Growth habit of polar crystals

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Abstract Using coordination polyhedron rule, growth habit of polar crystals such as ZnO, ZnS and SiO_2 is investigated. It shows that the growth rates in the positive and negative polar axis directions are different. The theoretical growth habit of ZnO crystal is hexagonal prism and the growth rates of its various faces are: $V_{\{0001\}} > V_{\{01\bar{1}\bar{1}\}} > V_{\{01\bar{1}0\}} > V_{\{01\bar{1}1\}} > V_{\{000\bar{1}\}}$. The growth habit of ZnS crystal is tetrahedron and its growth rates of different crystal faces are: $V_{\{111\}} > V_{\{001\}} > V_{\{001\}} = V_{\{100\}} = V_{\{010\}} > V_{\{\bar{1}\bar{1}\bar{1}\}}$. The growth rate relationship between positive and negative polar axis directions of SiO_2 crystal is $V_{[\bar{1}\bar{1}20]} > V_{[11\bar{2}0]}$. These results are in agreement with the growth habits observed under hydrothermal conditions. The different growth rates between positive and negative polar axis directions cannot be explained by PBC theory.

Keywords: ZnO crystal, ZnS crystal, SiO_2 crystal, growth habit.

The hydrothermal method[1] is a wet chemical route which is widely used to prepare oxide powder. The hydrothermal reaction generally proceeds under the non-limited conditions, and the supersaturation of solution is low. The as-prepared oxide crystal particles have good properties such as well-crystallized, no macroscopic agglomeration and narrow particle size distribution. So the hydrothermal technique is one of the ideal methods to investigate the growth habit of crystals.

The growth habit of a crystal consists of a lot of information which reflects the intrinsic structure of a crystal. The research on the growth habit is of great significance for the insight into the growth mechanism of a crystal. The theory models concerning crystal growth habit mainly include the BFDH law[2] and the PBC theory[3, 4]. The BFDH law, which starts from planar mesh density and takes the effects of the screw axis and glide plane on the crystal growth habit into consideration, predicts the theoretical growth habit of a crystal. The PBC theory describes quantitatively an ideal growth habit of a crystal in terms of bond chain types between molecules and attachment energy. But these models have some shortages of explaining the growth habit of a crystal, for example, they cannot reasonably explain the growth habit of polar crystal such as the SiO_2 crystal. The growth habit of a crystal results from the different growth rates among various crystal faces during the crystal growth process, so the growth

habit of a crystal is related to its growth mechanism and characteristics of interface. Therefore, in order to understand growth habit of crystals, the growth mechanism and characteristics of interface of the crystal should be studied firstly. Zhong et al.[5, 6] firstly presented the coordination polyhedron growth unit model in 1994, and according to this model, the cation is incorporated into the interface in the form of the anion coordination polyhedron growth unit during crystal growth. In 1999, Li et al.[7, 8] proposed a coordination polyhedra rule concerning growth habit (hereinafter designated as CPR) from the exposure to the elements (vertices, edge and face) of coordination polyhedron at the interface. Its main content is that the growth rates of various faces are related to the species which appears in the interface. First, the face which exposes the vertices of the coordination polyhedron has the fastest growth rate, the crystal face which exposes the face has the slowest rate and the face which exposes the edge has the growth rate between the two of the above. Secondly, if the elements exposed at the interface have the same species, for example, exposing vertices, the growth rates of different crystal faces are related to the numbers of exposed vertices. The more the exposed vertices are, the faster the growth rate is. In this note, we try to further explain the growth habit of various oxide crystal particles prepared by hydrothermal method according to this rule and to compare it with the results determined by the PBC theory.

1 Experiment

The reaction vessel adopted in the experiments is a silver-lined tube-type stainless steel autoclave with 30 mm inner diameter and about 215 mL capacity. The experiment method is the hydrothermal precursor-separated method[9]. The $Zn(CH_3COO)_2$ solution and aqueous $NH_3 \cdot H_2O$ are used as starting materials, where the $Zn(CH_3COO)_2$ solution is filled into crucible with 26 mm inner diameter and aqueous $NH_3 \cdot H_2O$ into the gap between the autoclave and crucible. The filling rate is 80%. After the hydrothermal reactions, the obtained powder is washed and then dried at 120℃ in the air for SEM morphological analyses and X-ray diffraction measurement.

2 Result and discussion

(i) Growth habit of the ZnS crystal. The growth habit of the ZnS crystal[10] is tetrahedron. The ZnS crystal belongs to the equiaxial crystal system, and its space group is T_d^2-$F\bar{4}3m$. In the zinc blende structure, the sulfur atoms are arranged in cubic closest packing, in which one half of the tetrahedral sites are filled with zinc atoms and the orientation of tetrahedron ZnS_4^{6-} is the same. The whole structure is of tetrahedron symmetry. Its structure is shown in fig. 1.

Fig. 2 shows the structure projection of the ZnS crystal along the $[1\bar{1}0]$ direction. In fig. 2, it can be seen that the two PBCs are bonded in the slice d_{222}, so the {111} faces are an F form. The slice d_{004}

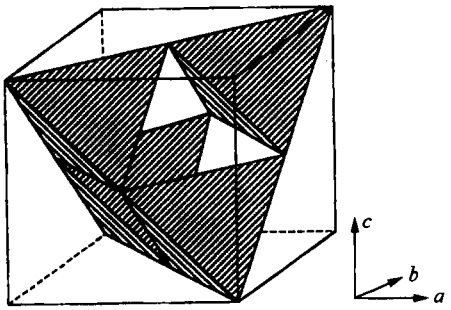

Fig. 1. Structure of ZnS crystal.

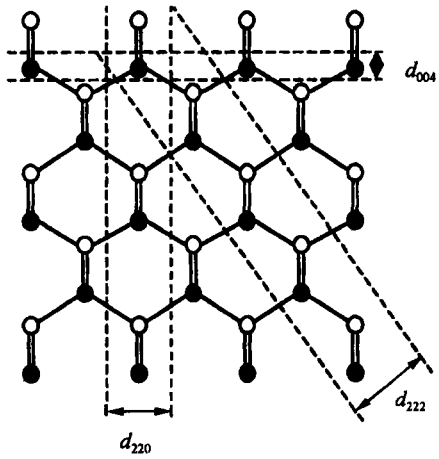

Fig. 2. Projection of structure of the ZnS crystal along the $[1\bar{1}0]$.