A New Class of All-Inorganic Perovskite Microplate for Lasing

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Abstract. We report a stable low-threshold amplified spontaneous emission performance from a new type of all-inorganic perovskite CsPb₂Br₅ microplate with superior crystallization, enhanced stability, and tunability under both one- and two-photon excitation for the first time.

1. Introduction

Recently there are many reports about solution-processed metal halide perovskite nanocrystal structures presenting a promising optoelectronic applications [1-5]. Especially, CsPbX₃ quantum dots (QDs) have exhibited bright emission with photoluminescence (PL) quantum yields (QYs) of 90%. Comparing with zero- and one-dimensional nanocrystals, perovskites with two-dimensional crystals have also shown excellent optical properties as the reason of its sufficient gain toward whispering gallery mode lasing [6]. Therefore, they are expected to play an important role as its potential building blocks for the optical devices in

Fig. 1 (a) Scanning emission microscopy and (b) transmission electron microscope image of an individual microplate. (c) Scanning emission microscopy images of CsPb₂Br₅ microplate with 1.5 h. (d) side view of the relaxed CsPb₂Br₅ unit cell, with a schematic of the alternating Cs⁺ and (Pb₂Br₅)⁻ layers strongly coupled with each other.
future based on the emergent perovskite materials. Comparing with liner absorption, multi-photon absorption and emission have several unique advantages including large penetration depth, high spatial resolution and little damage to the targeted samples, rendering wide applications in biological and medical fields. Therefore, two-photon pumping lasers have been regarded as a promising strategy to achieve frequency up-conversion [7,8]. In the present study, we report all-inorganic perovskite CsPb$_2$Br$_5$ with novel physical properties by material synthesis, characterization, optical measurement together with first principles calculations, which show that CsPb$_2$Br$_5$ crystallizes in a tetragonal phase with a unique sandwiched structure with alternating Cs$^+$ and (Pb$_2$Br$_5$)$^-$ layers chemically bonded with each other. We demonstrated the excellent amplified spontaneous emission (ASE) performance from a new type of all-inorganic perovskite CsPb$_2$Br$_5$ microplate with superior crystallization, enhanced stability, and tunable optical properties. To the best of our knowledge, this is the first report on the CsPb$_2$Br$_5$ microplate.

2. Results and discussion

2.1 The morphology and composition of perovskite microplate

Using a facile solution-phase synthesis approach, we prepared semiconductor perovskite CsPb$_2$Br$_5$ microplates which exhibit high stability with several months and excellent crystal quality with a uniform size. Figure 1a and b show scanning emission microscopy and transmission electron microscope image of CsPb$_2$Br$_5$ microplate with the size about micrometre scale. Being different from CsPbX$_3$, the growth process of CsPb$_2$Br$_5$ microplates displays a unique helical form crystal layered structure like bamboo, as shown in Fig 1c. To learn the crystallization of CsPb$_2$Br$_5$, we performed DFT-based first-principles calculations using the plane-wave-basis-set and the projector-augmented-wave method, as implemented in the Vienna ab initio simulation package (VASP) code to explore the atomic structure and electronic properties. It is found that CsPb$_2$Br$_5$ crystallizes in a tetragonal phase. It should be noted that CsPb$_2$Br$_5$ perovskite is characterized by a sandwiched structure with alternating Cs$^+$ and (Pb$_2$Br$_5$)$^-$ layers chemically bonding with each other (Fig. 1d).

2.2 The ASE characterization for perovskite microplate

As shown in Fig 2a, when CsPb$_2$Br$_5$ microplate is excited by a Ti$^{3+}$ doped sapphire pulse laser (700-1000 nm with peak at ~800 nm, ~100 fs, ~1 W, 1 kHz) stimulated emission could be obtained via coupling among the scattered light by individual CsPb$_2$Br$_5$ microplates. A bright ASE emission due to conduction-to-valence band transition located at the middle of the film was clearly observed in atmosphere condition when it was excited by 800 nm laser (Fig 2b). Figure 2c shows the power-dependent emission spectra of CsPb$_2$Br$_5$ microplate under the 800-nm fs-laser excitation. When the pumping density is under threshold, emission peak centre 528 nm and the intensity increases slowly with a full width at half maximum (FWHM) of 20 nm. However, above the threshold, the lasing peak red-shifted to ~540 nm with a FWHM of 6 nm appears. Figure 2d shows the corresponding lasing emission spectra under one-photon

Fig.2. (a) The schematic representation of CsPb$_2$Br$_5$ microplates excited by 800 nm fs pulse laser focused linearly on the sample with a cylindrical lens. (b) The photograph of the glass covered with CsPb$_2$Br$_5$ microplates excited by Ti$^{3+}$ doped sapphire pulse laser above lasing threshold excitation. (c) Pump-fluence dependence of the emission spectrum from CsPb$_2$Br$_5$ microplates under 800 nm and (d) 400 nm fs laser excitation.
excitation, which is consistent with the lasing excited by one-photon. Thus, CsPb Br may have great potential for two-photon excited up-conversion devices.

2.3 Two-photon absorption cross section in perovskite

The pump intensity dependence of intensity and FWHM of the ASE signal with one- and two-photon absorption (OPA and TPA) were measured. The results depicted in Fig. 3 and Fig. 4, respectively, clearly show threshold intensities of ASE. They are respectively $I_{th}(OPA) = 1.94 \text{mJ/cm}^2$ and $I_{th}(TPA) = 21.5 \text{mJ/cm}^2$. The threshold of the ASE when the population inversion is achieved by the pump pulse, which is common for OPA and TPA. This is given by the relation between OPA and TPA cross sections and TPA threshold flux $\sigma_{OPA} = \Phi_{th}(TPA)\sigma_{TPA}$. From the TPA threshold intensity above mentioned and the relation, $\sigma_{TPA}$ is estimated as $\sigma_{OPA} = \Phi_{th}(TPA)\sigma_{TPA} = 6200\text{GM}$ (Goeppert Myer: $10^{50}\text{cm}^4\text{s/photon}$). This cross section is very large in comparison with well known high TPA molecular crystal of anthracene, which is reported to have 4GM at $31.6 \times 10^3 \text{cm}^{-1}$ ($A_u$ absorption band) and 400GM at $33.4 \times 10^3 \text{cm}^{-1}$ (X absorption band). The material may be useful for nonlinear optical devices such as three dimensional optical memory device utilizing deep reaching photoexcitation inducing photochemical hole-burning thanks to the large TPA cross section.

3. Conclusion

In summary, we have studied CsPb$_2$Br$_5$ microplate as a typical material of all-inorganic perovskite, and demonstrated its large optical gain and corresponding emission. With a robust band gap of ~2.44 eV, CsPb$_2$Br$_5$ microplate exhibits stable low-threshold amplified spontaneous emission under both one- and two-photon excitation, which is related to its unique spatially distinguished valence/conduction band edge states originating from the intrinsic sandwiched structure. The material has extremely large two-photon absorption cross section. These results are expected to shed new light on future design and development of novel perovskite nanomaterials for optoelectronic devices including photoluminescence light sources and nonlinear material with gigantic two-photon absorbing medium.
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