Morphological Evolution during Synthesis of New $AlPO_4 \cdot H_2O$ Crystal

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(Received 12 April 2005)

A new crystal of aluminophosphate, $AlPO_4 \cdot H_2O$, is synthesized from two-batch aqueous solution under hydrothermal conditions. Three types of the crystal habits, i.e. the tetragonal double pyramid, the tetragonal prism and the plate-type tetragonal prism, are found from batch-A solution. Two types of the crystal habits, i.e. the hexagonal pyramid and the strip-type tetragonal prism, are found from batch-B solution. The change of crystal morphology is originated from the fluctuation of the synthesis conditions, such as the supersaturation, the temperature and the impurity content. It causes change of the step energies, the defect density and the step roughness, and further, change of the growth rates. Since the crystal morphology is sensitive to the mass transport mechanism, the crystal habits could be changed under the microgravity.

PACS: 81.10.Aj, 81.10.Dn, 81.10.Mx

In the past decade, experiments on space crystal growth have been conducted in the International Space Station,[1] Shen-Zhou (SZ-3) Spaceship,[2,3] Russia MIR Station,[4] US Space Shuttles,[5,6], EURECA,[7] Chinese Recoverable Satellite,[8−10] and Soviet rockets.[11] Although the scientific results to date have shown the benefits of experimentation under the microgravity environment, there are still problems that remain in further investigation in space and on the earth. The influence of microgravity on crystal morphology is one of the topics. Since the times of space experiments are limited, the research results on crystal morphology under microgravity environment are dispersed. For example, on space crystal growth of zeolite β, α-$LiIO_3$ and ZnSe, etc, no habit change was observed, i.e. the space-grown crystal has the same morphology as the terrestrial/control crystal.[1,4,8−10] For the $Ce{:}Bi_{12}SiO_{20}$ space experiment, the space-grown crystal has an external surface smoother than that on the earth.[2] For the space molecular sieve on ZSM-5, Mordenite and Offretite etc, the crystal morphology is markedly different from that in the ground cases.[11,12] In fact, the interpretation on the results of microgravity experiments is often hampered by the small amount of data available. With the intention of understanding the phenomena from the space experiments, we study the morphological evolution during the synthesis process of an $AlPO_4 \cdot H_2O$ crystal and report our experimental result.

A new crystal of aluminophosphate, $AlPO_4 \cdot H_2O$, is synthesized from two-batch aqueous solution under hydrothermal conditions. The working solution studied was prepared by Eq. (1):

$$Al_2O_3 - \zeta P_2O_5 - 1.5HCl - \chi DPA - 70H_2O, \quad (1)$$

where $\zeta = Al_2O_3/P_2O_5$ in mole, $\chi = Al_2O_3/DPA$ in mole, DPA is a template agent, the organic dipropylamine. All of chemicals are the analytical reagent. Table 1 shows the composition of the experimental solution on the study of crystal morphology. The aluminophosphate solution including both clear and milk states was used with the following procedure: the calculated quantities of $Al(OH)_3$ and H_3PO_4(85% water solution) were mixed and vigorously stirred at 100°C first. Then the calculated amount of HCl (36% water solution) was added slowly and the organic dipropylamine (DPA) was dropped. Finally, the distilled water was added until the reaction solution has a final volume.

Table 1. The composition of the solution system and the crystal habits.

Batches	ζ	χ	Crystal habits
A	2.0	2.0	Double pyramid
			Tetra-prism
			Plate-type tetragonal prism
B	1.5	4.8	Hexagonal pyramid
			Strip-type tetragonal prism

The hydrothermal crystallization experiments were carried out in stainless steel autoclaves. The autoclaves are consisted of the special cylindrical housing containing a polypropylene chamber in volume of 100 ml. The 20-ml supersaturated solution was sealed in the chamber. The reaction was carried out at 170°C for 15–60 h. The reaction products were washed with water and dried at 80°C for 20 h, 105°C for 15 h, and 120°C for 30 h, respectively. The composition for the as-synthesized product was analysed by a chemical method and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The crystalline phases were identified by x-ray diffraction (XRD) and thermogravimetry (TG), respectively. Scanning electronic microscopy (SEM) was used for identification of the

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crystal morphology.

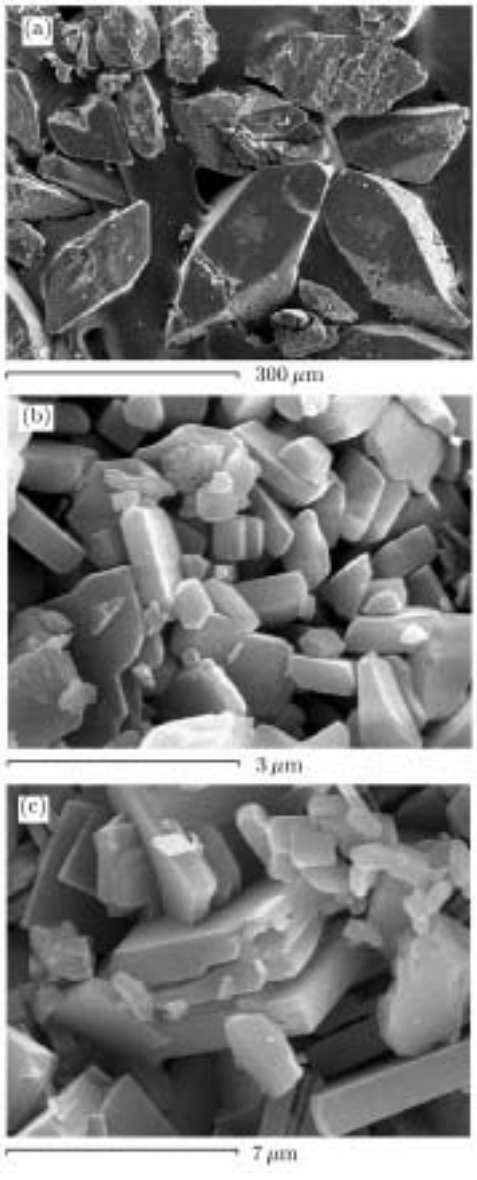

Fig. 1. SEM images of (a) the double pyramid $AlPO_4{\cdot}H_2O$, (b) the tetra-prism $AlPO_4{\cdot}H_2O$, and (c) the plate-type tetragonal prism $AlPO_4{\cdot}H_2O$, synthesized from the solution in batch A with $\zeta = 2.0$ and $\chi = 2.0$.

The experimental results identified by XRD, TG and ICP-AES indicated that the crystalline phases were as $AlPO_4.H_2O$, which is markedly different from the data reported in Ref. [13]. We have found the five types of the crystal habits by SEM and shown in Figs. 1 and 2. Three types of the crystal habits, such as the tetragonal double pyramid, the tetra-prism and the plate-type tetragonal prism, are synthesized from the batch-A solution with $\zeta = 2.0$ and $\chi = 2.0$, as shown in Figs. 1(a)–1(c). Two types of the crystal habits, i.e the hexagonal pyramid and strip-type tetragonal prism, are synthesized from the batch-B solution with $\zeta = 1.5$ and $\chi = 4.8$, as shown in Figs. 2(a)–2(b). Figure 3 shows the x-ray powder pattern of $AlPO_4{\cdot}H_2O$ synthesized from the solution in the two batches and indicates that although the crystal habits are different, the crystals have the same crystalline phase. In this Letter, we investigate the factors to affect the crystal morphology and the crystal habits under the microgravity. We also analyse the reasons for different habits appeared under the same synthesis conditions

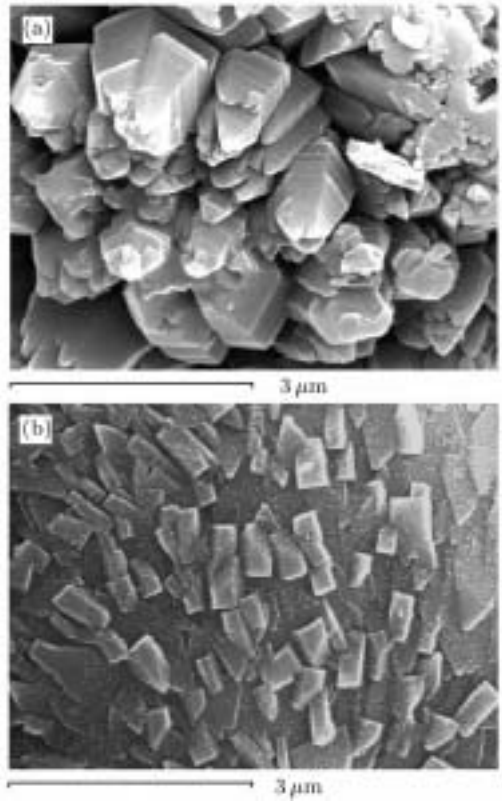

Fig. 2. SEM images of (a) the hexagonal pyramid $AlPO_4{\cdot}H_2O$ and (b) the strip-type tetragonal prism $AlPO_4{\cdot}H_2O$, synthesized from the solution in batch B with $\zeta = 1.5$ and $\chi = 4.8$.

According to the theoretic analysis on crystal growth, the crystal morphology is determined by the kinetics of crystal growth, i.e. the growth rates of crystal faces.[14] The normal growth rate of a face from solution is expressed as Eq. (2). All of the parameters used in the equation are listed in Table 2.

$$V = a\nu\sigma(a/\lambda_0)^2 \exp[-(E + \Delta H)/kT]. \qquad (2)$$

If we defined a parameter β as

$$\beta = a\nu([a/\lambda_0)^2/\Omega C_0] \exp[-(E + \Delta H)/kT], \qquad (3)$$

the relationship between the normal growth rate of a face, V, and the relative supersaturation σ obeys

$$V = \beta\Omega C_0\sigma. \qquad (4)$$

Table 2. The parameters used in Eq. (2).

Symbol of the parameter	Definition
a	Particle size
ν	Frequency of thermal vibration of an atom
σ	Relative supersaturation,
λ_0	Average distance between kinks
E	Activation energy of an atom
ΔH	Dissolution heat of crystal
k	Boltzmann's constant
T	Temperature
C	Solute concentration in solution
C_0	Equilibrium concentration of solute in solution
Ω	Volume occupied by a particle
β	Kinetic coefficient

From Eqs. (2)–(4), it is obvious that the growth rates of crystal faces are related to many factors. At present, although we cannot precisely affirm all the parameters mentioned above and it is difficult to quantitatively calculate the anisotropy of the surface growth rate, it is possible to analyse our experimental results qualitatively. Since the structure of the surface and the mechanism of growth essentially depend on the conditions of crystal growth, the habit of crystal depends not only on its structure, but also on the supersaturation, temperature and composition of the environment. For our experiments on the hydrothermal crystallization of $AlPO_4{\cdot}H_2O$ in batch A, the concentration of $AlPO_4$ in the working solution, C, is 44.6 wt.%, which is responsible for the solution composition with $\zeta = 2.0$, and on batch B, we obtain $C = 32.6$ wt.%. Based on the fact that the solute concentration C in batch A is 12 wt.% higher than that in batch B, the supersaturation in the former should be higher than the latter. Another fact is that the pH value in batch A is 0.25 unit less than that in batch B, which means that the impurity contents in the two batches are different. The adsorption of impurities rises to reduce their specific linear energy, thereby to increase the probability that two-dimensional nuclei will form. This effect increases the growth rate. That is why the crystal habits are different in both the batches. Why there are different habits under the same synthesis conditions? This is originated from the fluctuation of the synthesis conditions during the processes of nucleation and crystal growth. The small fluctuations of the supersaturation, the temperature and the impurity content cause the change of the step energies, the defect density and the step roughness. The rates of crystal faces by two dimensionally nuclei (homogeneous and heterogeneous) and that due to the effect of dislocations depend on the step energies and the spectrum of defects on the surface, they differ substantially for the various faces. Therefore at small deviations, the face growth velocities differ widely on nonlinear sections of $V(s)$ as expressed in Eq. (4).

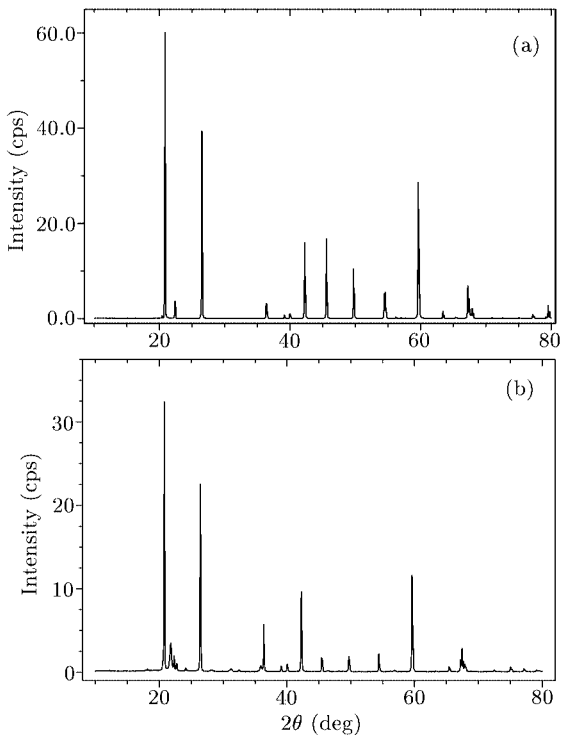

Fig. 3. X-ray powder pattern of $AlPO_4{\cdot}H_2O$ synthesized from the solution: (a) in batch A with $\zeta = 2.0$ and $\chi = 2.0$, (b) in batch B with $\zeta = 1.5$ and $\chi = 4.8$.

Nowadays, purely diffusion transport throughout the entire bulk of the mother medium is realized, for instance, during the growth of crystals in supersaturated solid solution, in gels or under zero gravity. How the crystal habits should be changed under the microgravity? The previous results from several experiments performed in space by Coker *et al.*[11] indicated that under the influence of different gravitational forces, the changes in convection and the sedimentation phenomena might influence crystallization in various aspects. Density-driven convective currents caused by thermal or compositional non-equilibrium are strongly reduced under microgravity. The advantageous conditions for crystal growth in space compared with on the earth are that: (a) the relatively large concentration gradients may arise and persist; (b) the surface phenomena, such as the Marangoni convection, become increasingly important; (c) the hydrostatic pressure within the fluid can be greatly dropped; (d) the sedimentation of the particles is minimized. These conditions often play a substantial role in growth kinetics. We have studied the influence of the gravity on interface shape during crystal growth from the computational analysis[15–17] and found that the radial segregation occurred and the interface shape became slightly flat under the microgravity. Whether or not should the crystal habits of $AlPO_4{\cdot}H_2O$ synthesized from the hydrothermal method be changed under the microgravity? Since the crystal morphology is sensitive to small fluctuation of the synthesis

conditions, the answer is affirmative.[18] However, at present, the experiments of crystal growth in space are more based on intuition and results and to a lesser extent on an understanding of how microgravity actually affects the hydrothermal synthesis. Ground-based fundamental research should be performed further for the interpretation of results of the experiments under microgravity.

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