Prismatic morphology of an ADP crystal grown in a defined crystallographic direction

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Herein, ammonium dihydrogen phosphate (NH₄H₂PO₄, ADP) crystals were grown in a defined crystallographic direction (θ = 90°, φ = 45°) in an aqueous solution using the point seed rapid growth method. Ex situ atomic microscopy (AFM) measurements were implemented to observe the prismatic growth micro-morphology of ADP and Cr³⁺-doped ADP in the defined crystallographic direction. It was found that with the increasing supersaturation, the growth morphology changed in turn to elementary steps, macro steps, and 2D nuclei. Moreover, the differences between ADP and Cr³⁺-doped ADP grown in the defined crystallographic direction have been discussed. The influence of Cr³⁺ on the growth of ADP crystals has been explored.

Introduction

The ammonium dihydrogen phosphate (NH₄H₂PO₄, ADP) crystal has various applications as a piezoelectric material and as a monochromator for X-ray crystal. It has also various applications as a piezo-electric material and as a monochromator for X-ray. Moreover, this method may improve the growth sections and macro steps, and 2D nuclei. Furthermore, Cr³⁺ was added to the growth solution to study the effects of Cr³⁺ on this growth direction as Cr³⁺ is a common impurity ion. Furthermore, prismatic morphology of the chromium-doped ADP crystals grown in the defined crystallographic direction was obtained. The differences between ADP and Cr³⁺-doped ADP in the defined crystallographic direction have also been discussed.

Experimental

The small ADP crystals grown in the defined crystallographic direction in our experiments were prepared using the point seed rapid growth method with the decreasing temperature. Moreover, seed crystal slices were obtained from the as-grown crystals in the direction of (θ = 90°, φ = 45°), as shown in...
where

\[ \sigma = \frac{C_0 - C_e}{C_e} \]  

(1)

where \( C_0 \) and \( C_e \) are the actual and equilibrium concentrations given in mass fractions. Thus, crystals suitable for surface microtopography, as shown in Fig. 2, could be obtained after a two-day growth process. The crystals were quickly withdrawn from the solution and dipped once or twice in a mixed solution of alcohol and propyl alcohol, which had the same temperature as the crystals and growth solution. Then, the mixed solution was removed with a piece of silk cloth. 

Fig. 1. Additionally, the initial growth temperature was about 50 °C. The supersaturation \( \sigma \) was created by decreasing the temperature of the solution, which could be calculated by\(^6,27\)

Fig. 2 Crystals suitable for surface microtopography (the yellow numbers represent the different \( \sigma \) values and the scale plate).

Fig. 1. The seed crystal slices in the direction of \( \theta = 90^\circ, \phi = 45^\circ \).

Fig. 2 Crystals suitable for surface microtopography (the yellow numbers represent the different \( \sigma \) values and the scale plate).

**Results and discussion**

**Prismatic growth micro-morphology of the ADP crystals**

The prismatic, namely (100) face, growth micro-morphologies of ADP at different supersaturations are shown in Fig. 3.

Fig. 3(a) shows the surface microtopography at a supersaturation of 0.6%; the average step height of the steps was measured to be about 0.366 nm, equal to half of the length of unit cell \( a \) or \( b \) (7.502 Å (ref. 6)). This can be named as the elementary step. Thus, it can be seen that only the spiral growth mechanism is observed, and the direction of the step bending points to the dislocation source. Additionally, the steps are equidistant and regular, showing a steady initial growth stage of the ADP crystal, and correspond well with the growth theory.\(^26\) It is illustrated in Fig. 3(b) that at a supersaturation of 0.8%, the height of the elementary step is about 0.490 nm, which is approximately equal to half of the length of the unit cell. At the edges of the elementary steps, some ridges and dents emerge; this occurs because the growth units prefer to be absorbed into the edges of the steps, forming ridges, or because the fluctuations impede the absorption of the growth units, forming dents with small fluctuations of the growth conditions. In Fig. 3(c), at a supersaturation of 1.0%, the average height of the step is 4.61 nm, which is equivalent to six times the length of \( a \). This indicates that the crystal surface is covered by macro steps, which are the result of a process called step bunching; the macro steps increase in height and terrace width with distance from the top of the hillock and integrate multiple micro steps. The shape of the macro steps is approximately regular; this indicates that the macro steps develop and step forward as a whole, rather than by respective growth of elementary steps. When the supersaturation increases to 1.2%, the process of step bunching continues, and the macro steps become larger, as shown in Fig. 3(d). In addition, the average height of the steps is about 12.3 nm, which is equal to 17 times the length of \( a \). A partial magnified image of Fig. 3(d) is shown in Fig. 3(d-1); this image clearly illustrates the topography of the macro steps and the process of step bunching. The macro steps are neither straight nor strictly parallel, but have more complicated shapes; this indicates that the crystal surface may be influenced not only by supersaturation but also by other factors. At a supersaturation of 1.4%, as shown in Fig. 3(e), the process of step bunching still occurs; the average height of the macro steps is about 20.8 nm, equal to 28 times the length of the unit cell. However, some islands without any signs of dislocation outcrop appear on the terraces between two steps, and their average radius is about 230 nm, much greater than the radius of the critical nucleus at this supersaturation. These islands are called 2D nuclei and are much more visible in Fig. 3(e-1), particularly in the magnified image shown in Fig. 3(c). When the supersaturation is increased to 1.8%, the radius of the 2D nuclei increases to about 1.107 \( \mu \)m, and the height of the macro steps is about 23.1 nm, as clearly shown in Fig. 3(f) and (f-1); moreover, the quantity of 2D nuclei obviously increases. The 2D nucleation mechanism is dominant in the crystal growth process.

Fig. 3(g) illustrates the (100) face growth micro-morphology at \( \sigma = 2.2\% \); it can be seen that the radius of the 2D nuclei increases to about 4.21 \( \mu \)m; this indicates that the 2D nuclei grow and step forward via step growth. The growth velocity of the 2D nuclei is anisotropic, as shown in Fig. 3(g). The velocity in the [001] direction is obviously smaller than that in the [010] direction, and this phenomenon is in good accordance with the
The chemical bond distribution shown in ref. 15. The chemical bond strengths of the \( \alpha \) and \( \beta \) bond chains are stronger than that of the \( \gamma \) bond chain;\(^{15}\) this leads to a low aspect ratio of the ADP crystals.

The relationship between the supersaturation and the step heights of the ADP crystals in the defined crystallographic direction is shown in Fig. 6. Thus, we can know that (1) the height of the elementary step is about half the height of the unit cell; (2) the growth steps are all elementary steps when \( \sigma \leq 0.8\% \), and this indicates that the process of crystal growth is stable, with few fluctuations influencing the crystal growth; (3) under the condition of \( \sigma \leq 1.2\% \), only the spiral step growth mechanism exists in the aqueous solution. Moreover, the elementary steps develop into macro steps, which integrate multiple micro steps via step bunching with the increasing supersaturation; (4) islands, namely 2D nuclei, without any signs of dislocation outcrop appear on the terraces between two steps when \( \sigma > 1.2\% \); thus, the spiral step growth mechanism and 2D nucleation mechanism coexist during the process of crystal growth. When the supersaturation is increased by decreasing the temperature, the 2D nucleation mechanism, whose velocity is anisotropic, will be dominant until the crystal growth is complete.

By comparing our results with those reported in ref. 15, in which (100) face growth morphologies have been obtained for ADP crystals grown in the \( Z \) direction at different supersaturations, we can determine the differences and similarities between the prismatic growth morphologies of the ADP crystals in the \( Z \) direction and the defined direction.
Similarities: (1) the variation trends of both growth mechanisms are the same, namely changing from the spiral step growth mechanism to the coexistence of spiral step growth and 2D nucleation mechanisms and then to a dominant 2D nucleation mechanism. (2) The exposed faces of the crystals during the growth processes are the same; in both cases, the faces are (100) and (101).

Fig. 4 The (100) face growth micro-morphologies of Cr³⁺-doped ADP at different supersaturations. (a) $\sigma = 0.4\%$; (b) $\sigma = 0.6\%$; (c) $\sigma = 0.8\%$; (c-1) partial enlarged view of (c); (d) $\sigma = 1.0\%$; (d-1) partial enlarged view of (d); (e) $\sigma = 1.2\%$; (f) $\sigma = 1.4\%$; (f-1) partial enlarged view of (f); (g) $\sigma = 1.6\%$; (g-1) partial enlarged view of (g); (h) $\sigma = 1.8\%$; (h-1) partial enlarged view of (h); and (i) $\sigma = 2.0\%$ (the white arrows indicate the direction of step movement).
Therefore, the impurity, namely Cr\textsuperscript{3+}, in our experiments may be in the form of Cr\textsuperscript{3+} inclusions, as shown in Fig. 4(b), with a height of 0.713 nm, equal to the height of the unit cell. The average height of the steps, as shown in Fig. 4, continues to increase with an anisotropic growth velocity. The average height of the macro steps is about 2.37 nm, far less than the height of the steps of the ADP crystals. As the supersaturation increases to 1.2%, as shown in Fig. 4(e), the step bunching continues; the average height of the macro steps is about 3.5 nm. In Fig. 4(f), at a supersaturation of 1.4%, a hollow core is observed; this proves that the impurity ion Cr\textsuperscript{3+} plays an important role in the formation of defects. When \( \sigma \) increases to 1.6%, as shown in Fig. 4(g), some 2D islands without any signs of dislocation outcrop appear on the terraces between two steps; their average radius is about 700 nm, much greater than the radius of the critical nucleus at this supersaturation.\textsuperscript{4} The quantity and radii of the 2D islands increase rapidly, and the islands are distributed regularly and in good proportion, as shown in Fig. 4(h); this indicates that the 2D nucleation mechanism is dominant. In Fig. 4(i), it can be seen that the two-dimensional islands continue to increase with an anisotropic growth velocity. The velocity in the [001] direction is obviously smaller than that in the [010] direction, same as the case with non-Cr\textsuperscript{3+}-doped ADP.

The overall relationship between the supersaturation and the step height of Cr\textsuperscript{3+}-doped ADP crystals in the defined crystallographic direction is shown in Fig. 6. Therefore, as \( \sigma \leq 1.4\% \), the spiral step growth mechanism controls the crystal growth. In the initial process, elementary steps originate from the outcrop of the dislocation source of maximum activity; moreover, the steps are bending and moving towards one another at the front edge. The impurities are pinned on the steps of the (100) face and form hollow cores, which may lead to the appearance of defects or inclusions. Then, macro steps occur via coalescence of multiple micro steps. When \( \sigma > 0.014 \), two-dimensional islands appear with an anisotropic growth velocity, \textit{i.e.} the velocity in the [001] direction is obviously smaller than that in the [010] direction. Moreover, as \( \sigma \) increases, 2D nuclei form and the 2D nucleation mechanism becomes dominant.

**Comparative analysis of the prismatic morphologies of ADP and Cr\textsuperscript{3+}-doped ADP**

As is known, the normal growth rate \( R \) in the spiral growth mechanism on the prismatic face of crystals depends on the steepness \( P \) of the dislocation hillock and the tangential growth rate \( V \) of the dislocation step.\textsuperscript{6,29,30}
The steepness $P$ of a hillock from an isotropic spiral is determined by the structure of the dislocation. Moreover, the steepness is given by:

$$ P = \frac{mh}{19r_c + 2L} \quad (4) $$

where $m$ is the number of unit steps in the Burgers vector of the dislocation, $h$ is the height of an elementary step, $r_c$ is the radius of a critical nucleus, and $2L$ is the length of the perimeter of dislocations. Furthermore, $r_c$ can be given by

$$ r_c = \frac{\Omega \gamma kT}{\sigma} \quad (5) $$

where $\gamma$ is the free energy of the step edge per unit length per unit step height, and $\Omega$ is the molecular volume in the solid. In addition, the parameters used to calculate the dependence of steepness on supersaturation are listed in Table 1. The $r_c$ values at the supersaturations where the 2D nuclei only started to appear (1.2% (undoped) and 1.4% (doped)) can also be calculated by the formula (5).

Therefore, the radius of a critical nucleus $r_c$ of ADP in the defined crystallographic direction at different supersaturations can be calculated as shown in Table 2.

The actual experimental curves of the steepness $P$ of the prismatic faces of the ADP crystals are shown in Fig. 7. Speculating that $m$ in the formula (4) equals 1–3 and according to (4) and (5), the $2L$ values of the ADP and Cr$^{3+}$-doped ADP crystals can be calculated, as shown in Table 2.

As shown in Table 3, for the ADP and Cr$^{3+}$-doped ADP crystals, the maximum value of $\sigma$, which meets the condition $2L \geq 0$, increases as $m$ increases. This indicates that as $\sigma$ increases, the number of layers of the dislocation source will increase. Moreover, as $m$ is constant, $2L_1$ increases initially and then decreases; however, $2L_2$ shows a decreasing trend with the increasing $\sigma$. Furthermore, $2L_3$ is larger than $2L_2$ at the same value of $m$ at low supersaturation ($\sigma \approx 0.8\%$) when the step heights are very low; as the macro steps propagate after $\sigma = 1.0\%$, Cr$^{3+}$ obviously decreases the overlay layers of the elementary steps and

<table>
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<th>$\Sigma$ (%)</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
<th>1.4</th>
<th>1.6</th>
<th>1.8</th>
</tr>
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<tr>
<td>$2L_1$ ($m = 1$) (nm)</td>
<td>—</td>
<td>475.9</td>
<td>496.4</td>
<td>28.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>$2L_1$ ($m = 2$) (nm)</td>
<td>—</td>
<td>1040.7</td>
<td>1059.5</td>
<td>110.0</td>
<td>5.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$2L_1$ ($m = 3$) (nm)</td>
<td>—</td>
<td>1605.5</td>
<td>1622.5</td>
<td>191.7</td>
<td>30.3</td>
<td>5.8</td>
<td>—</td>
<td>0.9</td>
</tr>
<tr>
<td>$2L_2$ ($m = 1$) (nm)</td>
<td>413.1</td>
<td>426.6</td>
<td>97.4</td>
<td>98.2</td>
<td>49.6</td>
<td>20.6</td>
<td>—</td>
<td>0.98</td>
</tr>
<tr>
<td>$2L_2$ ($m = 2$) (nm)</td>
<td>959.3</td>
<td>942.1</td>
<td>261.6</td>
<td>222.8</td>
<td>143.7</td>
<td>79.1</td>
<td>27.7</td>
<td>—</td>
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<tr>
<td>$2L_2$ ($m = 3$) (nm)</td>
<td>1505.6</td>
<td>1457.6</td>
<td>425.7</td>
<td>360.9</td>
<td>237.8</td>
<td>137.7</td>
<td>52.7</td>
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decreases the growth velocity of the (100) face. Therefore, it appears that Cr$^{3+}$ can impede the length of the perimeter of dislocations and the size of the dislocation cores. This leads to a smaller height of the steps for Cr$^{3+}$-doped ADP; thus, the growth velocity $R$ decreases at the same supersaturation and temperature. At the same supersaturation in both Cr$^{3+}$-doped ADP and undoped ADP crystals, the steps of spiral dislocation or 2D nuclei can expand in height and terrace width with time. Moreover, according to the formulas (2)-(4) and fitting of the two curves in Fig. 7, $\sigma$ increases dynamically with step growth and consumption of the solute; this leads to an increase in the growth velocity $R$ in both Cr$^{3+}$-doped ADP and undoped ADP crystals.

Conclusions

In this study, ADP crystals were grown in an aqueous solution in a defined crystallographic direction ($\theta = 90^\circ$, $\Phi = 45^\circ$, which is the direction of non-critical phase matching fourth harmonic generation) using the point seed rapid growth method. Ex situ atomic microscopy (AFM) measurements were implemented to observe the prismatic growth microscopic morphology of ADP. Moreover, the prismatic morphology of chromium-doped ADP crystal grown in the defined crystallographic direction was determined. For the ADP without Cr$^{3+}$ doping, under the condition of $\sigma \leq 1.2\%$, only the spiral step growth mechanism occurred in an aqueous solution. In addition, when $\sigma > 1.2\%$, the spiral step growth mechanism and 2D nucleation mechanism coexisted in the process of crystal growth. With regard to Cr$^{3+}$-doped ADP, when $\sigma \leq 1.4\%$, the spiral step growth mechanism controlled the crystal growth. Moreover, two-dimensional islands appeared with an anisotropic growth velocity when $\sigma > 0.014$. With the increasing $\sigma$, the 2D nuclei grow, and the 2D nucleation mechanism becomes dominant. The influence of Cr$^{3+}$ on the growth of ADP crystals in the defined crystallographic direction has been explored and discussed. For the ADP and Cr$^{3+}$-doped ADP crystals, the maximum value of $\sigma$, which meets with the condition $2L \geq 0$, increases as $m$ increases. This indicates that the larger the $\sigma$, the more the layers of the dislocation source. Moreover, as $m$ is constant, $2L$ increases initially and then decreases; however, $2L_2$ shows a decreasing trend with the increasing $\sigma$. Furthermore, $2L_1$ is larger than $2L_2$ at the same value of $m$ at low supersaturation ($\sigma \leq 0.8\%$) when the step heights are very low; as the macro steps propagate after $\sigma = 1.0\%$, Cr$^{3+}$ can obviously decrease the overlay layers of the elementary steps and slow the growth velocity of the (100) face. Therefore, this indicates that Cr$^{3+}$ can impede the length of the perimeter of dislocations and the size of the dislocation cores. This leads to a smaller step height in Cr$^{3+}$-doped ADP; thus, the growth velocity $R$ decreases at the same supersaturation and temperature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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