# Coordination polyhedron growth mechanism model and growth habit of crystals

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**Abstract** A new growth mechanism model, coordination polyhedron growth mechanism model, is introduced from the angle of the coordination of anion and cation to each other at the interface. It is pointed out that the force driving the growth unit to enter the crystal lattice is the electrostatic attraction force between ions, whose relative size can be approximately measured by the electrostatic bond strength (EBS) that reaches a nearest neighbor anion (or cation) in the parent phase from a cation (or anion) at the interface. The growth habits of NaCl, ZnS, $CaF_2$ and CsI crystals are discussed, and a new growth habit rule is proposed as follows. When the growth rate of a crystal is determined by the step generation rate, the growth habit of this crystal is related to the coordination number of the ion with the smallest coordination rate at the interface of various crystal faces. The smaller the coordination number of the ion at the interface, the faster the growth rate of corresponding crystal face. When the growth of a crystal depends on the step movement rate, the growth habit of this crystal is related to the density of the ion with the smallest coordination rate at the interface of various crystal faces. The smaller the densities of the ion at the interface is, the faster the growth rate of corresponding crystal face will be.

Keywords: **growth mechanism, growth habit, hydrothermal method.**

The growth habit of a crystal refers to a crystalline form that often occurs under certain conditions, which can date back to the time of Steno[1]. However, now, there are still a lot of mineralogists[2—4] engaged in this realm because the growth form contains a great deal of information that helps us understand the microcosmic growth mechanism of a crystal. The theories concerning crystal growth habit mainly include the BFDH law[5] and the PBC theory[6]. In recent years, the above theories[7,8] have made a certain progress, but they still cannot effectively predict the growth habit of some crystals and the habit change in crystals under different growth conditions. The main reason is that these theories are established on the basis of the structures of various crystal faces, ignoring the effect of growth conditions. The growth habit is an overall result of the growth process of a crystal, which is determined by the relative growth rate of various crystal faces. So, to disclose the relationship between the growth habit of a crystal and its structure, one should first study the growth mechanism of the crystal rather than the structure of the crystal.

The growth of a crystal is a complex process which involves the step generation, the step movement and the mass transfer. The theory[9] concerning growth mechanism of crystals mainly includes two-dimensional nucleation model and spiral growth model. With the improvement of

the testing tool[10,11], we are able to directly observe the movement of monosteps in a unit cell height on the monocrystalline terraces of reconstructed surfaces and in the vicinity of steps of well-crystalline crystal. But until now, no step generation mechanism model has been advanced on the molecular level, and the reaction mechanism of growth unit at the interface is not clear. So it is difficult to establish the relationship between the growth habit of a crystal and its interface structure in terms of the traditional growth mechanism models. The aim of this paper is to make clear this relationship through studying the growth mechanism of crystals on the atomic or ionic level from the angle of crystalline chemistry.

## 1    Coordination polyhedron growth mechanism model

To disclose the growth mechanism of a crystal on the atomic or ionic level, people have investigated the structure of melt or solution at the temperature domain before solidification by means of IR[12], Raman[13,14], neutron diffraction[15], etc. It was found that with the decreasing distance of the testing point away from the interface the coordination number of cations in the melt or solution approaches to that in the formed crystal. Moreover, in the structure of the formed ionic crystal, there not only exist the coordination structure of a cation, but also the coordination structure of an anion. So, an assumption is introduced that the formation mechanism of a crystal consists of two kinds of coordination processes occurring at the interface: one is the coordination of cations in the parent phase to anion to form the coordination group with the same coordination number as that of anions in the formed crystal, and the other is the coordination of anions in the parent phase to cation to form the coordination group with the same coordination number as that of cation in the formed crystal. In the formation of a crystal, the above two kinds of coordination processes proceed alternately at the interface. The above assumption is named the coordination polyhedron growth mechanism model. In the following, the NaCl crystal is taken as an example to describe this growth mechanism model.
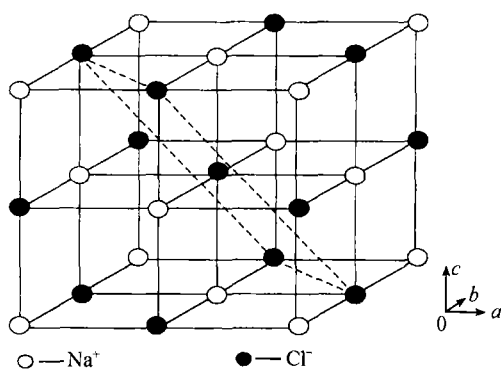


○ — Na⁺               ● — Cl⁻

Fig. 1.    Structure of the NaCl crystal cell.
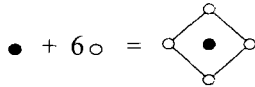
The space group of halite is $O_h^5$ = Fm3m, and the crystal lattice constant is $a$ = 0.5638 nm. In the structure of halite, the sodium and chlorine atoms are arranged alternately at the corners of a set of cubes, the atoms of either kind alone forming a face-centered cubic lattice. Each sodium atom is surrounded by six chlorine atoms and vice versa. The structure of a crystal cell is shown in fig. 1.

According to the coordination polyhedron growth mechanism model, the formation mechanism of the NaCl crystal consists of two complex processes at the interface: the coordination of Cl⁻ ions to Na⁺ ion to form the NaCl₆ group and the coordination of Na⁺ ions to Cl⁻ ion to form
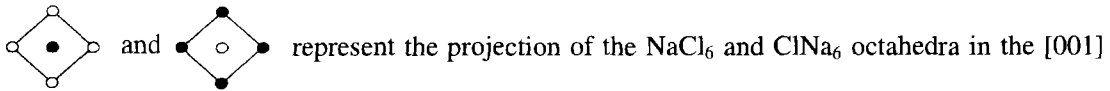
the $ClNa_6$ group. However, the formation rates of the above two groups are different at the interface. The formation rate of a coordination group at the interface is mainly related to its stability energy ($U$) which can be approximately calculated as follows:

$$U = -p \times \frac{(Z_1 e) \times (Z_2 e)}{r_1} + q \times \frac{(Z_2 e)^2}{r_2},$$    (1)

where $r_1$ represents the distance between central ion and ligand, $r_2$ the distance between neighboring ligands, $p$ the coordination number of central ion, $q$ the number of ligand-pair with distance $r_2$ and $Z_1$ and $Z_2$ stand for the charge number of central ion and ligand, respectively. The bigger the stability energy, the faster the formation rate of the coordination group at the interface. Moreover, the formation rate of a coordination group is also related to the radius of central ion. The smaller the radius of ion, the larger the formation rate of the coordination group. With eq. (1) the stability energy of both $NaCl_6$ and $ClNa_6$ groups is determined as 3.96 $e^2/r$, but their radii are different. The radii of $Na^+$ and $Cl^-$ ions are equal to 0.102 and 0.181 nm, respectively. So the formation rate of the $NaCl_6$ octahedron is faster than that of the $ClNa_6$ octahedron. Hence at the beginning of the formation of the NaCl crystal, the $NaCl_6$ octahedron is firstly formed by the coordination of $Cl^-$ ions to $Na^+$ ion,
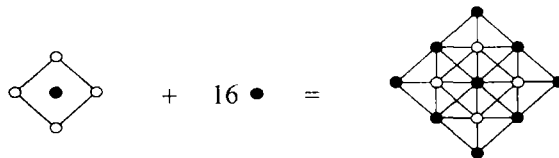


where the black circle represents the $Na^+$ ion, and the hollow circle represents the $Cl^-$ ion. Both

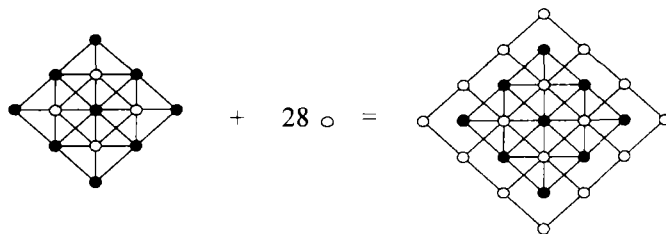 and  represent the projection of the $NaCl_6$ and $ClNa_6$ octahedra in the [001] direction.

The $Cl^-$ ions appear at the interface. In the structure of the NaCl crystal, the coordination number of $Cl^-$ ion is equal to 6. To meet the 6-coordination of $Cl^-$ ion, at the interface, each $Cl^-$ ion must coordinate with $Na^+$ ions to form the $ClNa_6$ group:



Thus, the $Na^+$ ions appear at the interface. Likewise, to meet the 6-coordination of $Na^+$ ion in the NaCl crystal, at the interface, each $Na^+$ ion must coordinate with $Cl^-$ ions to form the $NaCl_6$ group:

Consequently, the $Cl^-$ ions appear at the interface again. So the growth process of NaCl crystal is a process of alternate repeating between two coordinations at the interface. Note that the above equation only shows the growth process of the NaCl crystal in the direction perpendicular to [001]. When the size of clusters formed from this reaches the value required of the formation of the nucleus, the nucleus forms. In the formation of the 3D-nucleus, the growth unit entering into crystal lattice has to overcome the energy barrier caused by the increase in surface energy.

## 2  Growth habit of crystals

The growth habit of a crystal is related to the growth of the crystal. The growth of a crystal involves the step generation, the step movement and the diffusion of ion. For simplicity, we first discuss the growth habit of the perfect crystal. In a perfect crystal, the steps are created by the two-dimensional nucleation model. There, small islands are first formed and start to grow at the interface. After a certain time, the islands start to touch each other and steps disappear, until a complete layer is formed. So the growth rate of a crystal is related to the step generation rate and the step movement rate. In general, the rate of the step generation is slower than that of the step movement because the growth unit has to overcome the energy barrier caused by the increase in surface energy during the step generation showing that the growth rate of a crystal is mainly determined by the step generation rate. In the following, the NaCl crystal is taken as an example to elucidate the relationship between the growth habit of a crystal and the structure of its interface.

The above analysis indicates that the rate of coordination of $Cl^-$ ions in the parent phase to $Na^+$ ion to form the $NaCl_6$ group is bigger than that of $Na^+$ ions in the parent phase to $Cl^-$ ion to form the $ClNa_6$ group. In the growth procedure, the $Cl^-$ ions are easily exposed at the interface; that is, as soon as a layer of $Na^+$ ion forms, a layer of $Cl^-$ ions coordinate on top of it. So the generation process of the step observed during crystal growth at least consists of two coordination processes occurring at the interface: the coordination of $Na^+$ ions in the parent phase to $Cl^-$ ion to form $ClNa_6$ group and the coordination of $Cl^-$ ions in the parent phase to $Na^+$ ion to form $NaCl_6$ group, and the step generation rate is determined by the rate of coordination of $Na^+$ ions in the parent phase to $Cl^-$ ion at the interface. However, at the interface of the different crystal faces, the rate of the coordination of $Na^+$ ions to $Cl^-$ ion is different. At the interface where $Cl^-$ ions are present, the rate of the coordination of a $Na^+$ ion in the parent phase to $Cl^-$ ion can be determined by the electrostatic bond strength (EBS) that reaches a nearest neighbor $Na^+$ ion in the parent

phase from a $Cl^-$ ion which can be approximately calculated as follows:

$$EBS = \frac{Z}{N_C + 1},\qquad(2)$$

where $Z$ represents the charge on the cation (or anion), $N_C$ represents coordination number of anions or cations at the interface. So the step generation rate is related to the coordination number of ions at the interface. Note that the coordination number of ions at the interface of certain crystal faces can be obtained through drawing up the interface of this crystal face in the coordination structure of crystal. Fig. 2 shows the coordination structure of $Cl^-$ ion in the crystal.
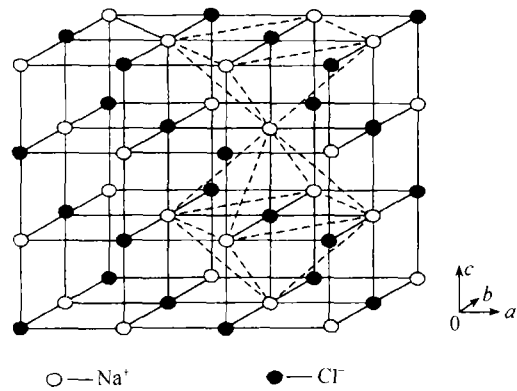


Fig. 2.  Coordination structure of $Cl^-$ ion in the NaCl crystal

○ — Na⁺      ● — Cl⁻

Fig. 2 indicates that the $ClNa_6$ octahedron has only one orientation in the NaCl structure. Suppose that the $ClNa_6$ octahedron is cut open by a plane through $Cl^-$ ions, such as the {001} face. By moving the upper part, the interface of the {001} face can be drawn up. Thus, it is easily obtained that the coordination number of $Cl^-$ at the interface of the {001} face is 5. In the same way, at the interface of the {101} and {111} crystal faces, the coordination number of $Cl^-$ ions is equal to 4 and 3, respectively. According to eq. (2), the electrostatic bond strength after a $Na^+$ ion in the parent phase complexing with a $Cl^-$ ion at the interface of the {001}, {101} and {111} crystal faces is equal to 1/6, 1/5 and 1/4, respectively. So, the step generation rate of various crystal faces decreases in the following order: $V_{\{111\}} > V_{\{101\}} > V_{\{001\}}$. Thus, when the growth rate of a crystal is determined by the rate of step generation, the growth rate of various crystal faces also decreases in the following order: $V_{\{111\}} > V_{\{101\}} > V_{\{001\}}$. The {001} face is a flat face. The morphology of the NaCl crystal is cubic which agrees with the morphology of NaCl crystal observed in aqueous solution[16]. Based on the above analysis, when the growth rate of a crystal is determined by the rate of step generation, the growth habit of the crystal can be determined through comparing the coordination number of the central ions with the smallest coordination rate (such as the $Cl^-$ ions in the NaCl crystal) at the interface. The more the coordination number of ions at the interface, the slower the growth rate of corresponding crystal face; the smaller the coordination number of ions at the interface, the faster the growth rate of corresponding crystal face. This relation represents rule 1.

In reality, the most prepared crystals are not perfect. There exist defects in the structure of this crystal. The outcrops of screw dislocation provide the source of step, which do not disappear in the growth procedure. So, for the defect crystal, the growth rate is determined by the step movement under low supersaturating conditions because the step always exists during the crystal

growth. Moreover, when the growing interface is shielded by the impurity ions, which makes the difference of step generation rate between various crystal faces decrease. The growth rate is also possibly determined by step movement rate. The bigger the step movement rate, the faster the growth rate of corresponding crystal face. From the above analysis, it can be obtained that the electrostatic bond strength after a $Cl^-$ ion complexing with a $Na^+$ ion has a big difference at the interface of {001}, {111} and {101} faces. It suggests that the effect of the environment of Cl ion on the growth habit of the NaCl crystal is great. The growth habit of the NaCl crystal is generally cubic. However, when there exist the impurity ions in the mother phase, the difference of the step generation rate between various crystal faces decreases due to the shielding effect of impurity ion. It is possible for the step movement rate to produce an important effect in the growth habit of the NaCl crystal. Obviously, the step movement rate is related to the density of $Cl^-$ ion at the interface of various crystal faces. The bigger the density of $Cl^-$ ion, the slower the step movement rate. So when the growth rate of a crystal is determined by the step movement rate, the growth habit of a crystal can be determined by comparing the density of the ion with the smallest coordination rate at the interface. The smaller the density of ion at the interface, the faster the growth rate of this crystal face and vice versa. This relationship represents rule 2. It should be noted that the density of ion at the interface of various crystal faces can be obtained through taking a 2-dimensional repeating unit at the interface, and then calculating the density of this ion within this unit. The atomic number located at the vertices, edge and face of repeating lattice is 1/8, 1/4 and 1/2, respectively. In fig. 1, it can be seen that for the {001}, {111} and {101} faces, the density of $Cl^-$ ions is different. According to the above density calculation method, at the interface of {001}

faces, the density of $Cl^-$ ions is equal to $\dfrac{\frac{1}{4} \times 4}{a_0^2}$ = 0.0003146 $nm^{-2}$; at the interface of {110} faces,

the density of $Cl^-$ ions is equal to $\dfrac{\frac{1}{4} \times 2 + \frac{1}{2} \times 1}{\sqrt{2}a_0 \times a_0}$ = 0.0002224 $nm^{-2}$; at the interface of {111}

faces, the density of $Cl^-$ ion is equal to $\dfrac{\frac{1}{8} \times 4 + \frac{1}{2} \times 1}{\dfrac{\sqrt{2}a_0}{2} \times \dfrac{\sqrt{6}a_0}{2}}$ = 0.0003633 $nm^{-2}$, which is calculated in

terms of the repeating unit with dotted line. According to rule 2, the growth rate of various crystal faces decreases in the following order: $V_{\{110\}} > V_{\{001\}} > V_{\{111\}}$. So when the growth rate of a crystal is determined by the step movement rate, the theoretical growth habit of the NaCl crystal is the octahedron, which is consistent with the growth habit of the NaCl crystal observed from the $NH_2CONH_2$ solution[16]. In order to confirm the feasibility of the above growth habit rules, the growth habits of ZnS, CsI and $CaF_2$ crystals are further discussed in the following.

## 2.1　Growth habit of ZnS crystal

The growth habit of the ZnS crystal observed in the nature[17] is the tetrahedron. Through the hydrothermal preparation experiment of ZnS crystal, Laudise et al.[18] confirmed that the growth rate of {111} face is fastest among various crystal faces. However, the above results were not reasonably explained. The ZnS crystal is an equiaxial crystal system; its space group is $T_d^2$ - $F\bar{4}3m$. In the zinc blende structure, the sulfur ions are arranged in cubic closest packing, in which half of the tetrahedral sites are filled with zinc atoms. Both the coordination number of sulfur and zinc are four. Its structure is shown in fig. 3. Fig. 4 shows the projection of the structure of the ZnS crystal along the $[1\bar{1}0]$ direction.
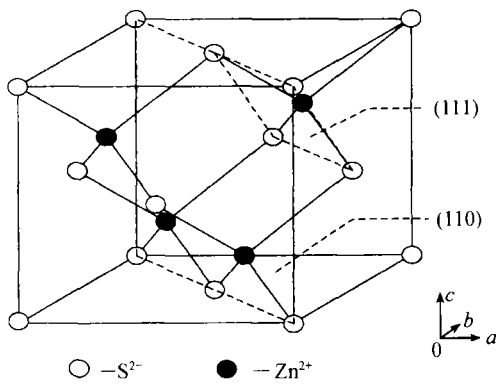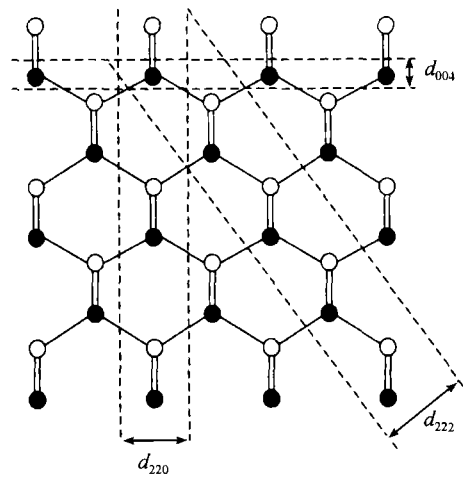


Fig. 3.　Structure of ZnS crystal cell.

Fig. 4.　Projection of structure of ZnS crystal along the $[1\bar{1}0]$ direction.

In fig. 4, it can be seen that the two PBCs are bonded in the slice $d_{222}$, so the {111} face is an F form. The slice $d_{004}$ is too thin to form a PBC, so the {001} face is a K face. The neighboring PBCs in the $d_{220}$ are not bonded, so the {110} is an S face. According to PBC theory, the velocities of various crystal faces are $V_{\{001\}} > V_{\{110\}} > V_{\{111\}} = V_{\{\bar{1}\bar{1}\bar{1}\}}$, and its theoretical growth habit is the octahedron. The result is not consistent with the growth habit of the ZnS crystal observed in the experiment. According to the coordination polyhedron growth mechanism model, the growth mechanism of the ZnS crystal consists of two kinds of coordination processes occurring at the interface: the coordination of $S^{2-}$ ions to $Zn^{2+}$ ions to form the $ZnS_4$ tetrahedron and the coordination of $Zn^{2+}$ ions to $S^{2-}$ ions to form the $SZn_4$ tetrahedron. From eq. (1), the stability energy of $ZnS_4$ and $SZn_4$ groups is equal to $-1.28\ e^2/r$. But the radii of $Zn^{2+}$ and $S^{2-}$ ions are equal to 0.060 and 0.138 nm, respectively. So the formation rate of the $ZnS_4$ tetrahedron is bigger than that of the $SZn_4$ tetrahedron. The coordination of $Zn^{2+}$ ions to $S^{2-}$ ions to form $SZn_4$ tetrahedron is the rate-determining step. The growth rate of various crystal faces is mainly related to the coordina-
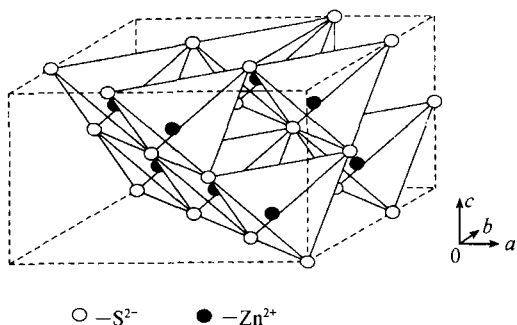
○ —S²⁻        ● —Zn²⁺

Fig. 5.   Coordination structure of Zn²⁺ ion in the ZnS crystal.

tion number and density of $S^{2-}$ ions at the interface. Fig. 5 shows the coordination structure of $Zn^{2+}$ ion in the ZnS crystal.

It can be seen from fig. 5 that at the interface of $\{001\}$, $\{111\}$ and $\{\bar{1}\,\bar{1}\,\bar{1}\}$ faces, every $S^{2-}$ ion coordinates with two, one and three $Zn^{2+}$ ions, respectively. So at the interface of $\{111\}$, $\{001\}$ and $\{\bar{1}\,\bar{1}\,\bar{1}\}$ faces, the coordination number of $S^{2-}$ ions is equal to 1, 2 and 3, respectively. According to rule 1, the growth rate of various crystal faces decreases in the following order: $V_{\{111\}} > V_{\{001\}} > V_{\{\bar{1}\,\bar{1}\,\bar{1}\}}$. So when the growth rate of a crystal is determined by the step generation rate, the morphology of the ZnS crystal is the tetrahedron $\{\bar{1}\,\bar{1}\,\bar{1}\}$. Moreover, the growth habit of the ZnS crystal is also related to the density of $S^{2-}$ ions at the interface of various crystal faces. It can be seen from fig. 3 that at the interface of the $\{001\}$, $\{111\}$ and $\{\bar{1}\,\bar{1}\,\bar{1}\}$ faces, the density of $S^{2-}$ ions is different, at the interface of $\{001\}$ face, the density of $S^{2-}$ ions is equal to

$$\frac{\dfrac{1}{8}\times4+\dfrac{1}{2}\times1}{a_0^2} = 0.0003418 \text{ nm}^{-2},$$ at the interface of $\{110\}$ face, the density of $S^{2-}$ ions is equal to

$$\frac{\dfrac{1}{8}\times4+\dfrac{1}{4}\times2}{\sqrt{2}a_0\times a_0} = 0.0002417 \text{ nm}^{-2}$$ and at the interface of $\{\bar{1}\,\bar{1}\,\bar{1}\}$ and $\{111\}$ faces, the density of

$S^{2-}$ ion is equal to $$\frac{\dfrac{1}{8}\times4}{\dfrac{\sqrt{2}a_0}{2}\times\dfrac{1}{2}\sqrt{a_0^2+\dfrac{1}{2}a_0^2}} = 0.0003947 \text{ nm}^{-2},$$ which is calculated in terms of the

repeating unit with dotted line. According to rule 2, the growth rate of various crystal faces decreases in the following order: $V_{\{110\}} > V_{\{001\}} > V_{\{\bar{1}\,\bar{1}\,\bar{1}\}} = V_{\{111\}}$. So when the growth rate of a crystal is determined by the step movement rate, the growth habit of the ZnS crystal is an octahedron $\{111\}$. However, according to eq. (2), the electrostatic bond strength after a $S^{2-}$ ion complexing with a $Zn^{2+}$ ion is 2/2, 2/3 and 2/4 respectively at the interface of $\{001\}$, $\{111\}$ and $\{\bar{1}\,\bar{1}\,\bar{1}\}$ faces which has a big difference. So the step generation rate plays an important role in the growth habit of the ZnS crystal. The theoretical growth habit of the ZnS crystal is a tetrahedron, not an octahedron. This result is consistent with the growth habit of the ZnS crystal observed in the nature and under hydrothermal conditions.

## 2.2   Growth habit of the CaF$_2$ crystal

Fig. 6 shows the SEM photograph of CaF$_2$ crystallites prepared by the hydrothermal method using CaF$_2$ as a precursor at 200℃. From fig. 6, it can be seen that the morphology of CaF$_2$ crystal is the octahedron. Fig. 7 shows the SEM photograph of CaF$_2$ crystallites prepared by the hydrothermal method using equal molar CaSO$_4$ and NaF as precursors at 200℃. From fig. 7, it can be seen that the morphology of CaF$_2$ crystal is a cube.
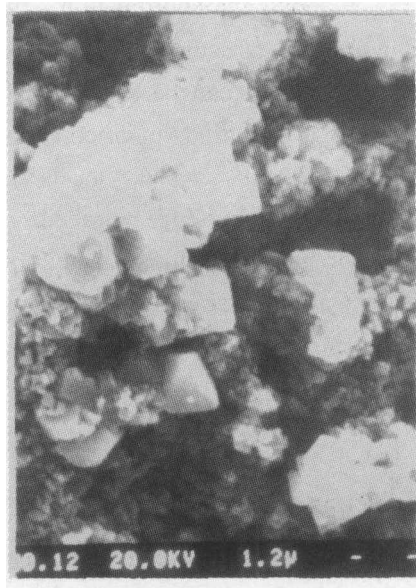


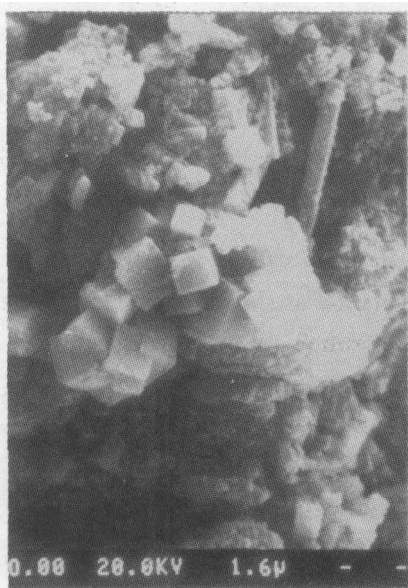Fig. 6.   SEM photograph of CaF$_2$ crystallites prepared by using CaF$_2$ as a precursor at 200℃.

Fig. 7.   SEM photograph of CaF$_2$ crystallites prepared by using CaSO$_4$ and NaF as precursors at 200℃.

CaF$_2$ crystal belongs to the equiaxial crystal system, and its space group is $O_h^5$-Fm3m. The crystal lattice constant is $a_0 = 0.56450$ nm. In the structure of CaF$_2$ crystal, the coordination number of Ca$^{2+}$ and F$^-$ is 8 and 4, respectively. Its structure is shown in fig. 8.

According to the coordination polyhedron growth mechanism model, the growth mechanism of CaF$_2$ crystal under hydrothermal conditions consists of both the coordination of F$^-$ ions to Ca$^{2+}$ ions to form CaF$_8$ group and the coordination of Ca$^{2+}$ ions to F$^-$ ion to form FCa$_4$ group at the interface. From eq. (1), it can be obtained that the stability energy of the CaF$_8$ and FCa$_4$ groups is equal to 3.76 e$^2$/r and
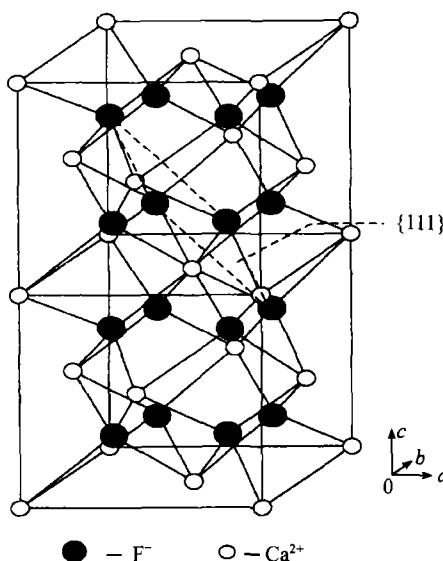


● — F$^-$        ○ — Ca$^{2+}$

Fig. 8.   Structure of CaF$_2$ crystal.

Fig. 9.   Coordination structure of F⁻ ion in the CaF₂ structure.

$\bullet - F^-$        $\bigcirc - Ca^{2+}$

6.72 $e^2/r$, respectively. The radii of both F⁻ ion and $Ca^{2+}$ ion are 0.131 and 0.112 nm respectively. So the formation rate of the $CaF_8$ group is faster than that of the $FCa_4$ group. The growth habit of $CaF_2$ crystal is mainly related to the density of F⁻ ion and its coordination number at the interface. Fig. 9 shows the coordination structure of F⁻ ion in the $CaF_2$ structure.

From fig. 9, it can be seen that the $FCa_4$ tetrahedron has two kinds of orientations in the structure of the $CaF_2$ crystal. One is similar to the orientation of the $ZnS_4$ tetrahedron in the ZnS crystal as shown in fig. 10; the other is similar to the orientation of the $SZn_4$ tetrahedron in the ZnS crystal as shown in fig. 11. So the structure of the $CaF_2$ crystal can be considered as the mutual insertion between fig. 10 and fig. 11. From fig. 10, it can be seen that at the interface of the $(\bar{1}\,\bar{1}\,\bar{1})$, $(11\bar{1})$, $(\bar{1}11)$ and $(1\bar{1}1)$ faces, the coordination number of F⁻ ion is equal to 1; from fig. 11, it can be seen that at the interface of the $(\bar{1}\,\bar{1}\,\bar{1})$, $(11\bar{1})$, $(\bar{1}11)$ and $(1\bar{1}1)$ faces, the coordination number of F⁻ ion is equal to 3. So at the interface of $(\bar{1}\,\bar{1}\,\bar{1})$, $(11\bar{1})$, $(\bar{1}11)$ and $(1\bar{1}1)$ faces, the coordination number of half of F⁻ ion is 1, the other half is 3. In the same way, at the interface of $(111)$, $(\bar{1}\,\bar{1}1)$, $(1\bar{1}\,\bar{1})$ and $(\bar{1}1\bar{1})$ faces, the coordination number of half of F⁻ ion is 1, the other half is 3. That is to say, at the interface of $\{111\}$, the coordination number of half of F⁻ ion is 1, the other half is 3. The growth rate of the $CaF_2$ crystal is determined by the coordination process of F⁻ ion with the coordination number of three at the interface. From fig. 9,
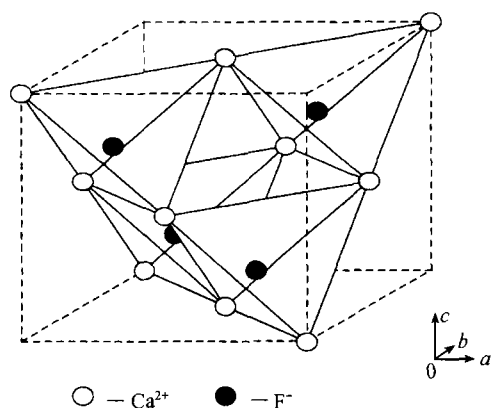


$\bigcirc - Ca^{2+}$     $\bullet - F^-$

Fig. 10.   Orientation of $FCa_4$ tetrahedron in the $CaF_2$ structure similar to orientation of $ZnS_4$ tetrahedron in the ZnS crystal.



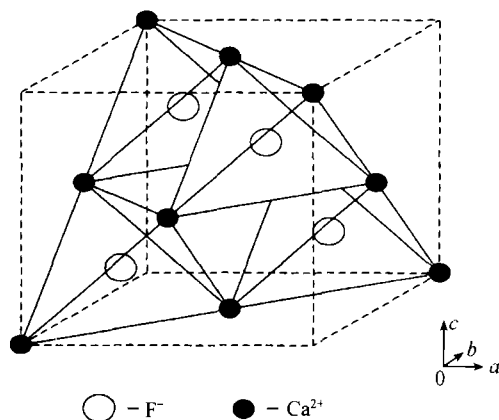$\bigcirc - F^-$     $\bullet - Ca^{2+}$

Fig. 11.   Orientation of $FCa_4$ tetrahedron in the $CaF_2$ structure similar to orientation of $SZn_4$ tetrahedron in the ZnS crystal.

it can be seen that at the interface of the {001} face, the coordination number of $F^-$ ion is equal to 2. According to rule 2, the growth rate of various crystal faces decreases in the following order: $V_{\{001\}} > V_{\{111\}}$. When the crystal growth depends on the step generation rate, the growth habit of the $CaF_2$ crystal is the octahedron. Namely, when the interface is not shielded by the impurity ions, the growth habit of the $CaF_2$ crystal is the octahedron which is consistent with the result of fig. 6.

Moreover, from the above analysis, it can be obtained that the electrostatic bond strength after a $F^-$ ion complexing with a $Ca^{2+}$ ion has a small difference at the interface of {111} and {001} faces. So when the interface is shielded by the impurity ions, the relative growth rate of various crystal faces is mainly determined by the step movement rate. From fig. 8, it can be seen that at

the interface of {001} face, the density of $F^-$ ion is equal to $\dfrac{\frac{1}{8} \times 4}{\left(\dfrac{a_0}{2}\right)^2} = 0.0012548$ $nm^{-2}$; at the

interface of {101} face, the density of $F^-$ ion is equal to $\dfrac{\frac{1}{8} \times 4}{\sqrt{2}\left(\dfrac{a_0}{2}\right) \times \left(\dfrac{a_0}{2}\right)} = 0.0008872$ $nm^{-2}$ and

at the interface of {111} face, the density of $F^-$ ion is equal to $\dfrac{\frac{1}{8} \times 4}{\sqrt{2}\left(\dfrac{a_0}{2}\right) \times \sqrt{2}\left(\dfrac{a_0}{2}\right) \times \dfrac{\sqrt{3}}{2}} =$

$0.0010868$ $nm^{-2}$, which is calculated in terms of the repeating unit with the dotted line. According to rule 2, the growth rate of various crystal faces decreases in the following order: $V_{\{101\}} > V_{\{111\}} > V_{\{001\}}$. So when the growth rate is determined by the step movement rate, the growth habit of $CaF_2$ crystal is a cube, which is consistent with the result of fig. 7.

## 2.3 Growth habit of CsI crystal

The growth habit[16] of the CsI crystal crystallized from aqueous solution is the dodecahedron {110} and cube {001}. According to the coordination polyhedron growth mechanism model, the growth process of CsI crystal can be regarded as $Cs^+$ ion and $I^-$ ion coordinative to each other to form the $CsI_8$ and $ICs_8$ groups at the interface respectively. According to eq. (1), the stability energy of $CsI_8$ and $ICs_8$ groups is the same. However, the radii of $Cs^+$ ion and $I^-$ ion are 0.169 and 0.216 nm, respectively. So the formation rate of the $CsI_8$ group is faster than that of the $ICs_8$ group. The coordination of $Cs^+$ ion to $I^-$ ion to form the $ICs_8$ groups at the interface is the rate-determining step. The growth habit of CsI crystal is mainly related to the coordination number and density of $I^-$ ion at the interface. The CsI crystal belongs to cubic crystal system, and its space group is $P\bar{4}3m$. The crystal lattice constant is $a = 0.4121$ nm, $Z = 1$. In the structure of CsI
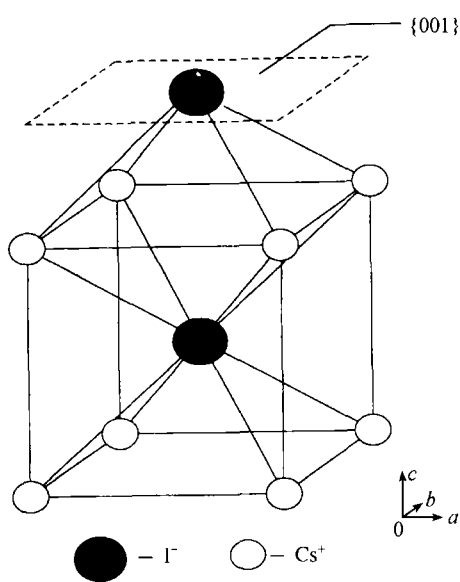
Fig. 12.   Coordination structure of $I^-$ ion in the CsI crystal.

crystal, each $I^-$ ion is surrounded by eight $Cs^+$ ions and vice versa. The coordination structure of $I^-$ ion in the CsI crystal is shown in fig. 12.

From fig. 12, it can be seen that the $ICs_8$ cube has only one orientation in the CsI crystal structure. Suppose that the $ICs_8$ cube is cut open by a plane through $I^-$ ions, such as the {001} face. By moving the upper part, the interface of the {001} face is drawn up. Thus, it is easy to obtain that the coordination number of $I^-$ ion is 4 at the interface of the {001} face. In the same way, at the interface of the {101} and {111} crystal faces, the coordination number of $I^-$ ion is equal to 6 and 4, respectively. In terms of rule 1, the growth rate of various crystal faces de-

creases in the following order: $V_{\{001\}} = V_{\{111\}} > V_{\{110\}}$. So when the growth rate of crystal is determined by step generation rate, the growth habit of CsI crystal is the dodecahedron {110}. Moreover, the growth rate of CsI crystal is related to the density of the ion as well as the coordination number of ions at the interface. Fig. 13 shows the structure of CsI crystal where $I^-$ ions are located in the corner.

From fig. 13, it can be seen that for the {001}, {111}, and {110} faces, the density of $I^-$ ions is different. According to the above density calculation method, at the interface of {001} face, the density of $I^-$ ions is equal to $\dfrac{\dfrac{1}{8}\times 4}{a_0^2}$ = 0.00029442 $nm^{-2}$; at the interface of {110} face, the density of $I^-$ ions is equal to $\dfrac{\dfrac{1}{8}\times 4}{\sqrt{2}a_0 \times a_0}$ = 0.00020819 $nm^{-2}$ and at the interface of {111} face, the density of $I^-$ ion is equal to $\dfrac{\dfrac{1}{8}\times 4}{\dfrac{1}{2}\times \sqrt{2}a_0 \times \sqrt{6}a_0}$ = 0.00016998 $mm^{-2}$, which is calculated



Fig. 13.   Structure of CsI crystal.

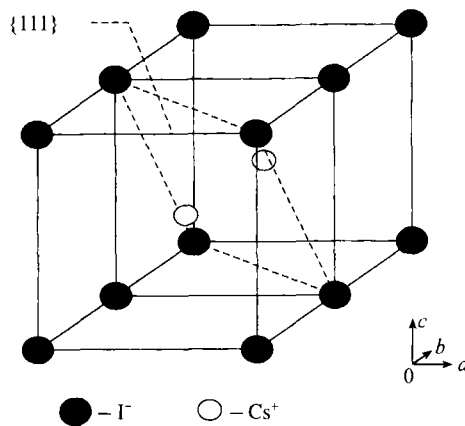in terms of the repeating unit with dotted line. According to rule 2, the growth rate of various

crystal faces decreases in the following order: $V_{\{111\}} > V_{\{110\}} > V_{\{001\}}$. So when the growth rate of crystal depends on the step movement rate, the growth habit of CsI crystal is a cube. So the growth habit of the CsI crystal predicted by rules 1 and 2 is the dodecahedron $\{110\}$ and cube $\{001\}$, which is consistent with the morphology of the CsI crystal observed in the solution.

## 3 Conclusions

The successful explanation on the growth habit of crystals with different structures indirectly confirms the reasonability of the assumption of growth mechanism model and the growth habit rule deduced on this basis. Namely, ( i ) step generation consists of at least two coordination processes occurring at the interface: the coordination of anions (cations) in the mother phase to cations (anions) and the coordination of cations (anions) in the mother phase to anions (cations); ( ii ) when the growth rate of a crystal is determined by the step-generation rate, the growth habit of this crystal is related to the coordination number of the ions with the smallest coordination rate at the interface of various crystal faces. The smaller the coordination number of the ions at the interface, the faster the growth rate of corresponding crystal face. When the crystal growth depends on the step movement rate, the growth habit of this crystal is related to the density of this ion at the interface of various crystal faces. The smaller the density of the ion at the interface, the faster the growth rate of corresponding crystal face.

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