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Random lasing in $MAPbI_3$ single crystal

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Received January 11, 2022
Revised January 23, 2022
Accepted February 15, 2022

Halide perovskites are a promising medium for the creation of microlasers. Random lasing in single crystals can provide principal information on the nature of laser radiation in these materials. This paper demonstrates random lasing in a $MAPbI_3$ $(MA^+{=}CH_3NH_3^+)$ single crystal at a temperature $T = 30$ K and pulsed optical excitation with a repetition rate of 80 MHz. The observed laser radiation has a multimode composition with a quality factor of individual modes $Q \sim 1200$ and threshold behavior. The paper also proposes a method for separating the background non-polarized photoluminescence and lasing signals.

Keywords: halide perovskites: random lasing: $MAPbI_3$.

DOI: 10.21883/EOS.2022.05.54440.8-22

Introduction

Initially, a surge of attention to halide perovskites about ten years ago was associated with the possibility of using this new class of ionic semiconductors as absorbers in solar cells [1–3]. It quickly became clear that halide perovskites are also excellent light sources and can be used as an active medium for lasers. Another feature of these materials is a simple liquid-phase synthesis, which makes it possible to create various laser structures on their basis.

Using spin-coating, halide perovskites can be deposited in the form of polycrystalline films with thickness on the order of hundreds of nanometers. Polycrystalline films of halide perovskites demonstrate enhanced spontaneous emission [4]. Simple technology for depositing such films allows them to be embedded in various types of lasing resonators: lasers with distributed feedback [5,6], coated microspheres [7], microdiscs [8], vertically-emitting lasers [9] etc. Despite the successful demonstration of amplification and lasing in such structures, the study of the processes underlying these phenomena is difficult due to the imperfection of the polycrystalline material and heterogeneous broadening of optical resonances.

The most fundamental results could be obtained in single crystal samples. In this case, the defect density can be minimized and optical resonances can be significantly narrowed due to a decrease in the area of crystal boundaries and the homogeneity of high-quality single crystals [10]. The problem that arises in this case is the embedding of such single crystals in optical resonators. An unexpected solution that makes it possible to obtain lasing in single crystals is random lasing. Cracks that arise in single crystals during temperature growth or change can lead to formation of random optical resonators between the planes of microcrystalline fragments with preservation of their single-crystal quality. Such random lasing was observed in the green region of the spectrum in $MAPbBr_3$ $(MA^+ = CH_3NH_3^+)$ single crystals at temperature of 4 K [11].

In this article, we demonstrate random lasing in a $MAPbI_3$ halide perovskite single crystal at temperature $T = 30$ K. This material is the most extensively studied halide perovskite with a band gap in the near-IR range. Previously, a detailed study of the spectral properties of the photoluminescence of $MAPbI_3$ single crystals made it possible to establish the spectral regions of various resonances of excitons and their complexes [12]. Comparison of these regions with those obtained in this article allows us to conclude that lasing occurs predominantly in the region of exciton states bound at defects. We also carried out a detailed study of the polarization properties of random lasing.

Results

Single crystals of halide perovskite $MAPbI_3$ were synthesized by crystallization with counter diffusion in a gel [13,14]. This method is based on the difference in the solubility of perovskite $MAPbI_3$ and lead halides PbI_2 in hydrogen iodine HI. Silica gel was used as a growth medium in the absence of organic solvents. Slow interpenetration of MAI and PbI_2 solutions led to the slow growth of crystals of rather large size and high optical quality. The optical properties of the synthesized single crystals are studied in detail in [12].

A single crystal of perovskite with size of about 3 mm was placed in Montana Instruments closed-cycle helium cryostat and cooled to temperature of $T = 30$ K. The sample was excited by a Spectra-Physics Tsunami titanium-sapphire laser with pulse repetition rate of 80 MHz and pulse duration of 3 ps. A confocal scheme with a Mitutoyo 10× microlens was used to excite the sample and collect the

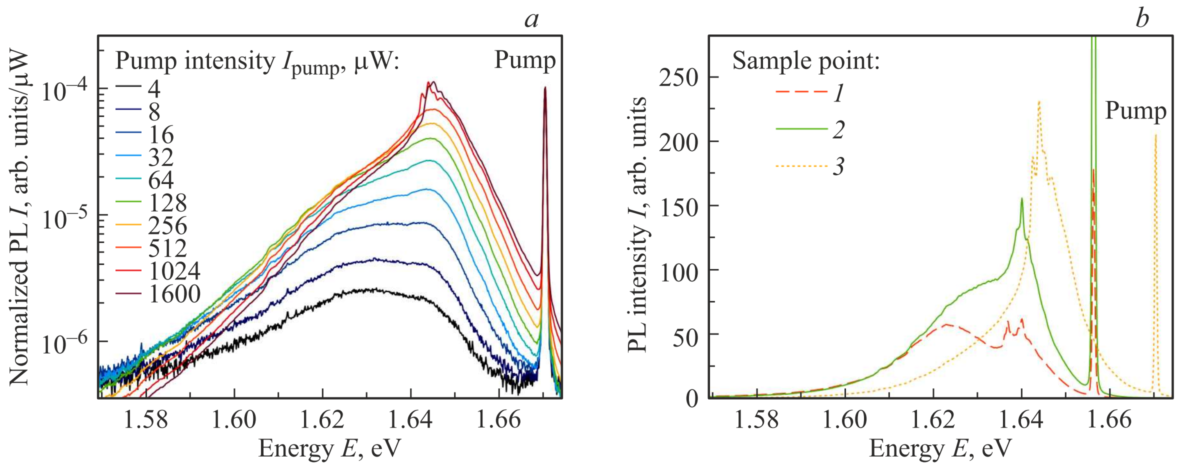

Figure 1. (a) PL spectra normalized to pump intensity I_{pump}. (b) PL spectra above the generation threshold at various points of the sample.

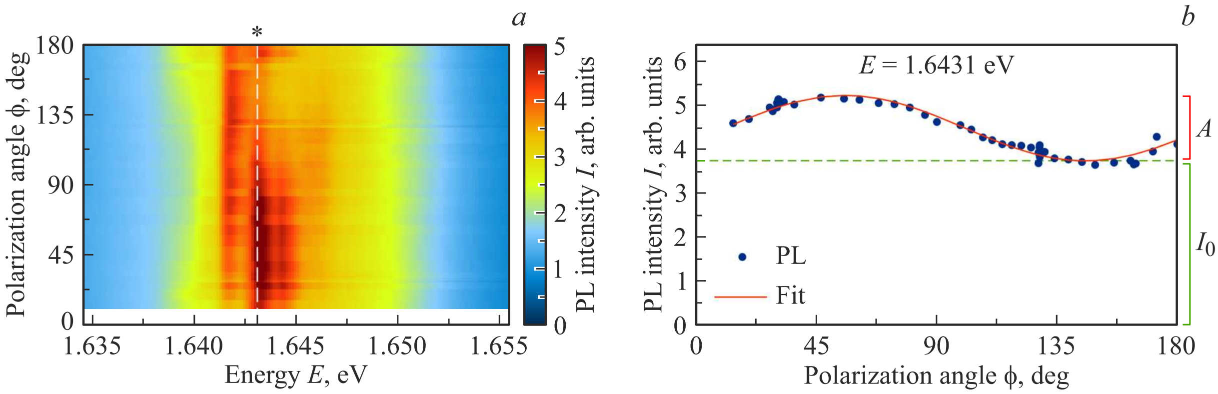

Figure 2. (a) Dependence of the PL spectra on the angle of the polarization plane ϕ. (b) Dependence of the PL signal on the angle of the polarization plane for $E = 1.6431$ eV (marked *). Points — experimental data, red curve — approximation by a polarized signal with a stand.

photoluminescence (PL) signal. The diameter of the laser spot focused on the sample was about 15 μm. Signals were recorded using a spectrometer based on an MDR-4 monochromator and Andor iDus cooled CCD-matrix. A phase achromatic plate $\lambda/2$ and a thin-film polarizer were installed in front of the entrance slit of the spectrometer to measure the polarization properties of the PL signal.

Figure 1, a shows the PL spectra at various laser pump intensities I_{pump} with energy of 1.67 eV, normalized to the pump intensity. The PL signal grows superlinearly with increasing pumping. At some points of the sample, a threshold dependence is observed — above a certain pump intensity, narrow lines appear in the PL spectrum, which grow very rapidly with the pump intensity. In Fig. 1, a such behavior is observed at $I_{pump} \sim 1$ mW. We associate the superlinear behavior of PL with enhanced spontaneous emission, and the appearance of narrow lines — with random lasing by analogy with the results for $MAPbBr_3$ single crystals [11]. Figure 1, b shows the PL spectra above the lasing threshold for several points of the sample, in which random resonators were formed due to cracks and crystal planes. In all cases, lasing lines at $T = 30$ K were observed in the region of 1.63–1.65 eV, which coincides with the spectral region of radiative recombination at defects [12]. Lasing was observed only upon pulsed excitation. Continuous excitation at the same wavelength with the same and higher intensity did not lead to the appearance of lasing, which indicates its pulsed nature with a characteristic pulse duration much shorter than the laser pulse repetition period (12 ns).

One of the features of laser radiation is its high degree of polarization. Figure 2, a shows the dependence of the PL spectra above the generation threshold on the analyzer angle ϕ. It can be seen on the spectra that the signal consists of two components — polarized lasing and unpolarized PL, which can be associated both with emission from the sample outside the random resonator and with amplified spontaneous emission. To separate these contributions, the polarization dependences of PL $I(\phi)$ for each of the energies were approximated by the following expression:

$$I(\phi) = I_0 + A\cos(\phi + \phi_0)^2, \quad (1)$$

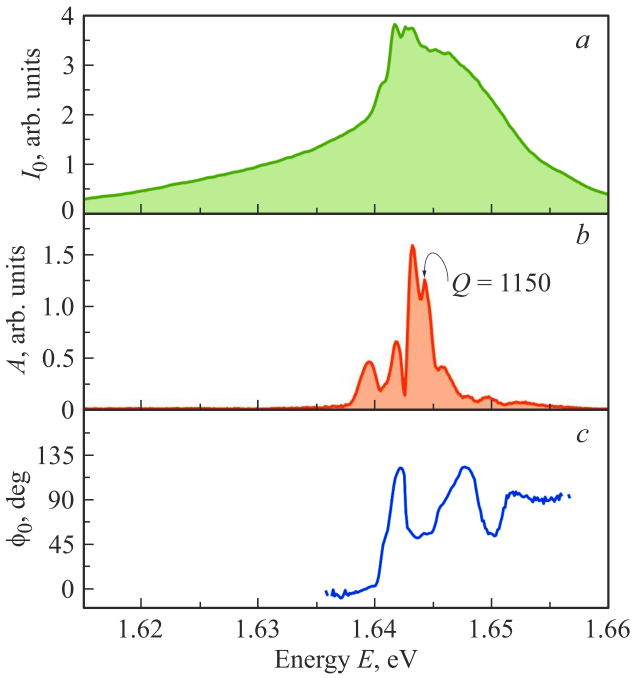

Figure 3. The result of the approximation of the polarization dependence by the Malus law: the unpolarized PL intensity I_0 (a), the lasing intensity A, and the lasing polarization rotation angle ϕ (c). In the Figure (b), the arrow marks the laser mode, for which the quality factor is indicated.

which is the sum of the contribution of unpolarized PL I_0 and polarized laser radiation with intensity A with polarization plane angle ϕ_0 given in the form of the Malus law. Figure 2, b shows an example of such approximation for $E = 1.6431$ eV and the extracted PL and lasing contributions.

Figure 3 shows the spectral dependences of the parameters extracted as a result of the approximation. The proposed model makes it possible to reliably separate unpolarized PL (Fig. 3, a) from lasing (Fig. 3, b). At this point of the sample, multimode lasing is observed. For individual laser modes, the quality factor Q can be found using the following formula:

$$Q = \frac{\lambda}{\Delta\lambda}, \qquad (2)$$

where λ — central radiation wavelength, $\Delta\lambda$ — full width at half maximum. The obtained values of $Q \sim 1200$ for the narrowest lines are comparable with the previously observed random lasing in $MAPbBr_3$ single crystals [11].

The random nature of the resonator leads not only to a random mode composition of the radiation, but also to a random polarization of individual modes (Fig. 3, c).

Conclusion

In the present article, random lasing in a halide perovskite $MAPbI_3$ single crystal was demonstrated. Lasing was observed at low temperature ($T = 30$ K) in a pulsed regime under pulsed laser pumping with pulse repetition rate of 80 MHz. Polarization measurements of the PL spectra made it possible to distinguish laser modes against the background of unpolarized PL, to determine their quality factor and the polarization plane rotation angle. The random nature of the resonator led to random spectral distribution of modes in the luminescence region of excitons bound at defects and to a random polarization of individual modes. Despite the random nature of the resonators under study, low-temperature measurements in single crystals will make it possible to study finer features of lasing and study their nature.

Funding

This work was supported by the RSF grant 19-72-10034 for using the equipment of the „Nanophotonics“ Resource Center of the St. Petersburg State University and the Laboratory of Photoactive Nanocomposite Materials (Pure ID 91696387).

Conflict of interest

The authors declare that they have no conflict of interest.

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