

## Article

# Purification and Improved Photoelectric Properties of Lead-Free Perovskite $\text{Cs}_3\text{Bi}_2\text{Br}_9$ Crystals

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**Abstract:** The lead-free halide perovskite  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  is a promising semiconductor material for room-temperature X-ray detection due to its excellent properties. However, material purity and crystal quality still limit the use of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals as detectors. In this work, we present a highly efficient purification method using continuous vacuum extraction to sublimate  $\text{BiBr}_3$  precursors for  $\text{Cs}_3\text{Bi}_2\text{Br}_9$ . Impurity analysis via inductively coupled plasma mass spectroscopy showed that the purification method successfully removed most of the impurities in  $\text{BiBr}_3$  precursors and improved the purity by at least one order of magnitude. Centimeter-sized  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  single crystals were grown by the vertical Bridgman method. The improved properties after purification were confirmed by UV-Vis-NIR spectra, infrared transmittance, and current–voltage (I–V) measurements. The results showed that the average transmittance of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals significantly increased from 62% to 75% in the 0.5–20  $\mu\text{m}$  spectral range. Additionally, the resistivity increased by nearly three orders of magnitude from  $5.0 \times 10^9 \Omega\cdot\text{cm}$  to  $2.2 \times 10^{12} \Omega\cdot\text{cm}$ , meaning the material will have low leakage currents and be suitable for developing applications for room temperature radiation detection.

**Keywords:** purification; lead-free perovskites;  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals; trace element analysis; Bridgman method



**Citation:** Nan, W.; Li, C.; Zhou, B.; Fu, Q.; Li, D.; Yu, H.; Hu, Z.; Wu, Y. Purification and Improved Photoelectric Properties of Lead-Free Perovskite  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  Crystals. *Crystals* **2023**, *13*, 871. <https://doi.org/10.3390/cryst13060871>

Academic Editor: Maria Gazda

Received: 9 May 2023

Revised: 23 May 2023

Accepted: 24 May 2023

Published: 26 May 2023



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## 1. Introduction

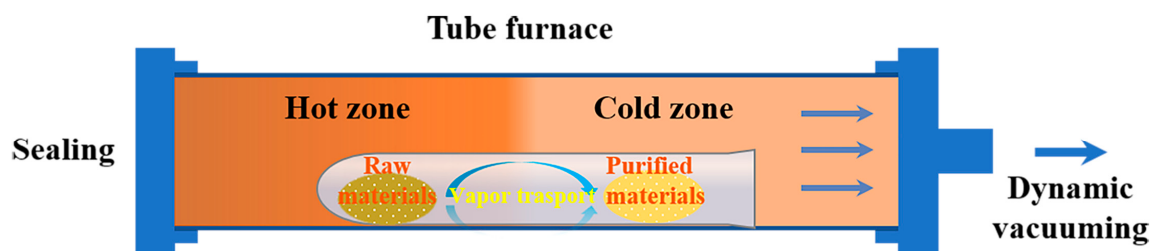
Bismuth-based halide perovskite crystals have sparked great interest due to their excellent physical properties and promising applications in X/γ-ray detection [1,2], photovoltaic devices [3,4], ultraviolet photodetectors [5,6], and light-emitting diodes [7,8], etc. As with most halide perovskite crystals, their photoelectric properties, such as resistivity, carrier mobility lifetime product ( $\mu\tau$ ), band gap, and optical transmittance, are strongly dependent on chemical impurities as well as crystalline quality. Therefore, purification techniques, such as the low-cost mass production of halide perovskite crystals with good properties, are in high demand. Over the past few decades, different purification techniques have been developed for the fabrication of high-quality crystals (zone refining method [9,10], physical vapor transport method-PVT [11–13], recrystallization [14,15]), which greatly improved the optical and electrical properties of crystals. Among these techniques, the PVT method is widely used because of its cost-effectiveness and simplicity. During the PVT process, the initial material is usually sealed in a quartz tube and placed in a high-temperature zone, while the purified material is deposited in a low-temperature zone. Zheng et al. [12] purified thallium bromide (TlBr) salt using the PVT method, and trace impurities after purification were reduced to the ppb/ppm level. The resistivity of the resultant TlBr crystals increased from  $2.58 \times 10^8 \Omega\cdot\text{cm}$  to  $3.98 \times 10^9 \Omega\cdot\text{cm}$  and the average infrared transmittance increased from 27% to 48%. Kwon et al. [13] analyzed  $\text{Hg}_2\text{Br}_2$  powders purified by the PVT method and found that the purity of  $\text{Hg}_2\text{Br}_2$  increased from 4 N (99.99%) to 5 N (99.999%). Subsequently, high-quality  $\text{Hg}_2\text{Br}_2$  crystals with little lattice distortions were obtained

using purified raw materials. Lin et al. [16] used the PVT method to remove most of the impurities in  $\text{TlI}_4$  raw materials, as evidenced by GDMS analysis, resulting in the growth of high-performance  $\text{Tl}_6\text{SI}_4$  crystals with a high resistivity of  $5 \times 10^{12} \Omega \cdot \text{cm}$  and a high electron mobility of  $35 \pm 7 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ , achieving spectroscopic detection with an energy resolution of 27% for  $^{241}\text{Am}$   $\alpha$ -particles. It can be seen that removing impurities from raw materials using the PVT method can remarkably improve the photoelectric properties of semiconducting crystals. However, for raw materials with a low vapor pressure, the purification effectiveness of the PVT method is not sufficiently effective.

Bismuth-based halide perovskite  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals are the newly discovered promising candidates for X-ray detection due to their excellent properties [17,18]. Nevertheless, there are still great challenges in preparing low-cost, large-volume, high quality  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals for X-ray imaging systems. Herein, the purification technique was utilized to increase the purity of raw materials for the low-cost production of large-sized  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals with high performance. For  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals, the precursor reagents ( $\text{BiBr}_3$ ) have low vapor pressure [19], so a modified and high-efficient PVT method, namely the dynamic vacuum vapor transport method, was developed to purify the  $\text{BiBr}_3$  precursors, indirectly improving the purity of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals. The effectiveness of this purification process was evaluated via trace elemental analysis of  $\text{BiBr}_3$  precursors before and after purification. In addition, single, centimeter-sized  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals were grown by the Bridgman method using the purified  $\text{BiBr}_3$  precursors to further assess the effectiveness of the purification method in improving optical and electric properties. The effective purification process applied to the  $\text{BiBr}_3$  precursors resulted in an increased purity of at least one order of magnitude, increased resistivity of two orders of magnitude, and increased optical transmittance from 62% to 75%.

## 2. Materials and Methods

The precursors for the synthesis of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  polycrystals were  $\text{CsBr}$  and  $\text{BiBr}_3$ . The purification of  $\text{BiBr}_3$  precursors can indirectly reduce impurities in  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals grown later. Because of the low vapor pressure of  $\text{BiBr}_3$ , the conventional purification by physical vapor transport was not efficient enough for the purification of  $\text{BiBr}_3$ . In this work, we proposed a new and modified vapor transport (dynamic vacuum vapor transport method (DVT)) for the purification of  $\text{BiBr}_3$ . The DVT purification method differed from the traditional one in two aspects: the quartz ampule was not sealed and the furnace chamber providing the heat field was continuously vacuumed throughout the purification. It was worth noting that vacuuming was implemented from the cold end of the furnace. In this way, the raw materials were kept in a negative pressure environment (0.1–0.3 Pa) during the purification process, which greatly increased the sublimation rate of the raw materials so that the raw materials could be sublimated quickly at a low-temperature range (180–210 °C) to achieve the desired purification results. Figure 1 illustrates the principle of the DVT purification method. The detailed purification process of  $\text{BiBr}_3$  precursors using DVT is as follows. Commercial  $\text{BiBr}_3$  powders with a purity of 99% were loaded into the bottom of the quartz ampule in an argon-filled glovebox and then the ampule was fixed into a five-zone horizontal tube furnace to be subject to purification. The bottom and open end of the ampule were placed in the hot zone and cold zone, respectively. The temperature in the hot zone was below the melting point of  $\text{BiBr}_3$  and the temperature difference between these two zones was at least greater than 50 °C, which created a desirable temperature gradient. During purification, the furnace chamber was continuously vacuumed to less than 1 Pa, which markedly enhanced the sublimation and vapor transport of the  $\text{BiBr}_3$  powders. Finally, the purified  $\text{BiBr}_3$  was deposited near the open end of the ampule and collected for trace element analysis and crystal growth.



**Figure 1.** The principle of the dynamic vacuum vapor transport method for the purification of  $\text{BiBr}_3$ .

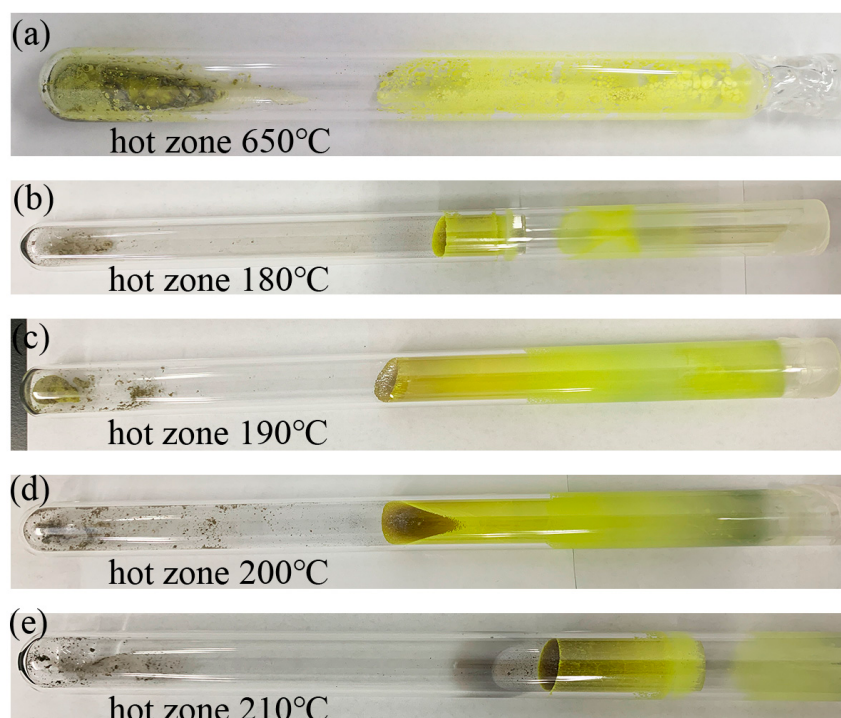
Before crystal growth, the quartz ampule with an inner diameter of 15 mm and a thickness of 2.5 mm was first cleaned with acetone, aqua regia, and deionized water, in turn.  $\text{CsBr}$  (3 N) powders and the purified  $\text{BiBr}_3$  with a molar ratio of 3: 2 were loaded into the cleaned ampule. The loaded ampule was sealed using an  $\text{H}_2\text{-O}_2$  torch at a dynamic vacuum of  $2\text{--}4 \times 10^{-5}$  Pa and then placed in a rocking furnace where polycrystalline  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  was synthesized at a soaking temperature of  $650^\circ\text{C}$ . Subsequently, the ampule with polycrystalline  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  was loaded into a six-zone growth furnace, and the growth program was run in the pre-designed temperature field with a growth temperature of  $630\text{--}635^\circ\text{C}$  and a temperature gradient of  $10\text{--}30\text{ K/cm}$  near the growth interface. During the growth, the translation rate of the heater was  $0.8\text{--}1.5\text{ mm/h}$ . After growth, the furnace temperature was slowly cooled to room temperature to reduce the thermal stress that induced structural defects (cracks, dislocations, etc.).

The as-grown  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  ingots were sliced perpendicular to the growth direction into wafers with dimensions of  $5 \times 5 \times 2\text{ mm}^3$  using a diamond wire saw (STX-202A, KEJING, Shenyang, China). The wafers were mechanically polished using SiC sandpapers and water-free  $\text{Al}_2\text{O}_3$  suspensions with a particle size of  $0.03\text{ }\mu\text{m}$  to obtain a mirror surface for analysis. The optical properties of the polished samples were characterized by a UV-Vis-NIR spectrophotometer (UH4150, HITACHI, Tokyo, Japan) with a scanning range of  $190\text{--}2500\text{ nm}$  and a Nicolet iS50 spectrometer (ThermoFisher, Waltham, MA, USA) with a scanning range of  $500\text{--}4000\text{ cm}^{-1}$ . Au electrodes were thermally evaporated on the top and bottom surface of the polished samples and then the I-V characteristic curves were obtained using a Keithley 6514B electrometer (Tektronix, Johnstown, OH, USA). The structure and crystalline quality of the grown  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals were investigated by X-ray diffraction with  $\text{Cu-K}\alpha 1$  radiation (XRD, Rigaku, Tokyo, Japan). In addition, impurities in  $\text{BiBr}_3$  precursors before and after purification were analyzed via inductively coupled plasma mass spectroscopy (ICP-MS, Agilent, Santa Clara, CA, USA) to evaluate the effectiveness of purification.

### 3. Results

For comparison, the traditional physical vapor transport method was used to purify  $\text{BiBr}_3$  precursors.  $\text{BiBr}_3$  powders with a weight of 10 g were sealed in the quartz ampule with a vacuum of  $2\text{--}4 \times 10^{-5}$  Pa. During purification, the hot zone was set to  $650^\circ\text{C}$  and held for 20 h, while the cold zone was set below the boiling point ( $462^\circ\text{C}$ ) of  $\text{BiBr}_3$  to facilitate  $\text{BiBr}_3$  vapor transport. The results showed that only a small number of  $\text{BiBr}_3$  powders were vaporized due to their low vapor pressure, and they were deposited in the cold end region of the ampule (Figure 2a), meaning the purification effect was not achieved by the traditional physical vapor transport method. To increase the vapor transport of  $\text{BiBr}_3$  powders at low temperatures, the dynamic vacuum vapor transport method (DVT method) was developed to purify  $\text{BiBr}_3$ , and the effect of temperature on purification was investigated. The hot zone was set to  $180^\circ\text{C}$ ,  $190^\circ\text{C}$ ,  $200^\circ\text{C}$ , and  $210^\circ\text{C}$ , respectively, while the cold zone was at least  $50^\circ\text{C}$  lower than the hot zone. It turned out that  $\text{BiBr}_3$  powders with a weight of 10 g began to sublime when the temperature in the hot zone reached  $180^\circ\text{C}$ , and then sublimated completely after holding for 5 h. The gray impurities from the initial  $\text{BiBr}_3$  powders remained at the bottom of the ampule in the hot zone, while the

purified  $\text{BiBr}_3$  transported by gasification was deposited near the open end of the ampule in the cold zone (Figure 2b). An optimal result was obtained when the temperature in the hot zone was increased to  $190^\circ\text{C}$ . It took only 6 h to purify the  $\text{BiBr}_3$  with a weight of 20 g, and the color of  $\text{BiBr}_3$  deposited at the cold end was bright yellow (Figure 2c), indicating that its purity was improved. If the temperature was further raised to  $200^\circ\text{C}$  or  $210^\circ\text{C}$ , the purification time was shortened to less than 4 h, but a small number of impurities were also transported along with the  $\text{BiBr}_3$  vapor phase and deposited on the cold end (Figure 2d,e), which significantly deteriorated the purity of the raw materials.

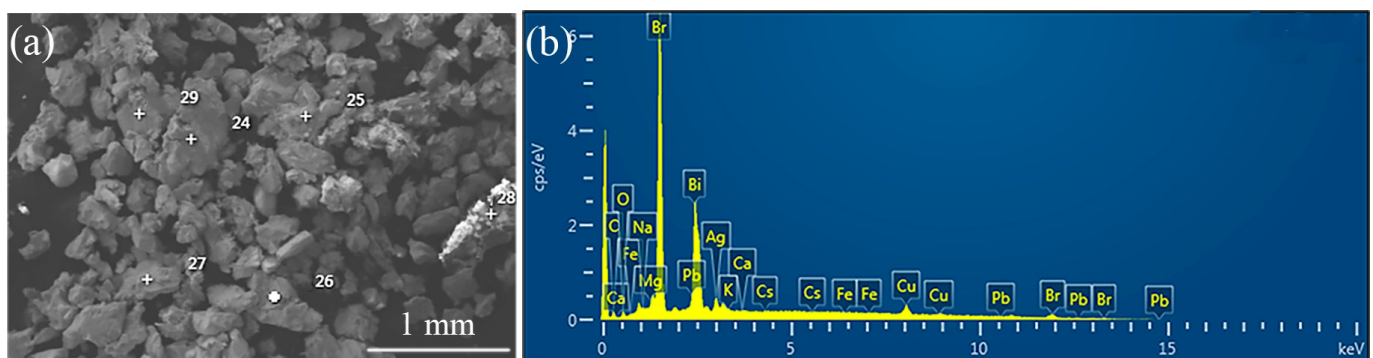


**Figure 2.** Purification of  $\text{BiBr}_3$  precursors by the dynamic vacuum vapor transport method at different temperatures (a)  $650^\circ\text{C}$ , 10 g  $\text{BiBr}_3$ , using the traditional physical vapor transport method, (b)  $180^\circ\text{C}$ , 10 g  $\text{BiBr}_3$ , (c)  $190^\circ\text{C}$ , 20 g  $\text{BiBr}_3$ , (d)  $200^\circ\text{C}$ , 20 g  $\text{BiBr}_3$ , (e)  $210^\circ\text{C}$ , 20 g  $\text{BiBr}_3$ .

Table 1 shows impurity concentrations in  $\text{BiBr}_3$  precursors before and after purification using the DVT method. It shows that the DVT method is highly effective in eliminating impurity elements, Na, K, Ca, Mg, Al, Fe, Cu, Ag, and Pb. The concentration of P increased after purification, which is attributed to the high volatility of P impurity. Before purification, the total impurity concentration was 6649.14 ppm, and its corresponding purity was 99.33%. However, after purification, the total impurity concentration was sharply reduced to 727.24 ppm, and the corresponding purity was 99.93%, indicating that the purity of  $\text{BiBr}_3$  had improved by an order of magnitude. In addition, the gray residual impurities remaining after purification were analyzed by a scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDS, FEI, Portland, OR, USA), as shown in Figure 3. The impurity elements and their contents in the grey residues were shown in Table 2. As can be seen, five main impurities were identified: C, O, Cu, Ag, and Na. These impurities were not uniformly distributed in the grey residues, with average mass fractions of 7.09% (C), 1.87% (O), 5.49% (Cu), 2.84% (Ag), and 0.12% (Na), respectively. The results of the impurity analysis indicated that the DVT method was quite effective in removing impurity elements, C, O, Cu, Ag, Na, K, Ca, Mg, Al, Fe, and Pb, and could improve the purity of  $\text{BiBr}_3$  by at least one order of magnitude, which would substantially decrease impurities in the resultant  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals.

**Table 1.** ICP-MS analysis of BiBr<sub>3</sub> precursors before and after purification.

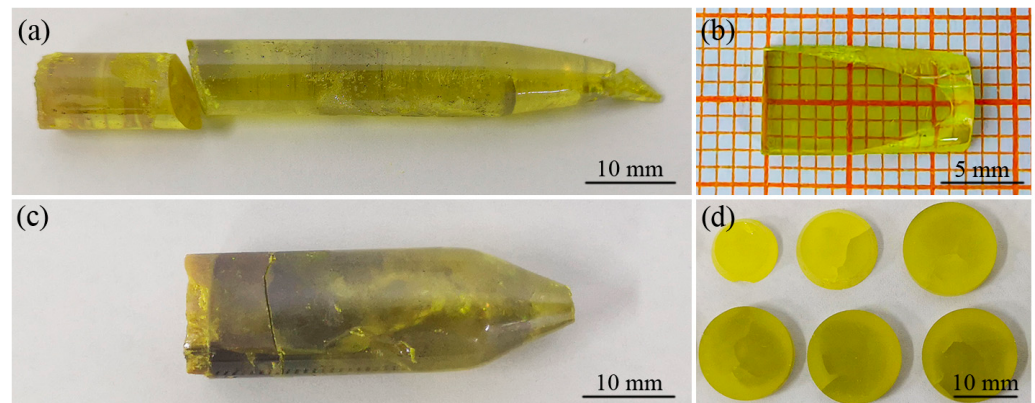
| Element | Before Purification (ppm) | After Purification (ppm) | Element | Before Purification (ppm) | After Purification (ppm) |
|---------|---------------------------|--------------------------|---------|---------------------------|--------------------------|
| Li      | 0.79                      | 0.14                     | As      | 0.09                      | 0.16                     |
| Be      | 0.02                      | <0.01                    | Se      | 22.21                     | 10.12                    |
| Na      | 1402.32                   | 183.38                   | Rb      | 19.94                     | 5.93                     |
| Mg      | 167.11                    | 53.71                    | Sr      | 1.90                      | 0.92                     |
| Al      | 138.01                    | 26.01                    | Y       | 0.15                      | 0.11                     |
| P       | 5.69                      | 9.43                     | Zr      | 1.83                      | 0.58                     |
| K       | 562.58                    | 92.81                    | Ag      | 984.57                    | 78.64                    |
| Ca      | 1075.56                   | 49.87                    | In      | 0.02                      | 0.03                     |
| V       | 2.22                      | 1.54                     | Sn      | 2.06                      | 1.98                     |
| Cr      | 2.25                      | 2.70                     | Sb      | 0.16                      | 0.12                     |
| Mn      | 1.19                      | 0.87                     | I       | 36.75                     | 14.64                    |
| Fe      | 694.78                    | 48.82                    | La      | 64.30                     | 21.43                    |
| Cu      | 1283.29                   | 26.45                    | Ce      | 3.88                      | 1.58                     |
| Zn      | 19.51                     | 7.11                     | Pb      | 153.49                    | 86.49                    |
| Ga      | 0.50                      | 0.15                     | Sc      | 1.97                      | 1.52                     |

**Figure 3.** SEM-EDS analysis of the residues left in the hot zone after purification (a) SEM image, (b) EDS spectra.**Table 2.** Impurities in the grey residues left in the hot zone after purification.

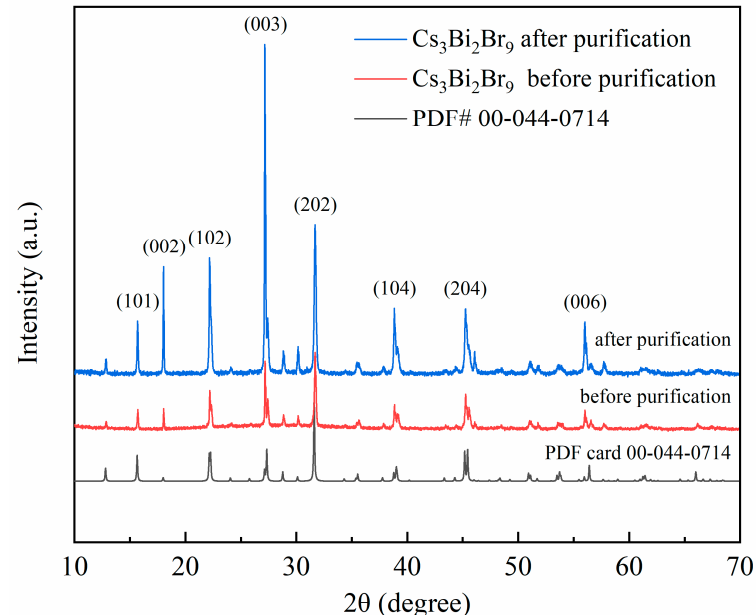
| Element | Position 1 (wt%) | Position 2 (wt%) | Position 3 (wt%) | Position 4 (wt%) | Position 5 (wt%) | Average (wt%) |
|---------|------------------|------------------|------------------|------------------|------------------|---------------|
| C       | 4.72             | 9.82             | 6.78             | 5.01             | 9.13             | 7.09          |
| O       | 0                | 1.46             | 0                | 2.14             | 5.76             | 1.87          |
| Cu      | 18.19            | 0                | 2.18             | 6.4              | 0.67             | 5.49          |
| Ag      | 2.75             | 0.23             | 5.64             | 4.66             | 0.9              | 2.84          |
| Na      | 0                | 0.13             | 0                | 0.27             | 0.18             | 0.12          |

Polycrystalline Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> was synthesized by a direct, stoichiometric chemical reaction of CsBr and BiBr<sub>3</sub> precursors and then used for crystal growth in a vertical Bridgman furnace. Figure 4a shows a single Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> crystal ingot with a diameter of 8 mm and a length of about 60 mm, grown by the Bridgman method using the purified BiBr<sub>3</sub> precursors. It can be seen that the ingot was transparent under ambient light, and the bright yellow color of the entire ingot was uniform (Figure 4a,b), suggesting that the grown crystals may have a good crystalline quality. However, using the unpurified BiBr<sub>3</sub> precursors, the grown Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> ingot with a diameter of 15 mm and a length of about 50 mm was polycrystalline and appeared opaque under ambient light (Figure 4c). The color of the ingot was inhomogeneous, being bright yellow at the tip and dark yellow at the tail (Figure 4d). The color inhomogeneity and the appearance of grain boundaries were attributed to

impurities and their segregation occurring in the melt during crystal growth. A similar result was observed by Hayashi [11] et al. In addition, XRD patterns of the grown  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals are shown in Figure 5, and all diffraction peaks were consistent with the standard PDF card (number: 00-044-0714), indicating that the grown crystals have a high phase purity and hexagonal structure. However, it was worth noting that the intensity of the diffraction peaks was significantly enhanced for the purified crystals, which generally indicates that the crystal has a good crystalline quality [20–22]. Therefore, these results demonstrated that it was beneficial to obtain single, high-quality, transparent  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals by purifying  $\text{BiBr}_3$  precursors to reduce impurities.



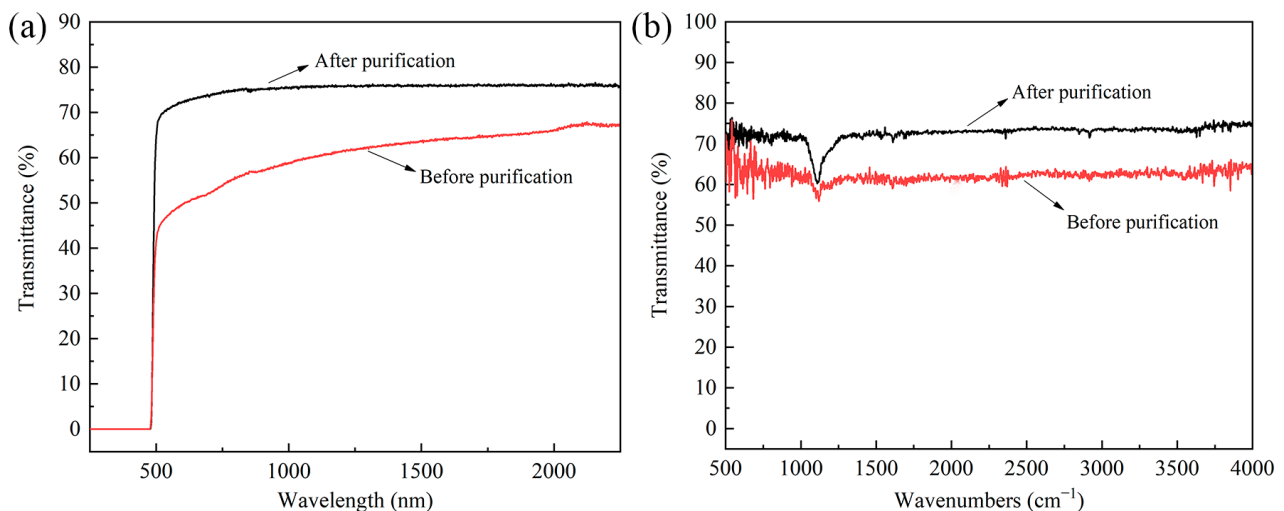
**Figure 4.**  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals grown from  $\text{BiBr}_3$  precursors before and after purification (a,b) after purification, (c,d) before purification.



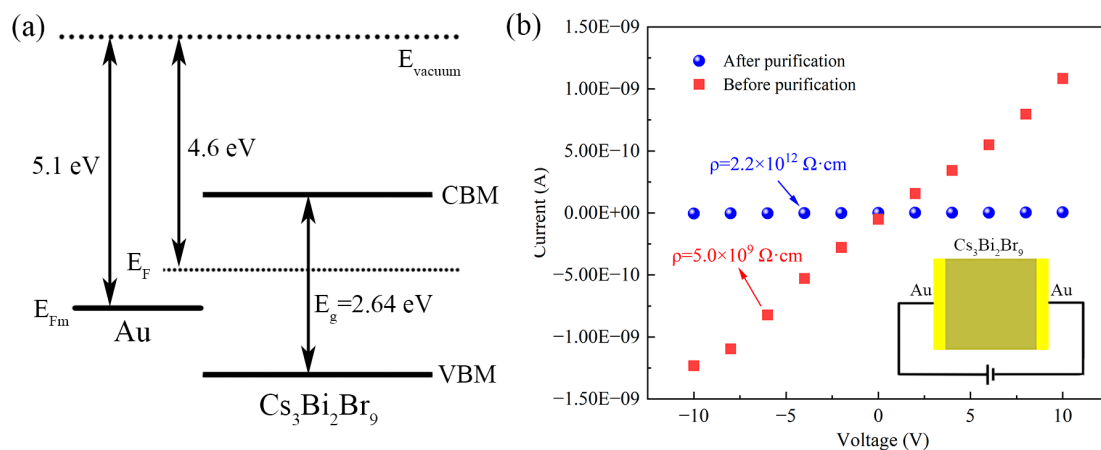
**Figure 5.** XRD patterns of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals before and after purification.

The optical characteristics of the grown  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals in the wavelength range of 0.2–20  $\mu\text{m}$  are shown in Figure 6. The UV-Vis-NIR spectra showed that the purified  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals had smaller absorption and larger transmittance in the wavelength range of 0.5–1.0  $\mu\text{m}$  compared to the unpurified  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals (Figure 6a), which may be attributed to the reduction of impurities after purification. In compound semiconductors, impurities usually acted as donor or acceptor defects, introduced corresponding donor or acceptor levels into the bandgap [23–25], such as Na (0.059 eV), Cu (0.22 eV), Ag (0.15 eV), Al (0.08 eV), Pb (1.28 eV), etc., and excited them to a higher level by absorbing photons

after illumination, which has a negative impact on the transmittance [26–28]. Therefore, the unpurified  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals with a high concentration of impurities exhibited strong absorptions, resulting in a low transmittance in the 0.5–1.0  $\mu\text{m}$  spectral range. It was also found that the average infrared transmittance of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals increased significantly from 62% to 75% after purification (Figure 6b). In the case of infrared irradiation, the infrared transmittance of the crystal is dominated by the absorption of free carriers [15], which are scattered by phonons, and then they transfer energy from the phonons to the lattices. Impurity ions in  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals resulted in the formation of lone electrons and holes. After absorbing photon energy, the lone electrons and holes may easily escape the bondage of impurity ions and become free carriers. That is to say, the higher the impurity concentration, the more free carriers will be formed. As a result, impurities were prominently reduced in the grown  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals after purification, resulting in a decrease in absorption and an increase in infrared transmittance. In addition, the increase in free carrier concentration caused by impurities led to a remarkable decrease in the resistivity of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals, which was confirmed by subsequent I–V measurements. To evaluate the resistivity, Au/ $\text{Cs}_3\text{Bi}_2\text{Br}_9$ /Au devices were fabricated based on  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  single crystals. The energy band diagram of the Au/ $\text{Cs}_3\text{Bi}_2\text{Br}_9$ /Au structure was shown in Figure 7a. The work function and the bandgap of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals are 4.6 eV and 2.64 eV, respectively [29], and the work function of Au is 5.1 eV [30]. The I–V characteristic curves of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals under a voltage range from  $-10$ – $10$  V were shown in Figure 7b. The resistivity of the purified crystals increased by nearly three orders of magnitude from  $5.0 \times 10^9 \Omega\cdot\text{cm}$  to  $2.2 \times 10^{12} \Omega\cdot\text{cm}$ , suggesting the material will have low leakage currents and be a good candidate for radiation detectors. Similar results have been observed in the literature [12,31–33], where it has been shown that the resistivity of materials decreased, or the conductivity increased, as the impurity concentration increased. The above results indicate that the DVT method has a high effectiveness of purification for  $\text{BiBr}_3$  precursors and could dramatically reduce the impurities in the resultant  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals, greatly improving the photoelectric properties.



**Figure 6.** Optical properties of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals before and after purification (a) optical absorption and transmission spectra in UV-Vis-NIR bands, (b) infrared transmission spectra.



**Figure 7.** I–V characteristic curves of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals before and after purification (a) the energy band diagram of the  $\text{Au}/\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{Au}$  structure, (b) I–V characteristic curves of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals. The inset shows a schematic diagram of the  $\text{Au}/\text{Cs}_3\text{Bi}_2\text{Br}_9/\text{Au}$  structure.

#### 4. Conclusions

In this work, the dynamic vacuum vapor transport (DVT) method was developed to purify  $\text{BiBr}_3$  precursors. ICP-MS impurity analysis showed that after purification, the purity of  $\text{BiBr}_3$  precursors increased by at least one order of magnitude, and the total impurity concentration, excluding carbon and oxygen, decreased significantly from 6649.14 ppm to 727.24 ppm. In addition, centimeter-sized  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals were grown using the vertical Bridgman method using  $\text{BiBr}_3$  precursors before and after purification. It was found that the  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  ingot grown with unpurified  $\text{BiBr}_3$  was opaque and changed colors from bright yellow at the tip to dark yellow at the tail, which may have been caused by impurities and their segregation. However, with purified  $\text{BiBr}_3$ , the grown ingot was transparent and uniformly bright yellow in color. Further studies on photoelectric properties showed that the average transmittance of  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  crystals increased prominently from 62% to 75% in the 0.5–20  $\mu\text{m}$  spectral range after purification, and the resistivity increased by nearly three orders of magnitude from  $5.0 \times 10^9 \Omega\cdot\text{cm}$  to  $2.2 \times 10^{12} \Omega\cdot\text{cm}$ .

**Author Contributions:** Methodology, W.N. and D.L.; investigation, W.N. and C.L.; validation, W.N. and B.Z.; data curation, W.N. and Q.F.; writing—original draft preparation, W.N.; writing—review and editing, B.Z. and H.Y.; project administration, B.Z., Z.H. and Y.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Natural Science Foundation of China (grant numbers 51902224, 51890864, and 51890865).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare that they have no conflict of interest.

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