Formation and Aging of Precipitates. X. An Electron Micro-Diffraction Study on Crystal Habit of Barium Sulfate Precipitates*

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The shapes of precipitated particles of sparingly soluble salts are usually classified into groups of perfect crystals having simple forms and dendrites having irregular forms. The author has previously reported the relationship between the condition of precipitation and the shape and size of precipitated particles of barium sulfate, by the direct mixing of reagents[1]. The rectangular perfect crystals were prepared from a solution below about 0.0005 M of initial concentration of barium sulfate, and the spindle-shaped dendrites having rugged edges were prepared in a range of initial concentration from about 0.001 to 0.2 M. Above 0.5 M, the precipitate was jelly-like at the beginning, but it changed gradually to the crystalline precipitate. Fischer[2] also studied the morphology of barium sulfate precipitates by electron microscopy and reported that the crystals formed as elevated temperature were somewhat more perfect than those formed at room temperature, and that the fairly perfect crystals were formed when very dilute solutions of reagents were mixed slowly by ionic diffusion through a thin membrane.

An attempt has been made in the present investigation to employ the electron micro-diffraction method for clarifying the crystal habit of barium sulfate.

Sample.—Solutions of 0.001 and 0.1 M barium chloride were placed in small beakers, which were kept at room temperature and at 80°C. Small thin films of Formvar were then floated on the surface of the solutions, and a drop of 0.001 M sulfuric acid was placed on each film. A few minutes were allowed for the reactant ions to diffuse slowly through the thin film and form the precipitates. Then the films with the drops were removed with the aid of a glass slide and refloated on the surface of water in another beaker. About ten minutes were allowed for diffusion of ions from the drop of mother liquid into the water below. Then the films with drops were scooped with specimen grids. After drying the specimen, the precipitates were observed with an electron microscope.

Rectangular perfect crystals were formed from 0.001 M solution independently of the reaction temperature. Dendrites were formed from 0.1 M solution. The growth direction of dendrite was dependent on the reaction temperature as mentioned later. The crystals formed by the diffusion mixing method are generally thin laminae, so they are suitable to study by the electron diffraction method. Crystals precipitated by the direct mixing of reagents have the same morphological characteristics as those precipitated by the diffusion mixing of ions, when the concentration and the reaction temperature are kept at the same condition.

Results

Morphology of Barium Sulfate Precipitates by Electron Microscopy.—A perfect crystal of barium sulfate is a rectangular platelet as shown in Fig. 1a. In a particular case of precipitation in dilute aqueous alcohol, octagonal or hexagonal platelet is formed as shown in Fig. 3a.

The dendrite prepared at room temperature is made of two main stems crossed perpendicularly to each other, which grow from the center of the crystal. Many primary and secondary branches are seen which grow from the main stems parallel to the stems (Fig. 4a). The dendrites prepared at elevated temperature are shown in Figs. 7a and 8a. The primary branches grow obliquely to the main stems crossed perpendicularly with each other (Fig. 7a). The main stems of the crystals shown in Fig. 8a has defects, and the large protuberances of these crystals correspond to the primary branches of the crystals shown in Fig. 7a. The secondary branchings are parallel to the primary branches, that is, they are oblique to the main stems (Figs. 7a and 8a). The relation of the main stems and the branches are shown in Figs. 9a and b.

* The nineth paper of this series, This Bulletin, **31**, 950 (1958).

1) E. Suito and K. Takiyama, ibid., **27**, 121, 123 (1954); **28**, 305 (1955).

2) R. B. Fischer, *Anal. Chem.*, **23**, 1667 (1951); R. B. Fischer and T. B. Rhinehammer, ibid., **25**, 1544 (1953).

The dendrite grows generally in two-dimension as shown by a replica of crystal in Fig. 10. The dendrite shown in Fig. 11 is sometimes observed. Here the platelet particle is set perpendicular to the supporting film. The crystal seems to be a twin, and twin planes estimated to be (110) were observed.

Analysis of N-Pattern Obtained by Electron Micro-Diffraction Method. — All electron diffraction patterns obtained from the crystals in the present study are N-patterns. The arrangement for orientation between the electron microscopic image and the electron diffraction pattern as well as the fixing of the index of each reflection spot were made as follows. The image of electron microscope is rotated at a certain angle with respect to the electron diffraction pattern owing to the difference of lens current. The method for an arrangement of these two images is described below, in Fig. 1 as an example. The electron diffraction pattern obtained from a selected crystal in Fig. 1a is shown in Fig. 1c. When the current of the intermediate lens is increased a little more than the value which gives the diffraction pattern, a pattern shown in Fig. 1b is obtained. In Fig. 1b the small bright field image appears at the center of the pattern and many small dark field images appear at the similar positions to the electron diffraction spots. The orientations of the bright and dark field images are the same, so the relative orientation of the electron microscopic image to the electron diffraction pattern can be known. All crystals are, of course, barium sulfate and belong to V_h^{16}. The reciprocal lattice of barium sulfate crystal and the intersection with Ewald sphere are obtained. Then N-pattern constructed is compared with that obtained by experiment (Fig. 1c), and the Miller's indices of reflection spots are fixed as shown in Fig. 2b.

Crystal Habit of Barium Sulfate Precipitates by Electron Micro-Diffraction Method. — All electron micrographs and diffraction patterns shown in this paper are arranged to the same orientation. Electron diffraction patterns obtained from most crystals are N-patterns same as that shown in Fig. 2b. From this, it has been revealed that the platelet crystals have grown along (100) plane. The laminae that give the N-pattern shown in Fig. 2b are perpendicular to the electron beam.

The short- and the long-axes of rectangular crystal shown in Fig. 1a are *b*- and *c*-axes respectively as shown in Fig. 2a. The normal to the platelet is *a*-axis. The normal to the octagonal lamina shown in Fig. 3a is also *a*-axis, and the side planes of that crystal are {010}, {011} and {001} groups.

The main stems of dendrite shown in Fig. 4a have grown to the direction along

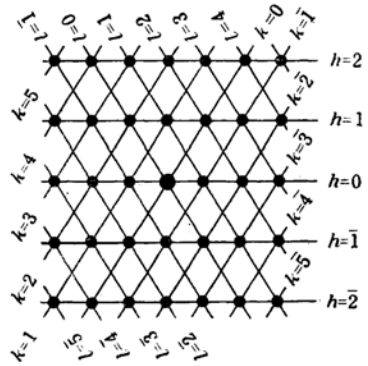
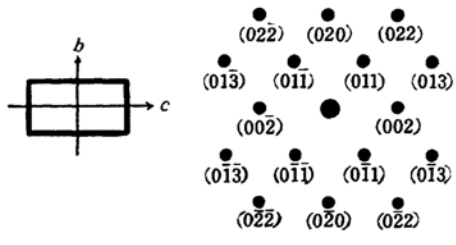
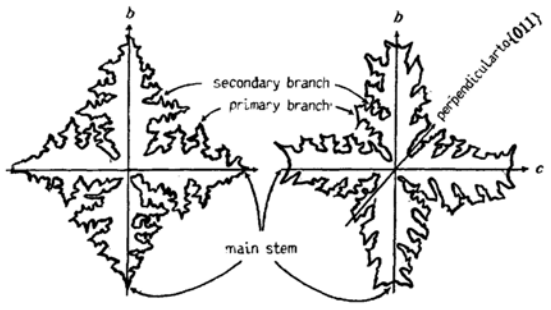


Fig. 6. The indices of electron diffraction pattern of dendrite of barium sulfate shown in Fig. 5.



(a) (b)

Fig. 2. The direction of axes and the indices of electron diffraction pattern of perfect crystal of barium sulfate shown in Fig. 1.



a b

Fig. 9. Schematic diagrams of two typical dendrites of barium sulfate crystals.
a: room temperature
b: 80°C

b- and *c*-axes. Small branchings also grow in parallel to these axes (Fig. 9a). The platelet of dendrite shown in Fig. 5a was placed inclined to the electron beam, and the angle between *a*-axis (normal to platelet) and the electron beam was proved 64° from the analysis of N-pattern as shown in Fig. 6. The main stems of the dendrite shown in Fig. 7a have grown along *b*- and *c*-axes, but the branches have grown to the direction perpendicular to the plane of {011} group (Fig. 9b). The dendrites shown in Fig. 8a have grown markedly to the direction perpendicular to the plane of {011} group.

Consideration

Generally speaking, when a crystal grows from a dilute reagent, the growth rate is so small that the perfect crystal is formed. The perfect crystal of barium sulfate is generally a rectangular platelet and the octagonal or hexagonal crystal is formed in a rare case.

Dendrite of barium sulfate crystal is formed in a range of initial concentration from about 0.001 M to 0.2 M. At the concentration above this range, the rate of nucleation is very rapid, so numerous nuclei appear but their growth immediately after mixing of reagents does not proceed. At the concentration below that range, the rate of nucleation is very slow and a small number of nuclei grows slowly to the perfect crystals. In the range of initial concentration mentioned above (0.001 to 0.2 M), both rates of nucleation and growth are a little more rapid than that in the case just mentioned above, and the edge or the corner of a crystal grows preferentially to form the dendrite.

Watson and Freemann[3] believed that the dendrite formed in an iron sol is composed of aggregated small cubic particles. However, the electron diffraction pattern of the dendrite of barium sulfate is N-pattern, which indicates a single crystal and that the crystal has grown from a single nucleus to the dendrite.

Summary

Barium sulfate precipitates in a form of rectangular perfect crystal from a solution of low initial concentration, and in a form of dendrite from a solution of higher initial concentration. They are platelets grown along (100) plane. The short- and long-axes of rectangular crystal are *b*- and *c*-axes respectively. The dendrite grows along *b*- and *c*-axes, or along the direction perpendicular to the plane of {011} group.

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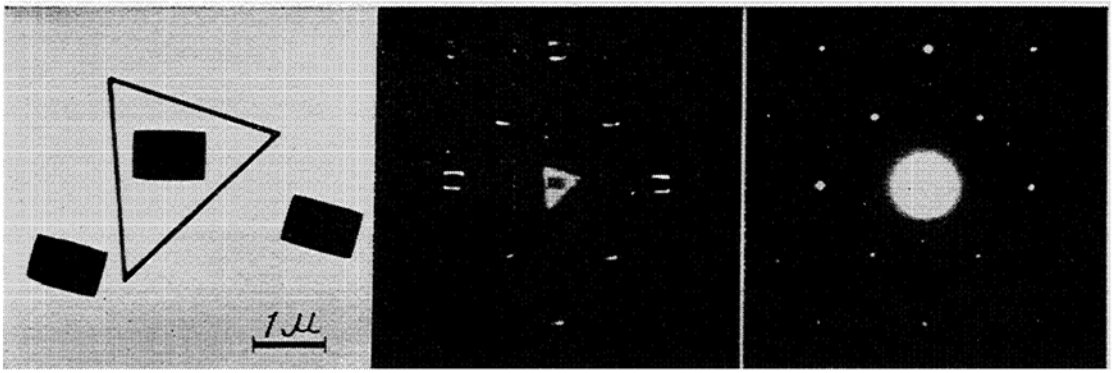
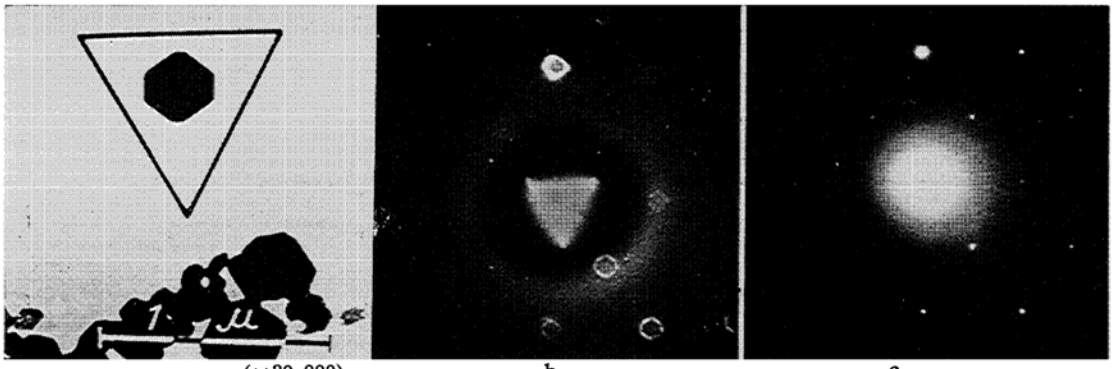
3) J. H. L. Watson and M. W. Freemann, *Kolloid-Z.*, **148**, 127 (1956).



a (×10,000) b c

Fig. 1. Perfect crystal of barium sulfate prepared by diffusion mixing of 0.001 M H_2SO_4 and 0.001 M $BaCl_2$ at room temperature.



a (×30,000) b c

Fig. 3. Perfect crystal of barium sulfate prepared by direct mixing of H_2SO_4 and $Ba(OH)_2$ at the initial concentration of 0.05 M in 2.5% aqueous alcohol medium at room temperature.

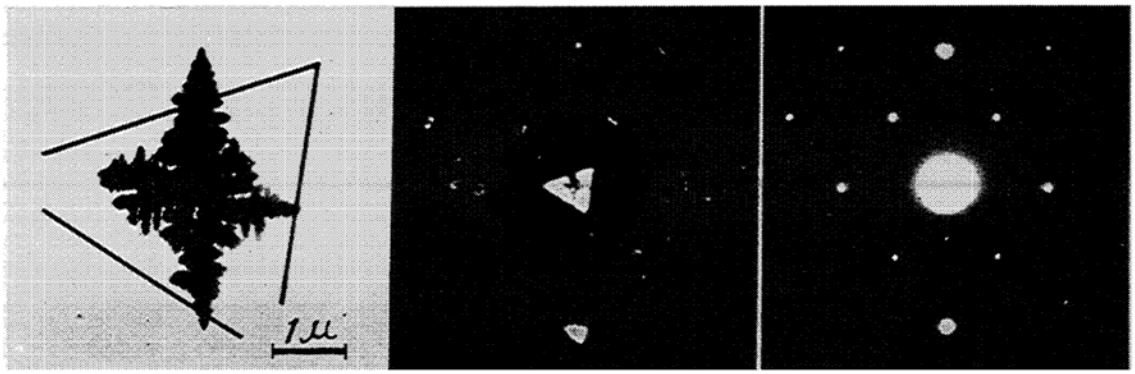
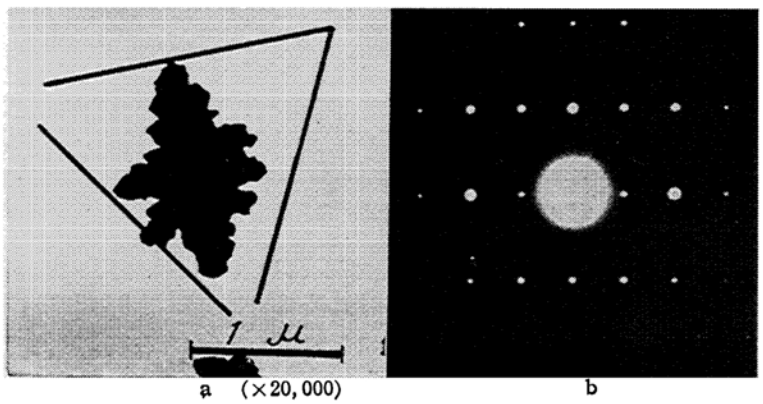
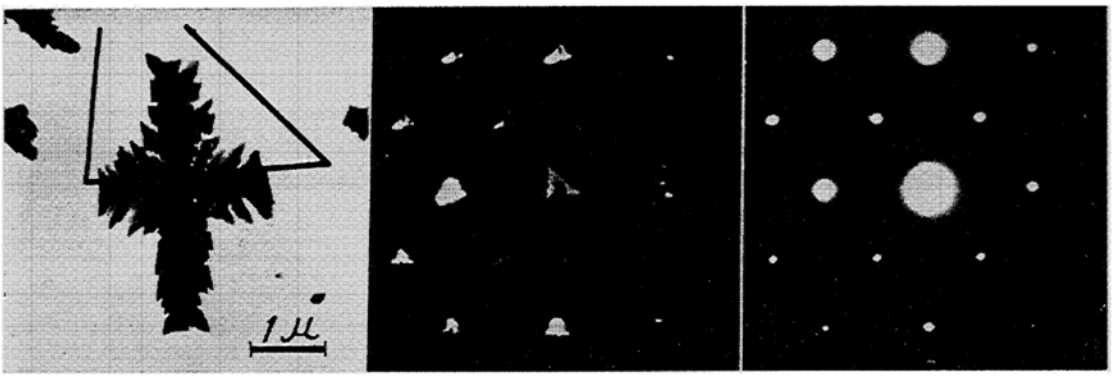


Fig. 4. Dendrite of barium sulfate prepared by diffusion mixing of 0.001 M H_2SO_4 and 0.1 M $BaCl_2$ at room temperature.



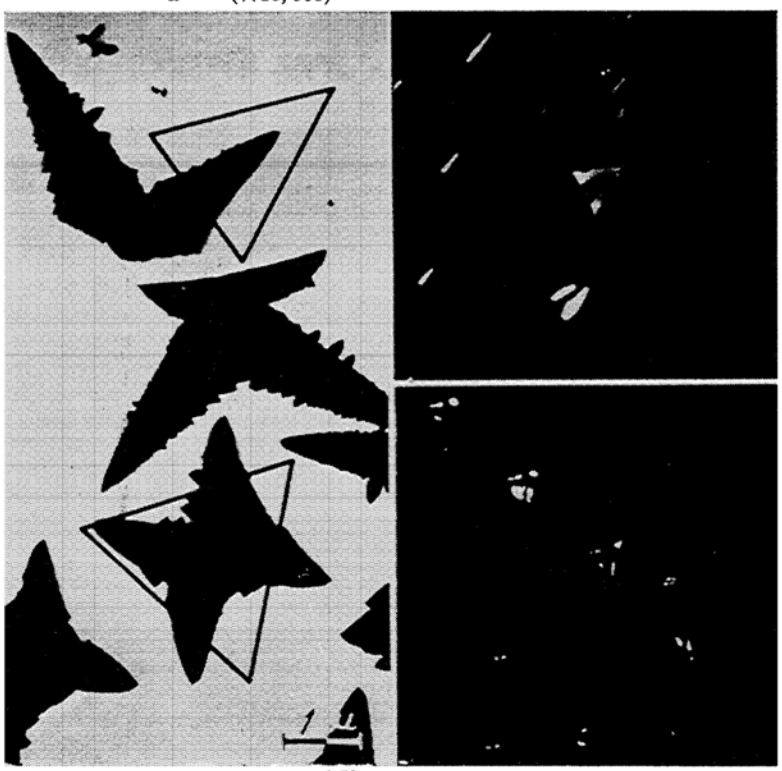
a (×20,000) b

Fig. 5. Dendrite of barium sulfate prepared by direct mixing of H_2SO_4 and $Ba(OH)_2$ at the initial concentration of 0.02 M at room temperature.



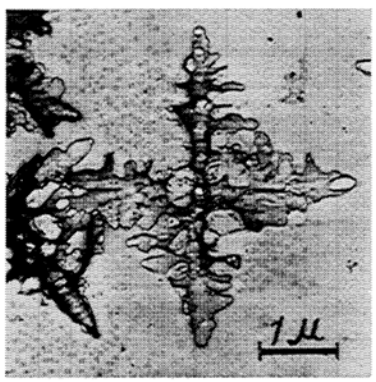
a (×10,000) b c

Fig. 7. Dendrite of barium sulfate prepared by diffusion mixing of 0.001 M H_2SO_4 and 0.1 M $BaCl_2$ at 80°C.



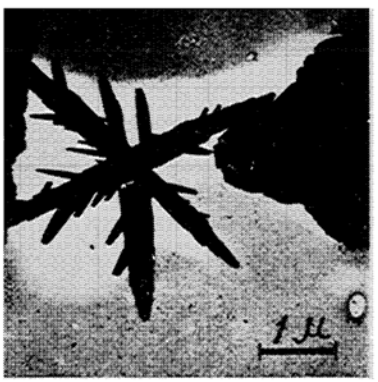
a (×10,000) b

Fig. 8. Dendrite of barium sulfate prepared by diffusion mixing of 0.001 M H_2SO_4 and 0.1 M $BaCl_2$ at 80°C.



(×10,000)

Fig. 10. Replica of dendrite of barium sulfate prepared by direct mixing of 0.001 M H_2SO_4 and 0.1 M $BaCl_2$ at room temperature.



(×10,000)

Fig. 11. Twin of dendrite of barium sulfate prepared by direct mixing of H_2SO_4 and $Ba(OH)_2$ at the initial concentration of 0.01M at room temperature.