

Research Article

# Strong nonlinear absorption in perovskite films

## RASHID A. GANEEV,<sup>1,2,4</sup> KONDA SRINIVASA RAO,<sup>1</sup> ZHI YU,<sup>1</sup> WEILI YU,<sup>1</sup> CHAONAN YAO,<sup>1</sup> YUE FU,<sup>1</sup> KE ZHANG,<sup>1</sup> AND CHUNLEI GUO<sup>1,3,5</sup>

<sup>1</sup>The Guo China-US Photonics Laboratory, State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

<sup>2</sup>Physical Faculty, Voronezh State University, Voronezh 394006, Russia

<sup>3</sup>The Institute of Optics, University of Rochester, Rochester, NY 14627, USA

<sup>5</sup>guo@optics.rochester.edu

Abstract: In this work, we report a comparative study of the nonlinear optical responses of  $CH_3NH_3PbX_3$  (where X is a chlorine, bromine, or iodine halogen atom) perovskite thin (~200 nm) films using 40 fs, 800 nm pulses. We found that these films possess strong nonlinear absorption coefficients comparable with the highest reported values for thin film structures (up to 7  $\times$  10<sup>-7</sup> cm W<sup>-1</sup>). We also analyze the photoluminescence emission from CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> film and demonstrate the quadratic dependence of emission intensity on the intensity of probe pulse indicating a two-photon mechanism of luminescence.

© 2018 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

OCIS codes: (190.4710) Optical nonlinearities in organic materials; (310.3840) Materials and process characterization; (300.6280) Spectroscopy, fluorescence and luminescence; (270.4180) Multiphoton processes.

#### References and links

- A. Oskooi, M. De Zoysa, K. Ishizaki, and S. Noda, "Experimental demonstration of quasi-resonant absorption in silicon thin films for enhanced solar light trapping," ACS Photonics 1(4), 304–309 (2014).
- P. Kuang, S. Eyderman, M.-L. Hsieh, A. Post, S. John, and S. Y. Lin, "Achieving an accurate surface profile of a photonic crystal for near-unity solar absorption in a super thin-film architecture," ACS Nano 10(6), 6116-6124 (2016).
- 3 C. E. R. Disney, S. Pillai, C. M. Johnson, and M. A. Green, "Self-assembled nanostructured rear reflector designs for thin-film solar cells," ACS Photonics 2(8), 1108-1116 (2015)
- O. Alvarez-Fregoso, J. G. Mendoza-Alvarez, and O. Zelaya-Angel, "Quantum confinement in nanostructured CdNiTe composite thin films," J. Appl. Phys. 82(2), 708-712 (1997).
- S. Baskoutas, P. Poulopoulos, V. Karoutsos, M. Angelakeris, and N. K. Flevaris, "Strong quantum confinement 5. effects in thin zinc selenide films," Chem. Phys. Lett. 417(4-6), 461-464 (2006)
- E. A. Muller, J. E. Johns, B. W. Caplins, and C. B. Harris, "Quantum confinement and anisotropy in thin-film 6 molecular semiconductors," Phys. Rev. B 83(16), 165422 (2011).
- A. I. Ryasnyansky, R. A. Ganeev, V. I. Redkorechev, T. Usmanov, G. Priebe, and K. Fostiropoulos, 7. "Competition of third- and fifth-order nonlinear optical processes in C<sub>60</sub> thin films," Fuller. Nanotub. Carbon Nanostruct. 13(2), 131-140 (2005).
- R. A. Ganeev, A. I. Ryasnyansky, M. K. Kodirov, and T. Usmanov, "Nonlinear optical characteristics of C<sub>60</sub> and 8. C<sub>70</sub> films and solutions," Opt. Commun. 185(4-6), 473-478 (2000).
- R. A. Ganeev, A. I. Ryasnyansky, M. K. Kodirov, and T. Usmanov, "Two-photon absorption and nonlinear refraction of amorphous chalcogenide films," J. Opt. A 4(4), 446-451 (2002).
- 10. R. A. Ganeev, A. I. Ryasnyansky, A. L. Stepanov, and T. Usmanov, "Saturated absorption and reverse saturated absorption of Cu:SuO<sub>2</sub> at  $\lambda$ =532 nm," Phys. Status Solidi, B Basic Res. **241**(3), R1–R4 (2004). R. A. Ganeev and A. I. Ryasnyansky, "Reflection Z-scan measurements of opaque semiconductor thin films,"
- 11. Phys. Status Solidi., A Appl. Mater. Sci. 202(1), 120-125 (2005).
- 12. H. P. Li, C. H. Kam, Y. L. Lam, and W. Ji, "Optical nonlinearities and photo-excited carrier lifetime in CdS at 532 nm," Opt. Commun. 190(1-6), 351-356 (2001).
- 13. R. A. Ganeev, A. I. Ryasnyansky, R. I. Tugushev, and T. Usmanov, "Investigation of nonlinear refraction and nonlinear absorption of semiconductor nanoparticles solutions prepared by laser ablation," J. Opt. A 5(4), 409-417 (2003).
- 14. E. Zheng, B. Yuh, G. A. Tosado, and Q. Yu, "Solution-processed visible-blind UV-A photodetectors based on CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> perovskite thin films," J. Mater. Chem. C Mater. Opt. Electron. Devices 5(15), 3796–3806

#323433 Journal © 2018 https://doi.org/10.1364/OME.8.001472

Received 16 Feb 2018; revised 12 Apr 2018; accepted 22 Apr 2018; published 9 May 2018

<sup>&</sup>lt;sup>4</sup>rashid@ciomp.ac.cn

(2017).

- Y. Fu, Q. Song, T. Lin, Y. Wang, X. Sun, Z. Su, B. Chu, F. Jin, H. Zhao, W. Li, and C. S. Lee, "High performance photomultiplication perovskite photodetectors with PC60BM and NPB as the interlayers," Org. Electron. 51, 200–206 (2017).
- D. Cortecchia, J. Yin, A. Bruno, S.-Z. A. Lo, G. G. Gurzadyan, S. Mhaisalkar, J. L. Brédas, and C. Soci, "Polaron self-localization in white-light emitting hybrid perovskites," J. Mater. Chem. C Mater. Opt. Electron. Devices 5(11), 2771–2780 (2017).
- V. Gonzalez-Pedro, E. J. Juarez-Perez, W. S. Arsyad, E. M. Barea, F. Fabregat-Santiago, I. Mora-Sero, and J. Bisquert, "General working principles of CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> perovskite solar cells," Nano Lett. 14(2), 888–893 (2014).
- S. Mirershadi and S. A. Kandjani, "Efficient thin luminescent solar concentrator based on organometal halide perovskite," Dyes Pigments 120, 15–21 (2015).
- Q. Wei, B. Du, B. Wu, J. Guo, M. Li, J. Fu, Z. Zhang, J. Yu, T. Hou, G. Xing, T. C. Sum, and W. Huang, "Twophoton optical properties in individual organic-inorganic perovskite microplates," Adv. Opt. Mater. 5(24), 1700809 (2017).
- K. N. Krishnakanth, S. Seth, A. Samanta, and S. V. Rao, "Broadband femtosecond nonlinear optical properties of CsPbBr<sub>3</sub> perovskite nanocrystals," Opt. Lett. 43(3), 603–606 (2018).
- G. Walters, B. R. Sutherland, S. Hoogland, D. Shi, R. Comin, D. P. Sellan, O. M. Bakr, and E. H. Sargent, "Two-photon absorption in organometallic bromide perovskites," ACS Nano 9(9), 9340–9346 (2015).
- S. Mirershadi, S. Ahmadi-Kandjani, A. Zawadzka, H. Rouhbakhsh, and B. Sahraoui, "Third order nonlinear optical properties of organometal halide perovskite by means of the Z-scan technique," Chem. Phys. Lett. 647, 7–13 (2016).
- B. S. Kalanoor, L. Gouda, R. Gottesman, S. Tirosh, E. Haltzi, A. Zaban, and Y. R. Tischler, "Third-order optical nonlinearities in organometallic methylammonium lead iodide perovskite thin films," ACS Photonics 3(3), 361– 370 (2016).
- K. Abdel-Baki, F. Boitier, H. Diab, G. Lanty, K. Jemli, F. Lédée, D. Garrot, E. Deleporte, and J. S. Lauret, "Exciton dynamics and non-linearities in two-dimensional hybrid organic perovskites," J. Appl. Phys. 119(6), 064301 (2016).
- W. Liu, J. Xing, J. Zhao, X. Wen, K. Wang, P. Lu, and Q. Xiong, "Giant two-photon absorption and its saturation in 2D organic–inorganic perovskite," Adv. Optical Mater. 5(7), 1601045 (2017).
- Y. Wang, X. Li, X. Zhao, L. Xiao, H. Zeng, and H. Sun, "Nonlinear absorption and low-threshold multiphoton pumped stimulated emission from all-inorganic perovskite nanocrystals," Nano Lett. 16(1), 448–453 (2016).
- F. O. Saouma, D. Y. Park, S. H. Kim, M. S. Jeong, and J. I. Jang, "Multiphoton absorption coefficients of organic–inorganic lead halide perovskites CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> (X = Cl, Br, I) single crystals," Chem. Mater. 29(16), 6876–6882 (2017).
- F. O. Saouma, C. C. Stoumpos, J. Wong, M. G. Kanatzidis, and J. I. Jang, "Selective enhancement of optical nonlinearity in two-dimensional organic-inorganic lead iodide perovskites," Nat. Commun. 8(1), 742 (2017).
- 29. R. Zhang, J. Fan, X. Zhang, H. Yu, H. Zhang, Y. Mai, T. Xu, J. Wang, and H. J. Snaith, "Nonlinear optical response of organic–inorganic halide perovskites," ACS Photonics **3**(3), 371–377 (2016).
- P. Li, Y. Chen, T. Yang, Z. Wang, H. Lin, Y. Xu, L. Li, H. Mu, B. N. Shivananju, Y. Zhang, Q. Zhang, A. Pan, S. Li, D. Tang, B. Jia, H. Zhang, and Q. Bao, "Two-dimensional CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite nanosheets for ultrafast pulsed fiber lasers," ACS Appl. Mater. Interfaces 9(14), 12759–12765 (2017).
- W. G. Lu, C. Chen, D. B. Han, L. H. Yao, J. B. Han, H. Z. Zhong, and Y. T. Wang, "Nonlinear optical properties of colloidal CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> and CsPbBr<sub>3</sub> quantum dots: a comparison study using Z-scan technique," Adv. Opt. Mater. 4(11), 1732–1737 (2016).
- J. Yi, L. Miao, W. Hu, W. Zhao, and S. Wen, "Third-order nonlinear optical response of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite in the mid-infrared regime," Opt. Mater. Express 7(11), 3894–3901 (2017).
- M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, and E. W. Van Stryland, "Sensitive measurement of optical nonlinearities using a single beam," IEEE J. Quantum Electron. 26(4), 760–769 (1990).
- 34. K. Kikuchi, Y. Takeoka, M. Rikukawa, and K. Sanui, "Architecture and optical properties of two-dimensional perovskite compounds containing fluoroamines," Synth. Met. **137**(1–3), 904–910 (2003).
- 35. X. Liu, S. Guo, H. Wang, and L. Hou, "Theoretical study on the closed-aperture Z-scan curves in the materials with nonlinear refraction and strong nonlinear absorption," Opt. Commun. **197**(4–6), 431–437 (2001).
- K. Dota, J. A. Dharmadhikari, D. Mathur, and A. K. Dharmadhikari, "Third-order nonlinear optical response in transparent solids using ultrashort laser pulses," Appl. Phys. B 107(3), 703–709 (2012).
- D. Blömer, A. Szameit, F. Dreisow, T. Schreiber, S. Nolte, and A. Tünnermann, "Nonlinear refractive index of fs-laser-written waveguides in fused silica," Opt. Express 14(6), 2151–2157 (2006).
- 38. P. B. Chapple, J. Staromlynska, J. A. Hermann, T. J. Mckay, and R. G. McDuff, "Single-beam Z-scan: measurement techniques and analysis," J. Nonlin. Opt. Mater. Phys. 6(3), 251–293 (1997).
- L. Yang, R. Dorsinville, Q. Z. Wang, P. X. Ye, R. R. Alfano, R. Zamboni, and C. Taliani, "Excited-state nonlinearity in polythiophene thin films investigated by the Z-scan technique," Opt. Lett. 17(5), 323–325 (1992).
- G. A. Swartzlander, H. Yin, and A. E. Kaplan, "Continuous-wave self-deflection effect in sodium vapor," J. Opt. Soc. Am. B 6(7), 1317–1325 (1989).
- 41. M. Samoc, A. Samoc, B. Luther-Davies, H. Reisch, and U. Scherf, "Saturable absorption in poly(indenofluorene): a picket-fence polymer," Opt. Lett. **23**(16), 1295–1297 (1998).

- 42. J. Li, S. Zhang, H. Dong, X. Yuan, X. Jiang, J. Wang, and L. Zhang, "Two-photon absorption and emission in CsPb(Br/I)<sub>3</sub>cesium lead halide perovskite quantum dots," CrystEngComm **18**(41), 7945–7949 (2016).
- J. Chen, K. Žídek, P. Chábera, D. Liu, P. Cheng, L. Nuuttila, M. J. Al-Marri, H. Lehtivuori, M. E. Messing, K. Han, K. Zheng, and T. Pullerits, "Size- and wavelength-dependent two-photon absorption cross-section of CsPbBr3 perovskite quantum dots," J. Phys. Chem. Lett. 8(10), 2316–2321 (2017).
- 44. M. Sheik-Bahae, D. C. Hutchings, D. J. Hagan, and E. W. van Stryland, "Dispersion of bound electronic nonlinear refraction in solids," IEEE J. Quantum Electron. **27**(6), 1296–1309 (1991).
- L. Brzozovski and E. H. Sargent, "Azobenzenes for photonic network Applications: third-order nonlinear optical properties," J. Mater. Sci. Electron. 12(9), 483–489 (2001).
- 46. T.-C. Wei, S. Mokkapati, T.-Y. Li, C.-H. Lin, G.-R. Lin, C. Jagadish, and J.-H. He, "Nonlinear absorption applications of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> perovskite crystal," Adv. Funct. Mater. 28(8), 1707175 (2018).
- 47. H. Linnenbank, M. Saliba, L. Gui, B. Metzger, S. G. Tikhodeev, J. Kadro, G. Nasti, A. Abate, A. Hadfeldt, M. Graetzel, and H. Giessen, "Temperature-dependent two-photon photoluminescence of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>: structural phase and exciton to free carrier transition," Opt. Mater. Express 8(3), 511–521 (2018).

#### 1. Introduction

Thin film materials have gained a great attentions due to their various potential applications [1-3]. Particularly, the unique properties of low-dimensional materials ignited numerous studies of their characteristics [4-6]. This peculiarity necessitates analysis of the optical and nonlinear optical features of thin films, which could be useful in various fields of optoelectronics and laser physics.

The availability of laser sources with ultra-short pulse duration allowed considerable increase in the laser intensities used in those experiments, therewith presenting the opportunity to investigate thin materials close to their optical breakdown intensities  $(10^{12}-10^{13})$ W cm<sup>-2</sup>). Particularly, the results of nonlinear refraction studies of  $C_{60}$  thin (100 nm) films have shown that their large third-order susceptibility causes strong self-focusing with a nonlinear refractive index ( $\gamma$ ) exceeding 2 × 10<sup>-9</sup> cm<sup>2</sup> W<sup>-1</sup> [7], similar to the data reported in Ref [8]. for  $C_{70}$ -doped polyimide films. Notice that fullerenes dissolved in toluene at similar concentration showed two orders of magnitude less nonlinear susceptibility. Chalcogenide films also demonstrate considerable values of optical nonlinearities. Studies of the nonlinear absorption coefficients ( $\beta$ ) of As<sub>20</sub>S<sub>80</sub> (3 × 10<sup>-6</sup> cm W<sup>-1</sup> at the wavelength  $\lambda$  = 532 nm) and 3As<sub>2</sub>S<sub>3</sub>/As<sub>2</sub>Se<sub>3</sub> (10<sup>-7</sup> cm W<sup>-1</sup> at  $\lambda$  = 1064 nm) have shown that some thin (200 nm) chalcogenide films possess large third-order nonlinear susceptibility [9]. Even in the case of thick media containing thin layers of active elements, such as nanoparticles, these layers have demonstrated enhanced nonlinear absorption and refraction. In particular, thin (60 nm) layers of copper nanoparticles implanted in silica glass caused strong nonlinear absorption ( $\sim 10^{-6}$ cm W<sup>-1</sup>) [10]. Furthermore, the nonlinear refraction of CdS thin films at  $\lambda = 532$  nm was measured to be  $-5.2 \times 10^{-11}$  cm<sup>2</sup> W<sup>-1</sup> [11], while the measured value of nonlinear refractive index of bulk CdS in this spectral region was reported to be  $-6 \times 10^{-13}$  cm<sup>2</sup> W<sup>-1</sup> [12], i.e. two orders of magnitude smaller than former structure. A considerable increase in the nonlinearity of thin films in those and other studies makes their nonlinear optical features close to those of nanoparticles [13].

In this connection, the perovskite films took large attention due to various potential applications of these structures. Rapid progresses in perovskite solar cells allowed power conversion efficiency reaching 22% [14]. The attractive photovoltaic properties of perovskites, such as strong optical absorption, simplicity of processing, long carrier diffusion length, tolerance to defects, high radiative efficiency, bandgap tunability, etc., can also be applied for other optoelectronic fields. By introducing suitable interlayers at the perovskite/electrode interfaces, the performance of the photodetectors improved significantly, which was attributed to the improved charge carrier collection efficiency [15]. Perovskite materials such as methylammonium lead halides are inexpensive to produce and simple to manufacture. The most studied perovskite absorbers are methylammonium lead trihalides ( $CH_3NH_3PbX_3$ , where X is a halogen atom such as iodine, bromine or chlorine), with an optical bandgap between 1.5 and 3.2 eV depending on halide content. These

methylammonium lead trihalide perovskites are commonly dubbed as MAPbI<sub>3</sub>, MAPbBr<sub>3</sub>, and MAPbCl<sub>3</sub>. Thin perovskite films are also attracting increasing interest, particularly as solution processable, white-light emissive materials [16].

Confining the organic molecules in the inorganic framework improves the nonlinear optical response of the organic-inorganic hybrids, because the inorganic framework restricts the motion of the organic molecules and prevents randomization of molecular orientation due to thermal relaxation. The organic-inorganic and all-inorganic perovskites have attracted the attention of the optical community, partially due to their exciting optical properties in addition to the potential applications in photovoltaic systems [17–20]. The first observation of nonlinear optical effects, such as two-photon absorption (2PA), in organometallic bromide perovskites was reported in Ref [21]. Since then, a number of isolated studies have been carried out in studying nonlinear optical responses of perovskites, but most of these studies were based on long pulses and at visible excitation wavelengths [19,20,22–32].

In this paper, we carry out a systematic comparative study of the nonlinear optical properties of Br-, I-, and Cl-containing  $CH_3NH_3PbX_3$  perovskite films using near infrared (800 nm) femtosecond radiation of frequently used Ti:sapphire lasers. Following analyzing the nonlinear absorption and nonlinear refraction of MAPbBr<sub>3</sub>, MAPbCl<sub>3</sub>, and MAPbI<sub>3</sub> thin (~200 nm) films using 40 fs, 800-nm pulses, we found that these films possess strong nonlinear absorption comparable to the highest reported values for all thin structures. We also analyze the photoluminescence emission from MAPbBr<sub>3</sub> film and demonstrate the 2PA mechanism of this process.

## 2. Experimental arrangements

Our Ti:sapphire laser (Spectra-Physics, Spitfire Ace) provided 40 fs, 800 nm pulses at 1 kHz pulse repetition rate. The standard Z-scan scheme [33] was applied in these studies. Laser radiation was focused by a 400-mm focal length spherical lens and was measured by a power meter. An open-aperture (OA) scheme with fully opened iris aperture placed in front of power meter allowed measurement of the nonlinear absorption of perovskite films during their propagation through the focal plane. When the aperture was closed to restrict propagation of ~10% of input radiation (closed-aperture scheme), the measurements of propagated radiation allowed determination of the nonlinear refractive index of our samples. We measured the normalized transmittances of our samples using both OA and closed-aperture (CA) schemes to calculate their  $\beta$  and  $\gamma$  respectively.

The Z-scan technique and the analysis of Z-scan traces are based on the assumption that the laser radiation source has a Gaussian beam profile. Hence, prior to Z-scan measurements, we characterized the probe beam using a CCD camera (Thorlabs) and confirmed that the beam profile in the focal area was close to Gaussian, which is a prerequisite for the analysis of the Z-scan traces using the relations developed for this technique. The corresponding full widths of the focused beam at half maximum and  $1/e^2$  maximum of intensity distribution were measured to be 40 and 68  $\mu$ m respectively.

The schematic of films preparation is shown in Fig. 1(a). The perovskite thin films were prepared by two-step method.  $PbX_2$  (X = Cl, Br, I) (1 M, in N,N-dimetylformamide for Cl, Br or  $\gamma$ -Butyrolactone for I) were resolved in solvents and stirred overnight. Then,  $PbX_2$  (X = Cl, Br, I) solution were spin-coated on the cleaned glass slides with a 3000 rpm for 50 s. Once the films were fully dried, MAX (X = Cl, Br, I) solution (15 mg/ml in isoproponal) was dropped onto the PbX<sub>2</sub> films. After waiting for 30 s, the solution was spin coated to dry and rinsed with isopropanol. The films were then put on hot plate for 2 min (MAPbCl<sub>3</sub> at 60 °C, MAPbBr<sub>3</sub> at 80 °C, and MAPbI<sub>3</sub> at 100 °C) to complete the preparation of samples before further optical experiments.

The UV and visible absorption spectra of the perovskite thin films were measured using a spectrophotometer (Agilent Technologies). They demonstrated growth of linear absorption at ~405, 540, and 780 nm in the case of MAPbCl<sub>3</sub>, MAPbBr<sub>3</sub>, and MAPbI<sub>3</sub> films respectively

[Fig. (1b)]. The corresponding bandgaps  $(E_g)$  of these films were defined as 3.01, 2.32, and 1.59 eV respectively. The inorganic layers in the conventional two-dimensional perovskites behave as a quantum well in which the organic layers play the role of the barrier, which causes sharp variations in the absorption and photoluminescence (PL) spectra [34]. The PL spectra of perovskite films were measured using a fiber spectrometer (Ocean Optics, USB4000). Particularly, PL spectrum of MAPbBr<sub>3</sub> was analyzed to determine the mechanism of this process in the case of 800 nm probe radiation.



Fig. 1. (a) Schematic of films preparation. (b) Absorption spectra of MAPbI<sub>3</sub>, MAPbBr<sub>3</sub>, and MAPbCl<sub>3</sub> films in the near infrared, visible and UV ranges. The bandgaps of above films were defined to be 1.59, 2.32, and 3.01 eV respectively. (c) Measurement of MAPbBr<sub>3</sub> film thickness using Tolansky interferometer. The shift of interference strips at the border of "perovskite-glass" shown on the CCD image is caused by phase shift, from which the thickness of film was calculated to be 240 nm. (d) SEM images of (from left to right) the MAPbBr<sub>3</sub>, MAPbCl<sub>3</sub>, and MAPbI<sub>3</sub> films. White lines correspond to 20  $\mu$ m (MAPbBr<sub>3</sub>), 0.5  $\mu$ m (MAPbCl<sub>3</sub>), and 1  $\mu$ m (MAPbI<sub>3</sub>).

The thickness and homogeneity of perovskites were measured using atomic force microscopy and Tolansky interferometry. The film thickness (<300 nm) was significantly less than the Rayleigh length of focused radiation to fulfill the thin sample approximation condition, which allows the application of Z-scan relations to fit with the experimental results. The shift of the interference pattern in Tolansky interferometry during reflection of HeNe laser beam defined the roughness and the thickness of films. Particularly, the thickness of MAPbBr<sub>3</sub> film was measured from those interference images to be 240 nm [Fig. 1(c)]. Other films had the thickness of 225 nm (MAPbCl<sub>3</sub>) and 150 nm (MAPbI<sub>3</sub>).

SEM studies of the surfaces of perovskites were performed to analyze the structural properties of our films. These images [Fig. 1(d)] showed the irregularities of surface structure, which is characteristic of polycrystalline perovskites.

#### 3. Results

CA Z-scan allows distinction of the two abovementioned processes (nonlinear absorption and nonlinear refraction) when they are presented simultaneously. In the general case of the joint contribution of both those processes, the variation of normalized transmittance of samples along z-axis, *T*, can be presented as follows [35]:

$$T = 1 + \frac{4x}{(x^2 + 9)(x^2 + 1)} \Delta \Phi_0 - \frac{2(x^2 + 3)}{(x^2 + 9)(x^2 + 1)} \Delta \Psi_0, \tag{1}$$

where  $x = z/z_0$ ,  $z_0 = k(w_0)^2/2$  is the Rayleigh length,  $k = 2\pi/\lambda$  is the wave number,  $w_0$  is the beam waist radius at the  $1/e^2$  level of intensity distribution, and  $\Delta \Phi_0 = k\gamma I_0 L_{\text{eff}}$  and  $\Delta \Psi_0 = \beta I_0 L_{\text{eff}}/2$  are the phase changes due to nonlinear refraction and nonlinear absorption, respectively. Here  $I_0$  is the laser radiation intensity in focal plane,  $L_{\text{eff}} = [1-\exp(-\alpha_0 L)]/\alpha_0$  is the effective length of the medium,  $\alpha_0$  is the linear absorption coefficient, and L is the thickness of our samples.

By making the substitution  $\rho = \beta/2k\gamma$ , one can determine the relation between  $\Delta \Phi_0$  and  $\Delta \Psi_0 (\Delta \Psi_0 = \rho \Delta \Phi_0)$ . Thus, Eq. (1) can be re-written as follows:

$$T = 1 + \frac{2(-\rho x^2 + 2x - 3\rho)}{(x^2 + 9)(x^2 + 1)} \Delta \Phi_o$$
(2)

This equation was used for fitting theoretical dependences with measured normalized transmittances taking into account our experimental conditions. After fitting  $\rho$  and  $\Delta \Phi_0$  we consequently found  $\gamma$  and  $\beta$ . We also carried out the  $\beta$  measurements of these films using OA Z-scan technique. One can get the data on nonlinear refraction and nonlinear absorption coefficients of materials in some particular cases from the CA Z-scan. OA Z-scan can be performed to test the results of nonlinear absorption measurements obtained from the fitting of nonlinear curve using Eq. (2). Notice that uncertainty in calculation of the nonlinear absorption coefficients using OA Z-scans was smaller compared with CA Z-scans, thus prompting us to analyze this process using the former configuration.

We calibrated our Z-scan measurements using 1-mm-thick fused silica plate. The calculations using the fitting procedure allowed measurement of the nonlinear refractive index of this material using 800 nm, 40 fs pulses, which was found to be  $(3.0 \pm 0.5) \times 10^{-16}$  cm<sup>2</sup> W<sup>-1</sup>. This value is similar to earlier reported measurements of the  $\gamma$  of fused silica (3 ×  $10^{-16}$  cm<sup>2</sup> W<sup>-1</sup> [36], (2.7 ± 0.3) ×  $10^{-16}$  cm<sup>2</sup> W<sup>-1</sup> [37]).



Fig. 2. Closed-aperture Z-scans of (a) MAPbBr<sub>3</sub> and (b) MAPbCl<sub>3</sub> films. The corresponding nonlinear optical parameters are shown on the graphs. The fitting curves correspond to Eq. (2). (a) The intensity of 800 nm radiation in the focal plane was  $7 \times 10^{11}$  W cm<sup>-2</sup> ( $E = 1 \times 10^{-6}$  J). The corresponding  $\Delta \Phi_0$  was found to be 0.76. (b) The intensity of 800 nm radiation in the focal plane was  $1.7 \times 10^{11}$  W cm<sup>-2</sup> ( $E = 0.25 \times 10^{-6}$  J). The corresponding  $\Delta \Phi_0$  and  $\rho$  were found to be 0.9 and 0.05.

The error bars ( $\pm$  5%) of these and other measurements of perovskites were the same during the entire course of the experiments. The error bars of definition of the absolute values of  $\gamma$  and  $\beta$  were estimated to be  $\pm$  25% due to uncertainty in the measurements of the intensity of laser pulses in the focal plane.

Figures 2(a) and 2(b) show the CA Z-scans of MAPbBr<sub>3</sub> and MAPbCl<sub>3</sub> films. Several data acquisitions were performed and compared with each other at the same point of the sample in order to ensure that no sample degradation occurs during the experiment. The characteristic valley followed by the peak in the dependence of the normalized transmittance of films on their position on the z-axis indicated the positive nonlinear refraction in those two films. MAPbI<sub>3</sub> film did not show the nonlinear refractive properties until the intensities reached the optical damage threshold of this sample ( $4 \times 10^{12}$  W cm<sup>-2</sup>). Notice that at the used intensities (up to  $10^{12}$  W cm<sup>-2</sup>), no any nonlinear optical processes were observed (neither nonlinear absorption nor nonlinear refraction) in the substrates without perovskites. Thus the glass slides do not contribute to our Z-scans. We compared the Z-scans using high (1 kHz) and low (10 Hz) pulse repetition rates and did not find significant difference between them, thus confirming that thermal effects related to heat accumulation do not play an important role in these studies.

The fitting procedure of CA Z-scans [solid curves in Fig. 2] allowed calculation of the  $\gamma$  of MAPbBr<sub>3</sub> and MAPbCl<sub>3</sub> films to be  $(7 \pm 2) \times 10^{-13}$  cm<sup>2</sup> W<sup>-1</sup> and  $(3.4 \pm 0.8) \times 10^{-12}$  cm<sup>2</sup> W<sup>-1</sup>, respectively. Asymmetry was observed in CA data for MAPbCl<sub>3</sub> films. The reason of this asymmetry is the influence of 2PA on the CA curve. One can estimate from presented CA data the  $\beta$  of this film (2.7 × 10<sup>-8</sup> cm W<sup>-1</sup>). Notice that the estimates of  $\beta$  from these CA Z-scans were larger than those obtained from the fitting of the OA Z-scans (1.5 × 10<sup>-8</sup> cm W<sup>-1</sup>).

Figures 3(a) and 3(b) show the OA Z-scans of MAPbCl<sub>3</sub> and MAPbBr<sub>3</sub> and their fitted curves. As the pump power is increased, a decrease in the normalized transmittance was observed. The normalized transmittance for the OA Z-scan is given as follows [38]:

$$T = q^{-1} \ln(1+q), \tag{3}$$

Here  $q = \beta I_0 L_{eff}/(1 + z^2/z_0^2)$ . The fitting of Eq. (3) to the experimental data is depicted in Fig. 3 by the solid curves. The theoretical dependences of *T* calculated using the two-photon absorption model (3) has coincided with the experimental data of OA Z-scans of our films [Fig. 3]. This coincidence confirms the prevailing influence of the third-order nonlinearities over the higher-order nonlinear optical processes (in particular, three-photon absorption). Indeed, the absorption spectra [Fig. 1(b)] show that the decrease in propagation of the 800 nm radiation through these films can be explained by the 2PA mechanism.

The ratio between  $E_g$  and photon energy of radiation used (1.55 eV) lies in the range between 1 and 2 at which the probability of three-photon absorption in most cases is smaller as compared to the 2PA process. Meanwhile, if 2PA at 800 nm is possible, based on energetic alone, three-photon absorption is also possible and very little can be said about the relative magnitude of the cross sections. There are no reported data on that matter. In the meantime, it is a common case when three-photon absorption cross section is smaller than the same for 2PA. Obviously, for some specific cases three-photon absorption can overpass 2PA cross section, however, it is a rare case.

The 2PA-induced nonlinear absorption coefficients under 800 nm, 40 fs pulse excitation were determined through the fitting procedure to be  $\beta = (1.5 \pm 0.4) \times 10^{-8}$  cm W<sup>-1</sup> and  $(5 \pm 1.2) \times 10^{-8}$  cm W<sup>-1</sup> for MAPbCl<sub>3</sub> and MAPbBr<sub>3</sub> films respectively. We used different intensities to analyze variation of  $\beta$  in those films. This parameter remained almost unchanged until the optical breakdown intensities for MAPbBr<sub>3</sub> and MAPbBr<sub>3</sub> films  $(5 \times 10^{12} \text{ W cm}^{-2} \text{ and } 3 \times 10^{12} \text{ W cm}^{-2}$  respectively) were reached.

As already mentioned, we also found  $\beta$  of MAPbCl<sub>3</sub> film from the known  $\rho$ , which was determined from the fitting of CA experimental data, and  $\gamma$ . Since any step in this procedure provides some systematic errors, the definition of nonlinear absorption coefficient by this method becomes less accurate, compared with direct method of fitting the open-aperture Z-scan data. Thus smaller uncertainty in calculation of  $\beta$  arises from a single step including the fitting of OA Z-scan curve.



Fig. 3. Open-aperture Z-scans of (a) MAPbCl<sub>3</sub>, (b) MAPbBr<sub>3</sub>, and (c) MAPbI<sub>3</sub> films. The corresponding nonlinear optical parameters are shown on the graphs. The fitting curves correspond to Eq. (3) describing TPA and phenomenological model of saturable absorption. (a) The intensity in the focal plane was  $3.5 \times 10^{11}$  W cm<sup>-2</sup> ( $E = 0.5 \times 10^{-6}$  J). *q* was found to be 0.105. (b) The intensity in the focal plane was  $5.2 \times 10^{11}$  W cm<sup>-2</sup> ( $E = 0.75 \times 10^{-6}$  J). *q* was found to be 0.5. (c) The intensity in the focal plane was  $2 \times 10^{11}$  W cm<sup>-2</sup> ( $E = 0.32 \times 10^{-6}$  J) and q = 2.  $I_{sat}$  was found to be  $8 \times 10^{11}$  W cm<sup>-2</sup>.

The OA Z-scan of MAPbI<sub>3</sub> film showed joint influence of two types of nonlinear absorption, 2PA and saturable absorption (SA). The absorption spectrum of MAPbI<sub>3</sub> shows a peak near 750 nm. Similar absorption spectrum for this perovskite has been reported in Ref [23,25]. The bandwidth of our 800 nm pulse was 26 nm, thus the wing of the spectral distribution of laser pulse centered at 800 nm was partially overlapped with the absorption edge, which led to absorption of the shorter-wavelength part of laser pulse at 780 nm ( $E_g = 1.59 \text{ eV}$ ). Probably, this overlap was the reason of the SA in MAPbI<sub>3</sub>, since linear absorption at the excitation wavelength is needed if the SA effect is the one responsible for the observed bleaching of the film.

To fit the Z-scan of MAPbI<sub>3</sub> film comprising simultaneous influence of SA and 2PA [Fig. 3(c)], one has to multiply the normalized transmittance induced by the 2PA described by Eq. (3) and the normalized transmittance induced by SA. There are different models of SA. A simplest phenomenological model is often used when the SA is considered in terms of depletion of the ground state concentration due to high fluence of radiation. It can be described by relation [39]

$$\alpha(z) = \alpha_0 / \left[ 1 + I(z) / I_{\text{sat}} \right], \tag{4}$$

where  $\alpha(z)$  is the absorption coefficient varying along z axis, I(z) and Isat are the laser radiation intensity and saturation intensity.  $I_{sat}$  is related with the concentration of the active centers in the medium, the effective cross-sections, and the lifetimes of the transitions populated upon the excitation.

#### Research Article

## Optical Materials EXPRESS

The absorption coefficient in the case of the two-level system possessing heterogeneously broadened states can also be written as [40]

$$\alpha(z) = \alpha_0 / \left[ 1 + I(z) / I_{\text{sat}} \right]^{0.5}.$$
(5)

Another model that can be expressed empirically as

$$\alpha(z) = \alpha_0 / \left\{ 1 + \left[ I(z) / I_{\text{sat}} \right]^{0.5} \right\}$$
(6)

was also used for the analysis of SA [41]. Finally, Eq. (3) could also be considered as the simplified analytical absorption model assuming the negative sign of nonlinear absorption coefficient. The corresponding normalized transmittances can be presented as  $T(z) = 1 + I_0/I_{sat} \times (1 + z^2/z_0^2)$ ,  $T(z) = [1 + I_0/I_{sat} \times (1 + z^2/z_0^2)]^{0.5}$ , and  $T(z) = 1 + [I_0/I_{sat} \times (1 + z^2/z_0^2)]^{0.5}$  for the phenomenological, two-level, and empirical models respectively.

Most materials demonstrate SA using short pulses, but often only at very high optical intensities (*i.e.* close to the optical damage). At sufficiently high incident light intensity, atoms in the ground state of a saturable absorber material become excited into an upper energy state at such a rate that there is insufficient time for them to decay back to the ground state before the ground state becomes depleted, and the absorption subsequently saturates. Our experimental conditions were better fitted by the phenomenological model [39].



Fig. 4. Photoluminescence from MAPbBr<sub>3</sub> film. (a) Dependence of the PL intensity on the laser pulse energy. This dependence shows the almost quadratic slope ( $l \approx 2$ ) up to the pulse energy of ~1  $\mu$ J for different components of a broad PL spectrum centered at 543 nm. Inset shows the band structure of perovskite. (b) Dependence of PL intensity on the rotation of polarization angle of laser radiation in the case of MAPbBr<sub>3</sub> polycrystalline film by pumping with 400 nJ, 800 nm, 40 fs pulses. Inset shows the photoluminescence of thin film during illumination through the mask containing the acronym for Guo Photonics Laboratory. (c) PL spectra observed from singly-crystalline (left side) and polycrystalline (right side) MAPbBr<sub>3</sub> perovskites using different energies of 800 nm pulses.

To accurately fit the experimental data of joint influence of SA and 2PA, one has to choose the conditions when these processes are clearly distinguished from each other, like it is shown in Fig. 3(c). At larger intensity of 800 nm pulses one can get purely 2PA pattern, when the SA-related growth of transmittance becomes fully masked by the strong 2PA. In that case it is impossible to determine the influence of SA on the whole pattern of Z-scan curve. Another extreme is a relatively small energy of 800 nm pulses when only SA plays dominating role, i.e. when only bleaching process, without the decrease of transmittance at the focal plane related with the influence of 2PA, appears. At such conditions one cannot properly determine the 2PA parameters.

The ratio of the maximum intensity of probe pulse and saturation intensity was calculated from the fit shown in Fig. 3(c) to be  $I_0/I_{sat} = 0.25$ . One can calculate the  $I_{sat}$  to be  $8 \times 10^{11}$  W cm<sup>-2</sup> assuming the maximal intensity of 800 nm pulse in the focal plane ( $2 \times 10^{11}$  W cm<sup>-2</sup>) used in this experiment, The nonlinear absorption coefficient of MAPbI<sub>3</sub> film was deduced from this fitting procedure to be  $\beta = (5 \pm 1.2) \times 10^{-7}$  cm W<sup>-1</sup>. This value of nonlinear absorption is one of the largest reported for thin films.

We did not observe scattering in the MAPbI<sub>3</sub> film in our experiments. The reason in relatively large nonlinearity attributed to 2PA is probably related with the large cross section of absorption. It is difficult to estimate the cross section of this process due to absence of pump-probe measurements of this process. The fitting of our OA curve for MAPbI<sub>3</sub> film showed that the 2PA becomes stronger than SA at relatively large energy of pulses. Earlier reported values of negative nonlinear absorption related with SA in this film were in the range of  $-10^{-5}$  cm W<sup>-1</sup> [25]. One can anticipate that, with the growth of laser energy, the SA will be totally overpassed by 2PA leading to domination of the positive nonlinear absorption.

Below we address the mechanism of photoluminescence in perovskite film. We show that PL is another process induced by nonlinear effects in the studied perovskites. Here we present the results of PL studies of MAPbBr<sub>3</sub> since this film has demonstrated the most interesting properties. The PL in MAPbBr<sub>3</sub> was a direct evidence that our samples in-fact absorb the 800 nm radiation through 2PA, since the bandgap of this perovskite (2.32 eV) is larger than photon energy (1.55 eV). Figure 4(a) shows the dependence of PL emission on the excited pulse energy. One can see an almost quadratic slope of this dependence for the PL spectral components (538 and 550 nm) until 1  $\mu$ J pulse energy, which confirms the 2PA mechanism of the formation of this emission. The inset to this figure shows the band structure of MAPbBr<sub>3</sub> demonstrating the scheme of PL emission centered at 543 nm. The electrons in the valence band can absorb two photons at the same time and transmit to the conduction band. Intensity of PL emission did not depend on the polarization of 800 nm radiation [Fig. 4(b)], which is the expected result, taking into account the polycrystalline structure of this film. The PL emission spectrum showed a peak at 543 nm using variable probe pulse energy [right side of Fig. 4(c)]. We also present here the PL spectrum produced by 1-mm-thick single crystalline MAPbBr<sub>3</sub> sample [left side of Fig. 4(c)]. The broader PL spectrum in the latter case was centered at 555 nm and showed asymmetric shape.

### 4. Discussion

The useful parameter for determination of the order of nonlinearity using Z-scan technique is a valley-to-peak distance of the normalized transmittance ( $\Delta Z_{vp}$ ). This parameter is equal to  $1.7z_o$  in the case of the third-order nonlinear optical processes and  $1.2z_o$  in the case of the fifth-order ones [33]. In our experimental conditions ( $\lambda = 800$  nm,  $w_o = 34 \mu$ m), the Rayleigh length  $z_o$  was calculated to be 4.5 mm. In that case, a distance between the valley and peak of the T(z) dependence should be equal to 7.65 and 5.4 mm in the case of the third- and fifthorder nonlinear optical refraction processes, respectively. The experimental valley-to-peak distance in these experiments was  $\Delta Z_{vp} \approx 7.4$  mm [Figs. 2(a) and 2(b)], in good agreement with the theoretical consideration of the third-order nonlinear optical processes involved at the pulse intensities used. Notice that our measurements of the nonlinear optical

characteristics of perovskites were carried out up to intensities of  $\sim 3 \times 10^{11}$  W cm<sup>-2</sup>, i.e. below the optical damage thresholds of these films using 40 fs pulses. Nevertheless, no fifth-order processes were observed at these conditions.

Among a variety of third-order nonlinear optical processes (intermolecular interaction, molecular reorientational Kerr effect, electronic Kerr effect, etc.) contributing to the nonlinear addition of the perovskite films' refractive index, the electronic Kerr effect seems to be most important mechanism in the case of short (femtosecond) pulses. Meanwhile, our attempts to observe the nonlinear optical effects in perovskites using long (200 ps) pulses did not show any of these processes due to relatively small intensity ( $1 \times 10^{10}$  W cm<sup>-2</sup>) of picosecond pulses that could be applied to our films without degradation and damage. Further growth of focused picosecond radiation intensity led to the optical damage of our thin films, probably due to accumulative effect of heating even with small absorption of 800 nm radiation using 1 kHz pulse repetition rate. The measured thresholds of optical damage of these films in the case of 200 ps pulses were  $3 \times 10^{10}$  W cm<sup>-2</sup> (MAPbBr<sub>3</sub>),  $6 \times 10^{10}$  W cm<sup>-2</sup> (MAPbI<sub>3</sub>), and  $2 \times 10^{10}$  W cm<sup>-2</sup> (MAPbCl<sub>3</sub>), while the same in the case of 40 fs pulses were  $5 \times 10^{12}$  W cm<sup>-2</sup> (MAPbBr<sub>3</sub>),  $4 \times 10^{12}$  W cm<sup>-2</sup> (MAPbI<sub>3</sub>), and  $3 \times 10^{12}$  W cm<sup>-2</sup> (MAPbCl<sub>3</sub>).

We did not evaluate the 2PA cross-sections of MAPbX<sub>3</sub> films. These parameters have earlier been reported only for all-inorganic (CsPbX<sub>3</sub>) perovskite films in a few studies [20,31,42,43]. To evaluate this parameter in the case of MAPbX<sub>3</sub> films one has to define the carrier density generated by the combination of linear and nonlinear absorption, which is a difficult task in the case of organic-inorganic compounds. Organometallic perovskites strongly differ from each other by this parameter, so the lack of accurate measurements of free electron density did not allow the estimation of the 2PA cross-sections of studied perovskites. Because of that no evaluations of 2PA in MAPbX<sub>3</sub> films were reported so far, to our best knowledge.

Below we discuss the sign of the nonlinear refractive index of investigated films. An important characteristic of the most commonly used perovskites, the methylammonium lead halides, is a bandgap controllable by the halide content. The analysis of nonlinear refraction of the MAPbBr<sub>3</sub> and MAPbCl<sub>3</sub> films at  $I_0 = 3 \times 10^{11}$  W cm<sup>-2</sup> showed that they demonstrate self-focusing properties [Fig. 2(a)]. The nonlinear Kramers-Kronig relations predict the selffocusing in semiconductors for which the relation  $\hbar\omega/E_g < 0.69$  takes place [44]. Here  $\hbar$  is the Planck's constant and  $\omega$  is the frequency of laser radiation. As already mentioned, the values of  $E_g$  for MAPbBr<sub>3</sub> and MAPbCl<sub>3</sub> films were estimated from the absorption curves to be 2.32 and 3.01 eV, respectively. The corresponding  $\hbar\omega/E_g$  values for our films at  $\lambda = 800$  nm were calculated to be 0.67 (MAPbBr<sub>3</sub>) and 0.51 (MAPbCl<sub>3</sub>). Thus, one can expect a positive sign of  $\gamma$  in these two films, which was confirmed in our experiments [Fig. 2]. Note that the analysis of nonlinear optical properties of such materials using the Kramers-Kronig transformations is possible only when the photon energy is less than the bandgap energy  $(\hbar\omega < E_{\sigma})$ , which corresponds to our case for MAPbBr<sub>3</sub> and MAPbCl<sub>3</sub> films. The reason of relatively small values of nonlinear refractive indices of perovskite films at 800 nm was related with the closeness of their  $\hbar\omega/E_g$  values to 0.69 where the sign of  $\gamma$  changes from positive to negative.

Our studies of perovskites demonstrate the domination of nonlinear absorption over nonlinear refraction. The Stegeman figure of merit  $T_{\rm S} = |2\beta\lambda/\gamma|$  [45] for our samples also shows the prevailing influence of nonlinear absorptive properties of used perovskites over their nonlinear refraction ( $T_{\rm S} \approx 7$  and 300 in the case of MAPbBr<sub>3</sub> and MAPbCl<sub>3</sub>, respectively).

Finally, we address the applicability of studied samples. Either  $\gamma$  or  $\beta$  can be utilized for specific purposes, but their coexistence in a single material often causes undesirable effects that limit the performance. For instance, a large  $\gamma$  is required for self-focusing applications but an inherently related large  $\beta$  value lowers the laser-induced damage threshold, which ultimately leads to optical damage of the material via efficient 2PA. In our case (large

nonlinear absorption and relatively moderate nonlinear refraction), the utilization of perovskite films is possible in the case of optical limiters and optical switchers. Such a perspective has recently been discussed in Ref [46]. Besides that, the application of 2PA-induced PL spectroscopy can be considered as a power tool for characterization of organic-inorganic halide perovskites [47].

#### 5. Conclusions

In conclusion, we performed the comparative study of the third-order nonlinear optical processes in thin perovskite films using short infrared pulses. We have shown that perovskite films possess strong nonlinear absorption comparable with the highest reported values for other thin structures. We have analyzed the photoluminescence emission from MAPbBr<sub>3</sub> film and demonstrated the nonlinear optical origin of this process in the case of 800 nm pulses.

In particular, we reported studies of the  $\gamma$  and  $\beta$  of MAPbBr<sub>3</sub>, MAPbCl<sub>3</sub>, and MAPbI<sub>3</sub> thin (~200 nm) films using 40 fs, 800 nm pulses. Those films have demonstrated large values of nonlinear absorption coefficients (up to  $5 \times 10^{-7}$  cm W<sup>-1</sup>) and moderate values of nonlinear refractive indices ( $\leq 3 \times 10^{-12}$  cm<sup>2</sup> W<sup>-1</sup>). The values of nonlinear absorption coefficients are comparable and even higher than the best reported data for thin films, suggesting that organometallic perovskites are promising materials for optical switching, optical limiting, and bistability applications. SA and 2PA in the case of the MAPbI<sub>3</sub> film demonstrated both positive and negative nonlinear absorption. The results using different perovskites can be interpreted as the manifestation of 2PA or SA + 2PA processes in the case of 40 fs pulses. The processes of 2PA in perovskites could be useful for optical limiting.

Finally, we analyzed the PL emission from MAPbBr<sub>3</sub> film and demonstrated the quadratic dependence of emission intensity on the intensity of 800 nm probe pulse, thus showing the defining role of 2PA in this process. Our studies have shown that strong nonlinear optical properties, especially nonlinear absorption, of some CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> perovskites can fulfill the potential for using these compounds in optoelectronics.

Our studies revealed large (compared to newly emerged all-inorganic perovskites) nonlinear absorption in three films. Those values are in the upper range of reported data for 2PA absorption coefficients  $(10^{-6} \text{ to } 10^{-8} \text{ cm W}^{-1} \text{ [25,27]})$ . As for the nonlinear refraction related with electronic Kerr effect, this process was rarely observed in the case of MAPbX<sub>3</sub> perovskites, contrary to all-inorganic species, such as CsPbX<sub>3</sub>. We discussed the measurements of nonlinear refraction in two perovskites, with  $\gamma$  in the range of  $10^{-12} \text{ cm}^2 \text{ W}^{-1}$ . Our values were smaller than earlier reported data [23], though those measurements were carried out using 532 nm nanosecond pulses. Notice that these parameters were one to two orders of magnitude larger compared to the all-inorganic perovskite films. Overall, methylammonium lead iodide perovskites have shown to be the highly nonlinear optical materials, possessing strong third-order nonlinearity.

#### Funding

Natural Science Foundation of China (NSFC, 21404015, 61774155, 61705227); National Key Research and Development Program of China (2017YFB1104700); and Jilin Science and Technology Department Project (20150204019GX).