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Growth and Characterization of All-inorganic Perovskite $CsPbBr_3$ Crystal by a Traveling Zone Melting Method

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Abstract: A self-designed traveling zone melting method was employed to fabricate perovskite $CsPbBr_3$ crystals, which is helpful for impurities removing and moisture excluding. A large-size $CsPbBr_3$ crystal with a dimension of ϕ25 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℃ and 131.25℃, 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 $CsPbBr_3$ crystal preparation.

Key words: traveling zone melting method; $CsPbBr_3$ crystal; transmittance; band gap

During the past several years, a series of all-inorganic version of the lead bromide perovskite ($CsPbX_3$, X= Cl, Br, I) has attracted great attention due to its outstanding performance and broad potential applications in opto-electronic fields[1-6]. Among them, cesium lead bromine ($CsPbBr_3$) is a representative material. For example, the mobility lifetime product $\mu\tau$ of $CsPbBr_3$ crystal for electrons could up to 1.7×10^{-3} cm^2/V that is comparable to the CdZnTe crystal, and the $\mu\tau$ value for holes is 1.3×10^{-3} cm^2/V which is about ten times higher than that of CdZnTe, such excellent properties make $CsPbBr_3$ 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, $CsPbBr_3$ 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 $CsPbBr_3$ crystal has become much significant. However, it is regrettable that the obtained $CsPbBr_3$ crystals are always in small size although many growth techniques have been employed in past years. For example, Stoumpos, *et al*[2] fabricated $CsPbBr_3$ crystal *via* a vertical Bridgman method, but the as-grown crystal is only about ϕ7 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 ϕ8 mm×58 mm. Rakita *et al*[11] produced $CsPbBr_3$ crystals through a solution-grown method under a low temperature condition (90℃–110℃), however, the largest crystal is millimeter-sized. Therefore, it is obvious that some novel techniques are still expected to grow $CsPbBr_3$ crystal. In this work, a self-designed traveling zone melting method is introduced and a large-size $CsPbBr_3$ crystal about ϕ25 mm× 60 mm in dimensions is successfully produced, besides, the crystal quality and its properties are also investigated.

1 Experiment

1.1 Synthesis of $CsPbBr_3$ polycrystalline

$CsPbBr_3$ polycrystalline was synthesized from 99.99% purity of CsBr and $PbBr_2$ powders with mole ratio of 1∶1 (the total weight was about 132 g). Considering CsBr and $PbBr_2$ were both water sensitive, the weighting and loading process was conducted under N_2 atmosphere in a glove box. The raw materials were loaded into a ϕ25 mm quartz tube which was carefully cleaned by

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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℃ that was about 50℃ higher than the melting point of $CsPbBr_3$. 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 $CsPbBr_3$ synthesis homogeneous. Finally, the furnace was naturally cooled to room temperature. Table 1 lists the parameters for $CsPbBr_3$ polycrystalline synthesis. Fig. 1 is the obtained $CsPbBr_3$ 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 $CsPbBr_3$ was suggested to be clarified that would do benefit to guide the choice of furnace temperature. Fig. 2

Table 1 Conditions for $CsPbBr_3$ polycrystalline synthesis and crystal growth

Materials	Method	Conditions
$CsPbBr_3$ polycrystalline Synthesis	Synthesis method	Rocking technique
	Raw material	99.99% CsBr and $PbBr_2$, 132 g
	Crucible	Quartz tube
	Vacuum	<10^{-3} Pa
	Synthesis temperature	620℃
	Rocking rate	30 r/min
	Rocking time	20 min
$CsPbBr_3$ crystal growth	Growth method	Traveling zone melting
	Crucible	Quartz tube
	Vacuum	<10^{-3} Pa
	Furnace temperature	585℃
	Temperature gradient	30℃/cm–40℃/cm
	Growth rate	1.0 mm/h
	Cooling rate	50℃/h

Fig. 1 Synthesized $CsPbBr_3$ polycrystalline

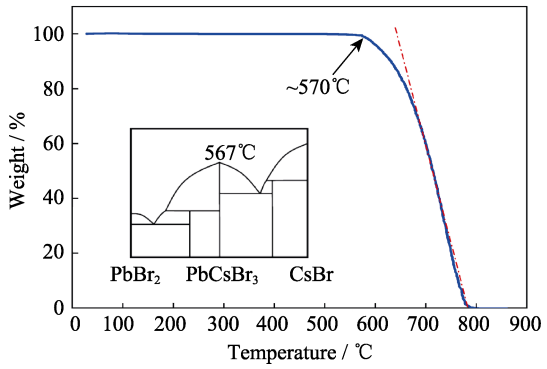

Fig. 2 TG curve of $CsPbBr_3$ material

shows the relationship between weight percentage and temperature examined by thermogravimetry equipment (TG-DTA 8121, Japan) with 5℃/min increasing rate. It was observed no weight losing took place from room temperature to 570℃. The result means $CsPbBr_3$ is stable under melting point (see inserted $PbBr_2$-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, $CsPbBr_3$ was totally exhausted as temperature reached 800℃. Such behavior illustrated that $CsPbBr_3$ was easily volatilized above melting point. Therefore, the furnace temperature for $CsPbBr_3$ 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℃. Fig. 3(b) is the temperature profile along vertical direction, and the melting zone was only 20 mm–25 mm in height. $CsPbBr_3$ 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 $CsPbBr_3$ polycrystalline/melt. After the $CsPbBr_3$ 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, $CsPbBr_3$ crystal growth was started and the temperature gradient in the solid-liquid interface was about 30-40℃/cm. Finally, after all of the solution was crystallized, the furnace was cooled down to room temperature at a rate of 50℃/h. The parameters for $CsPbBr_3$ crystal growth were listed in Table 1.

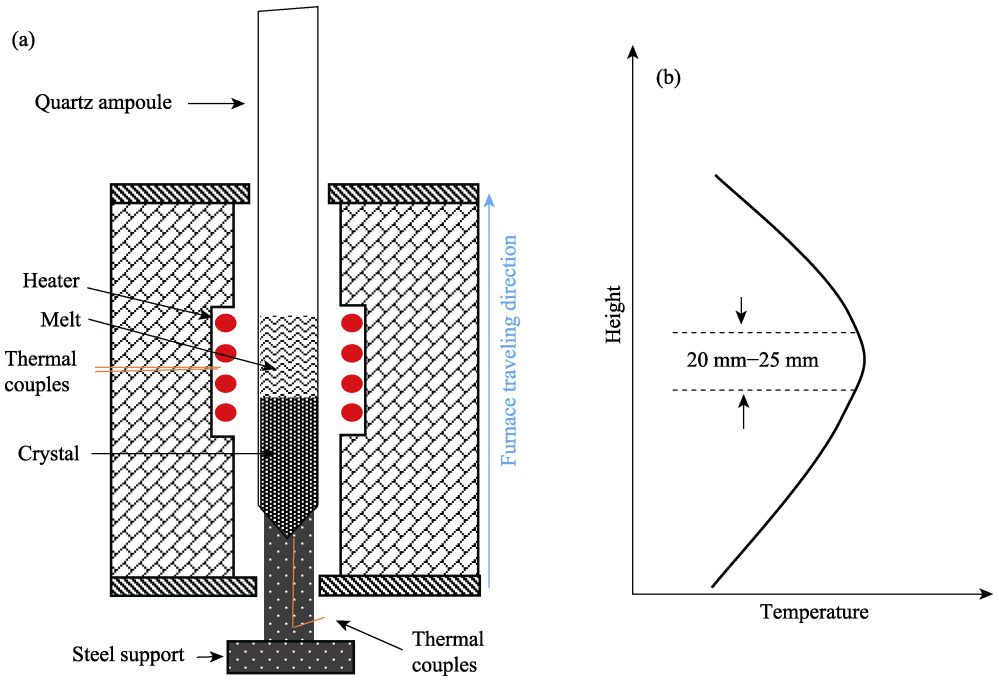

Fig. 3　Schematic diagram of $CsPbBr_3$ crystal growth (a) and temperature profile along vertical direction in the furnace (b)

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 $CsPbBr_3$ from moisture absorption. $CsPbBr_3$ wafers are ground by 200 μm SiC powder and polished by 20 μm Al_2O_3 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 $CsPbBr_3$ 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 $CsPbBr_3$ 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

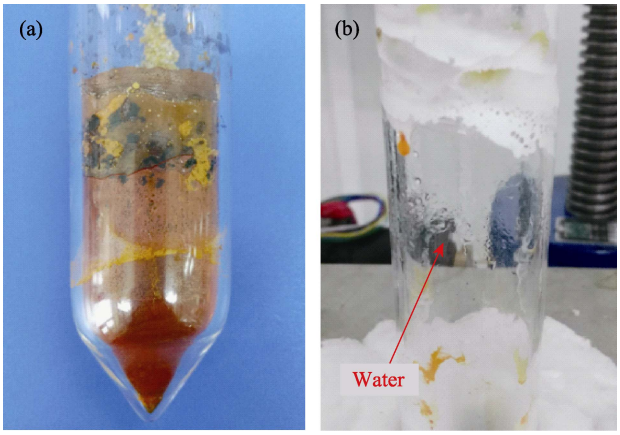

Fig. 4　As-grown $CsPbBr_3$ crystal in quartz tube (a) and attached water on the inside wall of quartz (b)

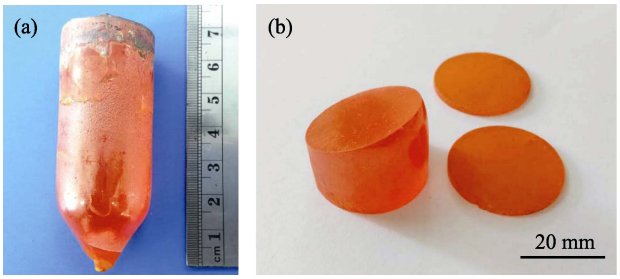

Fig. 5　As-grown $CsPbBr_3$ crystal (a) and some cutting samples (b)

the as-grown crystal. It is found that all the diffraction patterns can be indexed as the room temperature $CsPbBr_3$ 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 crystallity

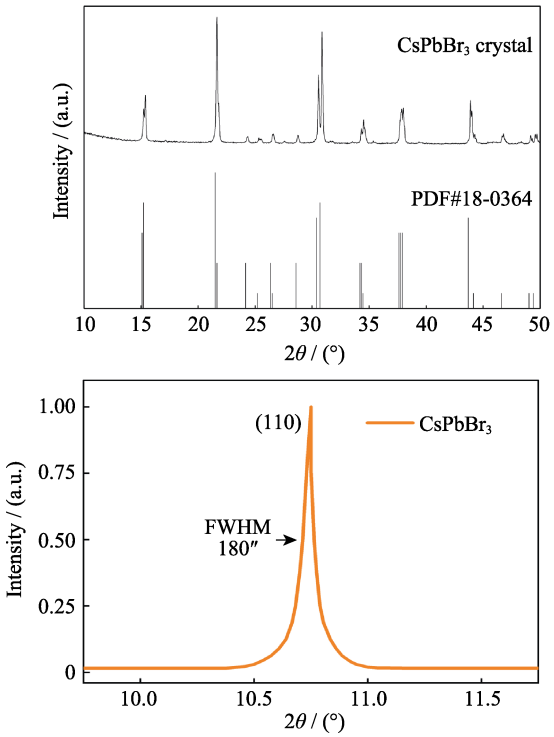

Fig. 6 XRD patterns of $CsPbBr_3$ crystal powders (a) and the rocking curve of $CsPbBr_3$ crystal

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/mbm) 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 $CsPbBr_3$ 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/mbm) is 88.1℃, and the value T_{TC} for Tetragonal (P4/mbm) to Cubic (Pm3m) is 131.25℃.

Fig. 8 is the transmittance spectrum of $CsPbBr_3$ 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 $CsPbBr_3$ powder in the range of 200 nm-1800 nm wavelength. According to Kubelka-Munk equation[12]:

$$F[R]=(1-R)^2/2R \quad (1)$$

Where R is diffuse reflection ratio. The band gap E_g of $CsPbBr_3$ can be induced from the relationship of $[F(R)hv]^{1/2}$ with hv as $CsPbBr_3$ is considered to be a direct band gap semiconductor[2]. As a result, the E_g of $CsPbBr_3$ 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 $CsPbBr_3$ 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 $CsPbBr_3$ crystal preparation. Besides, some of their properties, including crystal structure, phase transition temperature and band gap are found basically the same, however, the present $CsPbBr_3$ crystal displays relative higher transmission performance, which proves this crystal growth technique is a better choice for high quality $CsPbBr_3$ crystal fabrication in the future.

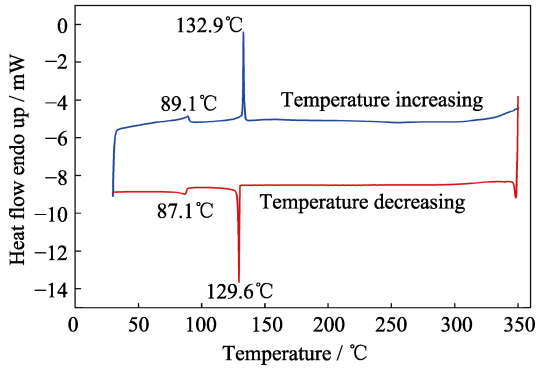

Fig. 7 DSC thermal analysis of $CsPbBr_3$ crystal

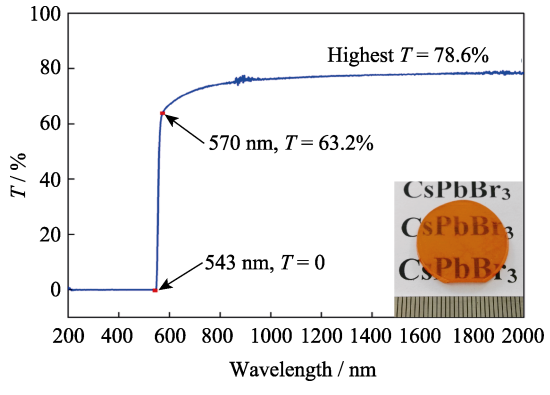

Fig. 8 Transmittance spectrum of $CsPbBr_3$ crystal

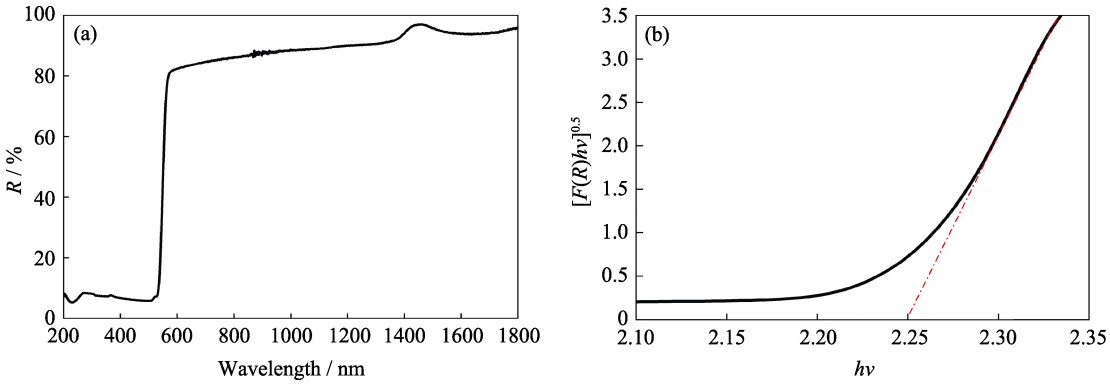

Fig. 9　Diffuse reflection spectroscopy of $CsPbBr_3$ (a) and transformed Kubelka−Munk spectrum of $CsPbBr_3$ (b)

Table 2　Growth results and properties of $CsPbBr_3$ crystal

Growth method	Crystal size/mm^3	Color	Band gap, E_g/eV	Highest transmittance/%	Phase transition temperature/℃		Ref.
Traveling zone melting	ϕ25×60	Orange	2.250	78.6	Orthorhombic→ Tetragonal 88.1	Tetragonal→ Cubic 131.25	This work
Vertical Bridgman	ϕ7×12	Orange	2.250	–	88	130	[2]
Solution grown	7×2×4	Orange	2.254	–	–	–	[11]
Electronic dynamic gradient	ϕ8×58	Orange	2.252	75	87	127	[10]

3　Conclusions

In this work, a self-designed traveling zone melting method was adopted to grow $CsPbBr_3$ crystal and the $CsPbBr_3$ polycrystalline was synthesized in advance for impurities removing and moisture excluding due to the special temperature distribution. By optimizing growth conditions, a large size $CsPbBr_3$ 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 $CsPbBr_3$ crystal growth.

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移动区熔法生长全无机钙钛矿型 $CsPbBr_3$ 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 $CsPbBr_3$ 晶体, 事先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 $CsPbBr_3$ 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达 78.6%的优异透光性能。热分析表明, 所得 $CsPbBr_3$ 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 $CsPbBr_3$ 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 $CsPbBr_3$ 晶体的生长方法。

关 键 词: 移动区熔法; $CsPbBr_3$ 晶体; 透过率; 带隙

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