Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2021, **31**, 456–458

Mendeleev Communications

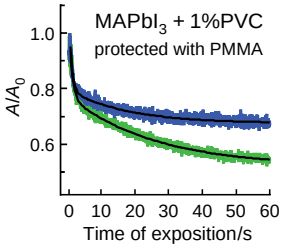
Thin films of $MAPbI_3$ and $MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$ perovskites under femtosecond laser irradiation: nonlinear optical absorption and kinetics of photodegradation

Dmitry V. Khudyakov,*[a] Daniil V. Ganin,[a] Andrey D. Lyashedko,[b] Lubov A. Frolova,[c] Pavel A. Troshin[c] and Anatoly S. Lobach[c]

[a] *Prokhorov General Physics Institute, Russian Academy of Sciences, Physics Instrumentation Center, 108840 Troitsk, Moscow, Russian Federation. E-mail: dimakh65@gmail.com*
[b] *Optosystems Ltd., 108840 Troitsk, Moscow, Russian Federation*
[c] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation*

DOI: 10.1016/j.mencom.2021.07.006

The thin $MAPbI_3$ and $MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$ perovskite films have strong nonlinear absorption with coefficients of 443 ± 20 and 830 ± 50 cm GW^{-1}, respectively, due to two-photon absorption at 1064 nm. The photochemical degradation of perovskite films was observed upon irradiation with femtosecond pulses at 532 nm, and the depth of photodegradation decreased in perovskite films protected with a PMMA polymer layer.



Keywords: organometallic halide perovskites, thin perovskite films, nonlinear optical absorption, femtosecond laser irradiation, photodegradation.

Metal halide perovskites are of interest because of their excellent optical and electronic properties. The perovskite materials can be considered as potential media for nonlinear optical modulators.[1,2] In this work, we employed a Z-scan technique to investigate the nonlinear optical response of thin perovskite films (PFs) under pulsed femtosecond laser irradiation at 1064 and 532 nm. Perovskite films of $MAPbI_3$ + 1%PVC (thickness, 65 nm)[3] and $MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$ (thickness, 45 nm),[4] where MA and FA are methylammonium and formamidinium cations, respectively, and PVC is poly(9-vinylcarbazole), on glass substrates were obtained by a spin-coating method in an inert atmosphere in a nitrogen glove box (O_2 and H_2O levels, < 0.1 ppm) as described previously.[3] To prevent contacts of PFs with ambient moisture and oxygen, the samples were covered (encapsulated) with a thin PMMA polymer layer.

A pulsed Yb-doped fiber laser at 1064 nm with an output pulse duration of 400 fs was used as an excitation source for Z-scan experiments. The pulse repetition rate was 10 kHz with a pulse energy of 1.5 μJ. The open aperture Z-scan experiments were carried out for recording nonlinear absorption only. The band gaps of the samples were in the range E_g = 1.49–1.62 eV,[5] which exceeds an excitation photon energy of 1.16 eV. However, it becomes possible to transfer photoexcited electrons to a conduction band by two-photon absorption (TPA). Depending on the incident intensity I_0 and sample thickness L along the Z axis, the transmittance is described by the equation:[5]

$$T(I_0) = \frac{I_1}{I_0} = \frac{1}{1 + \beta L I_0}, \quad (1)$$

where β is the nonlinear absorption coefficient (TPA coefficient), and I_1 is the intensity of radiation transmitted through the sample.

Figure 1 shows the dependence of the normalized transmittance on the incident pulse peak intensity for the thin PFs taken from the experimental Z-scan curves at z = 0.

The best approximations of experimental curves using equation (1) gave the nonlinear absorption coefficients of 443 ± 20 cm GW^{-1} for $MAPbI_3$ + 1%PVC and 830 ± 50 cm GW^{-1} for $MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$. The found TPA coefficients are consistent with the coefficients determined earlier.[6–9] As noted by Ferrando *et al.*,[10] the nonlinear NIR absorption coefficients of the PFs are higher by two orders of magnitude than those of ordinary semiconductors (Si, ZnSe, and CdSe). We did not find the dependence of the nonlinear properties on the protective PMMA layer in the perovskite samples under femtosecond irradiation at 1064 nm. The experimental Z-scan signals at

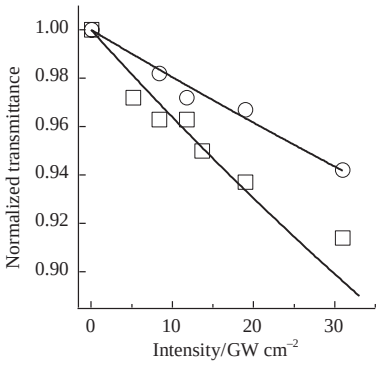


Figure 1 Normalized transmittance *vs.* incident pulse peak intensity for (circles) $MAPbI_3$ + 1%PVC and (squares) $MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$; solid lines show the best approximations by equation (1).

1064 nm were repeatable, and they did not change from one experiment to another.

We carried out similar Z-scan experiments at 532 nm with the photon energy E = 2.33 eV > E_g. The duration and energy of excitation pulses at wavelength of 532 nm were 300 fs and 150 nJ, respectively, with a pulse repetition rate of 10 kHz. The experimental Z-scan curves showed the bleaching of the samples with increasing intensity in the waist of a laser beam. The signal of bleaching was unrepeatable, and it increased every time when the sample passed through the waist region to confirm photochemical decomposition in the area of irradiation. We studied the kinetics of photobleaching of PFs under exposure to high-intensity light at 532 nm. The samples were installed in the waist of a laser beam, and optical transmittance was measured at an incident power density of 53 W cm^{-2} and a peak intensity 18 GW cm^{-2} on the perovskite sample surface. The effect of a protective PMMA layer on the rate of degradation was examined. Figure 2 shows the kinetics of photodegradation.

The kinetics of photodegradation of PFs was described by the following equation:

$$\frac{A}{A_0} = a\exp(-k_1 t) + b\exp(-k_2 t) + C. \qquad (2)$$

Table 1 summarizes the results of the approximation of experimental curves by equation (2).

As follows from Table 1 and Figure 2, the kinetics of photodegradation is decomposed into two photochemical processes with different rates. At the first stage, the rates from 0.68 to 0.98 s^{-1} did not depend on the encapsulation of PFs with PMMA layers within the experimental error, whereas the rates from 0.02 to 0.06 s^{-1} at the second stage and the coefficient b depended on the encapsulation. In unprotected films, the rate k_2 was lower and the coefficient b was higher; therefore, long exposure times led to a lower normalized absorbance level of 47–48%, as compared to a level of 64–69% in protected films.

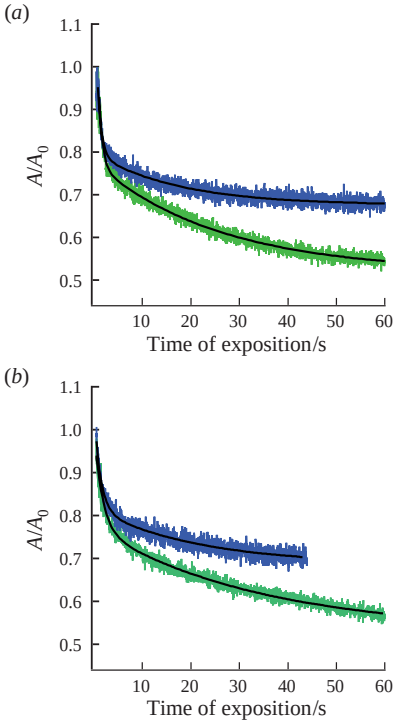


Figure 2 Kinetics of photodegradation of PFs under irradiation at a wavelength of 532 nm. The time dependence of the normalized optical density of (*a*) $MAPbI_3$ + 1%PVC and (*b*) $MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$. Blue and green curves refer to PFs encapsulated with a PMMA layer and nonencapsulated PFs, respectively, and black lines show approximations using equation (2).

Table 1 Fitting parameters for experimental curves of photodegradation using equation (2) for PFs encapsulated with a PMMA polymer layer and nonencapsulated PFs.

Sample	a/b	k_1/s^{-1}	k_2/s^{-1}	C (%)
$MAPbI_3$ + 1%PVC	1.21	0.93 ± 0.05	0.037 ± 0.002	47
$MAPbI_3$ + 1%PVC + PMMA	2.27	0.98 ± 0.05	0.060 ± 0.002	64
$MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$	0.79	0.68 ± 0.04	0.020 ± 0.001	48
$MA_{0.15}FA_{0.75}Cs_{0.1}PbI_3$ + PMMA	1.69	0.77 ± 0.05	0.047 ± 0.002	69

At the first stage, fast photochemical and thermal (local heating of the film under laser irradiation) decomposition reactions occurred inside the PFs, and this process was independent of the presence or absence of the protective PMMA layer. We assume the following decomposition reactions of perovskites: $APbI_3 \rightarrow AI + PbI_2$ (A is a cation),[11] $PbI_2 \rightarrow Pb^0 + I_2\uparrow$[12] and $CH_3NH_3PbI_3 \rightarrow PbI_2 + CH_3NH_2\uparrow + HI\uparrow$.[13]

At the second stage, the perovskites and their decomposition products reacted with ambient water and oxygen, which diffused into the reaction zone. The overall reaction of light- and oxygen-induced degradation was $2CH_3NH_3PbI_3 + xO_2 + h\nu \rightarrow 2CH_3NH_2\uparrow + PbI_2 + 2I_2\uparrow + PbO_{(2x-1)} + H_2O\uparrow$.[14] The products CH_3NH_2 and PbI_2 decomposed to CH_3I, NH_3, I_2 and Pb^0 upon irradiation with ligh.[15] Perovskites were also hydrolyzed with ambient water to form CH_3NH_2, PbI_2 and HI.[16] In this case, the presence of a polymer layer reduced the rates of delivery of water and oxygen to the reaction zone and the rates of removal of gaseous reaction products; therefore, it affected the rates of processes at the second stage. Thus, the encapsulation of PFs with PMMA polymer layers allowed us to decrease the depth of photodegradation (or to increase the level of residual absorbance) under irradiation with femtosecond pulses at 532 nm by a factor of 1.4.

Thus, the nonlinear absorption coefficients of the thin films of halide perovskites, which exceed analogous coefficients for conventional semiconductors by several orders of magnitude, were measured on femtosecond laser irradiation at 1064 nm. Under irradiation with femtosecond pulses at 532 nm, the photochemical degradation of perovskite films with fast and slow process kinetics was recorded. The rates of photodegradation and the depth of absorbance change were measured depending on the encapsulation of the films with PMMA polymer layers. A decrease in the photodegradation depth by a factor of 1.4 was detected in the encapsulated films.

This work was performed within the framework of a state contract no. AAAA-A19-119032690060-9 (A.S.L.) and Russian Ministry of Science and Education (project AAAA-A19-119071190044-3, L.A.F. and P.A.T.).

References

1 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, *ACS Appl. Mater. Interfaces*, 2017, **9**, 12759.
2 R. Zhang, J. Fan, X. Zhang, H. Yu, H. Zhang, Y. Mai, T. Xu, J. Wang and H. J. Snaith, *ACS Potonics*, 2016, **3**, 371.
3 L. A. Frolova, A. I. Davlethanov, N. N. Dremova, I. Zhidkov, A. F. Akbulatov, E. Z. Kurmaev, S. M. Aldoshin, K. J. Stevenson and P. A. Troshin, *J. Phys. Chem. Lett.*, 2020, **11**, 6772.
4 Z. Song, C. Wang, A. B. Phillips, C. R. Grice, D. Zhao, Y. Yu, C. Chen, C. Li, X. Yin, R. J. Ellingson, M. J. Heben and Y. Yan, *Sustainable Energy Fuels*, 2018, **2**, 2460.
5 D. V. Khudyakov, D. V. Ganin, A. D. Lyashedko, L. A. Frolova, P. A. Troshin and A. S. Lobach, *Quantum Electron.*, 2021, **51**, 211.
6 F. O. Saouma, C. C. Stoumpos, J. Wong, M. G. Kanatzidis and J. I. Jang, *Nat. Commun.*, 2017, **8**, 742.

7 J. Zhang, T. Jiang, X. Zheng, C. Shen and X. Cheng, *Opt. Lett.*, 2017, **42**, 3371.
8 C. Redondo-Obispo, I. Suárez, S. J. Quesada, T. S. Ripolles, J. P. Martínez-Pastor, A. L. Alvarez, A. de Andrés and C. Coya, *J. Phys. Chem. Lett.*, 2020, **11**, 2188.
9 I. Suárez, M. Vallés-Pelarda, A. F. Gualdrón-Reyes, I. Mora-Seró, A. Ferrando, H. Michinel, J. R. Salgueiro and J. P. Martínez-Pastor, *APL Mater*., 2019, **7**, 041106.
10 A. Ferrando, J. P. Martínez-Pastor and I. Suárez, *J. Phys. Chem. Lett.*, 2018, **9**, 5612.
11 N. N. Udalova, A. S. Tutantsev, Q. Chen, A. Kraskov, E. A. Goodilin and A. B. Tarasov, *ACS Appl. Mater. Interfaces*, 2020, **12**, 12755.
12 A. F. Akbulatov, L. A. Frolova, N. N. Dremova, I. Zhidkov, V. M. Martynenko, S. A. Tsarev, S. Yu. Luchkin, E. Z. Kurmaev, S. M. Aldoshin, K. J. Stevenson and P. A. Troshin, *J. Phys. Chem. Lett.*, 2020, **11**, 333.
13 B. Philippe, B.-W. Park, R. Lindblad, J. Oscarsson, S. Ahmadi, E. M. J. Johansson and H. Rensmo, *Chem. Mater*., 2015. **27**, 1720.
14 S. Ruan, M.-A. Surmiak, Y. Ruan, D. P. McMeekin, H. Ebendorff-Heidepriem, Y.-B. Cheng, J. Lu and C. R. McNeill, *J. Mater. Chem. C*, 2019, **7**, 9326.
15 P. H. Joshi, L. Zhang, I. M. Hossain, H. A. Abbas, R. Kottokkaran, S. P. Nehra, M. Dhaka, M. Noack and V. L. Dalal, *AIP Adv.*, 2016, **6**, 115114.
16 J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde and A. Walsh, *Nano Lett*., 2014, **14**, 2584.

Received: 3rd March 2021; Com. 21/6477