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Three-Dimensional CA-LBM Numerical Model and Experimental Verification of $\text{Cs}_2\text{AgBiBr}_6$ Perovskite Single Crystals Grown by Solution Method

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Abstract: A three-dimensional cellular automata-lattice Boltzmann (CA-LBM) coupling model is established to simulate the facet growth process and the controlled cooling growth process of $\text{Cs}_2\text{AgBiBr}_6$ perovskite single crystals. In this model, the LBM method is used to calculate the real-time solute field, the CA method is used to simulate the crystal growth process driven by supersaturation of solute, and the geometric parameter g related to the adjacent grid is introduced to reduce the influence of grid anisotropy. The verification of the model is achieved by comparing the simulation results with the experimental results. The comparison results show that a smaller cooling rate is helpful for the growth of large-size single crystals, which verifies the rationality and correctness of the model.



Citation: Chen, H.; Wu, C.; Li, R.; Chen, H. Three-Dimensional CA-LBM Numerical Model and Experimental Verification of $\text{Cs}_2\text{AgBiBr}_6$ Perovskite Single Crystals Grown by Solution Method. *Crystals* **2021**, *11*, 1101. <https://doi.org/10.3390/cryst11091101>

Academic Editor: Konrad Świerczek

Received: 17 August 2021

Accepted: 7 September 2021

Published: 10 September 2021

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Keywords: solution method; $\text{Cs}_2\text{AgBiBr}_6$ single crystals; facet growth; cellular automaton; experimental verification

1. Introduction

Recently, perovskite materials have received widespread attention due to their excellent photoelectric properties [1]. A perovskite single crystal has extremely low defect density and minimal interface defects compared to polycrystalline materials [2–5]. However, the application of solution methods to perovskite single-crystal materials has strict solvent requirements [3], so it is difficult to obtain single crystals with large sizes. Large-sized perovskite single crystals are of great significance for improving their optical and electrical properties [5].

Organic–inorganic hybrid perovskite materials ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $X = \text{I}, \text{Br}, \text{Cl}$) have attracted wide attention in the fields of solar cells [6–8], photodetectors [9–13], light-emitting diodes [14], etc., because of their excellent optical and electrical properties [15,16]. However, organic–inorganic hybrid perovskite materials have two important disadvantages: (1) their properties are easily affected by temperature, humidity, and light; and (2) the Pb^{2+} contained in the component leads to their toxicity and decreased environmental friendliness [16,17], and the application of these perovskite is limited to some extent.

Lead-free double perovskite $\text{Cs}_2\text{AgBiBr}_6$ is a stable and nontoxic photoelectric material [16–19] with suboptimal photon to charge carrier conversion efficiency. Compared with other lead-free double perovskites, $\text{Cs}_2\text{AgBiBr}_6$ perovskite has better stability in response to moisture, air, heat, and light [20], which is very suitable for high-energy photon detection applications [21].

So far, scholars have conducted much research on the growth of perovskite crystals by the solution method. The most common method is the solution temperature-lowering (STL) route. Su et al. [15] synthesized high-purity polycrystalline $\text{Cs}_2\text{AgBiBr}_6$ powder by the solution method by using hydrobromic acid as a solvent; millimeter-sized $\text{Cs}_2\text{AgBiBr}_6$ crystals were obtained. Yin et al. [22] obtained $\text{Cs}_2\text{AgBiBr}_6$ single crystals with smooth

surfaces and relatively high resistivity with good reproducibility by controlling cooling. Zhang et al. [23] grew $\text{Cs}_2\text{AgBiBr}_6$ crystals with maximum dimensions of 10 mm and a flat plane by the solution cooling method with the addition of toluene. Zhu et al. [24] proposed an additive CH_3COONa -controlled nucleation route toward the generalized growth of all inorganic double perovskite single crystals. A $\text{Cs}_2\text{AgBiBr}_6$ single crystal with a maximum size of 13 mm was successfully grown by this method. Dang et al. [25] successfully grew centimeter-sized $\text{Cs}_2\text{AgBiBr}_6$ single crystals by the TSSG method, using MABr as the flux in the mother solution.

The above methods are all experimental studies that do not fully reveal the growth mechanism of $\text{Cs}_2\text{AgBiBr}_6$ perovskite crystals. The numerical simulation method can reproduce the evolution process of crystal growth from the perspective of the full space and time domain and provide process guidance for crystal preparation. For example, Zhang et al. [26–28] studied the directional growth of polycrystalline silicon by numerical simulation based on the cellular automaton (CA) method and studied the growth mechanism of facet silicon crystals in detail. Chen et al. [29], based on the phase field (PF) method, studied the growth of arbitrary symmetry facet dendrites. Although the driving force for the growth of silicon crystals is temperature and that of $\text{Cs}_2\text{AgBiBr}_6$ perovskite crystals is solution supersaturation, both of them are facet crystals, so the same numerical method can be used to reveal the growth mechanism of $\text{Cs}_2\text{AgBiBr}_6$ perovskite.

In this paper, the solution temperature-lowering growth process of $\text{Cs}_2\text{AgBiBr}_6$ single crystals is simulated by the CA-LBM method and compared with the experiment to verify the correctness of the model. Then, in order to guide the preparation of larger-size single crystals, the CA-LBM method is used to simulate the growth behavior of single crystals at different cooling rates. In this paper, the experimental and simulation results are respectively compared qualitatively and quantitatively to further verify the model.

2. Preparation of $\text{Cs}_2\text{AgBiBr}_6$ Single Crystals by the Solution Method

Materials: CsBr (99.9%) and BiBr_3 (99%) were purchased from Xi'an Polymer Light Technology Corp. (PLT) and Alfa Aesar, respectively. AgBr (99.9%) and hydrobromic acid (HBr , 48% wt % in H_2O) were purchased from Aladdin. All these commercially available chemicals were used without any further purification.

Facet Growth Procedure: The concentration was calculated from the solution volume and the mass of the solute evaporated from the sample. First, the precursor of a target concentration (0.1 M, M is the concentration unit: mol/L) was prepared by CsBr , AgBr , BiBr_3 , and 3 mL HBr acid ($\text{CsBr}:\text{AgBr}:\text{BiBr}_3 = 2:1:1$) in a 5 mL glass bottle. Every point was averaged from three samples for a more accurate result. The bottle was sealed by a silicone plug and silicone grease and heated at 120 °C in an oil bath. Second, after the solute fully dissolved, the temperature was lowered at a rate of $0.5\text{ }^\circ\text{C}\cdot\text{h}^{-1}$ to 60 °C to avoid excessive nucleation and crystal growth. Then, the crystals were obtained by pouring out the residual solution.

Controlled Cooling Rate Growth Procedure: The $\text{Cs}_2\text{AgBiBr}_6$ crystals were grown by the method of controlling the cooling rate. First, 3 mL of the respective precursor solution with the same concentration (0.1 M) was prepared in four 5 mL glass bottles. The preparation method of the precursor solution followed the Facet Growth Procedure. Second, the sealed glass bottles were heated at 120 °C in an oil bath to fully dissolve the solute and then cooled to 60 °C at the cooling rates of $2\text{ }^\circ\text{C}\cdot\text{h}^{-1}$, $1.5\text{ }^\circ\text{C}\cdot\text{h}^{-1}$, $1\text{ }^\circ\text{C}\cdot\text{h}^{-1}$, and $0.5\text{ }^\circ\text{C}\cdot\text{h}^{-1}$, respectively. Then, the crystals were obtained by pouring out the residual solution.

3. Numerical Model of $\text{Cs}_2\text{AgBiBr}_6$ Single-Crystal Growth Based on the CA Method

A three-dimensional CA-LBM coupling model with interface energy anisotropy was established to simulate $\text{Cs}_2\text{AgBiBr}_6$ single-crystal growth. The solute field was calculated by the LBM method, the solid-liquid interface advancing process was calculated by the CA method, and the CA method and LBM method were coupled according to the solute

content decreased by the solid-state rate growth of $\text{Cs}_2\text{AgBiBr}_6$ crystals. The experimental results were compared with the simulation results to verify the rationality and correctness of the model.

3.1. LBM Model

The D3Q15 model [28,30], with the single relaxation time lattice Bhatnagar–Gross–Krook (LBGK) method, was used to calculate the solute field.

$$g_i(r + e_i \Delta t, t + \Delta t) - g_i(r, t) = (g_i^{eq}(r, t) - g_i(r, t)) / \tau_c + G_i \quad (1)$$

$$G_i = -1000 \rho_s \omega_i \Delta f_s M \cdot (C_{max} - C_{min}) \quad (2)$$

where r , t , Δt , and τ_c represent location, time, time step, and the relaxation time of the solute field, respectively; g_i is the distribution function of particle solute content; and g_i^{eq} is the equilibrium distribution function of particle solute content. G_i is the solute sink term, which represents solute content consumed due to crystal growth. ρ_s and M represent the solid density and molar mass, respectively, of $\text{Cs}_2\text{AgBiBr}_6$ perovskite. $(C_{max} - C_{min})$ represents the difference between the initial content and the end content, which is used for the dimensionless solid density.

3.2. CA Model

In this paper, the three-dimensional CA model was used to simulate the growth of perovskite single crystals. Due to the slow growth rate of the $\text{Cs}_2\text{AgBiBr}_6$ single crystals and the limitations of computation capacity, it was difficult to simulate the growth of the perovskite crystals in the macro scale. In order to reduce the calculation time as much as possible under the condition of ensuring calculation accuracy, $61 \times 61 \times 61$ cube cells were selected in the calculation area, and the cell size was $1 \mu\text{m}$.

The following is a three-dimensional model to simulate the nucleation, growth, and capture of $\text{Cs}_2\text{AgBiBr}_6$ single crystals.

3.2.1. Model for the Nucleation

The continuous nucleation model based on Gaussian distribution is used in the nucleation model [31].

$$n(S) = \int (dn/dS) dS \quad (3)$$

$$dn/dS = n_{max} \cdot (2\pi S_\sigma)^{-1/2} \cdot \exp(-0.5((S - S_{mea})/S_\sigma)^2) \quad (4)$$

Here, S is supersaturation, and dn/dS is the nucleation distribution function. n_{max} , S_σ , and S_{mea} represent the maximum nucleation density, standard deviation supersaturation, and average nucleation supersaturation, respectively. These three parameters are determined by the experimental conditions.

For the nucleation on the wall of a three-dimensional container, the nucleation probability in a time step can be expressed as

$$P = \delta n \cdot V_C \quad (5)$$

where δn is the increasing nucleation density in one time step, and V_C is the volume of a cell.

When the supersaturation of a cell is higher than the critical supersaturation of nucleation, and the probability of nucleation is greater than a random number of 0–1, the cell nucleates. The nucleation position is randomly selected in the cell space that satisfies the basic conditions of nucleation.

3.2.2. Crystal Growth Model

In the process of crystal growth, the transition from interface cell to solid cell is determined by the growth of the solid fraction. For solution growth, without considering the evaporation of the solution, the solid fraction increment can be expressed by

$$\Delta f_s = g \cdot S \cdot M / 1000 \rho_s \quad (6)$$

where S is the supersaturation of the solution, and M and ρ_s represent the molar mass and solid density of $\text{Cs}_2\text{AgBiBr}_6$, respectively. In order to maintain the solid-liquid interface of the single layer as well as the solidification and growth, the geometric parameter g related to the state of the adjacent grid is introduced [28].

$$g = \min((\sum \zeta_m^{\chi_1} + 2^{-1/2} \sum \zeta_m^{\chi_2}) / 2, 1) \quad (7)$$

$$\zeta^{\chi_1}, \zeta^{\chi_2} = 0, (f_s < 1) \quad \zeta^{\chi_1}, \zeta^{\chi_2} = 1, (f_s = 1) \quad (8)$$

Here, ζ^{χ_1} is the state parameter of the nearest six grid cells, and ζ^{χ_2} is the state parameter of the next nearest 12 grid cells.

In this model, the driving force of growth is the saturation (S) of the solution, which is the difference between the solution concentration (C) and solubility (C_{sat}) at a certain temperature.

$$S = C - C_{sat} \quad (9)$$

The nucleation and growth concentrations are two key factors to control crystal growth. The temperature-concentration distribution curve of $\text{Cs}_2\text{AgBiBr}_6$ in HBr can be divided into three zones by the solubility curve and supersolubility curve [22], as shown in Figure 1.

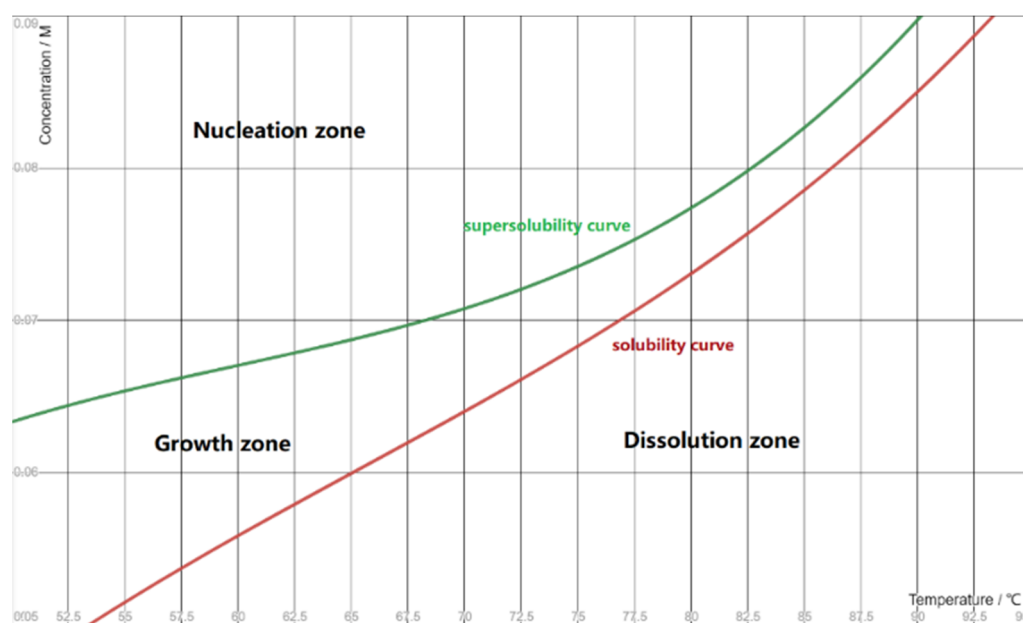


Figure 1. The temperature–concentration distribution curve of $\text{Cs}_2\text{AgBiBr}_6$ in HBr.

In Figure 1, nucleation can occur when the concentration is in the nucleation zone. When the concentration is in the growth zone, the crystal can grow stably without nucleation. Therefore, in order to grow larger single crystals, the concentration should be controlled in the growth range as much as possible. By fitting the above two curves, the solubility and supersolubility of $\text{Cs}_2\text{AgBiBr}_6$ can be expressed as polynomials of temperature as Equations (10) and (11), respectively.

$$C_{sat} = 3.34174 \times 10^{-7} T_t^3 - 6.57362 \times 10^{-5} T_t^2 + 5.11715 \times 10^{-3} T_t - 0.08669 \quad (10)$$

$$C_{ssat} = 4.77122 \times 10^{-7} T_t^3 - 8.58122 \times 10^{-5} T_t^2 + 5.46878 \times 10^{-3} T_t - 0.05521 \quad (11)$$

Here, C_{sat} is solubility, and C_{ssat} is supersolubility. T_t is the equivalent temperature after considering the influence of interface energy anisotropy and the curvature of the interface, which can be calculated using Equation (12).

$$T_t = T + \Gamma \cdot wmc \quad (12)$$

Here, T is the liquidus temperature, Γ is the Gibbs–Thomson coefficient, and wmc is the weighted mean curvature. For cubic crystals with a fourfold anisotropy, wmc can be calculated from Equation (13) [32]:

$$wmc = (3\varepsilon - 1) \cdot (\partial_x n_x + \partial_y n_y + \partial_z n_z) - 48\varepsilon \cdot (n_x^2 \cdot \partial_x n_x + n_y^2 \cdot \partial_y n_y + n_z^2 \cdot \partial_z n_z) + 12\varepsilon \cdot Q \cdot (\partial_x n_x + \partial_y n_y + \partial_z n_z) + 12\varepsilon \cdot (n_x \cdot \partial_x Q + n_y \cdot \partial_y Q + n_z \cdot \partial_z Q) \quad (13)$$

where ε is the degree of anisotropy of the surface energy, and $n_x = \partial_x f_s / |\nabla f_s|$, $n_y = \partial_y f_s / |\nabla f_s|$, $n_z = \partial_z f_s / |\nabla f_s|$, where $|\nabla f_s| = \sqrt{(\partial_x f_s)^2 + (\partial_y f_s)^2 + (\partial_z f_s)^2}$. $Q \equiv n_x^4 + n_y^4 + n_z^4$.

3.2.3. Model for the Capture

During the CA simulation, the transition of the cell state from liquid to interface is governed by the capture rule. Since the change of cellular state has a great influence on the subsequent growth process, it is particularly important to choose an appropriate capture rule.

For the three-dimensional CA model, the number of adjacent cells is large, so the 3D capture rule is more complex than the 2D capture rule. The traditional capture rules are Von Neumann's and Moore's rules, but no matter which capture rule, it will inevitably lead to artificial anisotropy. Therefore, based on Von Neumann's rule, this paper introduces the geometric parameter g [28] to reduce the artificial anisotropy, and a three-dimensional low anisotropy capture model is established.

4. Results and Discussion

4.1. The Physical Parameters of $\text{Cs}_2\text{AgBiBr}_6$ Precursor Solution

The physical parameters used in the present computations are listed in Table 1.

Table 1. Physical properties and calculation parameters used in the present model.

Property	Value
Initial solution concentration, C (M)	0.1
Initial temperature, T (K)	393.0
Solid density, ρ ($\text{g}\cdot\text{cm}^{-3}$)	4.915
Liquid solute diffusion coefficient, D ($\text{m}^2\cdot\text{s}^{-1}$)	3.0×10^{-9}
Gibbs–Thomson coefficient, Γ (mK)	2.6×10^{-7}
Anisotropic coefficient of interface energy, ε	1.5×10^{-2}
Maximum nucleation density, n_{max} (m^{-3})	8.4×10^{10}
Standard deviation supersaturation, S_σ (M)	1.0×10^{-3}
Maximum nucleation supersaturation, S_{max} (M)	1.0×10^{-2}
Cell size, a (m)	1.0×10^{-6}
Time step, Δt (s)	5.0×10^{-5}

4.2. Simulation and Verification of Facet Growth

In order to reveal the growth rule of $\text{Cs}_2\text{AgBiBr}_6$, a $\text{Cs}_2\text{AgBiBr}_6$ facet growth morphology is simulated firstly.

Since both the simulation and experiment adopt the all-area synchronous cooling method, $61 \times 61 \times 61$ cubic cells with the same cooling conditions are selected in the calculation area, and the cell size is 1 μm . The initial simulation conditions are set as central point nucleation, and the all-area temperature is cooled by 0.5 $^\circ\text{C}$ every 1800 time steps.

The physical parameters used in the calculation are listed in Table 1, which contains both the initial temperature and the initial concentration. Crystal growth is calculated by the CA model driven by solute supersaturation, and the temperature–solubility curve used is shown in Figure 1.

The calculation results when the time steps are 100,000, 140,000 and 180,000 are shown in Figure 2a–c, respectively. The real time after conversion is 55.5 h, 77.7 h, and 100 h, respectively. The upper part of each drawing shows the 3D simulation result, and the lower part shows the solute distribution and the solid-liquid interface of the Y–Z section corresponding to the 3D drawing.

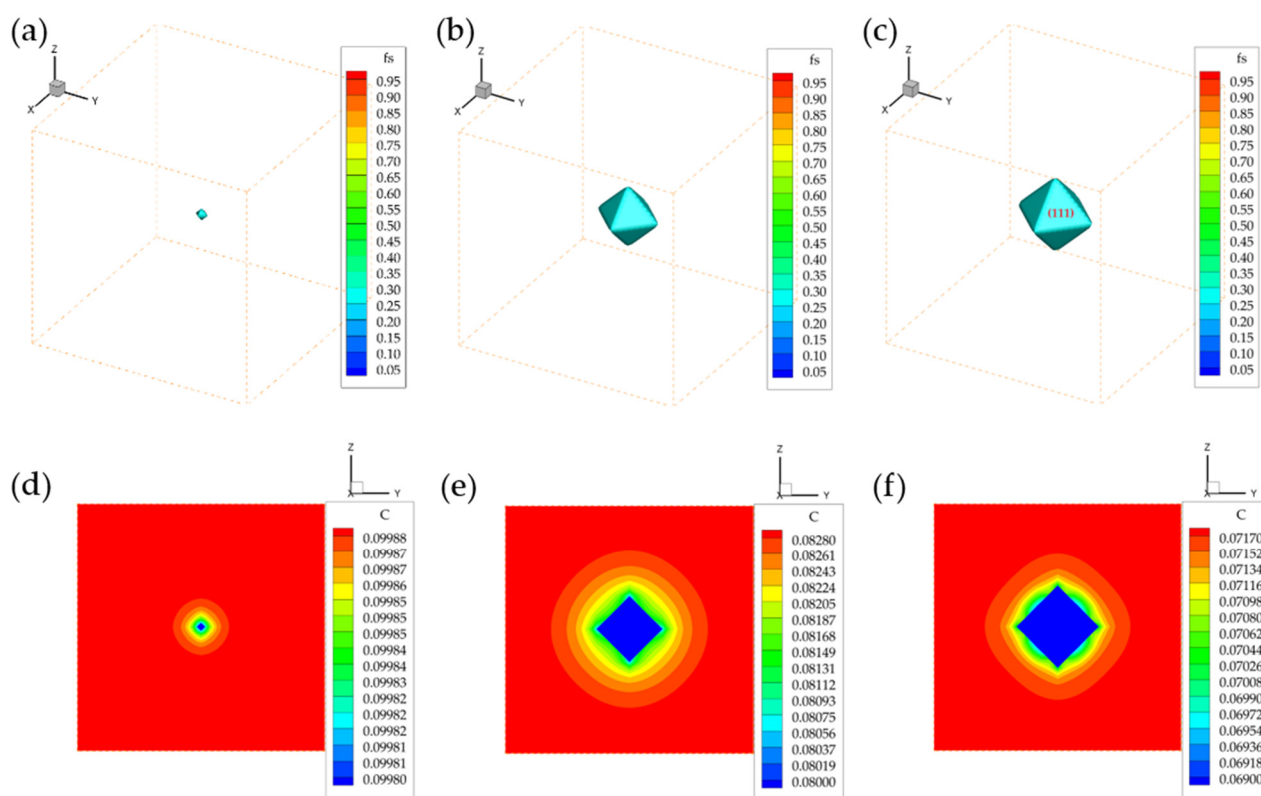


Figure 2. Numerical simulation results of different time steps: (a) $t = 100,000 \Delta t$ (55.5 h); (b) $t = 140,000 \Delta t$ (77.7 h); (c) $t = 180,000 \Delta t$ (100 h); (d–f) the corresponding Y–Z section of solute distribution.

The facet morphology cannot be seen clearly in Figure 2a because it is in the early stage of growth after nucleation. The corresponding solute cross-section figure shows that the solute distribution is quite uniform, and the anisotropy is not relatively distinct. Figure 2b shows that the crystal is in an octahedral shape, and the morphology of facet growth appeared after a period of growth. The corresponding solute cross-section in Figure 2e shows that under the influence of anisotropy and geometric parameters g , the growth of the $\langle 111 \rangle$ direction (45° direction) is restrained, and crystal growth occurs along the $\langle 100 \rangle$ direction (axial direction). The solute in the $\langle 100 \rangle$ direction is poorer than that in the $\langle 111 \rangle$ direction, resulting in faster growth in the $\langle 111 \rangle$ direction, thus maintaining the facet growth morphology. It can be seen from Figure 2c that the crystal is characterized by four-fold anisotropic symmetry and continues to grow in an octahedral shape.

The analysis of the above simulation results reveals the growth mechanism of $\text{Cs}_2\text{AgBiBr}_6$; the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions restrict each other during the growth process due to the influence of solute content, forming alternating growth behaviors of the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, and finally forming a typical octahedral morphology.

The concentration of solute has a great influence on the process of grain growth. As shown in Figure 3, the grain growth is divided into two stages, namely nucleation and

growth. The concentration curve in Figure 3 does not change, and the grain length is 0 before 42 h (about 95 °C). After 42 h, nucleation occurs and enters the growth stage, and the solute concentration decreases with the increase in grain length. It is worth noting that the solute consumption rate has an obvious acceleration process and then gradually slows down. This is due to the increase in solute capture rate at the solid–liquid interface with the cooling growth process, and with the gradual consumption of solute, the supersaturation of solution decreases, which is not enough to maintain rapid growth. When the cooling is stopped, the supersaturation tends to 0, and the solution concentration tends to a certain value.

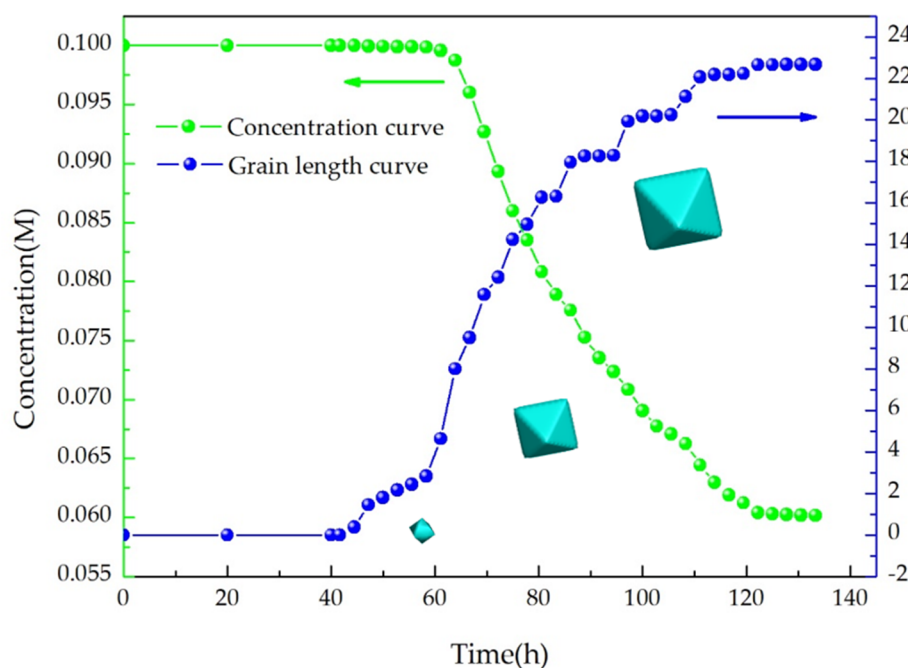


Figure 3. Evolution diagram of concentration at the origin of the coordinate (0, 0, 0) and grain length.

It can be seen from the above analysis that the concentration curve in Figure 3 shows that the trend of constant-gradient decline tends to be stable. This trend can be explained by comparison with Figure 1. At the beginning stage of cooling growth, the solute concentration is lower than the solubility curve and supersolubility curve, indicating that the concentration is in the dissolution zone. During this period, neither nucleation nor growth can occur. As the temperature gradually lowers, the solute concentration enters the nucleation zone, where nucleation occurs and consumes part of the solute and then enters the growth zone. In the subsequent cooling process, it alternately enters the nucleation zone and growth zone, so the concentration curve in Figure 3 shows a gradient declining trend. In the final stage of growth, the solute concentration is close to the solubility, and the growth stops and reaches a stable state, as seen in Figure 3. The above analysis shows that the concentration curve in Figure 3 is consistent with the change trend of the temperature–solubility curve in Figure 1, which verifies the correctness of the CA model driven by supersaturation in this paper.

The grain length curve in Figure 3 does not increase linearly but has some steps. This is because the supersaturation of the solution is consumed after a certain period of growth at a certain temperature, resulting in temporary slow growth. When the solution is cooled, the supersaturation increases again, resulting in the acceleration of growth again. Therefore, a stepped curve is formed.

Analysis of the above simulation results shows that the grain will continue to grow with an octahedral morphology. Therefore, in this paper, the simulation results can be approximately compared with the experimental results to verify the rationality and correct-

ness of the model. Figure 4 shows the comparison between simulation results (Figure 4a,b) and experimental results (Figure 4c,d) of $\text{Cs}_2\text{AgBiBr}_6$ single-crystal growth.

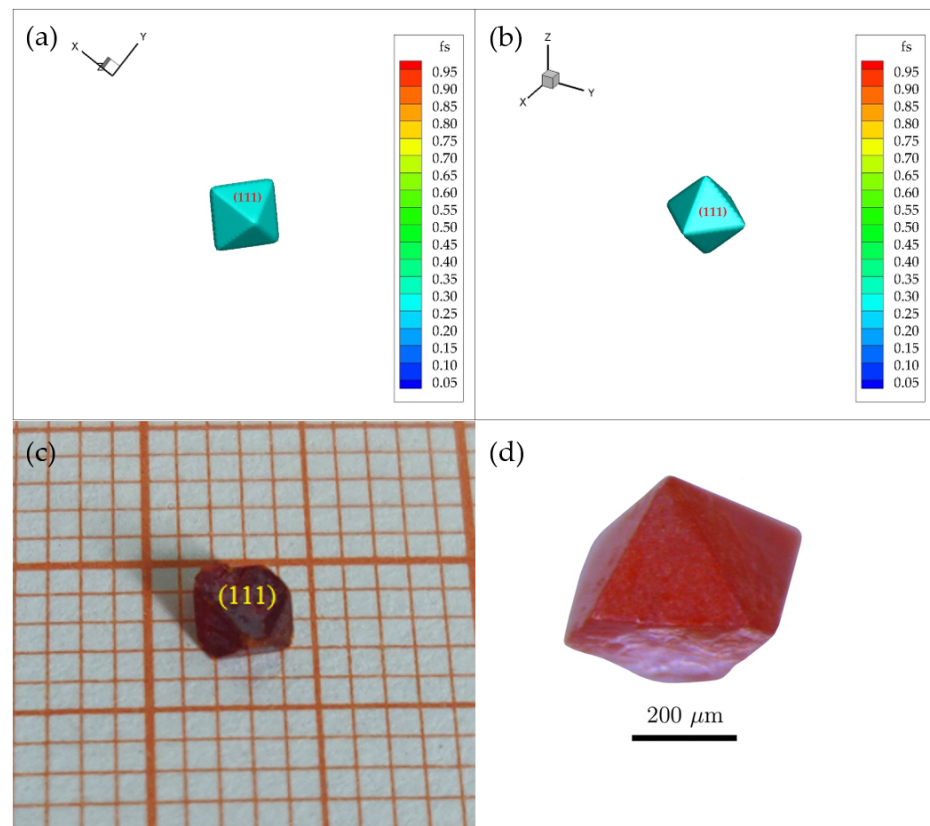


Figure 4. Comparison between simulation results and experimental results of $\text{Cs}_2\text{AgBiBr}_6$ single-crystal growth. (a) Simulation results after coordinated axis rotation; (b) simulation results without rotating axis; (c) experimental results in this paper; (d) experimental results in Ref. [16].

Figure 4c is the single-crystal morphology prepared by the author of this paper by the solution method, while Figure 4d is the single crystal prepared in Reference [16]. The comparison between Figure 4a and c show that the (111) characteristic surface of the simulated single crystal is in good agreement with the experimental results. The comparison between Figure 4b and d show that the simulation results are also in good agreement with the experimental results in Reference [16]. The two sets of results are cross-validated, which demonstrate that the model established in this paper can simulate the facet growth morphology of $\text{Cs}_2\text{AgBiBr}_6$ correctly. The surface of the single crystal in Figure 4c is comparatively rough, which is caused by the simultaneous growth of many nucleation sites, while in Figure 4a, only one nucleation site is set, so the single-crystal surface is smooth.

4.3. Simulation and Verification of Controlled Cooling Growth

In order to reveal the effect of solution cooling rate on the size and number of the $\text{Cs}_2\text{AgBiBr}_6$ single crystal, the grain growth process at different cooling rates is simulated.

The calculation area also selects $61 \times 61 \times 61$ cubic cells with the same cooling conditions, and the cell size is $1 \mu\text{m}$. In order to facilitate the observation of the grain size distribution, the initial conditions are set as random point nucleation on the $Z = 30$ plane (central horizontal plane), and the all-area temperature is cooled by 2°C , 1.5°C , 1°C , and 0.5°C every 1800 time steps, respectively. The physical parameters used are listed in Table 1. The crystal growth process is also calculated by the CA model driven by the supersaturation.

Figure 5 shows the simulation and experimental results when the cooling rate is $2\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, $1.5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, $1\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, and $0.5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$. The upper part of each drawing shows the 3D simulation results, and the lower part shows the experimental results corresponding to the 3D drawing.

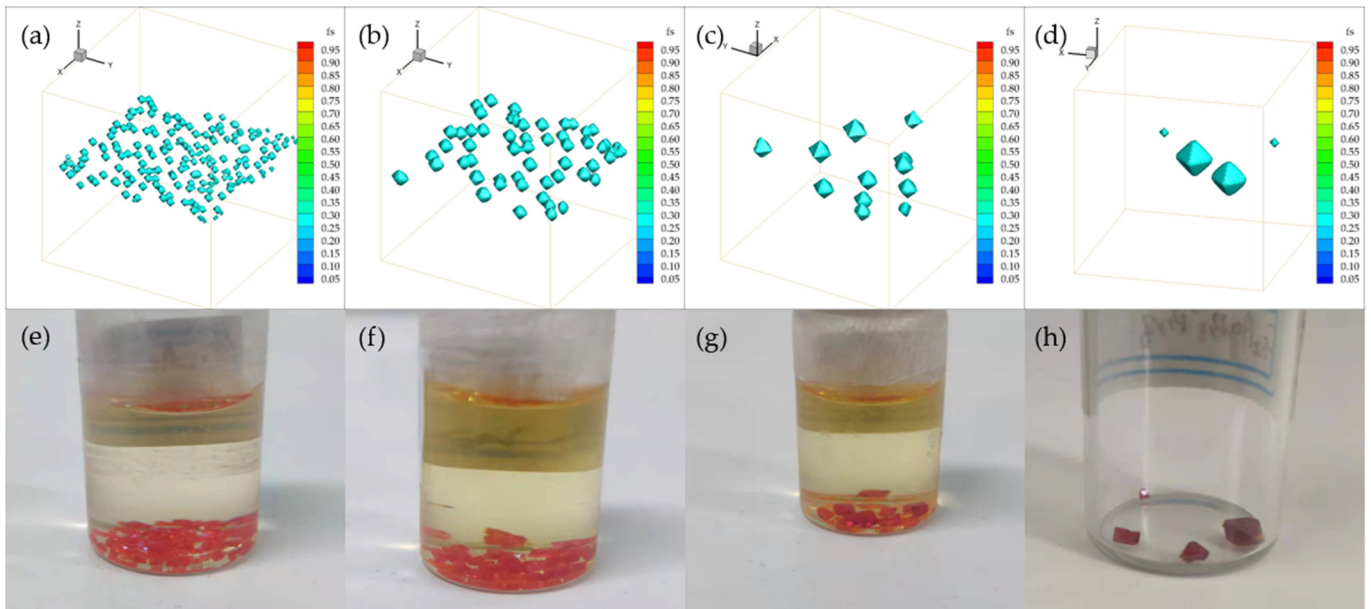


Figure 5. Grain size distribution at different cooling rates. (a–d) The simulation results of $2\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, $1.5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, $1\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, and $0.5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, respectively; (e–h) the experimental results corresponding to the respective upper simulation results.

From the above analysis, it can be predicted that the number of final grains will gradually decrease as the cooling rate decreases, and the maximum grain size will gradually increase. The comparison results of Figure 5d,h verify this prediction. When the cooling rate is reduced to $0.5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$, the number of final grains is reduced to 4, and the maximum grain size increases considerably.

There are some very small grains in Figure 5d,h, which is because the number of initial nucleation is small, resulting in the solute mass required for grain growth being insufficient to deplete the supersaturated solute mass increased by cooling and then precipitate in the form of a few grains. However, the solute content at this time can no longer maintain its rapid growth, so the subsequent precipitated grain size is much smaller than the initial grain.

The qualitative comparison between the above simulation results and the experimental results verifies the rationality of the model established in this paper. In order to verify the correctness of the model, Figure 6 shows the quantitative comparison between the simulation results and experimental results. Due to the limitation of the amount of calculation, the volume of the calculation area is smaller than the volume of the actual growth solution, and the quantitative comparison results cannot be clearly presented by using the maximum grain size. Therefore, the dimensionless method is adopted for treatment—the grain size corresponding to different cooling rates is divided by the maximum grain size corresponding to $0.5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$ to obtain the dimensionless grain size corresponding to different cooling rates (grain size ratio).

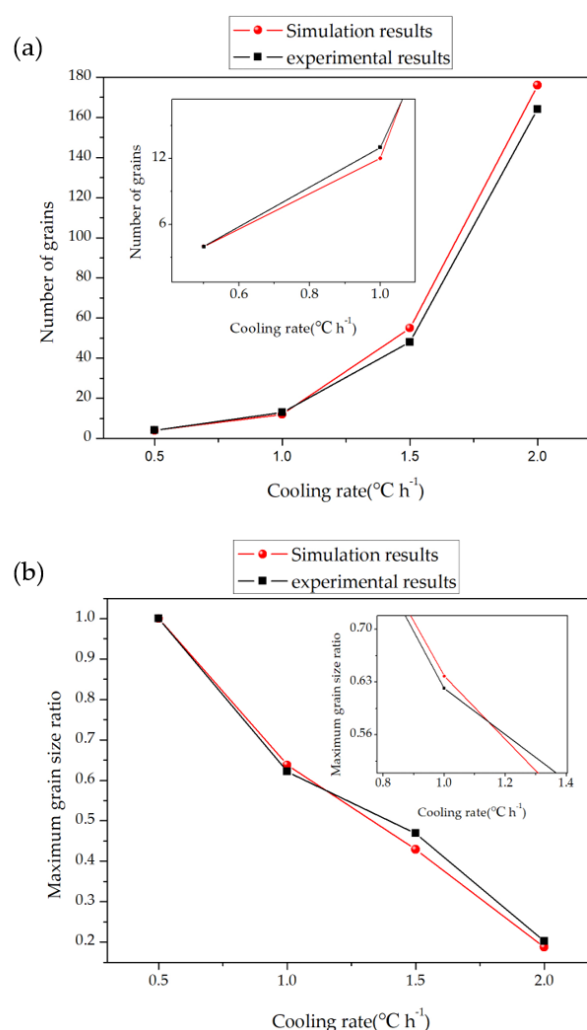


Figure 6. Quantitative comparison between simulation results and experimental results. (a) Cooling rate-number of grains curve (the inset is the detailed view), and (b) cooling rate-maximum grain size ratio curve (the inset is the detailed view).

It can be seen intuitively from Figure 6a,b that as the cooling rate increases, the number of grains gradually increases, while the maximum grain size shows a decreasing trend. The two curves in Figure 6a are in good agreement, and there is a slight deviation when the cooling rate is larger. This is because the random nucleation model is adopted in this paper, the number of nucleations will be within a certain range, and the nucleation position is random, so it is more in line with the real grain growth situation.

In Figure 6b, when the cooling rate is larger, the simulation results are lower than the experimental results. This is because the simulation results have more grains than the experimental results when the cooling rate is larger, resulting in a smaller size of the simulated grains than the experimental grains. The quantitative comparison between Figure 6a,b shows that the simulation results are in good agreement with the experimental results, which verifies the correctness of the model established in this paper.

5. Conclusions

In this paper, a three-dimensional CA-LBM coupling model is established to simulate the facet growth process and controlled cooling growth process of $\text{Cs}_2\text{AgBiBr}_6$ perovskite single crystals. The CA model takes the supersaturation of solute as the driving force and considers the influence of interface energy anisotropy on the morphology of the liquid–solid interface. The geometric parameter g is introduced to reduce the influence of grid anisotropy. The qualitative and quantitative comparison between the simulation results

and the experimental results verified the rationality and correctness of the model, indicating that the model established in this paper can reproduce the solution growth process of the $\text{Cs}_2\text{AgBiBr}_6$ perovskite single crystal well and can guide the preparation of larger-size $\text{Cs}_2\text{AgBiBr}_6$ single crystals.

Author Contributions: Conceptualization, R.L. and H.C. (Hongjian Chen); data curation, H.C. (Hui Chen); formal analysis, H.C. (Hui Chen); methodology, C.W., R.L. and H.C. (Hongjian Chen); software, H.C. (Hui Chen); validation, H.C. (Hui Chen) and C.W.; investigation, H.C. (Hui Chen); resources, C.W., R.L. and H.C. (Hongjian Chen); writing—original draft preparation, H.C. (Hui Chen); writing—review and editing, H.C. (Hui Chen), R.L. and H.C. (Hongjian Chen); supervision, R.L. and H.C. (Hongjian Chen); project administration, R.L. and H.C. (Hongjian Chen); funding acquisition, H.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by grants from the National Natural Science Foundation of China (grant No. 51475138 and No. 51975182) and the 2019 Tongliao Science and Technology Innovation Guidance Incentive Fund.

Data Availability Statement: Not applicable.

Acknowledgments: Hui Chen would like to thank Cuncun Wu, Ri Li and Hongjian Chen (Hebei University of Technology) for providing materials used for experiments and academic guidance.

Conflicts of Interest: The authors declare no conflict of interest.

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