Synthesis of Some Crystal Forms of Strontium Sulfite by Metasilicate Gel Method and Crystal Form Control

Takayuki Kohiruimaki* **and Keizo Matsuda†**

Department of Technology, Hachinohe Institute of Technology, 88-1 Myou-oobiraki, Hachinohe 031

†Department of Chemistry, School of Science, Tokai University, 1117 Kitakaname, Hiratsuka 259-12

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The purpose of this study is to synthesize strontium sulfite crystals with characteristic forms by a metasilicate gel-growth method and to determine the optimum conditions for synthesis of the crystals. Strontium ions were diffused into metasilicate gel including sulfite ions in order to synthesize strontium sulfite crystals. The crystals were synthesized in the pH range of 4.0 to 11.0, at a diffusion temperature between 5 and 40 °C, in the following concentration ranges: sodium sulfite, 0.2 to 1.5 mol dm^{-3}, and strontium chloride, 0.2 to 3.0 mol dm^{-3}. As a result, strontium sulfite crystals were obtained in the following four forms: spherical, poly-spherical, ellipsoidal, and spindle. The cause of the crystal form change was found to be a difference in the growth side by comparison of X-ray diffraction patterns. In addition, the optimum conditions which controlled the crystal form were influenced by the pH value in the gel and the temperature.

A gel-growth method is known as the synthesis method of a few mm diameter single crystals of calcium tartrate, lead iodide and other crystals.[1—8]

We have studied the gel-growth method from a slightly different view point to establish a control method of the poly-crystal forms. We have prepared various crystal forms of calcium sulfite hemihydrate by a gel-growth method. Calcium sulfite hemihydrate could be made six different forms of crystal: three poly-spherulites, the poly-columnar form, the poly-plate form, and the plate-particular form.[9] The crystal forms are changed by the effect of pH and of ionic product in the gel. Nucleation of calcium sulfite hemihydrate is governed by pH control. We concluded that the rate of nucleation and the crystal forms changed with the amount of calcium ions and sulfite ions.

This paper deals with strontium sulfite crystal, which has the same alkaline earth metal sulfite as calcium sulfite hemihydrate. The spherulite of strontium sulfite was formed in agar–agar gel. Then, the crystal structure and the optimum condition for the formation were investigated.[10,11] The crystal size of strontium sulfite was compared with the other alkaline earth metal (Ca and Ba) sulfites. A linear relationship existed between the square of diameter of the spherulite and the concentration of sulfite ion in the gel.

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Experimental

Sodium sulfite and strontium chloride, regent grade from Wako Pure Chemical Industry Ltd., were used as strontium sulfite source without further purification. The method of gel-growth is shown in Fig. 1. To begin with, the aqueous solution of sodium sulfite and acetic acid were added into the aqueous solution of sodium metasilicate (32.8 wt%). Acetic acid was used as the pH adjustment and the gelling agent in this case. Next, the pre-obtained solutions were injected into a 25 mm inner diameter test tube, the mixed solution was gelled and the metasilicate gel was kept for 1 week. We will use the term "top solution" to refer to the aqueous solution of strontium chloride in this study. The top solution was poured

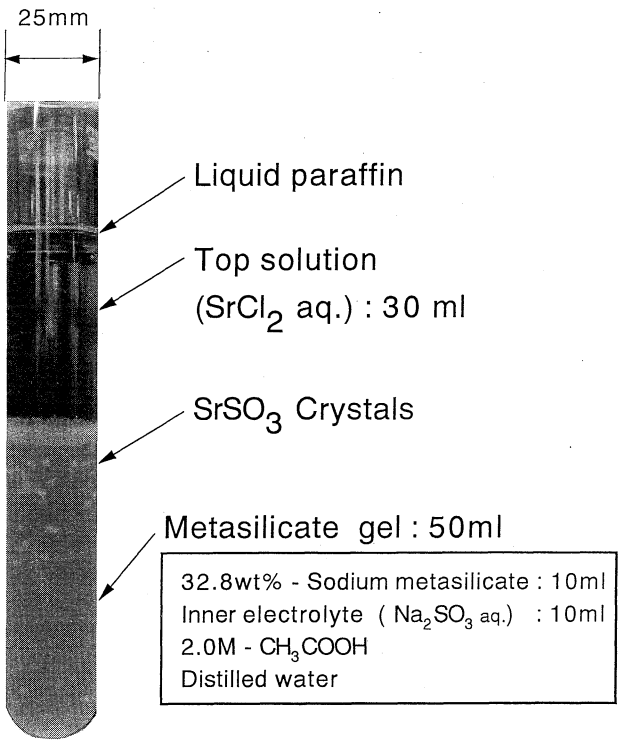


Fig. 1. Method of crystal growth.

upon the gel. The strontium ion in the top solution diffused into the gel, and then the strontium sulfite crystals were synthesized in the gel. The gel and the top solution were sealed with liquid paraffin so as not to oxidize the sulfite ions.

The conditions of synthesis are shown in Table 1 as follows: the pH range, 4.0 to 11.0; the diffusion temperature, 5 to 40 °C; the concentration of Sodium Sulfite, 0.2 to 1.5 mol dm^{-3} and Strontium Chloride, 0.2 to 3.0 mol dm^{-3}

Table 1. Conditions

	Inner	Top solution
Electrolyte	Na_2SO_3	$SrCl_2$
Concentration of electrolyte	0.2—1.5 mol dm^{-3}	0.2—3.0 mol dm^{-3}
pH	4.0—11.0	
Temperature	5—40 °C	
Diffusion time	15 d	

In order to establish the condition of the control method of crystal forms, the measurements of pH in the gel and concentrations of sulfite ion and strontium ion were analyzed. The crystals which grew in the gel was classified in each form into 4 groups. The crystals grown in the gel were classified into each form; the gel which included each form was cut and its pH was measured with the pH testing papers from Advantec MFS. Inc.

The top solution was studied after diffusing into the gel. The concentration of electrolytes in the gel was measured as follows: After the prescribed time, the gel was pulled out by a glass-pipe; then it was cut at 15 mm intervals from upper gel. The cut gels were dissolved in the distilled water, degassed, and samples were

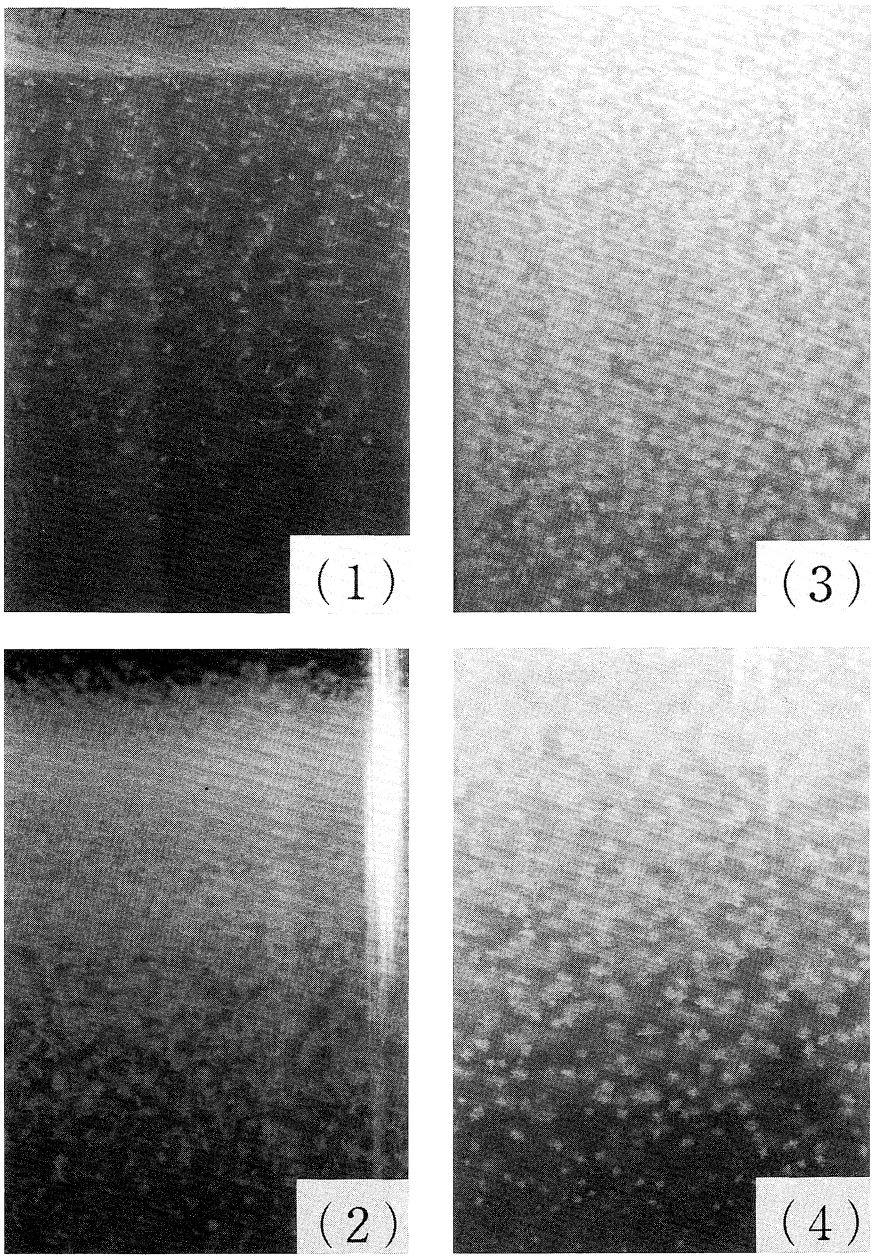


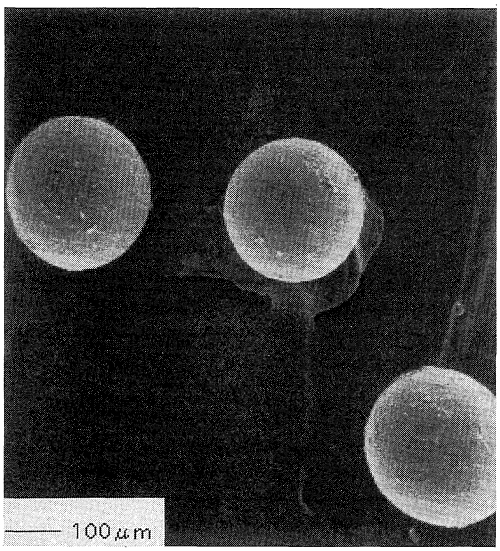
Fig. 2. $SrSO_3$ crystals in gel. Temperature: 40 °C. Concentration of top solution (Na_2SO_3): (1) 0.5 mol dm^{-3}; (2) 1.0 mol dm^{-3}; (3) 2.0 mol dm^{-3}; (4) 3.0 mol dm^{-3}.

sealed in a beaker to prevent oxidation. Then they were frozen for more than 24 h. The samples were thawed and were filtered. The concentration of strontium ions in the filtrate was determined by an atomic absorption photometer AA-670, a product of Shimadzu Seisaku Co.. The concentration of the sulfite ion in the filtrate was determined by an absorptiometric method using an absorptiometer V-550, a product of JASCO Co..

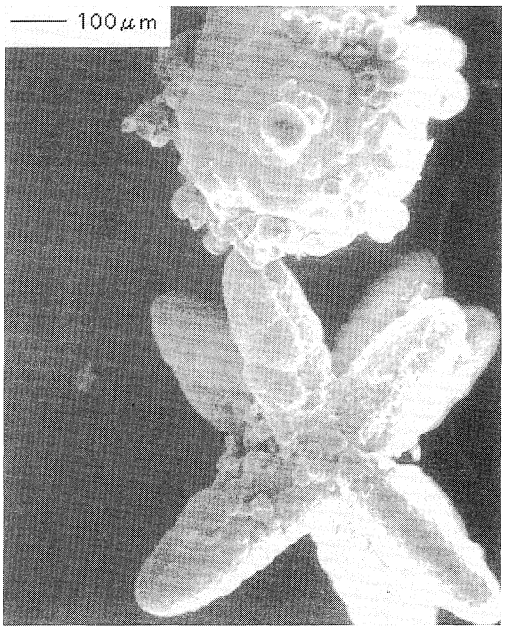
The estimation of the obtained crystals were carried out as follows: the obtained crystal was separated from the gel, washed with deaired distilled water, and dried in a vacuum desiccator. The structures of these crystals were analyzed by X-Ray Diffraction and SEM. X-ray powder diffraction patterns were measured using RAD-C, a product of Rigaku Co., and solubility measurements were performed using Cu $K\alpha$ radiation (40 kV, 30 mA) and Ni filter.

Results and Discussion

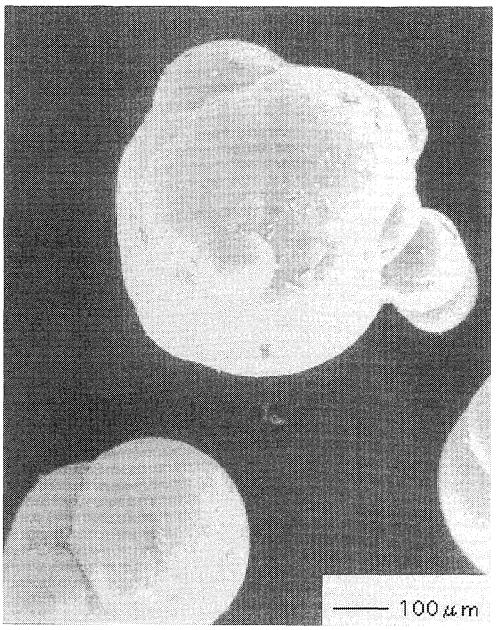
Syntheses of the Various Forms of Crystal. As a beginning, we investigated how to prepare the crystals in the gel. The state in the gel after 2 weeks of crystal growth is shown in Fig. 2. The photographs indicate a crystal obtained under the following conditions: 40 °C, pH=7.6 and the elec-



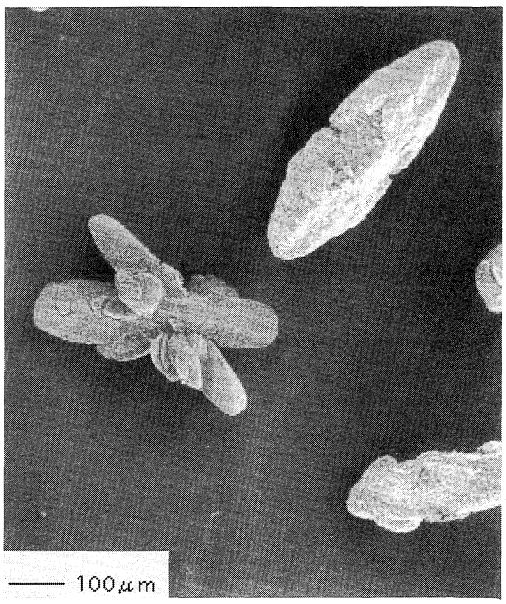
Spherulite (A)



Ellipsoidal form (C)



Poly-spherulite (B)



Spindle form (D)

Fig. 3. SEM of $SrSO_3$ crystals.

trolytes concentrations of 0.5, 1.0, 2.0, and 3.0 mol dm^{-3}. It was recognized that the crystals grew up from the upper part of the gel. First, a spherulite of strontium sulfite was prepared in the upper part of gel. Then, the spherulite was transformed in the course of successive changes of ellipsoidal form in less than 15 d. After 15 d, crystal shape and size underwent no further changes. The ellipsoidal form crystals were seen in the gel under such conditions. The amount of crystals increased and the diameter of crystal lengthened with increasing the concentration of electrolytes.

Figure 3 shows SEM pictures of some crystal forms of strontium sulfite taken out in the gel. The crystals could be classified into four forms: the spherulite, the poly-spherulite, the ellipsoidal form, and the spindle form. These are the mean diameter values of the crystals: the spherulite had average size of 150 μm, the poly-spherulite had 300 μm, both the ellipsoidal form and the spindle form had average crystals of 450 μm. All crystals are polycrystalline substances comprised of particles with the mean diameter of 0.2 to 0.5 μm.

To clarify the structure of the crystals, the cross sections of the crystals are shown in Fig. 4. The spherulite and the poly-spherulite consisted of fibrous crystals which were arranged minutely in a radial manner from the center, as seen in Fig. 4(A) and (B). The ellipsoidal form crystal consisted of an aggregation of plate-shaped crystals, as shown in Fig. 4(C). As a cleavage plane could be seen from the section of the inside of the spindle form crystal, it has become apparent that this crystal was a single crystal, as shown in Fig. 4(D). Figure 3(D) shows a coarse surface due to the gel and powder crystals which adhered on the surface.

X-Ray diffraction patterns of the spherulite and the poly-spherulite obtained at 20 °C and the ellipsoidal form, the spherulite, and the spindle form crystals obtained at 40 °C are shown in Fig. 5 from top to bottom, respectively. The X-ray diffraction patterns of each crystal coincided with that of the standard reagent of strontium sulfite.[12,13] The highest peak was (040) face in all crystals. The peak of (111) face of the spherulite and the poly-spherulite were separated in the ellipsoidal form and the spindle form crystals. By observing the change of the peak of (111) face, we can proved that the crystals making the meeting body of the spherulite and the poly-spherulite are different from those making that of the ellipsoidal form and the spindle form crystals. The full

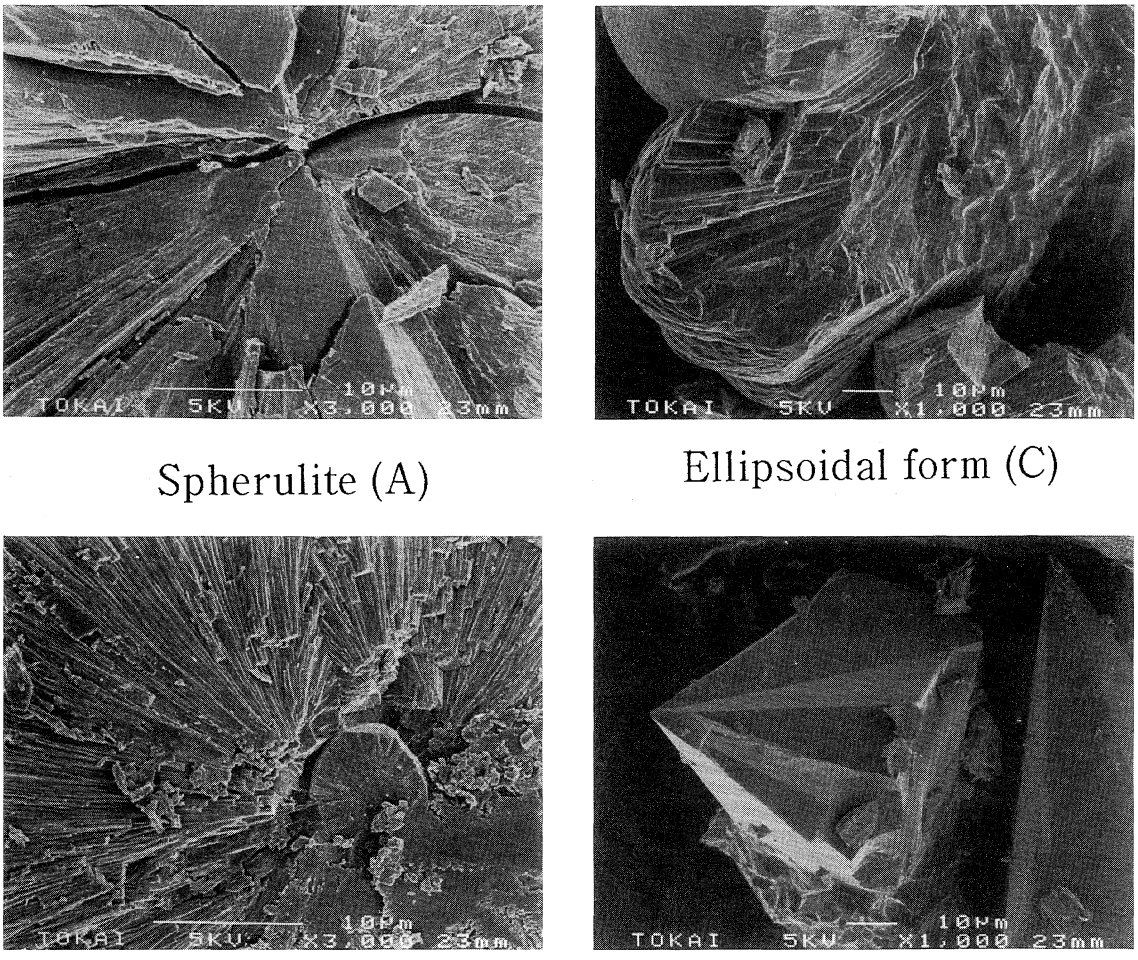


Fig. 4. SEM of cross section of $SrSO_3$ crystals.

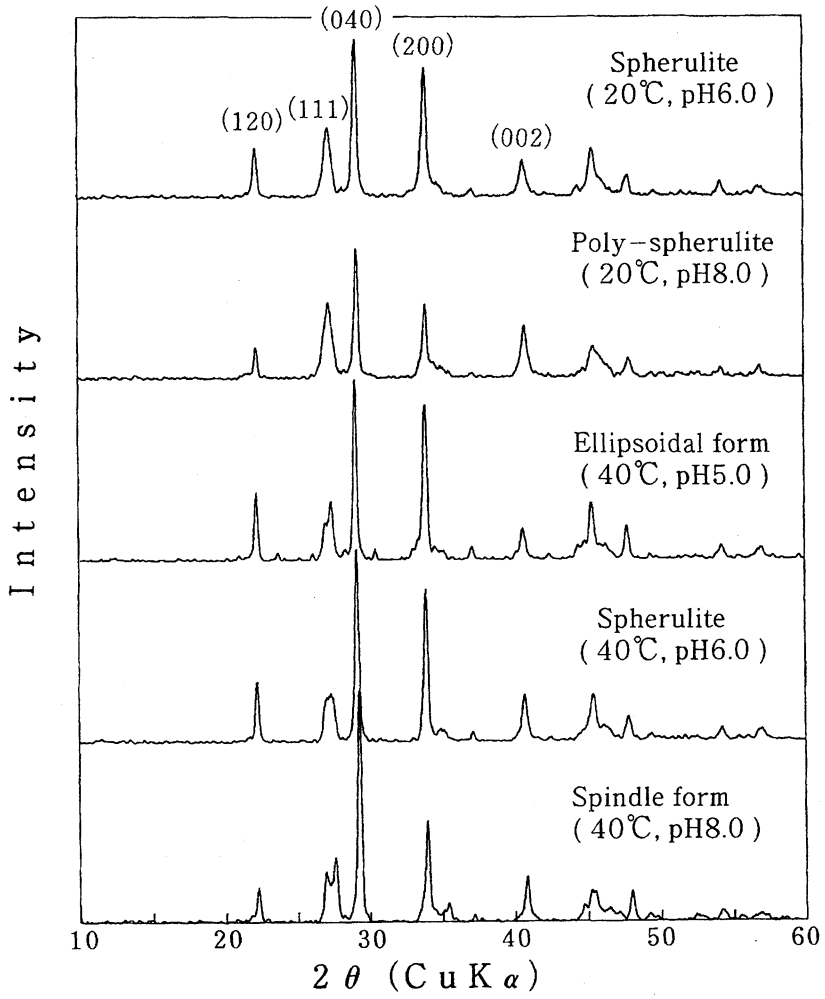


Fig. 5. X-Ray diffraction patterns of $SrSO_3$.

width at half maximum intensity (FWHM) of (111) face changed in all crystal forms. FWHM ratios of (111) face of the spherulite obtained at 20 and 40 °C were 0.7 and 0.43—0.58, respectively, against that of the poly-spherulite obtained at 20 °C taken as base of one. The FWHM ratios of (111) face of the ellipsoidal form crystal and of spindle form crystals obtained at 40 °C were 0.33—0.39. It follows from comparison of FWHM of (111) face that the crystallization of the ellipsoidal form and the spindle form crystals obtained at 40 °C progressed. FWHM values of the other peaks of each form show little differences. The peaks of (111) face and (040) face of the spindle form crystals obtained at 40 °C shifted to high 2θ angles.

These results made it clear that the crystallinity was decreased with successive changes of crystal forms: the spindle, the ellipsoidal, and the spherulite obtained at 40 °C, and the spherulite and the poly-spherulite obtained at 20 °C.

Synthesis Condition of Each Crystal. Next, we will investigate the relation between gel conditions and crystal forms. In Fig. 6, the vertical line shows the concentration of Top Solution and the horizontal line showed the initial pH in the gel at 20 °C. The spherulites were prepared in the acidic gel, and the poly-spherulite in the alkaline gel at 20 °C. The relations between the gel conditions and the crystal formed

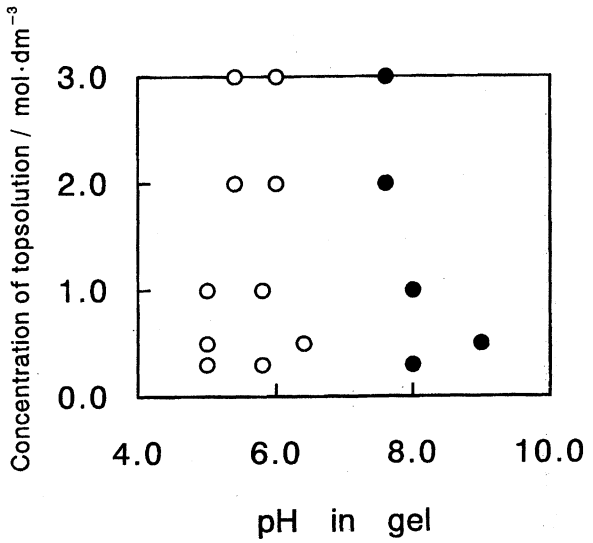


Fig. 6. Relation between crystal form and gel conditions. Temperature: 20 °C. Crystal forms: (○) Spherulite, (●) Poly-spherulite.

at 40 °C were shown in Fig. 7. The spherulite and the poly-spherulite were prepared in the acidic gel, and the ellipsoidal form and the spindle form crystals in the alkaline gel at 40 °C generally. From such results, we expected that the optimum conditions which controlled the crystal form were influenced with the pH value and the temperature in the gel.

First, the effects of pH inside the gel on the crystal forms were investigated. The relations between the ionic product of sulfite ion and strontium ion ($[Sr^{2+}][SO_3^{2-}]$) and pH in the gel are shown in Fig. 8. The ionic product of each ion increases with decreasing of pH below 5.0 in the gel, and strontium sulfite is difficult to dissolve in the alkaline gel. The ionic product of $[Ca^{2+}][SO_3^{2-}]$ is represented by a solid line in Fig. 8. If the acid condition increased, the ionic

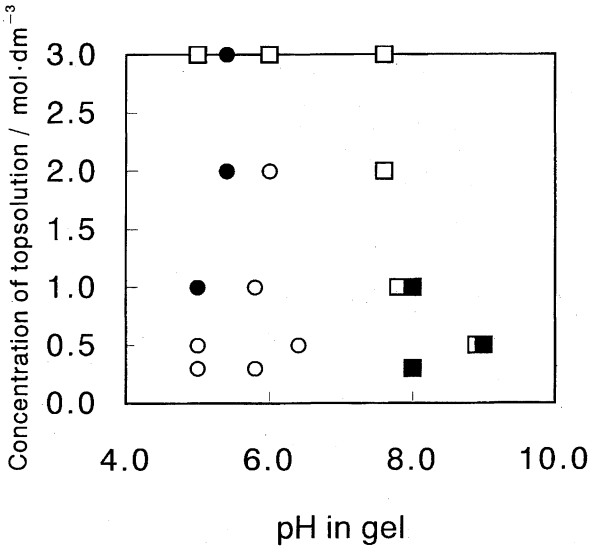


Fig. 7. Relation between crystal form and gel conditions. Temperature: 40 °C. Crystal forms: (○) Spherulite, (●) Poly-spherulite, (□) Ellipsoidal, (■) Spindle.

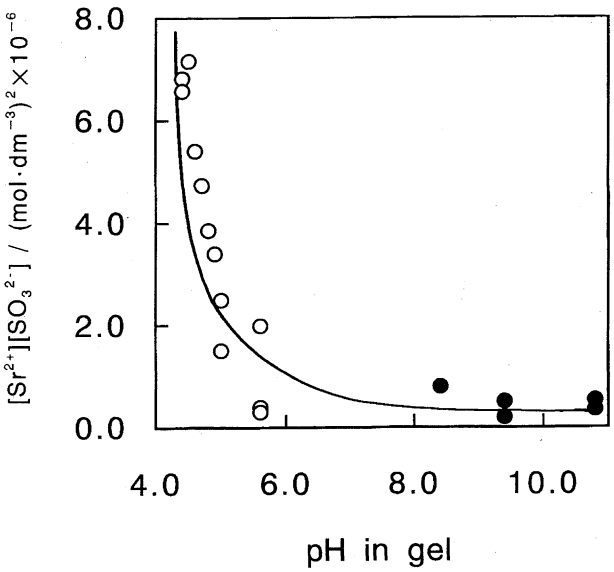


Fig. 8. Relation between ionic products and pH in gel. Temperature: 20 °C. Crystal forms of $SrSO_3$: (○) Spherulite, (●) Poly-spherulite,
—: Ionic product of $CaSO_3 \cdot 1/2H_2O$.

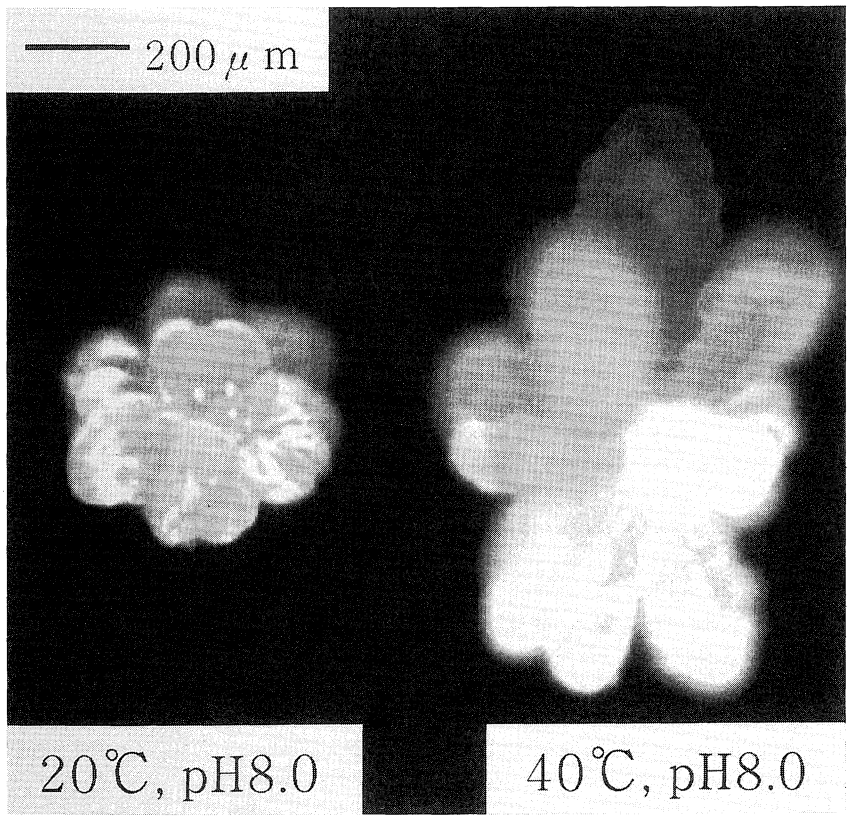


Fig. 9. Comparison of crystal size.

product of $[Sr^{2+}][SO_3^{2-}]$, spherulite could be prepared. A radiation-formed crystal such as ellipsoidal form and the spindle form could be easy to get in the alkaline condition because the ionic product of $[Sr^{2+}][SO_3^{2-}]$ decreased and the deposit of the crystal was quick. The ionic products of $[Sr^{2+}]$-$[SO_3^{2-}]$ and $[Ca^{2+}][SO_3^{2-}]$ have the same change tendency; thus we see the crystal form change factors of strontium sulfite agree with those of calcium sulfite hemihydrate. From these results, we conclude that nucleation is produced slowly in the acidic gel, and that a lot of nuclei are produced and aggregated in the alkaline gel. The crystal forms change with the pH value in the gel.

Nest, we observed the effect of temperature in controlling the crystal forms. The comparison of crystal sizes at the different temperature is shown in Fig. 9. The crystal size grew with the rising of temperature. This result could be explained as follows. The diffusion rate of strontium ion and sulfite ion into the gel will be changed with the temperature effect, and the crystal form will be changed with the differences of ionic products.

Conclusion

These results lead to the conclusion that we synthesized four forms of strontium sulfite crystals which included the new crystal forms. We recognized from comparison of X-ray diffraction patterns that the cause of the crystal form change was a difference in the growth side.

In addition, we revealed that the optimum conditions which control the crystal form were influenced with the pH value in the gel and the temperature effect. Due to the pH in the gel and the temperature effect, the ionic product of $[Sr^{2+}][SO_3^{2-}]$ and solubility limit of strontium sulfite crystal from the gel will be changed, and due to the amount of nuclei in the gel, the crystal form will be changed.

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