Growth and Characterization of All-inorganic Perovskite CsPbBr₃ Crystal by a Traveling Zone Melting Method

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Abstract: A self-designed traveling zone melting method was employed to fabricate perovskite CsPbBr₃ crystals, which is helpful for impurities removing and moisture excluding. A large-size CsPbBr₃ crystal with a dimension of φ 25 mm× 60 mm is successfully obtained. The as-grown crystal shows orange color and displays an excellent transmittance of 78.6% in the range of 600 nm – 2000 nm wavelength. It is revealed by DSC analysis that there is phase transition at 88.1°C and 131.25°C, respectively. The band gap $E_g$ of the crystal is calculated to be 2.25 eV. The above results prove that the traveling zone melting method is indeed a potential approach for large size and high quality CsPbBr₃ crystal preparation.

Key words: traveling zone melting method; CsPbBr₃ crystal; transmittance; band gap

During the past several years, a series of all-inorganic version of the lead bromide perovskite (CsPbX₃, X= Cl, Br, I) has attracted great attention due to its outstanding performance and broad potential applications in optoelectronic fields[1-6]. Among them, cesium lead bromine (CsPbBr₃) is a representative material. For example, the mobility lifetime product $\mu \tau$ of CsPbBr₃ crystal for electrons could up to 1.7×10⁻³ cm²/V that is comparable to the CdZnTe crystal, and the $\mu \tau$ value for holes is 1.3×10⁻³ cm²/V which is about ten times higher than that of CdZnTe, such excellent properties make CsPbBr₃ crystal a promising candidate material for X- and γ-ray radiation detection at room temperature[2]. Besides, the measured high resistivity (343 GΩ·cm) implies it is favorable for photon detection[7]. In addition, CsPbBr₃ crystal is also considered as a fast decay scintillator as its decay time is only 10 ps–20 ps[8-9]. Based on the bright application prospect, the preparation of large and high quality CsPbBr₃ crystal has become much significant. However, it is regrettable that the obtained CsPbBr₃ crystals are always in small size although many growth techniques have been employed in past years. For example, Stoumpos, et al[2] fabricated CsPbBr₃ crystal via a vertical Bridgman method, but the as-grown crystal is only about φ 7 mm× 12 mm in dimensions. Zhang, et al[10] conducted crystal growth by a creative electronic dynamic gradient (EDG) method and the crystal is about φ 8 mm×58 mm. Rakita et al[11] produced CsPbBr₃ crystals through a solution-grown method under a low temperature condition (90°C– 110°C), however, the largest crystal is millimeter-sized. Therefore, it is obvious that some novel techniques are still expected to grow CsPbBr₃ crystal. In this work, a self-designed traveling zone melting method is introduced and a large-size CsPbBr₃ crystal about φ 25 mm× 60 mm in dimensions is successfully produced, besides, the crystal quality and its properties are also investigated.

1 Experiment

1.1 Synthesis of CsPbBr₃ polycrystalline

CsPbBr₃ polycrystalline was synthesized from 99.99% purity of CsBr and PbBr₂ powders with mole ratio of 1 : 1 (the total weight was about 132 g). Considering CsBr and PbBr₂ were both water sensitive, the weighting and loading process was conducted under N₂ atmosphere in a glove box. The raw materials were loaded into a φ 25 mm quartz tube which was carefully cleaned by
aqua regia and ~18 MΩ-cm DI water. The quartz tube was sealed by oxyhydrogen flame with <10⁻³ Pa vacuum, then, it was placed into a rocking furnace. The furnace temperature was controlled at 620°C that was about 50°C higher than the melting point of CsPbBr₃. After the raw materials were melted and soaked for half an hour, the rocking system was started to work at a rate of 30 r/min for 20 min to enhance CsPbBr₃ synthesis homogeneous. Finally, the furnace was naturally cooled to room temperature. Table 1 lists the parameters for CsPbBr₃ polycrystalline synthesis. Fig. 1 is the obtained CsPbBr₃ polycrystalline that kept in quartz tube, the polycrystalline exhibited brown color and was easily separated from quartz wall. Importantly, no cracking phenomenon was found in the quartz tube, which implied the following crystal growth via such quartz tube would be safe.

### 1.2 Crystal growth

Before crystal growth, the volatility behavior of CsPbBr₃ was suggested to be clarified that would do benefit to guide the choice of furnace temperature. Fig. 2 shows the relationship between weight percentage and temperature examined by thermogravimetry equipment (TG-DTA 8121, Japan) with 5°C/min increasing rate. It was observed no weight losing took place from room temperature to 570°C. The result means CsPbBr₃ is stable under melting point (see inserted PbBr₂-CsBr phase diagram in Fig. 2). However, as temperature was continuously increased, the weight percentage was decreased sharply. Based on the TG curve, the average volatilization speed above melting point was calculated to be ~2.5% per minute. Finally, CsPbBr₃ was totally exhausted as temperature reached 800°C. Such behavior illustrated that CsPbBr₃ was easily volatilized above melting point. Therefore, the furnace temperature for CsPbBr₃ crystal growth should be designed as low as possible.

Fig. 3(a) shows the schematic diagram of the self-designed traveling zone melting furnace. It was heated by winding Fe-Cr-Al resistance wires which were located in middle position of furnace. The furnace temperature was detected by a couple of Pt/Pt-10%Rh thermocouples and monitored via DWT-702 with a proportional integral differential (PID) controller. In this experiment, the furnace temperature was set as 585°C. Fig. 3(b) is the temperature profile along vertical direction, and the melting zone was only 20 mm–25 mm in height. CsPbBr₃ polycrystalline with vacuumed quartz tube was placed on a steel support. A Pt/Pt-10%Rh thermocouples were installed near the bottom of quartz tube for indicating the temperature of CsPbBr₃ polycrystalline/melt. After the CsPbBr₃ polycrystalline was melted and soaked for 8 h, the motor system was started to work and the furnace was traveled upward with 1.0 mm/h speed. Then, CsPbBr₃ crystal growth was started and the temperature gradient in the solid-liquid interface was about 30–40°C/cm. Finally, after all of the solution was crystallized, the furnace was cooled down to room temperature at a rate of 50°C/h. The parameters for CsPbBr₃ crystal growth were listed in Table 1.

### Table 1 Conditions for CsPbBr₃ polycrystalline synthesis and crystal growth

| Material          | Method       | Conditions                          |
|-------------------|--------------|-------------------------------------|
| Synthesis method  | Rocking technique | 99.99% CsBr and PbBr₂, 132 g       |
| Raw material      |              |                                     |
| Crucible          | Quartz tube  |                                     |
| Vacuum            | <10⁻³ Pa     |                                     |
| Synthesis         | 620°C        |                                     |
| temperature       |              |                                     |
| Rocking rate      | 30 r/min     |                                     |
| Rocking time      | 20 min       |                                     |
| Growth method     | Traveling zone melting |          |
| Crucible          | Quartz tube  |                                     |
| Vacuum            | <10⁻³ Pa     |                                     |
| Furnace temperature | 585°C        |                                     |
| Temperature gradient | 30°C/cm–40°C/cm |                 |
| Growth rate       | 1.0 mm/h     |                                     |
| Cooling rate      | 50°C/h       |                                     |

Fig. 2 TG curve of CsPbBr₃ material
1.3 Characterization

Phase structure of the samples were analyzed by X-ray diffraction (Bruker D8, Germany) using CuKα radiation (λ=0.15406 nm) at room temperature. Crystal cutting was carried out by a diamond wire cutting machine (STX-1202A, China) using absolute alcohol as lubricant to prevent CsPbBr3 from moisture absorption. CsPbBr3 wafers are ground by 200 μm SiC powder and polished by 20 μm Al2O3 powder. Phase transition temperature is tested by Differential Scanning Calorimetry (Flash DSC 2+, China). Crystal transmittance and diffuse reflection are analyzed by ultraviolet visible near infrared spectrophotometer (LAMBDA, China).

2 Results and discussion

Benefit from zone melting temperature profile of the furnace, there are two outstanding advantages for CsPbBr3 crystal growth in this experiment: (i) The existing impurities in raw material could be removed from bottom to top gradually, as shown in Fig. 4(a). Some black impurities are noticed on tail part of the ingot; (ii) Most of the water could be excluded due to the special furnace temperature distribution, and the excluded water is re-condensed on the cold part of quartz tube, as shown in Fig. 4(b). Large size CsPbBr3 crystal with a dimension of about φ25 mm × 60 mm was shown in Fig. 5(a) and (b) are some samples cut from the ingot. The as-grown crystal and the cutting samples display orange color and look uniformity.

Fig. 6(a) is the XRD powder diffraction diagram of the as-grown crystal. It is found that all the diffraction patterns can be indexed as the room temperature CsPbBr3 phase (PDF#18-0364), indicating an Pnma space group, and the crystal lattices are calculated to be a= 0.8205 nm, b= 0.8250 nm and c= 1.1754 nm. To evaluate the crystallinity...
Fig. 6 XRD patterns of CsPbBr₃ crystal powders (a) and the rocking curve of CsPbBr₃ crystal of as-grown crystal, the double rocking curve was measured by DX-9BG X-ray orientation. Fig. 6(b) shows the rocking curve with the central peak at 10.75°, which corresponds to the (110) diffraction peak. The full width at half maximum of the peak (FWHM) is about 180 arc sec.

Fig. 7 exhibits the DSC thermal analysis results with temperature from 30 ℃ to 350 ℃. As the temperature is increased, there are two endothermic peaks at 89.1 ℃ and 132.9 ℃, respectively, which correspond to the phase transitions to tetragonal (P4/mmb) and cubic (Pm3m). On the contrary, as the temperature is decreased, two exothermic peaks appeared at 87.1 ℃ and 129.6 ℃, respectively. This result means the phase transitions of CsPbBr₃ crystal are reversible. Considering the slight different transform temperature, we define here that the average phase transition point $T_{OT}$ for Orthorhombic (Pnma) to Tetragonal (P4/mmb) is 88.1 ℃, and the value $T_{TC}$ for Tetragonal (P4/mmb) to Cubic (Pm3m) is 131.25 ℃.

Fig. 8 is the transmittance spectrum of CsPbBr₃ crystal in the range of 200 nm-2000 nm wavelength. It is noticed that the crystal is absolutely opaque under 543 nm which corresponds to its absorption edge. Then, the transmittance is rapidly raised as wavelength increasing. For example, when wavelength reaches 570 nm, the transmittance value arrives at 63.2%. Subsequently, as wavelength continuously increases, the transmittance increasing tendency becomes moderately, and the highest value is about 78.6% in the range of 600 nm-2000 nm wavelength. In fact, the insert figure showed good transmittance in visible light, which means the as-grown crystal has better quality than the samples in literatures[2,7].

Fig. 9(a) is the diffuse reflection spectroscopy of CsPbBr₃ powder in the range of 200 nm-1800 nm wavelength. It is noticed that the crystal is absolutely opaque under 543 nm which corresponds to its absorption edge. Then, the transmittance is rapidly raised as wavelength increasing. For example, when wavelength reaches 570 nm, the transmittance value arrives at 63.2%. Subsequently, as wavelength continuously increases, the transmittance increasing tendency becomes moderately, and the highest value is about 78.6% in the range of 600 nm-2000 nm wavelength. In fact, the insert figure showed good transmittance in visible light, which means the as-grown crystal has better quality than the samples in literatures[2,7].

Fig. 8 is the transmittance spectrum of CsPbBr₃ crystal in the range of 200 nm-2000 nm wavelength. According to Kubelka-Munk equation[12]:

$$F[R] = \frac{(1-R)^2}{2R}$$

Where $R$ is diffuse reflection ratio. The band gap $E_g$ of CsPbBr₃ can be induced from the relationship of $[F(R)h\nu]^{1/2}$ with $h\nu$ as CsPbBr₃ is considered to be a direct band gap semiconductor[2]. As a result, the $E_g$ of CsPbBr₃ is calculated to be 2.25 eV (in Fig. 9(b)).

In Table 2, we summarized the growth results of the present work compared with other CsPbBr₃ crystals grown by various methods. It is concluded that the crystal size in this work is the largest that implies such traveling zone melting method is indeed a simple and effective approach for CsPbBr₃ crystal preparation. Besides, some of their properties, including crystal structure, phase transition temperature and band gap are found basically the same, however, the present CsPbBr₃ crystal displays relative higher transmission performance, which proves this crystal growth technique is a better choice for high quality CsPbBr₃ crystal fabrication in the future.
3 Conclusions

In this work, a self-designed traveling zone melting method was adopted to grow CsPbBr₃ crystal and the CsPbBr₃ polycrystalline was synthesized in advance for impurities removing and moisture excluding due to the special temperature distribution. By optimizing growth conditions, a large size CsPbBr₃ crystal up to 25 mm in diameter and 60 mm in length was obtained. The as-grown crystal displays orange color and excellent transmittance. The crystal structure, phase transition point and band gap are investigated in accordance well with the literatures previously reported. The growth results imply the traveling zone melting method is indeed a better choice for large and high quality CsPbBr₃ crystal growth.

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移动区熔法生长全无机钙钛矿型 CsPbBr₃ 晶体及其性能研究

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摘 要: 利用自制移动区熔炉生长了 CsPbBr₃ 晶体, 先后采用相同工艺合成了高纯多晶原料以去除杂质和水分。通过工艺优化获得了大尺寸 CsPbBr₃ 晶体, 达到 φ25 mm × 60 mm。该晶体呈橘红色, 在 600~2000 nm 波长范围内具有透过率为 78.6%的优异透光性能。热分析表明, 所得 CsPbBr₃ 晶体在 88.1℃和 131.25℃时存在正交-四方和四方-立方相变。计算得到 CsPbBr₃ 晶体的带宽 $E_g = 2.25$ eV。上述结果表明移动区熔法是一种具有应用潜力的制备高质量大尺寸 CsPbBr₃ 晶体的生长方法。

关 键 词: 移动区熔法; CsPbBr₃ 晶体; 透过率; 带隙

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