order nonlinear process and thus the SHG intensity should have quadratic dependency on the incident pump power. The slopes of the measured power-intensity correlations were estimated to be 1.74 and 1.76 for PEA₂MAPb₂I₇ and MePEA₂MAPb₂I₇, respectively, which is close to quadratic law (Fig. 2, *a*, *b*), proving the occurrence of SHG. The SHG threshold was estimated to be 0.4 mJ/cm² for both compositions. The intensity of the SHG signal for both methyl-substituted and usual PEA-based crystals were obtained at the same pump power and normalized to the most intense signal value (Fig. 2, *c*, *d*). The difference in intensity of normalized signal may be attributed to different thickness of structures, as it was previously reported in other works [3].

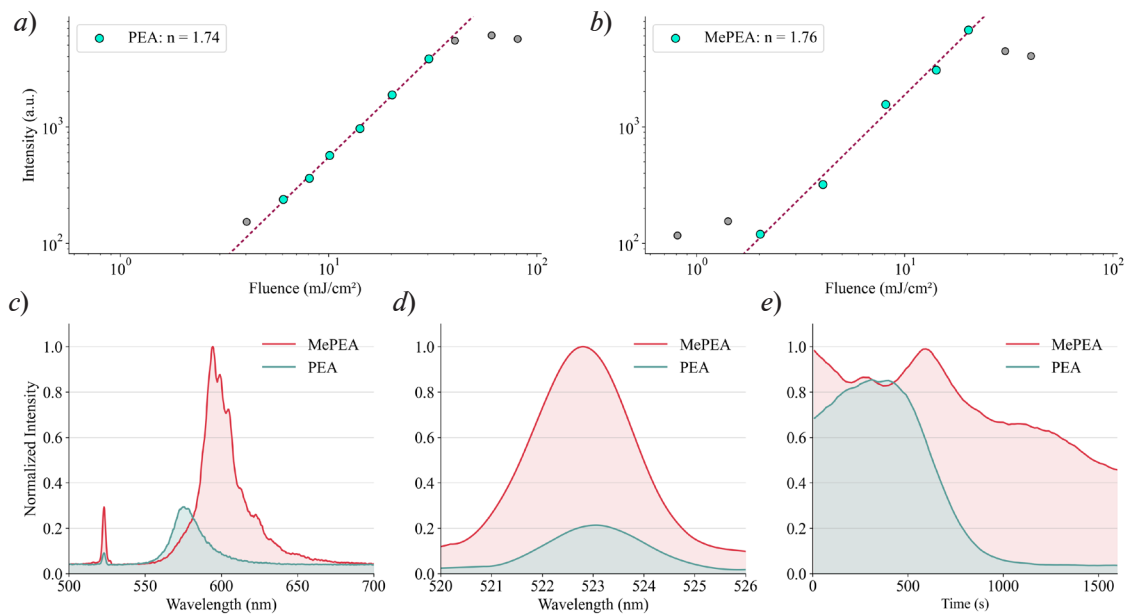


Fig.2. Dependence of the SHG peak intensity on the optical pump power in a logarithmic scale for the composition PEA₂MAPb₂I₇ (*a*) and MePEA₂MAPb₂I₇ (*b*); 2PL spectra with SHG peak for compositions PEA₂MAPb₂I₇ and MePEA₂MAPb₂I₇, at low fluence (1.2 mJ/cm²) (*c*); SHG spectra for MePEA₂MAPb₂I₇/PEA₂MAPb₂I₇ crystals at the same pump fluence (6 mJ/cm²) (*d*); temporal dependency of SHG peak intensity under continuous pump fluence (6 mJ/cm²) (*e*)

In addition, for the MePEA₂MAPb₂I₇ crystal, the 2PL spectra presented a non-uniform shape compared to PEA₂MAPb₂I₇ (Fig. 2, *c*). Such a shape, with multiple peaks in the 2PL spectra, might be attributed to the impact from other phases with *n* ranging from 3 to 6, however the *n* = 2 peak remains dominant. Thus, the exact role of additional methyl group on quasi-2D crystal phase formation and their SHG intensity remains under discussion, and additional structural characterization is required.

To compare the SHG stability of both compositions, the SHG intensity was measured under continuous excitation at 6 mJ/cm² incident fluence for 1600 seconds (Fig. 2, *e*). It was revealed that the SHG signal disappeared after 1000 s for the PEA₂MAPb₂I₇ crystal, whereas the SHG signal for MePEA-based crystal remained by the end of the measurements. During the continuous optical pump, the perovskite crystal degradation is mainly attributed to the heating of sample and additional oxidation or adsorption of water molecules from the air. Previously, it was established that MePEA-based perovskite films demonstrated better structural stability against polar solvents exposure compared to regular PEA-based structures [7]. Thus, MePEA may also impact the temporal stability of the SHG signal in MePEA₂MAPb₂I₇ crystals as it provides better structural stability.

Conclusion

In conclusion, our research demonstrates the occurrence of SHG in both MePEA₂MAPb₂I₇ and PEA₂MAPb₂I₇ compositions. Notably, the MePEA-based quasi-2D perovskite crystal exhibits enhanced stability compared to its PEA-based counterpart. Specifically, the operational half-lifetime at 6 mJ/cm² incident fluence for SHG intensity in the MePEA-based crystal is approximately twice as long, measuring 25 minutes compared to 12.5 minutes for the PEA-based crystal. These findings prove the significant relationship between organic spacer composition and the stability of SHG in iodine-based perovskite crystals. Consequently, this work contributes valuable insights toward the development of quasi-2D perovskite materials for advanced photonic applications.

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