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Growth mechanism and growth habit of oxide crystals

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Abstract

In this paper, the growth mechanism and growth habit of oxide crystals are investigated. Firstly, from the kinetics viewpoint, the growth mechanism of ZnO powders under hydrothermal condition is disclosed starting from the hypothesis of growth unit. It is concluded that the growth mechanism of oxide crystals contains the formation of growth units and the incorporation of growth units into the crystal lattice by a dehydration reaction. Then, a new growth interface model of oxide crystals in solution is established on the basis of an ideal growth mechanism of oxide crystals, which considers the interface structure of the crystal as the stacking order of coordination polyhedrons with OH^- ligands. Finally, a new rule concerning the growth habit is deduced considering the relation between the growth rate and the orientation of the coordination polyhedron at the interface. It is concluded that the direction of the crystal face with the corner of the coordination polyhedron occurring at the interface has the fastest growth rate; the direction of the crystal face with the edge of the coordination polyhedron occurring at the interface has the second fastest growth rate; the direction of the crystal face with the face of the coordination polyhedron occurring at the interface has the slowest growth rate. In terms of this rule, the growth habit of ZnO crystal particles and AlO(OH) crystal particles, and the effect of reaction medium on the growth habit are successfully explained. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Growth unit; Growth habit; Hydrothermal method; Interface

1. Introduction

The hydrothermal method [1] is one of the wet chemical methods for the preparation of metal oxide powders of high quality. The powders prepared by the hydrothermal method have good crystallinity, good dispersity, and do not show macroscopic agglomeration. Because the supersaturation of the solution during hydrothermal reaction is low, the particles prepared by the hydrothermal method tend to have a regular polyhedral crystal face. So the hydrothermal method is also an ideal method that is used to investigate the growth habit of crystals.

The growth habit of crystals is mainly determined by the internal structure of a given crystal, and affected by external conditions such as temperature, supersaturation, pH value of the solution etc. So the study of the crystal growth habit can reveal the growth mechanism of the crystal and vice versa.

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The theoretical models concerning crystal growth habit mainly include the BFDH law [2] and the PBC theory [3]. The BFDH law starting from planar mesh density, and considering the effects of screw axis and glide plane on crystal growth habit, provides a predicted theoretical growth habit of the crystal. The PBC theory provides an ideal growth habit of crystals in terms of bond chain types between molecules and attachment energy. But the above mentioned models have some shortages in explaining or predicting the crystal growth habit. For example, they cannot reasonably explain the growth habit of polar crystal and the change of growth habit of oxide crystal in different crystallization conditions. Moreover, from the angle of crystal growth, it can be found that the change of crystal growth habit is due to the change of relative growth rate at various crystal faces. So, studying the growth habit of an oxide crystal must start from the growth mechanism of the crystal. Wei-zhuo Zhong [4] was the first to put forward the growth unit model, which hypothesizes that in the crystallization procedure, cations exist in the form of complexes whose ligands are OH^- ions, and the complex whose coordination numbers are equal to that of the crystal formed is called a growth unit. The paper will reveal crystal growth mechanisms, and try to advance a new rule of crystal growth habits that is applied to different crystals.

2. Experimental procedure

The reaction vessel adopted in the experiments is a silver-lined tube-type stainless steel autoclave with a capacity of about 215 ml and an inner diameter of 30 mm. In the upper part of the autoclave, a discharge valve for releasing gas and a gas manometer are located. The $Zn(CH_3COO)_2$ solution or the newly-prepared hydroxide colloids $Zn(OH)_2$ by adding the proper quantity of ammonia hydroxide to the chloride solution are used as starting materials. Various solvents involving pure water and different concentrations of sodium hydroxide solutions are employed. The reaction temperature ranges from 200 to 350°C. The crystallites are naturally crystallized after the hydrothermal reactions, then washed and filtered. The obtained powder is dried at 120°C for 24 h in the air for X-ray diffraction measurements, and TEM or SEM morphological analyses.

3. Result and discussion

The ZnO crystal obtained by the hydrothermal method belongs to the hexagonal crystal system. Due to its higher solubility under hydrothermal conditions, the growth rate of the ZnO crystal is smaller, which allows the ZnO particles to have good crystallinity and regular polyhedral crystal faces. So the ZnO crystal tends to be a good material for studying the crystal growth habit. Laudise [5,6] was the first to describe the idealized growth habit of a ZnO crystal, preparing the ZnO single crystal by the hydrothermal method in an alkaline (1–2 mol/l NaOH) medium. It has been observed that the maximal crystal growth velocity is fixed in the $\langle 0\,0\,0\,1\rangle$ direction and the following relationship between the velocities of crystal growth to different directions is found to be: $V_{\langle 0\,0\,0\,1\rangle} > V_{\langle 0\,1\,\bar{1}\,0\rangle} > V_{\langle 0\,0\,0\,\bar{1}\rangle}$, its idealized growth habit is shown in Fig. 1. In order to confirm the above

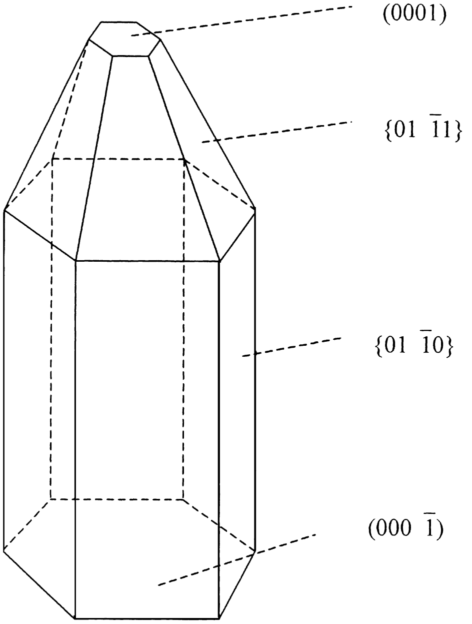

Fig. 1. Idealized growth habit of the ZnO crystal.

idealized growth habit of the ZnO crystal, the experiment is done by hydrothermal salt solution pressure-relief using $Zn(CH_3COO)_2$ solution as the precursor. Fig. 2 shows the SEM micrograph of the powder prepared using 0.5 mol/l $Zn(CH_3COO)_2$ solution as the precursor at 250°C.

From Fig. 2, it can be seen that the morphology of the particle is prismatic; the relative growth rate of the (0 0 0 1) face and the $(0\,0\,0\,\bar{1})$ face shows a difference, which is consistent with the idealized growth habit of the ZnO crystal described by Laudise.

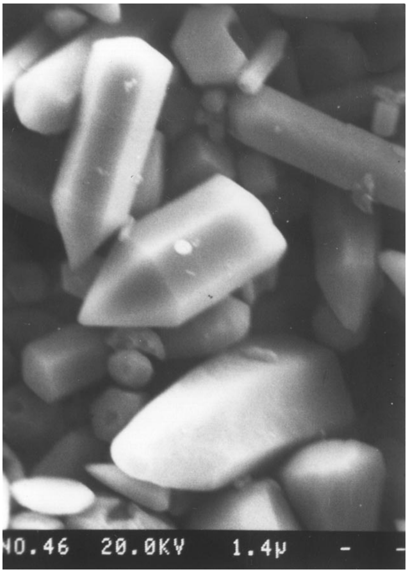

Fig. 2. SEM micrograph of powder prepared by hydrothermal salt solution pressure-relief using 0.5 mol/l $Zn(CH_3COO)_2$ solution as precursor at 250°C.

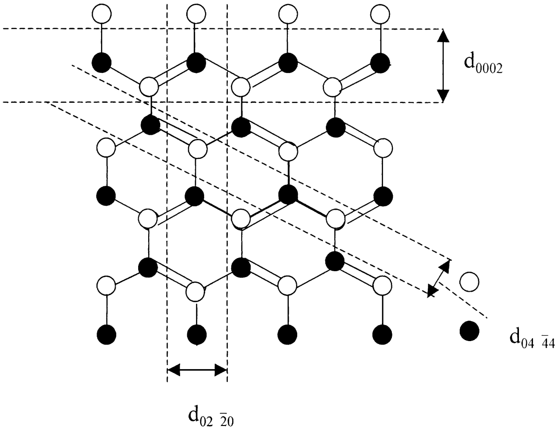

Fig. 3. Projection along $[1\,\bar{2}\,\bar{2}\,0]$. Black circles represent zinc atoms, white circles represent oxygen atoms.

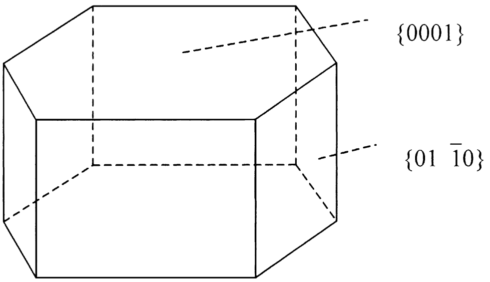

Fig. 4. Theoretical growth form of ZnO crystal.

ZnO is a polar crystal, whose polar axis is the c-axis, its space group is $C_{6v}^4 = p6_3mc$. In the ZnO structure, each Zn^{2+} ion is surrounded by four O^{2-} ions and vice versa. Fig. 3 shows a projection along $[1\,\bar{2}\,\bar{2}\,0]$. From Fig. 3, it can be found that the PBCs are bonded in the slice $d_{0\,0\,0\,2}$, so the $\{0\,0\,0\,1\}$ is an F form. The neighboring PBCs in the $d_{0\,4\,\bar{4}\,4}$ are not bonded, so $\{0\,1\,\bar{1}\,1\}$ is an S form. The slice $d_{0\,2\,\bar{2}\,0}$ is too thin compared to a PBC, so $\{0\,1\,\bar{1}\,0\}$ is a K form. According to PBC theory, the velocities of crystal growth in different directions is found to be: $V_{\langle 0\,1\,\bar{1}\,0\rangle} > V_{\langle 0\,1\,\bar{1}\,1\rangle} > V_{\langle 0\,0\,0\,\bar{1}\rangle} = V_{\langle 0\,0\,0\,1\rangle}$, its theoretical growth form is shown in Fig. 4. This is not consistent with the growth habit of the ZnO crystal observed by the hydrothermal experiment. So, the PBC theory cannot reasonably explain the growth habit of the ZnO crystal under hydrothermal conditions. The growth habit of the crystal is due to the difference of relative growth rates at various crystal faces. So, the study of crystal growth habit must consider the effect of growth mechanism and interface characteristics on crystal growth habit.

From a kinetics point of view of crystal growth, it has to be assumed that the growth mechanism mainly contains the formation of growth units and the incorporation of growth units into the crystal lattice at the interface. The problem is to clarify what the growth units are for a given location and then how growth units are incorporated into the crystal lattice. From the analysis of IR spectra, [7,8] Raman spectra [9,10] and low angle diffraction of X-ray [11,12] of the solution structure, it can be found that there exist complexes whose ligands are OH^- in the supersaturation solution, especially near the interface of the oxide crystal. Moreover, from the calculation value of the stability energy of the complex with OH^- ligands [13], it can also be found that the cation existing in the form of a given complex is more stable than a single cation. So, we introduce the hypothesis that the growth unit is the complex formed by the attraction of cation and OH^- ions, whose coordination numbers is equal to that of the cation in the crystal to be formed. For example, in the ZnO crystal, the coordination number of Zn is four, and then according to our hypothesis the growth units of the ZnO crystal are the complex $Zn(OH)_4^{2-}$.

In order to reveal the formation mechanism of ZnO powder by the hydrothermal salt solution pressure-relief method, the experiments are carried out using the $Zn(CH_3COO)_2$ solution as the precursor under no pressure-relief. The result shows that whether the relief valve is opened or not,[1] this has a greater effect on the experimental result. When the relief valve is not opened, the hydrolysis reaction of $Zn(CH_3COO)_2$ solution does not occur, which shows the hydrolysis reaction of $Zn(CH_3COO)_2$ solution only proceeds under pressure-relief condition. So, when the relief valve is opened, the reaction that takes place in the reactor can be considered to be as follows:

$$Zn(CH_3COO)_2 + H_2O = ZnO + 2CH_3COOH(l), \tag{1}$$

$$CH_3COOH(l) = CH_3COOH(g). \tag{2}$$

Based on the above hypothesis of the character of the growth unit, the growth mechanism of ZnO powders prepared by hydrothermal salt solution pressure-relief is represented as follows. Firstly, when the relief valve is opened in high pressure, due to the CH_3COOH in the solution vaporizing and being discharged from the autoclave, the equilibrium of hydrolysis of CH_3COO^- move to the right which has an increased concentration of OH^-, as shown in Eq. (4). At the same time, $Zn(OH)_4^{2-}$ is formed, as shown in Eq. (5):

$$CH_3COOH(l) = CH_3COOH(g), \tag{3}$$

$$CH_3COO^- + H_2O = CH_3COOH(l) + OH^-, \tag{4}$$

$$\begin{aligned} Zn^{2+} + 2OH^- + 2H_2O &= Zn(OH)_2 + 2H_2O \\ &= Zn(OH)_4^{2-} + 2H^+. \end{aligned} \tag{5}$$

Then, in the greater supersaturation solution, due to the diffusion of ions, and deregulation movement among molecules and ions, growth units $Zn(OH)_4^{2-}$ are bonded together through a dehydration reaction ($OH^- + OH^- = H_2O + O^{2-}$) forming the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$, as shown in Eqs. (6) and (7). When the critical size of the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ reaches the value required for the formation of ZnO powder, the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ is precipitated:

$$Zn(OH)_4^{2-} + Zn(OH)_4^{2-} = Zn_2O(OH)_6^{4-} + H_2O, \tag{6}$$

$$\begin{aligned} &Zn_xO_y(OH)_z^{(z+2y-2x)-} + Zn(OH)_4^{2-} \\ &\quad = Zn_{x+1}O_{y+1}(OH)_{z+2}^{(z+2y-2x+2)-} + H_2O, \end{aligned} \tag{7}$$

where, the subscript "x, y, z" represents the numbers of "Zn^{2+}, O^{2-}, OH^-" within the crystal, respectively.

From the above analysis of the formation mechanism of the ZnO crystal, it can be found that the oxide crystal is the stacking order of the coordination polyhedron by sharing elements (corner, edge or face of the coordination polyhedron). In the interior of the crystal, coordination polyhedra are connected together by sharing O^{2-}; while at the interface of crystal, the terminal vertex of the element (corner, edge or face) of the coordination polyhedron that occurs at the interface is the OH^- ligand, which has been proved by IR [14] and

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[1] The experimental procedure of no pressure-relief is that hydrothermal reaction is preceded using $Zn(CH_3COO)_2$ solution as the precursor. When the temperature reaches the desired value for a given reaction period, cut off the power to make the autoclave cool to room temperature keeping the autoclave sealed.

Raman data [15–17]. For example, at the interface of ZnO crystals along the [0 0 0 1] direction, every coordination polyhedron has a corner present, and the terminal vertex of the corner contains an OH^- ligand, as shown in Fig. 5. Moreover, compared with the number of ions contained in the interior crystal particle, the number of OH^- ions contained at the interface is very small. So the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ to be precipitated is customarily represented as ZnO.

The growth habit of crystals is related to the relative growth rate of various crystal faces bounding the crystal. The difference of the growth rate of various crystal faces results in different growth habits. Under hydrothermal conditions, the viscosity of a solution is lower; the diffusion of ions (including complex) is not the main factor affecting the growth rate, so the growth rate of various crystal faces is mainly related to their interface structure. From the coordination structure of the oxide crystal, it can be found out that the orientation of the coordination polyhedron at different interfaces is different, namely, the elements of the coordination polyhedron present at different interfaces are different. So the growth rate of various crystal faces is mainly related to the elements of the coordination polyhedron present at the interface. In the ZnO crystal, the coordination number of O^{2-} is four, so the terminal vertex of a corner of the coordination polyhedron can still bond with three growth units; the terminal vertex of the edge of the coordination polyhedron can still bond with two growth units; an terminal vertex of the face of the coordination polyhedron can only bond with one growth unit. This shows that the terminal vertex of the corner of the coordination of the polyhedron has the strongest bonding force; the terminal vertex of the edge of the coordination polyhedron has the second strongest binding force; the terminal vertex of the face of the coordination polyhedron has the smallest binding force. So, the crystal face with the corner of the coordination polyhedron present at the interface has the biggest growth rate; the crystal face with the edge of the coordination polyhedron present at the interface has the second biggest growth rate; the crystal face with the face of the coordination polyhedron present at the interface has the smallest growth rate. Thus, we can judge the growth habit by making use of the different elements[2] of the coordination polyhedron which are present at the interface. Namely, if the type of elements of the coordination polyhedron that are present at the interface are different, the growth rate of various crystal faces is related to the type of element of the coordination polyhedron that is present at the interface. The direction of the crystal face with the corner of the coordination polyhedron present at the interface has the fastest growth rate; the direction of the crystal face with the edge of the coordination polyhedron present at the interface has the second fastest growth rate; the direction of the crystal face with the face of the coordination polyhedron present at the interface has the slowest growth rate. Moreover, if the types of elements of the coordination polyhedron that are present at the interface are equal, the growth rate of the various crystal faces is related to the number of elements that every coordination polyhedron presents at the interface. For example, in an SiO_2 crystal, only the corner of the coordination polyhedron is present at the interface of various crystal faces, the growth rate of various crystal faces is related to the number of corners which every coordination polyhedron present at the interface. Crystal faces with more corners of coordination polyhedrons present per unit area at the interface have faster

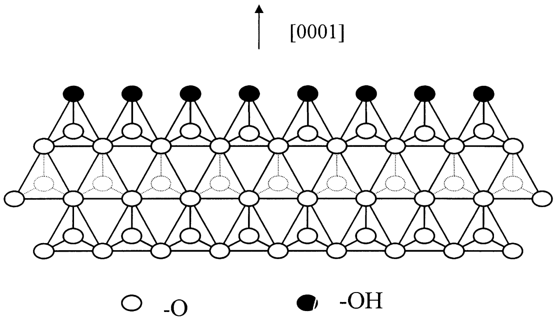

Fig. 5. Idealized interface structure image of ZnO crystal in [0 0 0 1] direction.

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[2] Element is referred to as corner, edge or face.

growth rate. So, when determining the relative growth rate of various crystal faces or predicting the growth habit of the crystal, we first find out the number of kinds of elements of the coordination polyhedron present at various interfaces making use of the coordination structure of the crystal. Then, according to the above new rule, determine the difference of growth rate at the different crystal faces.

In the coordination structure of the ZnO crystal, the coordination number of Zn is four; all the tetrahedrons are connected together by corner sharing. The orientation of the Zn–O$_4^{6-}$ tetrahedron between adjacent sheets is different. The orientation of the Zn–O$_4^{6-}$ tetrahedron in every sheet is obtained by rotating the adjacent sheet by 180° around the c-axis of the hexagonal lattice, as shown in Fig. 6.

From Fig. 6 one can see that the type of element of the coordination tetrahedron that is present at the interface is different for various crystal face directions. In the [0 0 0 1] direction, every coordination tetrahedron has a corner present at the interface. In the [0 0 0 $\bar{1}$] direction, every coordination tetrahedron has a face present at the interface. In the prism face direction, half of the coordination tetrahedrons have a corner present at the interface; the other half have a face present at the interface. In the direction of pyramidal faces $\{0\ 1\ \bar{1}\ \bar{1}\}$, half of the coordination tetrahedrons have a corner present at the interface; the other half have an edge present at the interface. In the direction of pyramidal faces $\{0\ 1\ \bar{1}\ 1\}$, half of the coordination tetrahedrons have a face present at the interface; the other half have an edge present at the interface. According to the new rule of growth habit, one can find out that the growth rate in the [0 0 0 1] direction is the fastest; the following relationship between the velocities of crystal growth in the different directions is found: $V_{\langle 0\,0\,0\,1\rangle} > V_{\langle 0\,1\,\bar{1}\,\bar{1}\rangle} > V_{\langle 0\,1\,\bar{1}\,0\rangle} > V_{\langle 0\,1\,\bar{1}\,1\rangle} > V_{\langle 0\,0\,0\,\bar{1}\rangle}$. Moreover, from Fig. 6, one can also see that the crystal face (0 0 0 1) with the corner of the coordination polyhedron present is a kinked face; the crystal face (0 0 0 $\bar{1}$) with the face of the coordination polyhedron present is a flat face; the other crystal faces with the edge of the coordination polyhedron present is between a kinked face and a flat face. This confirms that the [0 0 0 1] direction has the fastest growth rate, while the [0 0 0 $\bar{1}$] direction has the slowest growth rate. This is consistent with the growth habit of the ZnO crystal particle observed by the hydrothermal experiment. It has been known that crystal faces whose growth rate is slow easily appear and the crystal face whose growth rate is fast easily disappear, so the crystal face (0 0 0 1) and (0 1 $\bar{1}$ $\bar{1}$) of the crystal particle prepared by the hydrothermal salt solution pressure-relief method disappear. In the practical growth procedure, whether the crystal face is present or not is still related to the growth condition.

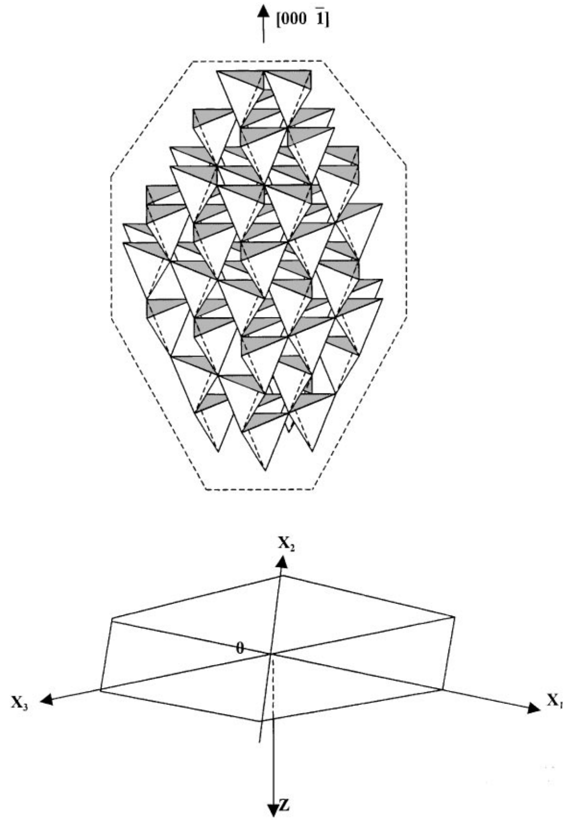

Fig. 6. View of the ZnO crystal structure image represented in the form of the coordination tetrahedron along the x-direction.

In order to disclose the effect of reaction mediums on the growth habit of powders obtained, the experiment is done by the hydrothermal crystallization method using newly prepared hydroxide colloids $Zn(OH)_2$ as precursors at 350°C in various mediums. The SEM micrograph of the ZnO powder prepared in a neutral medium is shown in Fig. 7. The SEM micrograph of the ZnO powders prepared in an alkali condition (4 mol/l NaOH) is shown in Fig. 8. From Figs. 7 and 8, one can find that the morphology of the ZnO powder prepared by hydrothermal crystallization in a neutral medium is in the elongated prismatic form; whereas it is in the shortened prismatic form when prepared in the alkali medium. Their growth habits approach shown in Figs. 9 and 10, respectively. From Figs. 9 and 10, one can find that the growth rates of the (0 0 0 1) and (0 0 0 $\bar{1}$) faces are different; and in an alkaline medium, the (0 1 $\bar{1}$ $\bar{1}$) face easily appears, while in a neutral medium, the (0 1 $\bar{1}$ $\bar{1}$) face easily disappears.

Based on the above hypothesis of growth unit, the growth mechanism of the ZnO crystal prepared by hydrothermal crystallization is represented as follows: first, in the supersaturation solution, zinc hydroxide gel dissolved in the solution complex with OH^- ions forms growth units by the attraction

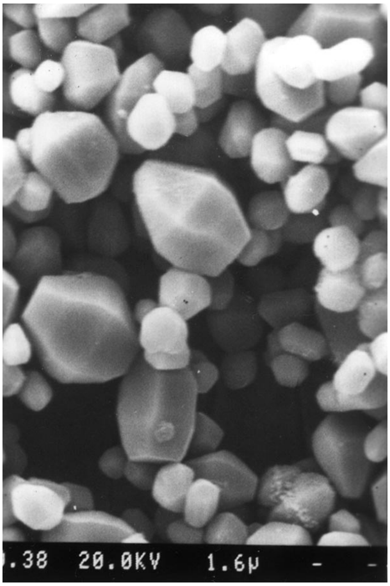

Fig. 8. SEM micrograph of the ZnO powder prepared by the ordinary hydrothermal method using newly prepared hydroxide colloids $Zn(OH)_2$ as precursor at 350°C for 24 h in an alkali medium (4 mol/l NaOH).

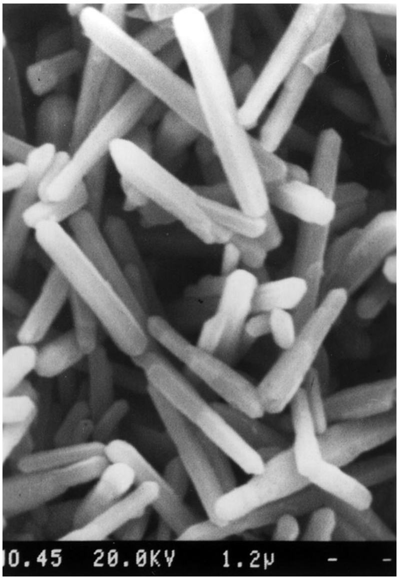

Fig. 7. SEM micrograph of the ZnO powder prepared by the ordinary hydrothermal method using newly prepared hydroxide colloids $Zn(OH)_2$ as precursor at 350°C for 24 h in a neutral medium.

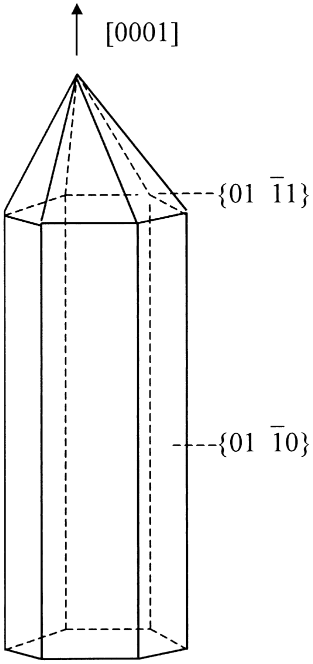

Fig. 9. Growth habit image of the ZnO crystal prepared by the ordinary hydrothermal method using newly prepared hydroxide colloids $Zn(OH)_2$ as precursor at 350°C for 24 h in a neutral medium.

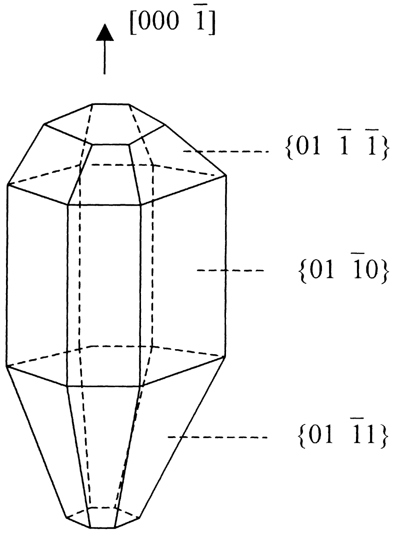

Fig. 10. Growth habit of the ZnO crystal prepared by the ordinary hydrothermal method using newly prepared hydroxide colloids $Zn(OH)_2$ as precursor at 350°C for 24 h in an alkali medium (4 mol/l NaOH).

of ions:

$$Zn(OH)_2(gel) + 2H_2O = Zn^{2+} + 2OH^- + 2H_2O = Zn(OH)_4^{2-} + 2H^+. \quad (8)$$

Then, due to heat convection, diffusion of ions and deregulation movement among molecules and ions in the solution, the clusters $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ are formed by the dehydration reaction of growth units. When the particle size of the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ reaches a certain value, the ZnO nucleus is formed, as shown in Eqs. (9) and (10). Consequently, the ZnO is precipitated:

$$Zn(OH)_4^{2-} + Zn(OH)_4^{2-} = Zn_2O(OH)_6^{4-} + H_2O, \quad (9)$$

$$Zn_xO_y(OH)_z^{(z+2y-2x)-}(\text{nucleus}) + Zn(OH)_4^{2-} = Zn_{x+1}O_{y+1}(OH)_{z+2}^{(z+2y-2x+2)-} + H_2O, \quad (10)$$

where, the subscripts x, y and z represent the number of Zn^{2+}, O^{2-} and OH^- within crystal, respectively.

From the above analysis of the formation mechanism of ZnO powders, it can be considered that the growth unit incorporating into the crystal lattice take place by the dehydration reaction between OH^- ligands, so the growth habit of the ZnO crystal is related to OH^- ligands at the interface. When the hydrothermal reaction proceeds in a different solution, a part of the OH^- ligands of the surface of clusters $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ can be shielded by the other ions in the medium, forming the cation surface with H_2O [15,16] or other ions in the structure, so the growth habit of crystal particle is related to the reaction medium. In a neutral medium, the exterior condition has a smaller effect on the OH^- ligands at the interface, so the crystal growth habit is mainly affected by the interior structure. According to the new rule of growth habit, the growth rate of the (0 0 0 1) face is the fastest among the various crystal faces, and the growth rates of various crystal faces have a bigger difference, so the morphology of the particle is in the elongated prism form. In an alkali medium, during the crystallization, the growth unit is shielded by OH^- ion, forming a complex such as $Zn(OH)_{4-x}(ONa)_x^{2-}$, so that the coordination polyhedron clusters formed by the dehydration reaction between shielded growth units also have a cation surface with ONa^- ions at the interface, such as $Zn_xO_y(OH)_{z-1}(ONa)_m^{(z+2y-2x+m)-}$. Their shielding mechanisms are shown as follows:

$$Zn(OH)_4^{2-} + x\text{NaOH} = Zn(OH)_{4-x}(ONa)_x^{2-} + H_2O, \quad (11)$$

$$Zn_xO_y(OH)_z^{(z+2y-2x)-} + m\text{NaOH} = Zn_xO_y(OH)_{z-1}(ONa)_m^{(z+2y-2x-1+m)-} + mH_2O. \quad (12)$$

Before growth units are incorporated into the crystal lattice by the dehydration reaction. The ONa^- ion matched with cations is first replaced by the OH^- ion. The replacement reaction tends to be a procedure of absorbing heat, which hinders the growth of crystals. Thus, due to the shielding effect of OH^- ions on the interface, the growth rate of various faces becomes slow. From the above analysis, one can conclude that the activation of the

OH^- ligand present at different interfaces is different, so the hindrance effect of OH^- ions on OH^- ligands at different interfaces is different. The larger the activation of the OH^- ligands present at the interface, the larger is the hindrance effect of OH^- ions on the interface, which makes the difference of various crystal faces in growth rates to become small. So the morphology of particles prepared in an alkaline medium is in the shortened prism form. Moreover, due to the larger shielding effect of OH^- ions at the interface of the (0 0 0 1) and $(0\,1\,\bar{1}\,\bar{1})$ faces, the growth rates of the (0 0 0 1) and $(0\,1\,\bar{1}\,\bar{1})$ faces have a greater decrease relative to other crystal faces. So the (0 0 0 1) and $(0\,1\,\bar{1}\,\bar{1})$ faces appear in the crystal prepared in an alkali medium.

In order to confirm the rules for the growth habit, the experiments are performed by the ordinary hydrothermal method. Fig. 11 shows a TEM micrograph of γ-AlO(OH) powder prepared by the ordinary hydrothermal method using $Al(NO_3)_3$ solution as precursor at 200°C for 8 h. From Fig. 11, it can be seen that the morphology of powders are elongated plate-like forms. In order to testify the elongated direction of the plate-like particle, it is analyzed by the ED instrument, whose type number is JEM-2010. The result is shown in Fig. 12, where the arrowhead points to the elongated direction of the plate-like particle. From Fig. 12, one can deduce that the particle is elongated along the *a*-axis. Its growth habit approaches that shown in Fig. 13.

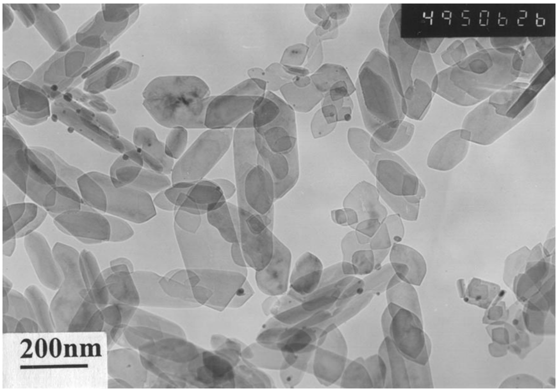

Fig. 11. TEM micrograph of γ-AlO(OH) powder prepared by the hydrothermal method using $Al(NO_3)_3$ solution as precursor at 200°C for 8 h.

Fig. 12. ED image of γ-AlO(OH) powder prepared by the hydrothermal method using $Al(NO_3)_3$ solution as precursor at 200°C for 8 h.

The γ-AlO(OH) crystal is an orthorhombic crystal system with point group D_{2h} mmm, space group Amam and a layer-shape structure. Al^{3+} ion occupies the site of Al-O6 octahedron. The chain is made up of corner sharing Al-O6 octahedra parallel to the *a*-axis. The wave-like layer is made up of edge-sharing chains parallel to the (0 1 0) face. Wave-like layers are connected together by the hydroxyl groups, in which H^+ near to O^{2-} tends to show OH^- bonding character; H^+ far from O^{2-} tends to show H^+ bonding character, its coordination structure is shown in Fig. 14. From Fig. 14, it can be seen that in the *a*-axis direction, every Al-O6 octahedral has a corner present at the interface; in the $\langle 1\,1\,0 \rangle$, $\langle 1\,\bar{1}\,0 \rangle$ direction, every Al-O6 octahedral has two edges present at the interface; In the *b*-axis or *c*-axis direction, every Al-O6 octahedral has an edge present at the interface, and in the *b*-axis direction, there exists a weak bonding. According to the new rule concerning crystal growth habit, one can conclude that the growth rate in the

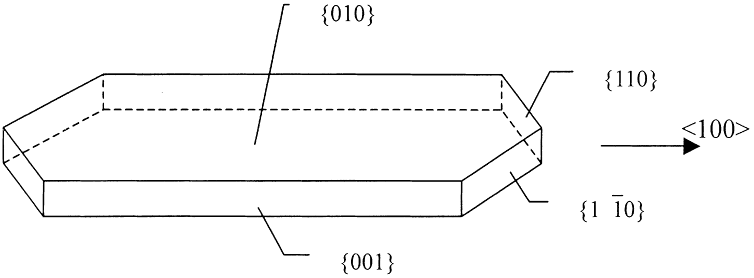

Fig. 13. Growth habit of the AlO(OH) crystal.

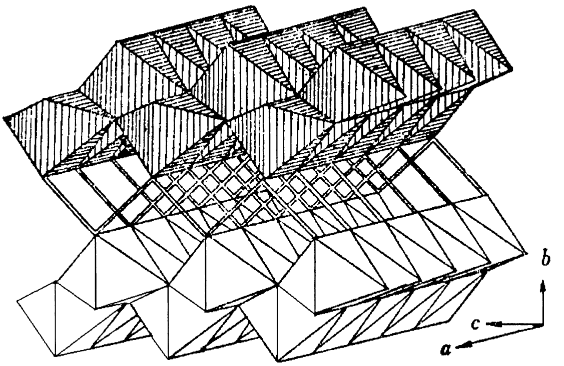

Fig. 14. Structure image of the γ-AlO(OH) crystal represented in the form of a coordination octahedron.

a-axis direction is the fastest; the following relationship between the velocities of crystal growth in various directions is found: $V_{\langle 1\,0\,0\rangle} > V_{\langle 1\,1\,0\rangle} = V_{\langle 1\,\bar{1}\,0\rangle} > V_{\langle 0\,0\,1\rangle} > V_{\langle 0\,1\,0\rangle}$. This result is consistent with the growth habit observed by the hydrothermal experiment.

4. Conclusions

The main results of this study may be summarized as follows:

1. In solution, the growth unit of a crystal is the complex that is formed by the connection of cation with OH^- ions. The ideal growth procedures of crystal contain the formation procedure of growth unit and the incorporating procedure of the growth unit at the interface. In practical growth procedures, due to the hindrance effect of external conditions on the interface, the replacement reaction of OH^- ligands with other ligands at the interface is contained except the above two procedures.
2. The ideal interface of the crystal can be considered as an ordered stack of the coordination polyhedron with OH^- ligands. The relation between the growth unit and the interface is established by the dehydration reaction.
3. The growth rate of the crystal is related to the orientation of the coordination polyhedron at the interface. Namely, the crystal face with the corner of the coordination polyhedron present at the interface has the fastest growth rate; the crystal face with the edge of the coordination polyhedron present at the interface has the second fastest growth rate; the crystal face with the face of the coordination polyhedron present at the interface has the slowest growth rate. This rule of growth habit connects the growth rate at various crystal faces with their interface structure, and considers the effect of external conditions on crystal growth habit. Moreover, this rule successfully explains the difference in growth rate between nonequivalent faces $(h\,k\,l)$ and $(\bar{h}\,\bar{k}\,\bar{l})$ of a polar crystal.

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