

Centimeter-Sized Inorganic Lead Halide Perovskite CsPbBr₃ Crystals Grown by an Improved Solution Method

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ABSTRACT: As a member of the lead-halide perovskite family, inorganic perovskite CsPbBr₃ exhibits excellent optical and electrical properties with higher stability to the environment. However, former efforts to obtain large-size CsPbBr₃ single crystals with satisfactory quality using low temperature solution methods reached limited results. In this work, we have studied the growth of CsPbBr₃ crystals using the antisolvent vapor-assisted crystallization (AVC) method. By adjusting the mole ratio of PbBr₂ and CsBr, the phase diagram of the final products is acquired. Five regions are identified, including the Cs₄PbBr₆ single phase region, Cs₄PbBr₆ and CsPbBr₃ two phases region, CsPbBr₃ single phase region, CsPbBr₃ and PbBr₂·2[(CH₃)₂SO] metastable two phases region, and CsPbBr₃ and PbBr₂·2[(CH₃)₂SO] two phases region. Three methods are adopted to improve the size and crystalline quality of CsPbBr₃. The growth rate is effectively tailored by diluting the antisolvent MeOH solution using DMSO to reduce the MeOH vapor pressure. Centimeter-size bright CsPbBr₃ crystals have been obtained. The room temperature bandgap of CsPbBr₃ is estimated at ~2.29 eV by the transmission spectra. The photoluminescence spectra show two strong emission peaks,



located at 530 and 555 nm, respectively, which are related to the free and bond excitons. The resistivity is as large as $2.1 \times 10^9 \Omega$ cm. Hall effect measurements demonstrate the CsPbBr₃ is p-type conductivity with a hole carrier concentration of 4.55×10^7 cm⁻³ and the mobility of 143 cm² V⁻¹ s⁻¹. The resulting Au/CsPbBr₃/Au device exhibits strong photoresponse to optical light, with an on–off ratio of two orders under a light emitting diode (~1 mW/cm²) with a wavelength of 365–420 nm. Our research would shed more light on the growth and the photoresponse properties of CsPbBr₃ crystals.

1. INTRODUCTION

Compared with the hybrid perovskites, all inorganic lead halide perovskites have excellent photoelectrical properties, as well as higher chemical stability to the environment. As a member of inorganic perovskites, CsPbBr₃ (CPB) has direct optical band gap, large optical absorption (~2.3 eV),^{1,2} narrow emission line width, high luminescence, and high quantum yield, which make it suitable for application in the fabrication of strong luminescent colloidal quantum dots (QDs),^{3–5} air-stable perovskite solar cells,⁶ highly sensitive visible light detectors,⁷ highly polarization-selective three-photon absorption,⁸ and high-energy detectors.^{1,9}

To understand the potential optoelectrical properties of CsPbBr₃, high quality of CsPbBr₃ bulk crystals are desirable. Stoumpos¹ reported CsPbBr₃ bulk crystals grown by the Bridgman method at high temperature (above 600 °C) used for X- and γ -rays detection. However, the obtained CsPbBr₃ single crystals suffered from phase transition (*Pm*3*m* above 410 K, *P4/mbm* from 410 to 375 K, *Pbnm* below 375 K) after the crystallization, resulting in a high density of grown-in defects.¹ Compared with melt growth, the solution growth can avoid the phase transition in the crystal and should be a favorable method for preparing CsPbBr₃ perovskite crystals. Two low temperature solution growth methods have been reported recently, including inverse temperature crystallization (ITC)⁹

antisolvent vapor-assisted crystallization (AVC),¹⁰ respectively. Dirin⁹ reported CsPbBr₃ crystals grown from DMSO using the ITC method and the related solutions. Millimeter-sized CsPbBr3 crystals were obtained. However, when it was used for γ -ray detection, only a broad photopeak was observed illuminated by a ²⁴¹Am source at 220 K, but no peak appeared at room temperature. The mobility lifetime product $(\mu\tau)$ is ~2 $\times 10^{-4}$ cm² V⁻¹, which is slightly lower than that of Bridgmangrown CsPbBr3 crystals.¹ The resistivity is about 2 G Ω ·cm, which is also smaller than that grown by the Bridgman method $(343 \text{ G}\Omega \cdot \text{cm})$.¹ Another AVC solution method is suggested by Rakita et al. and other groups.¹⁰⁻¹² Cha et al.,¹¹ Ding et al.,¹² and Miao et al.¹³ reported the photodetector properties of solution-growth CsPbBr3 crystals. However, only millimeter sized crystals with relative low resistivity (less than 1 G Ω ·cm) and poor mobility $\sim 13.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained due to the defects and impurities.¹³

Except for the low resistivities,⁹⁻¹³ mobilities,¹³ and lifetimes,⁹ due to the defects and impurities, a more essential problem is to control the phase in the Cs–Pb–Br system when growing CsPbBr₃ crystals from solution. From the phase

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Figure 1. (a) The schematic diagram of CsPbBr₃ crystals grown by the AVC method. (b) The pictures of the final crystals obtained from the precursor solution with *n* changing from 0.25 to 4, where *n* is the starting mole ratio of PbBr₂ and CsBr. (c) The obtained yellow, orange, and white crystals are determined as Cs₄PbBr₆, CsPbBr₃, and PbBr₂·2[(CH₃)₂SO] using the XRD patterns refinements.

diagram,¹⁴ it is seen that there are three phases including $CsPbBr_{3}$, $CsPb_2Br_5$, and Cs_4PbBr_6 , respectively. Rakita et al.¹⁰ and Saidaminov et al.² found that it is difficult to control the exact composition of the obtained crystals from the solution due to the complex factors, such as the ratio of the starting materials, the kinds of solution and antislovent, and even the temperature. $CsPbBr_3$ and Cs_4PbBr_6 tend to generate simultaneously if the ratios of the starting materials PbBr₂ and CsBr are not adjusted carefully.^{2,10} Only several millimeters size $CsPbBr_3$ crystals are obtained from the solution method.^{2,9,10}

So it is still a challenge to obtain large size $CsPbBr_3$ crystals with high quality by optimizing the growth conditions of the solution method. In this work, we study the low temperature solution growth of $CsPbBr_3$ crystal by the AVC method. The phase diagram of Cs-Pb-Br system is determined according to the ratio of $PbBr_2$ and CsBr. To control the growth rate, we propose a new method by using dilute antisolvent to reduce the vapor pressure of MeOH.

2. EXPERIMENTAL SECTION

2.1. Preparation of Precursors. CsBr (\geq 99.5%) and PbBr₂ (\geq 99.5%) were used as the starting materials, and methylalcohol (\geq 99.5%) and dimethyl sulfoxide (DMSO, \geq 99.5%) as the solvents for the growth of CsPbBr₃ crystals. Nine millimoles of PbBr₂ and 6 mmol of CsBr were dissolved by 15 mL of DMSO with continuous stirring for 1 h at room temperature. After that, the solution was filtered using 30 μ m-sized filter paper to remove the green-yellow precipitate. Then, the clear solution was titrated with MeOH until the orange precipitate no longer dissolved. Finally, the titrated mixed solution was filtered again to obtain the precursor for crystal growth. A series of variable precursors were obtained by changing the mole ratios of PbBr₂ and CsBr from 0.25 to 4.

2.2. Growth of CsPbBr₃ Single Crystals. CsPbBr₃ single crystals were grown by the AVC method. As shown in Figure 1a, about 20 mL of clear precursors were put in the inner container, and 30 mL of antisolvent (MeOH or diluted MeOH) was added in the outer container. MeOH solution was volatilized from the outer container to the inner one, forming a saffron yellow precipitation of CsPbBr₃. It is noted that the mole ratios of PbBr₂ and CsBr from 1 to 1.5 is required to form pure CsPbBr₃ crystals. This growing process lasted 3–14 days, depending on the composition of the mixed antisolvent. The final crystals were washed with dimethylformamide (DMF) solution at room temperature. By using the optimum conditions that the mole ratio of PbBr₂ and CsBr in the precursor is 1.5 and the mixed antisolvent composition is 50% MeOH and 50% DMSO, we obtained the largest CsPbBr₃ crystals with a size of $42 \times 5 \times 3$ mm³.

2.3. Characterizations and Measurements. The X-ray diffraction (XRD) patterns of both powders and single crystal were collected using D/Max2500PC with Cu $K_{\alpha1}$ in the range of 10–90° (2 θ) under a tube voltage of 40 kV and 40 mA. The UV–vis spectra of CsPbBr₃ crystals were carried out on a UV-2550 spectrometer with an integrating sphere over the spectral range of 400–800 nm. A FLS-920 fluorescence spectroscopy was used to collect photoluminescence (PL) spectra, with the excitation wavelength of 405 nm. Current–voltage (*I–V*) and current–time (*I–t*) were measured by electrical properties measurement system (Agilent 4155C). A light emitting diode (LED) (~1 mW/cm²) was employed as the illumination light to perform the time-dependent photoresponse with the wavelength of 365–420 nm.

3. RESULTS AND DISCUSSION

3.1. Phase Diagram in Cs–Pb–Br System. The starting mole ratio of PbBr₂ and CsBr is very important for the final crystallization from DMSO solution. Dirin⁹ and Saidaminov² found that if the ratio of PbBr₂ and CsBr is equal to 1:1, the resulting CsPbBr₃ is always mixed with Cs₄PbBr₆. Pure

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CsPbBr₃ phase can be achieved when the ratio was increased to 2:1. In our work, the variable mole ratios of PbBr₂ and CsBr (n:1) have been studied for the crystallization process, where *n* changes from 0.25 to 4. When the antisolvent MeOH volatilized into the precursors, complex crystallizations can be observed at the bottom of the container. Figure 1b shows the pictures of the evolution of the resulting crystallizations with a different mole ratio of PbBr₂ and CsBr (n:1). When n varies from 0.25 to 1, the colors of the obtained crystallization change from bright yellow to orange gradually. Further increasing nfrom 1 to 1.5, the color turns orange, and the grain sizes become large. When n changes from 1.5 to 4, another white stick-like crystallization was generated and mixed with the orange crystals. To determine the phases of crystallizations with different colors, the XRD patterns were measured, as illustrated in Figure 1c. After the refinements of XRD patterns, the yellow, orange, and white crystallizations were determined as Cs₄PbBr₆, CsPbBr₃, and PbBr₂·2[(CH₃)₂SO], respectively. It should be noted that the white stick-like crystals are not PbBr₂, but the organic crystal PbBr₂·2[(CH₃)₂SO].¹⁵ Its space group is Pmmn, and the lattice parameters are a = 11.108 Å, b = 12.400 Å, and c = 4.548 Å, respectively.

To identify the variable crystallizations at different values of n, the starting components dependent phase diagram is plotted in Figure 2a. It is suggested that when the value of n is between



Figure 2. (a) The phase diagram of the final products in Cs–Pb–Br systems grown from DMSO solution using MeOH as an antisolvent. It is noted that the metastable region (n = 1.3-1.5) is observed with the components of CsPbBr₃ and PbBr₂·2[(CH₃)₂SO]. (b) After a slight vibration of the solution, an increasing amount of the white PbBr₂·2[(CH₃)₂SO] crystals is observed over time.

1.3 and 1.5, the metastable region is observed. As shown in Figure 2b, the state of the solutions changes over time (0 s to 30 s) after a slight disturbance. At the beginning, only orange CsPbBr₃ crystals are generated at the bottom of the container. After a slight vibration, the white PbBr₂·2[(CH₃)₂SO] crystals are formed quickly. Thirty seconds later, the orange CsPbBr₃ crystals are almost covered by the white PbBr₂·2[(CH₃)₂SO] crystals.

According to the results of the crystallization experiments, five crystallization regions are obtained as a function of the value of n. We propose the following four reactions to explain the crystallization process.

$$\frac{1}{4} \text{PbBr}_2 + \text{CsBr} \to \frac{1}{4} \text{Cs}_4 \text{PbBr}_6 \left(n \le \frac{1}{4} \right) \tag{1}$$

$$nPbBr_{2} + CsBr \rightarrow \frac{1-n}{3}Cs_{4}PbBr_{6} + \frac{4n-1}{3}CsPbBr_{3}$$
$$\left(\frac{1}{4} < n < 1\right)$$
$$PbBr_{2} + CsBr \rightarrow CsPbBr_{3} (1 \le n < 1.3)$$

$$nPbBr_{2} + CsBr + 2(n - 1)(CH_{3})_{2}SO$$

$$\rightarrow CsPbBr_{3} + (n - 1)PbBr_{2} \cdot 2[(CH_{3})_{2}SO]$$

$$(1.3 \le n \le 1.5) \text{ (metastable) } (n > 1.5)$$

According to eq 1, when *n* is below 1/4, only green Cs_4PbBr_6 crystals precipitate from the solution. When *n* is between 1/4 and 1, green Cs_4PbBr_6 and orange $CsPbBr_3$ crystals can grow up simultaneously. When *n* is between 1 and 1.3, only the orange $CsPbBr_3$ crystals grow from the solution. When *n* is between 1.3 and 1.5, orange $CsPbBr_3$ crystals can grow up at first. After a slight vibration, the extra $PbBr_2$ in the solution can form the complex $PbBr_2 \cdot 2[(CH_3)_2SO]$ with DMSO gradually. This is a metastable region. When *n* is above 1.5, both orange $CsPbBr_3$ and white $PbBr_2 \cdot 2[(CH_3)_2SO]$ crystals are generated.

3.2. Control of the Crystal Growth. The crystallization process takes place once the precursor solubility is reduced by the interdiffusion of the antisolvent. Figure 3 shows the



Figure 3. Relationship of the obtained mass (or moles) of $CsPbBr_3$ crystals and the moles of MeOH volatilized into the precursor solution. Accordingly, the pictures of $CsPbBr_3$ crystals obtained in the solution are shown below this curve.

relationship between the mass (or molar quantity) of the resulting CsPbBr₃ crystals and the antisolvent MeOH volatilized in the precursor solution. The mole ratio of CsPbBr₃ and MeOH in the solution is about 7×10^{-3} . Accordingly, CsPbBr₃ crystals were generated from the precursor solution, as shown in the bottom of Figure 3. When 625 mmol of MeOH volatilized into the solution, the mass of CsPbBr₃ crystals can achieve at as large as 1.8 g. Therefore, the maximum volume could be 0.40 cm³ considering the density of CsPbBr₃ is about 4.55 g/cm³. This indicates that the antisolvent MeOH can produce large CsPbBr₃ crystals by reducing the solubility of the precursor solution.

In order to obtain large crystals with high quality, it is necessary to control the growth rate and the amount of nucleation. For this solution growth, three aspects should be taken into account, including (1) the diffusion of the



Figure 4. (a) The vapor pressures of the composited antisolvent MeOH and DMSO with changing X_{MeOH} , where X_{MeOH} is the mole ratio of MeOH. The value of X_{MeOH} of the green dash line is the concentration of MeOH in antisolvent solution of outer container, while the green dash line represents the concentrate of MeOH in the precursor solution in the inner container. When MeOH in the antisolvent solution is volatized into the precursor solution, the concentration of MeOH in two containers change along the pink line. Finally, they both have the same value of X_{MeOH} (b) The orange CsPbBr₃ crystals are obtained at the variable value of X_{MeOH} in the antisolvent solutions from 100% to 50%. With decreasing value of X_{MeOH} the maximum sizes of crystals are increased. (c) The XRD patterns of the CsPbBr₃ crystals are shown with a set of peaks identified as (0l0) faces.



Figure 5. (a) The transmittance and PL spectra of CsPbBr₃ crystals. (b) The energy gap is fitted as 2.29 eV by the Tauc plot curve. (c) The PL spectra are measured at the variable incident powers from 0.55 mW to 5.06 mW. The inset is the relationship between incident powers and PL intensities. The fitting values of γ for two peaks are 1.44 and 1.48, respectively. (d) The color picture presents the changes of PL intensities at variable powers and wavelengths.

antisolvent from the outside container to the inner one; (2) the concentration of Pb^{2+} and Br^{-} in the precursor solution; (3) the vapor pressure of the antisolvent MeOH in the outside container.

First, the sizes of the pores connecting inside and outside containers were adjusted for controlling the diffusion of antisolvent MeOH. When the areas of the pores were adjusted from several square centimeters to hundreds square microns, the crystallization rate did not result in a significant difference. Within 1-2 days, the amounts of crystal were not increased anymore. Because of the fast growth rate of CsPbBr₃ crystals, the maximum size of obtained crystals is usually only several millimeters, which is similar to the previous reports. This is

possibly because MeOH diffuses still too fast from the outside container into the inner one by controlling the area of pores, and thus this method is not effective to improve the size and quality of CsPbBr₃ crystals.

Second, increasing the amount of PbBr₂ could influence the crystallization rate. At the same growth time, the relative larger CsPbBr₃ crystals are generated by increasing the amount of PbBr₂, as shown in Figure 1b. Therefore, more Pb²⁺ and Br⁻ ions in the DMSO solution can decrease the CsPbBr₃ crystals dissolving speed. But when the PbBr₂ is too large amount, the white stick-like crystals PbBr₂·2[(CH₃)₂SO] will dissolve out from the DMSO solution. Further growth of CsPbBr₃ crystals, however, is prevented because of the appearance of these white

crystals. So the value of *n* is suggested at the metastable region (n = 1.3-1.5), which ensures the growth of a relatively large amount of PbBr₂ simultaneously, and avoids the formation of the white stick-like PbBr₂·2[(CH₃)₂SO] crystals.

Third, reducing the vapor pressure of the antisolvent MeOH can decrease the CsPbBr3 crystal growth rate effectively. According to the ideal solution partial pressure law, the vapor pressure of the antisolvent MeOH is controlled by mixed MeOH and DMSO. At room temperature, the vapor pressure of DMSO is about 49 Pa, which is three orders lower than MeOH $(1-2 \times 10^5 \text{ Pa})$. So the partial pressure of DMSO can be ignored for the calculation of the vapor pressure of MeOH in the mixed solution. As shown in Figure 4a, the vapor pressure of MeOH is reduced by decreasing the mole amount of MeOH. The precursor solution is consisted of DMSO and 30-40% MeOH, where MeOH is used to prepare the saturated solution. In order to ensure that MeOH in the outside container can enter into the precursor, the concentration of MeOH in the antisolvent solution should not be below 30-40%. By this diluted antisolvent method, the growth time can last from 2 days to 2 weeks. MeOH over DMSO with the mole ratios of 100%, 80%, 70%, 60%, and 50% are applied when n =1.5 for the crystal growth. As shown in Figure 4b, the sizes of orange CsPbBr3 crystals are increased from millimeters to centimeters. The maximum size of CsPbBr₃ crystals is about 42 \times 5 \times 3 mm³ at 50% MeOH in the antisolvent. The transparency of CsPbBr3 crystals obtained from diluted MeOH antisolvents is better than the ones from pure MeOH. XRD patterns of CsPbBr₃ single crystal from the diluted antisolvent exhibits a set of (0 l 0) diffraction surface, as shown in Figure 4c. The inset in Figure 4c is the crystal structure of CsPbBr₃, which is related to the space group Pnma. The lattice parameters are a = 8.37 Å, b = 8.425 Å, c = 12.011 Å, $\alpha = \beta$ $= \gamma = 90^{\circ}.$

3.3. Optical and Photoresponse Properties. The optical properties of CsPbBr3 grown by the improved AVC method have been studied at room temperature. Figure 5a shows the transmission spectra and the PL spectra from 400 to 800 nm. From the transmission spectrum, a sharp rise in the curve is observed at around 550 nm, which is in agreement with the previous reports.^{1,2,11} And a relative higher average transmittance of \sim 57% is obtained from 550 to 800 nm. By fitting the Tauc plot, the energy band gap (E_g) was calculated to be \sim 2.29 eV, demonstrated in Figure 5b, which is higher than 2.25 eV^1 that grown from the melt method, 2.16 eV^{12} and 2.21 eV^2 that grown by the solution method. It is noted that two peaks at around 530 and 555 nm, respectively, are observed with strong intensity in the room temperature PL spectrum under an incident power of 5.06 mW. Only one broad peak at around 550 nm in the PL spectra has been reported from the solutiongrown CsPbBr₃ crystals,^{2,9–11,15} while Stoumpos et al. observed two peaks at 46 K PL from the melt-grown CsPbBr₃ crystals.¹

In order to interpret the two peaks, the incident power dependent PL spectra were measured from 510 to 600 nm. Figure 5c shows the power dependent PL spectra from 5.06 mW to 0.5 mW. The positions of two peaks are constant with the value of 530 and 555 nm, respectively, under different incident powers. Analysis of the PL peak intensity (*I*) versus incident beam intensity (*F*) displays a power law dependence ($I \alpha F^{\gamma}$) for both the 530 nm and the 555 nm peaks. The inset picture of Figure 5c shows the values of the exponential coefficient γ are 1.44 and 1.48, respectively. The values between $1 < \gamma < 2$, generally, is indicative of PL emission through

strongly bound excitons.^{16,17} Because the free exciton is more close to the bandgap, we think the 530 nm peak is attributed to free exciton emission and the 550 nm peak is contributed by the bound-exciton emission. The color picture in Figure 5d also presents the changes of PL intensities at variable powers and wavelengths. The positions of two peaks are constant with the changing of incident powers. And the full width at halfmaximum (fwhm) of two peaks are around 17 nm, which are broadened slightly with the increased incident powers.

The photoresponse properties of CsPbBr₃ grown by the improved AVC method have also been evaluated. Au/CsPbBr₃/ Au structure device was fabricated by thermally evaporating Au contacts with the thickness of 60 nm on the opposite face of the wafers, as shown in Figure 6a. I–V curves are measured in dark



Figure 6. (a) The schematic diagram of the electrode structure with Au electrodes and the measurement of the photoresponse. (b) The I-V curves of CsPbBr₃ single crystal measured from -1 V to 1 V at dark. (c) The photoresponse of CsPbBr₃ are shown at variable wavelengths of 365–420 nm with the incident power about 1 mW/cm².

with bias from -1 to 1 V, Figure 6b. The dark current of CsPbBr₃ crystal is about 0.1 nA at 1 V. And the bulk resistivity of CsPbBr₃ crystal at room temperature is about $2.1 \times 10^9 \ \Omega$ · cm, which is close to that of CdTe crystals.¹⁸ This ensures the CsPbBr₃ as a potential semiconductor for room temperature Xor γ -rays detection with lower electronic noise. Figure 6c shows the photoresponse illuminated by an LED light in the wavelengths range of 365-420 nm and with the intensity of ~1 mW·cm⁻². The ON/OFF ratio is as high as about 10^2 at 1 V bias, which is several times higher than the data reported by Ding et al.⁵ Hall effect measurements are carried out on the asgrown CsPbBr₃ crystals. CsPbBr₃ exhibits p-type conductivity with a hole carrier concentration of 4.55×10^7 cm⁻³ and the mobility of 143 cm² V⁻¹ s⁻¹, as shown in Table 1. Except for the melt-grown CsPbBr₃, the CsPbBr₃ crystals grown in our lab have a higher quality than the reported crystals obtained by the solution method (including AVC and ITC).

4. CONCLUSIONS

Centimeter-size CsPbBr₃ crystals were grown by a modified AVC solution method at low temperature. By controlling the mole ratio of PbBr₂ and CsBr, the phase diagram with five regions was obtained, including Cs₄PbBr₆, CsPbBr₃, PbBr₂· 2[(CH₃)₂SO] single phase regions and the mixed phases regions. To improve the size and crystalline quality of CsPbBr₃ crystals, three methods were employed to tailor the growth speed. The most effective method is to dilute the MeOH solution with DMSO. The vapor pressure of the antisolvent MeOH is controlled by changing the diluted ratios. At the ratio of 50%, a CsPbBr₃ crystal with a size of $42 \times 5 \times 3$ mm³ was

Table 1. Electronic Paramet	ers of CsPbBr ₃	Single Crystals	Grown by	Different Methods ^a

crystal growth method	size (mm ³)	resistivity (Ω ·cm)	mobility (cm ² V ^{-1} s ^{-1})	carrier concentration (cm^{-3})	ref			
AVC	$42 \times 5 \times 3$	2.1×10^{9}	143	4.55×10^{7}	this work			
AVC	$2 \times 1 \times 1$	4.0×10^{6}	13.6	1.13×10^{10}	13			
AVC	$0.67 \times 2.0 \times 0.51$	6.2×10^{7}			11			
AVC	millimeter-sized	$\sim 1 \times 10^{6}$			12			
ITC	$3 \times 2 \times 1$	1×10^{8}	52 (electron)	1.1×10^9 (electron)	2			
			11 (hole)	1.4×10^{8} (hole)				
ITC	$7 \times 3 \times 2$	2×10^{9}			9			
melt-grown crystallization	centimeter-sized	3.43×10^{11}	1000		1			
^a Where AVC and ITC is antisolvent vapor-assisted crystallization method and inverse temperature crystallization method, respectively.								

obtained. The bandgap of CsPbBr₃ is 2.29 eV. Two strong emission peaks at 530 and 555 nm in the PL spectra were observed, which are attributed to the strong bond excitons. The obtained p-type CsPbBr₃ crystals exhibited high resistivity of $\sim 2.1 \times 10^9 \ \Omega$ -cm. The CsPbBr₃ device shows a promising photoresponse to the optical light, with an on-off ratio of ~ 100 under an LED light at the wavelength of 365–420 nm ($\sim 1 \text{ mW}\cdot\text{cm}^{-2}$).

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z. F.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G. *Cryst. Growth Des.* **2013**, *13*, 2722–2727.

(2) Saidaminov, M. I.; Haque, M. A.; Almutlaq, J.; Sarmah, S.; Miao, X. H.; Begum, R.; Zhumekenov, A. A.; Dursun, I.; Cho, N.; Murali, B.; Mohammed, O. F.; Wu, T.; Bakr, O. M. *Adv. Opt. Mater.* **2017**, *5*, 1600704.

(3) Li, G.; Rivarola, F. W. R.; Davis, N. J. L. K.; Bai, S.; Jellicoe, T. C.; de la Peña, F.; Hou, S.; Ducati, C.; Gao, F.; Friend, R. H.; Greenham, N. C.; Tan, Z.-K. *Adv. Mater.* **2016**, *28*, 3528–3534.

(4) Swarnkar, A.; Marshall, A. R.; Sanehira, E. M.; Chernomordik, B. D.; Moore, D. T.; Christians, J. A.; Chakrabarti, T.; Luther, J. M. *Science* **2016**, *354*, 92–95.

(5) Cottingham, P.; Brutchey, R. L. Chem. Mater. 2016, 28, 7574–7577.

(6) Saliba, M.; Matsui, T.; Domanski, K.; Seo, J.-Y.; Ummadisingu, A.; Zakeeruddin, S. M.; Correa-Baena, J.-P.; Tress, W. R.; Abate, A.; Hagfeldt, A.; Gratzel, M. *Science* **2016**, *354*, 206–209.

(7) Song, J.; Xu, L.; Li, J.; Xue, J.; Dong, Y.; Li, X.; Zeng, H. Adv. Mater. 2016, 28, 4861–4869.

(8) Clark, D. J.; Stoumpos, C. C.; Saouma, F. O.; Kanatzidis, M. G.; Jang, J. I. Phys. Rev. B: Condens. Matter Mater. Phys. 2016, 93, 195202. (9) Dirin, D. N.; Cherniukh, I.; Yakunin, S.; Shynkarenko, Y.; Kovalenko, M. V. *Chem. Mater.* **2016**, *28*, 8470–8474.

(10) Rakita, Y.; Kedem, N.; Gupta, S.; Sadhanala, A.; Kalchenko, V.; Bohm, M. L.; Kulbak, M.; Friend, R. H.; Cahen, D.; Hodes, G. *Cryst. Growth Des.* **2016**, *16*, 5717–5725.

(11) Cha, J. H.; Han, J. H.; Yin, W.; Park, C.; Park, Y.; Ahn, T. K.; Cho, J. H.; Jung, D. Y. J. Phys. Chem. Lett. **2017**, *8*, 565–570.

(12) Ding, J. X.; Du, S. J.; Zuo, Z. Y.; Zhao, Y.; Cui, H. Z.; Zhan, X. Y. J. Phys. Chem. C 2017, 121, 4917–4923.

(13) Miao, X.; Qiu, T.; Zhang, S.; Ma, H.; Hu, Y.; Bai, F.; Wu, Z. J. Mater. Chem. C 2017, 5, 4931–4939.

(14) Cola, M.; Massarotti, V.; Riccardi, R.; Sinistri, C. Z. Naturforsch., A: Phys. Sci. 1971, 26, 1328–1332.

(15) Baranyi, A. D.; Onyszchuk, M.; Page, Y. L.; Donnay, G. Can. J. Chem. 1977, 55, 849–855.

(16) Taguchi, T.; Shirafuji, J.; Inuishi, Y. Phys. Status Solidi B 1975, 68, 727-738.

(17) Schmidt, T.; Lischka, K.; Zulehner, W. Phys. Rev. B: Condens. Matter Mater. Phys. **1992**, 45, 8989.

(18) Takahashi, T.; Watanabe, S. IEEE Trans. Nucl. Sci. 2001, 48, 950-959.