

Growth of L- and D-Copper Tartrate Crystals from Silica Gels

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シリカゲル中での L-及び D-酒石酸銅結晶の成長

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Abstract : An *in-situ* observation of the crystal growth of copper tartrate by controlled diffusion in silica gels is reported. The change of a growth structure in the form of a polyhedron is discussed on the basis of the results through an *in-situ* observation. Several kinds of tartaric acids (L, D and DL) as a starting material were used. By examining the morphology on the surface of L- and D-copper tartrate crystals using a phase contrast microscope, we noticed that they formed two types of equilibrium structures, each one a mirror image of the other.

Key Words : silica gels, crystal growth, copper tartrate crystals

抄 録 : シリカゲル中での酒石酸銅結晶の成長過程を位相差顕微鏡を用いて連続観察した。形態観察より、出発物質として L-, D-及び DL-酒石酸を用いた場合、異なる成長形を示すことがわかった。互いに鏡像関係を示す平衡形が観察された。

索引語 : シリカゲル, 結晶成長, 酒石酸銅

1. Introduction

The principal advantage of crystal growth in silica gels is the control of nucleation conditions, which can give the possibility of large crystals of high quality for observations using a light microscope, and for measuring their physical properties.^{[1][2][3]} The insoluble compounds produced as reported here could not be grown from an aqueous solution as a large and strainless single crystal. However, several studies on the growth of tartrate crystals from silica gels have been done.^{[2][4]-[8]} There are very few *in-situ* observations during growth and studies of the

morphology of the surface of the grown crystals in relation to chirality.

We report here the growth of copper tartrate, especially focusing on their growth process and morphology. To distinguish the equilibrium structures of the grown crystals of L- and D- copper tartrate, surface roughness was examined by a phase contrast microscope. Although the chirality in tartaric acid originated by the famous discovery by L. Pasteur (1848), the influence of chirality on the morphology of equilibrium structures in silica gel growth is of great interest.

2. Experimental

The acid gel of pH 3.5 used for the present crystal-growing experiments was prepared as follows: 10cm³ of a sodium meta silicate solution (24.4g of sodium meta silicate + 100cm³ distilled water) was mixed with 10cm³ of 1M tartaric acid. Three types of tartaric acid (L-enantiomers, D-enantiomers and DL racemic compound) were used. A mixture of gel was allowed to set in a growth cell maintained at a thermostatted 35°C, the density of which was varied between 1.02~1.05g · cm⁻³. The growth cell was 4.5×1.2×1.2cm in size and made of a transparent quartz. After a gel was aged for about 48 hours, 2M copper nitrate solution of 2.8cm³ was carefully added to the top of the growth cell as an upper reactant. The growth cell was tightly sealed with a lid. When the upper reactant of copper nitrate diffused into the gel, the crystals started to grow and gradually became thicker. All the chemicals used in the present experiments were of reagent grade. The purity of the crystals is primarily governed by the purity of the starting materials.

The present apparatus developed for an *in-situ* observation of the crystals during growth is schematically illustrated in fig. 1. The water flowed out of the thermostat ① maintained at 35°C through the reservoir ② to control the flow speed of water induced into the bath ③. The growth cell ④ placed in the bath ③ in order to keep the temperature constant during growth. Temperature could be stabilized at 35.0 ± 0.05°C. The crystal growth proceeds through the diffusion of a copper nitrate solution into the gel impregnated with tartaric acid. The *in-situ* observation using a light microscope ⑤ was carried out through the growth cell with illumination from below. The observed images using the light microscope were recorded with the CCD camera ⑥ connected to the video recorder ⑦ and video printer ⑧. The personal computer ⑨ is for the processing of the observed images. In the present study, this system was used while a crystal was growing for about 6 hours.

After the *in-situ* observation, the grown crystals were taken out of the growth cell to observe in detail the morphology of the equilibrium structures using a phase contrast microscope. The observed crystals were grown for over 48 hours. By dissolving 0.03g of crystals in 1N HCl solution, the optical activity of the grown crystals was measured using a polarimeter. Powder X-ray diffraction patterns were taken of the grown crystals after being crushed into powders.

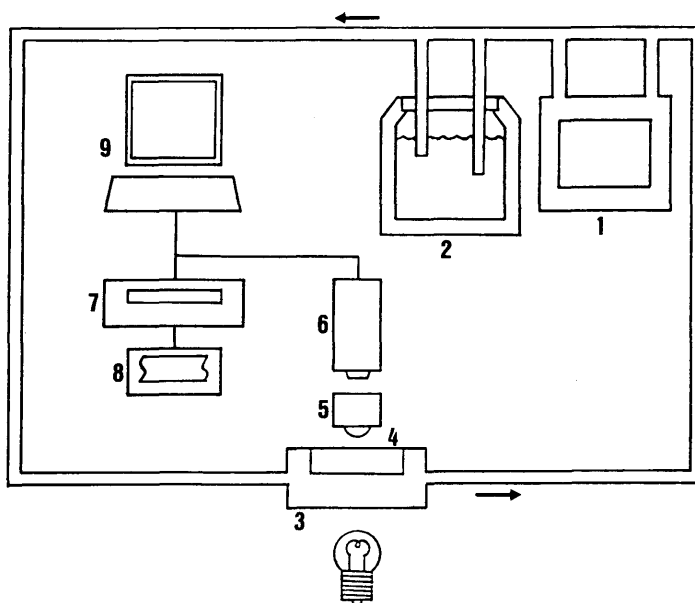


Fig. 1 The apparatus used for *in-situ* observations.

① thermostat maintained at 35°C ② reservoir to control the flow rate ③ bath for surrounding the growth cell ④ growth cell made of a transparent quartz ⑤ light microscope ⑥ CCD camera ⑦ video recorder ⑧ videoprinter ⑨ computer system for a processing of observed images.

3. Experimental Results and Discussion

Polyhedral single crystals of copper tartrate were grown in silica gels up to about 1mm in size. A powder X-ray diffraction analysis of both products obtained from L- and D-tartaric acid gave similar unit cell dimensions to those of copper tartrate crystals reported by C. Bridle et al.^[9]. But their X-ray diffraction patterns could be easily changed through dehydration. From all the experiments of copper tartrate crystals carried out here, the growth of polyhedra with a distinct crystal habit was observed. All the products were bright blue, well-faceted and optically clear crystals. Fig. 2 shows typical results of a series of *in-situ* observations for the crystals of copper tartrate grown from the reaction with L-tartaric acid and copper nitrate. The observed crystals were formed in the immediate vicinity of the gel reactant interface in the growth cell. The growth behavior for a period of about six hours is shown in figs. 2a~f, which were reproduced from the video tape. As the growth proceeded, a typical growing form appeared in the form of polyhedron including a small dent as indicated by the arrow in fig. 2b. A small dent grew with the advancement of a step and finally filled up as indicated by the arrows in figs. 2d, e. Finally the grown crystal showed a polyhedral form with a flat surface as shown in fig. 2f, which had been growing for over six hours. The advance rate of the step during growth was about 0.01~0.05mm/hr.

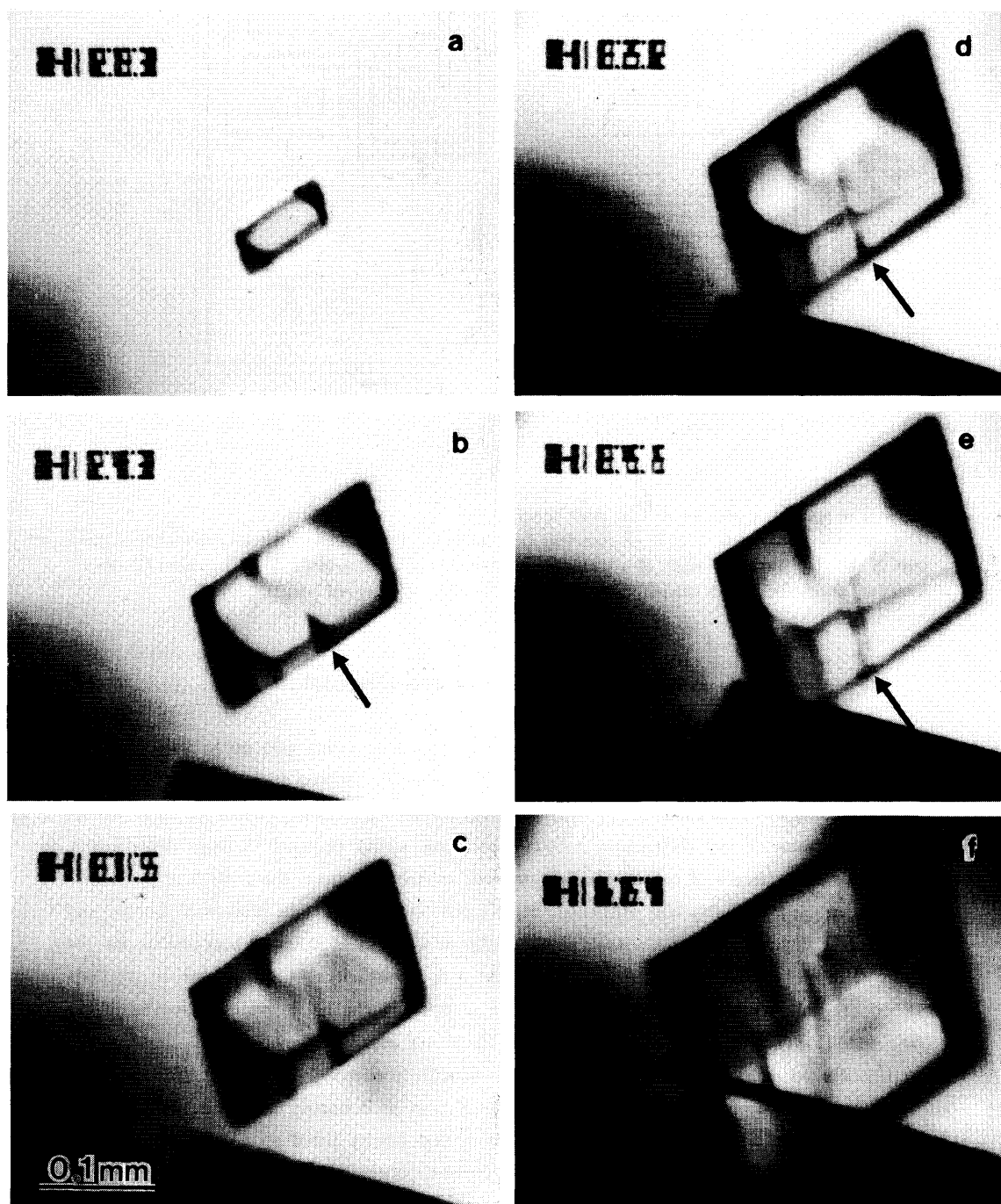


Fig. 2 A series of *in-situ* observations made during growth of L-copper tartrate crystals.

Similar results with regard to the macroscopic morphology and the advancement of a step on the surface during growth were obtained when D-tartaric acid was used. Therefore, it will be sufficient to describe the results by the *in-situ* observation obtained from one of these reactants. The measurements of the optical rotatory power for several products using L-and D-tartaric acid as the starting material were dextrorotatory and levorotatory, respectively.

On the other hand, a detailed examination of surface roughness revealed a difference in morphology between the two equilibrium structures of the L-and D-copper tartrate crystals. Figs. 3 and 4 show the images using a phase contrast microscope representing their characteristic crystal habits and surface roughness. Fig.5 illustrates the directions of observation using the phase contrast microscope. The figures lettered a~d in figs. 3 and 4 correspond to those areas shown in fig. 5. In figs. 3 and 4 they only differ in their surface structures. It is noticed that the areas lettered by p in figs. 3 and 4 are flat, while those lettered by q have rough surface. As far as the structures on the surface are concerned, they showed the two types of equilibrium structures, each one a mirror image of the other. The relationship of the enantiomorph for the surface morphology between the grown crystals of L-and D-copper tartrate is described by the illustrations in fig. 6. The hatched areas in fig. 6 represent the areas with a rough surface as observed in figs. 3 and 4. The mirror images between figs. 6a, b (L-copper tartrate) and figs. 6c, d

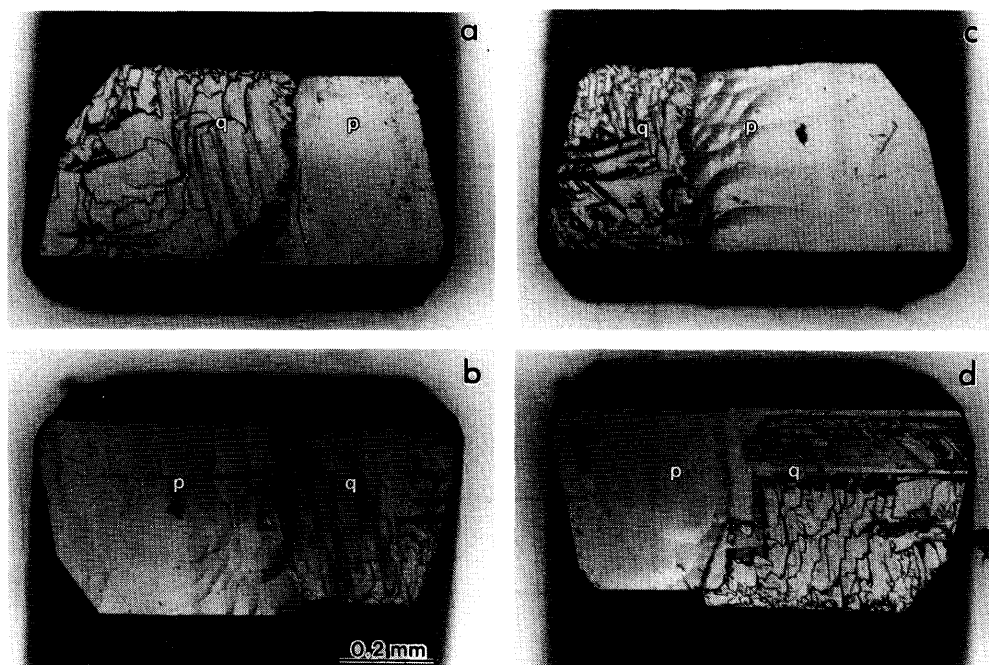


Fig. 3 The observed images of the grown L-copper tartrate crystals viewed from several directions using a phase contrast microscope. It was noticed that the areas lettered by p are flat while those lettered by q have a rough surface.

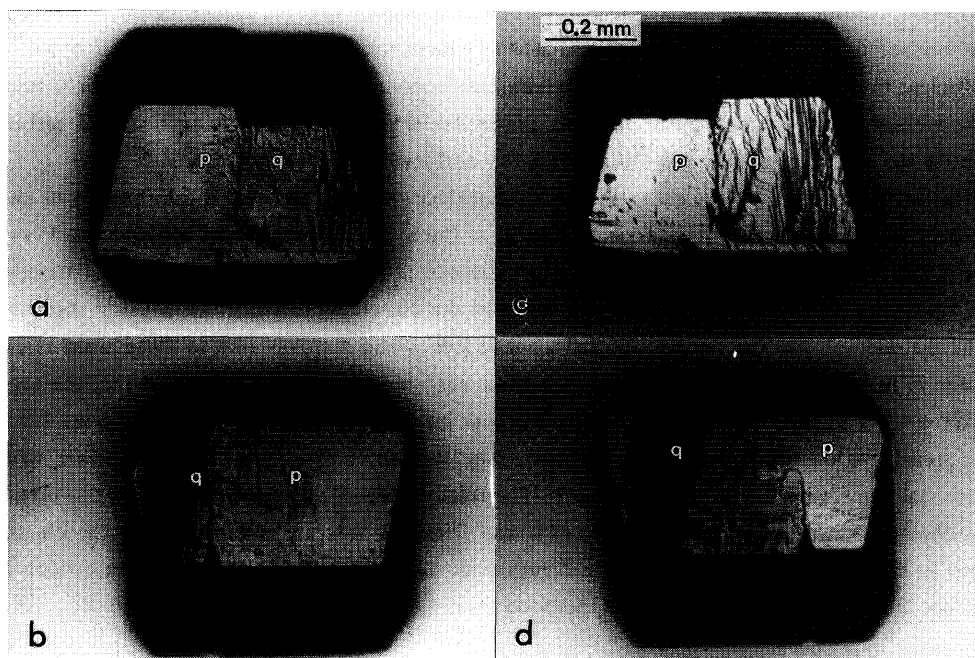


Fig. 4 The observed images of the grown D-copper tartrate using a phase-contrast microscope. Compare the scheme with that of fig. 3.

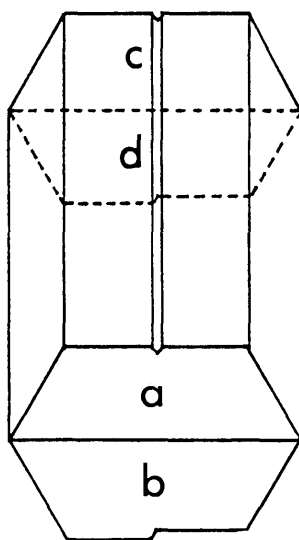


Fig. 5 The schematic illustration of the grown crystal representing the crystal habit and the notations of a~d corresponding to those of figs. 3 and 4.

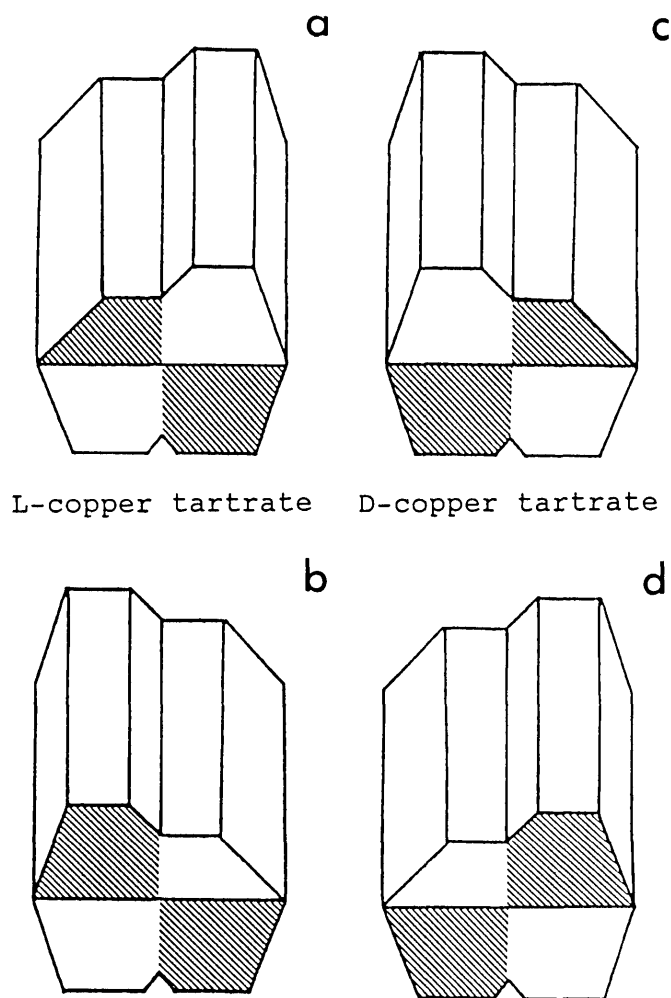


Fig. 6 Illustrations showing the relationship of the morphology on the surface between the equilibrium structures of L- (figs. a and b) and D- (figs. c and d) copper tartrate crystals. The hatched areas represent a rough surface as observed in figs. 3 and 4. Note that they formed two types of equilibrium structures, each one a mirror image of the other.

(D-copper tartrate) are also shown. The present relationships on the morphology of the grown crystals could be explained by considering the effect of chirality in tartaric acid used as the starting material. The microscopic morphology on the surface in the equilibrium structure could vary depending on the enantiomorph of tartaric acid used as a starting material. However, the mechanism of forming a rough surface on an atomic scale in relation to chirality could not be

examined. The growth structure observed during growth did not show a difference for the morphology on the surfaces between them.

Fig. 7 shows the grown crystals using DL-tartaric acid with an equimolar ratio of D and L types. They grew radially in the form of dendrites, which were oriented randomly with respect to each other. In this case, the growth mechanism, morphology and optimum conditions for the crystal growth have not yet been examined.

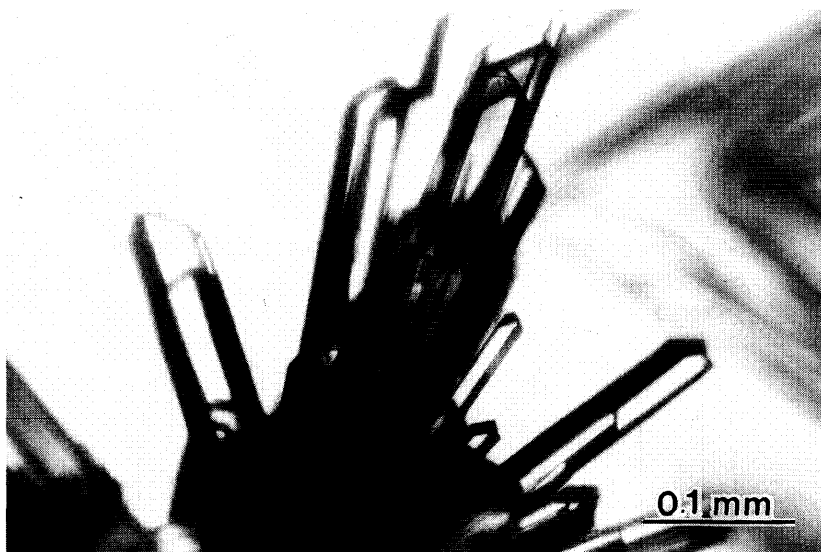


Fig. 7 The grown crystal using DL-tartaric acid as a starting material. The crystals grew radially in the form of dendrites, which were randomly oriented with respect to each other.

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