Formation of $SrSO_4 \cdot 1/2H_2O$ in an $SrSO_4$–H_2O System and Its Solid Solution in a $CaSO_4$–$SrSO_4$–H_2O System

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In an $SrSO_4$–H_2O system the formation of a new compound of $SrSO_4 \cdot 1/2H_2O$ has been found by coprecipitation from solutions of Sr^{2+} and SO_4^{2-}. This was found to have a similar crystal structure to $CaSO_4 \cdot 1/2H_2O$ of a hexagonal crystal system. The lattice constants thereof were calculated. It was also found that $SrSO_4 \cdot 1/2H_2O$ is not stable in water, but changes to a stable well-known orthorhombic anhydrous strontium sulfate. For a $CaSO_4$–$SrSO_4$–H_2O system, a series of solid solutions of $CaSO_4 \cdot 1/2H_2O$ and $SrSO_4 \cdot 1/2H_2O$ was prepared, which had similar X-ray diffraction patterns to $SrSO_4 \cdot 1/2H_2O$. These solid solutions were unstable in water, and converted with time to a mixture of stable anhydrous $SrSO_4$ and $CaSO_4 \cdot 2H_2O$.

The stable form for the $SrSO_4$–H_2O system at room temperature is known to be anhydrous strontium sulfate of an orthorhombic crystal system. It was reported that a flocculent and amorphous precipitate,[1] or needle-like hydrate,[2] was initially formed and afterwards changed to stable anhydrous strontium sulfate when the aqueous solution of strontium was reacted with that of sulfate at room temperature. However, no data for this hydrate were shown in JCPDS and the details were not clear.

On the other hand, two stable forms are well-known for the $CaSO_4$–H_2O system at room temperature: calcium sulfate dihydrate and II-anhydrous calcium sulfate (anhydrite). Calcium sulfate hemihydrate is a metastable form. Generally, when the aqueous solution of calcium salt is reacted with that of sulfate, calcium sulfate dihydrate is produced at rom temperature and hemihydrate at a temperature above 97 °C.

The $CaSO_4$–$SrSO_4$–H_2O system is important in relation to such industrial problems as the gypsum industry, or problems involving the impurities of strontium in gypsum. Concerning this system, the authors[3] have investigated the incorporation of strontium into dihydrate gypsum, and reported on the limit of the solubility and its dependence on the temperature.

Moreover, in studies concerning this system by means of synthesis through a coprecipitation method, a short note[4] was reported regarding the existence of a new double salt of $CaSO_4 \cdot 2SrSO_4$ composition, for which no details have been given. It was reported[5] thereafter that strontium sulfate is chemically inactive to all forms of calcium sulfate, and does not produce any double salts with the latter.

In the present study, the products in $SrSO_4$–H_2O and $CaSO_4$–$SrSO_4$–H_2O systems were investigated through synthesis by a coprecipitation method, and new products were found other than anhydrous strontium sulfate and calcium sulfate dihydrate, the well-known stable forms in these systems.

Experimental

Preparation of Samples. The samples were synthesized at 25 °C by adding 250 cm^3 of a mix-solution of $CaCl_2$+$SrCl_2$ (mixing ratio of Ca^{2+}: 0—80 mol%) of 1 mol dm^{-3} concentration and 250 cm^3 of a Na_2SO_4 solution of the same concentration into 250 cm^3 of pure water in one portion under stirring. Parts of the product were picked out at predetermined intervals, washed first with water, then with ethanol and finally with acetone to fix them, and dried at 45 °C.

As the mixing ratio of Ca^{2+} in the mix-solution increased at a reaction temperature of 25 °C, the product was not purely new phase, but a mixture containing more calcium sulfate dihydrate. Therefore, in case of a mixing ratio of Ca^{2+} of 52.5—100 mol%, the reactions were carried out at a temperature above 97 °C by the use of a solution amount of 50 cm^3.

Measurements. Identification and the lattice constants of the samples produced were determined using a powder X-ray diffractometer (RAD-II A by RIGAKU). For chemical analyses of Ca^{2+} and Sr^{2+}, an ion-chromatograph (2000i/sp DIONEX) was used. For chemical analyses of SO_4^{2-}, samples were dissolved by an ion-exchange method by Sakurai.[6] The characteristics of the samples were further measured by TG-DTA, FT-IR, and SEM.

Results and Discussion

$SrSO_4$–H_2O System. X-Ray Diffraction of the Products. The X-ray diffraction patterns of the samples synthesized at 25 °C for the $SrSO_4$–H_2O system are shown in Fig. 1. A sample picked out 10 min after precipitation ((B) in Fig. 1) gave a diffraction pattern which seems to be single phase and quite different from that of anhydrous strontium sulfate. This pattern suggests the formation of a new product in the $SrSO_4$–H_2O system. Also, this is quite similar to the pattern of $CaSO_4 \cdot 1/2H_2O$ ((A) in Fig. 1), except that the angles of diffraction shift to a lower side than do those of the latter.

The pattern of the sample remaining in the reacted solution for 120 min after precipitation ((C) in

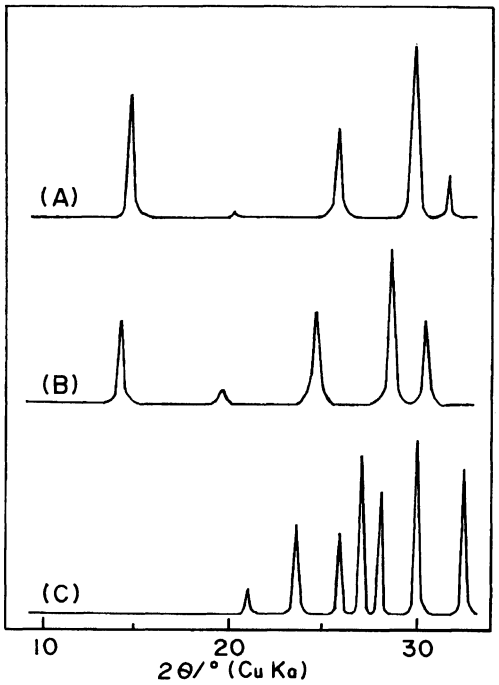

Fig. 1. X-Ray diffraction patterns for samples of the $SrSO_4$–H_2O system synthesized at 25 °C. (A): β-$CaSO_4 \cdot 1/2H_2O$ for control, (B): sample 10 min after precipitation (new product), (C): sample 120 min after precipitation (anhydrous $SrSO_4$).

Fig. 1) was not the same as that of the sample mentioned above, but coincided with that of pure anhydrous $SrSO_4$.

Change of the Products in Water. The change in the products mentioned above (synthesized at 25 °C) in water with time is shown in Fig. 2 in terms of the diffraction intensity of the line of 14° of 2θ for the new product and 30° for anhydrous $SrSO_4$. The line of the new product reduced with time about 20 min after preparation, and disappeared after 120 min; the line of anhydrous $SrSO_4$, however, appeared in about 20 min and grew successively. This suggests that the new product could exist as a pure single phase for a period of about 10 min.

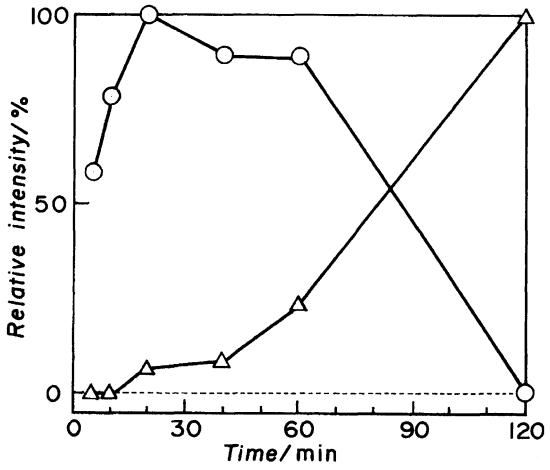

Fig. 2. Change of the new products of the $SrSO_4$–H_2O system in water with time. ○: relative diffraction intensity for new products (2θ=14°), △: relative diffraction intensity for anhydrous $SrSO_4$ (2θ=30°).

It was thus found that the new product, which was different from the conventional stable form of anhydrous $SrSO_4$, would have been formed during the initial stage of the reaction and was converted to stable $SrSO_4$ with time in water. The new product was confirmed to be stable in the dry state.

$CaSO_4$–$SrSO_4$–H_2O System. X-Ray Diffraction of the Products. The results of the X-ray diffraction of samples for the $CaSO_4$–$SrSO_4$–H_2O system are shown in Fig. 3. The samples produced at 25 °C from the original mix-solution containing 25 and 50% of Ca^{2+}, respectively, indicated, as can be seen in (A) and (B) of Fig. 3, the patterns of neither calcium sulfate dihydrate nor anhydrous $SrSO_4$, but rather patterns similar to that of the new product described above. This suggested the formation of new products to also exist in this system. These new products were found to be formed almost purely in terms of X-ray analysis in the range up to 70 mol% of the mixing ratio of Ca^{2+}; however, they contained a large amount of $CaSO_4 \cdot 2H_2O$ when the mixing ratio was more than 80% of Ca^{2+}. On the other hand, the sample produced at 97 °C indicated, as can be seen in (C) of Fig. 3, a similar pattern. The

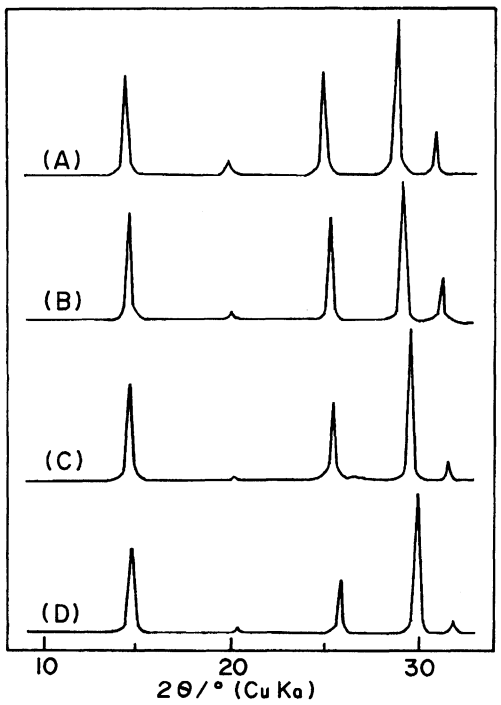

Fig. 3. X-Ray diffraction patterns for samples synthesized in the $CaSO_4$–$SrSO_4$–H_2O system. (A): Ca^{2+} mixing ratio in original soln; 25 mol% (at 25 °C), (B): 50 mol% (at 25 °C), (C): 70 mol% (above 97 °C), (D): 100 mol% (above 97 °C).

pattern of the sample ((D) in Fig. 3) for 100 mol% of Ca^{2+} (for the $CaSO_4$–H_2O system) coincided with the pattern of $CaSO_4 \cdot 1/2H_2O$.

Thus, pure new products which gave X-ray diffraction patterns similar to that of $CaSO_4 \cdot 1/2H_2O$ were obtained over the range of various mixing ratios of Ca^{2+} and Sr^{2+} in the $CaSO_4$–$SrSO_4$–H_2O system.

Change of the Products in Water. The change of the products of this system in water is shown in Fig. 4. The X-ray diffraction intensity of the new product formed by using a mix-solution containing 40 mol% of Ca^{2+} slightly increased with time until 360 min, and then decreased to zero in 960 min. Instead, the pattern of anhydrous $SrSO_4$ appeared after 180 min and $CaSO_4 \cdot 2H_2O$ after 360 min, and grew successively. It is suggested that the new product could exist in water as a single phase for about 120 min.

Thus, it was found that the new product (as mentioned above) was formed during the initial period of reaction for all ranges of the Ca^{2+} content in the $CaSO_4$–$SrSO_4$–H_2O system. Further, although it was not stable in water at 25 °C, it decomposed with time to anhydrous $SrSO_4$ and $CaSO_4 \cdot 2H_2O$. The new product could be kept as a single phase for a longer time than that of the $SrSO_4$–H_2O system.

Characteristics of the New Products. Chemical Compositions. The results of chemical analyses of the new products described above are shown in Table 1 (measurement error: less than ± 5%). As can be seen, each new products has a different amount of Ca^{2+} content, depending on the Ca^{2+} content in the original mix-solution. The mol ratio of the anion (SO_4^{2-}) to the cation ($Ca^{2+}+Sr^{2+}$) is approximately 1 for all products; nevertheless, they give the same X-ray diffraction patters as those mentioned above. It is thus understandable that the new products are not compounds comprising compositions of definite proportion.

TG-DTA. All of the new products indicated, as shown in the TG-DTA curves of Fig. 5, endothermic peaks with a weight decrease at the vicinity of 190—140 °C and an exothermic peak at about 400—323 °C. The endothermic peak is seemingly due to the combined water, and the peak temperature shifts to the lower side as the Ca^{2+} content increases. The exothermic peak was considered to be similar to the peak which is usually observed on the transition from III-$CaSO_4$ to II-$CaSO_4$; it also shifts to the lower side along with an increase in the Ca^{2+} content. For the sample of the $CaSO_4$–$SrSO_4$–H_2O system, except for the sample of the end composition, it was indicated that a sample with a greater content of Ca^{2+} gives a bigger area of the exothermic peak; the reason for this is not clear.

Further, the weight decrease due to the combined water amounted to the about 5—7%; the correlation of the weight decrease and the Ca^{2+} content is shown in Fig. 6. The broken line in Fig. 6 corresponds to the curve for the theoretical value of the combined water of the new products, symbolized as (Ca_x, Sr_{1-x}) $SO_4 \cdot 1/2H_2O$.

IR Spectra. Generally, the absorption bands by H_2O molecules in $CaSO_4 \cdot 1/2H_2O$ are observed at 4000—3200 cm^{-1} (stretching vibration) and 1700—1600 cm^{-1} (deformation vibration),[7] and H_2O molecules in $CaSO_4 \cdot 1/2H_2O$ are considered to contain hydrogen bonds.[8]

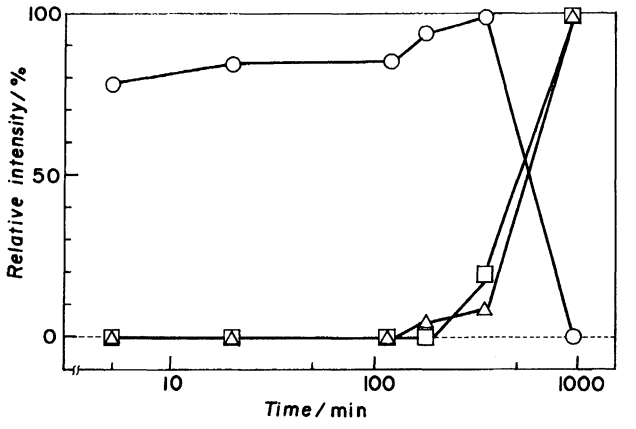

Fig. 4. Change of the new products of the $CaSO_4$–$SrSO_4$–H_2O system in water with time (Ca^{2+} mixing ratio in original soln: 40 mol%). ○: diffraction intensity for new product ($2\theta=14°$), □: diffraction intensity for $CaSO_4 \cdot 2H_2O$ ($2\theta=11.7°$), △: diffraction intensity for anhydrous $SrSO_4$ ($2\theta=30°$).

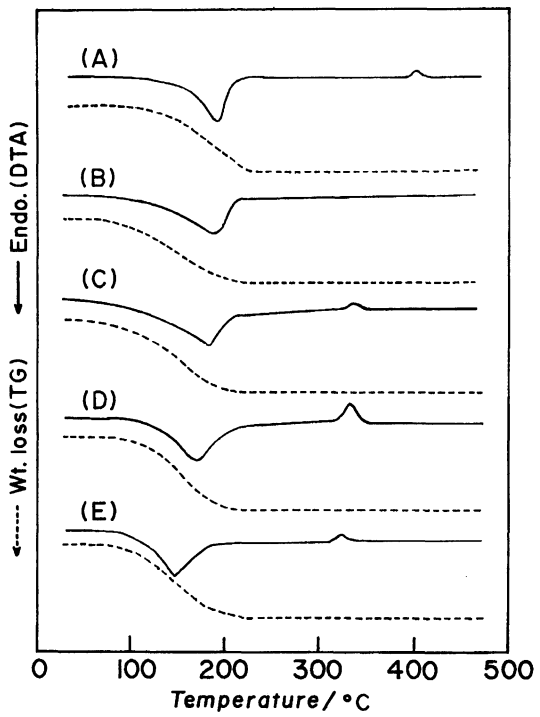

Fig. 5. TG-DTA curves for the synthesized samples for the $CaSO_4$–$SrSO_4$–H_2O system. (A): Ca^{2+} mixing ratio in original soln; 0 mol% (at 25 °C), (B): 25 mol% (at 25°C), (C): 50 mol% (at 25 °C), (D): 70 mol% (above 97 °C), (E): 100 mol% (above 97 °C).

Table 1. Chemical Composition of the Synthesized Samples

Ca^{2+} in original solution/mol%	Reaction temp/°C	$Ca^{2+}/(Ca^{2+}+Sr^{2+})$ in synthesized samples/mol%	$SO_4^{2-}/(Ca^{2+}+Sr^{2+})$ in synthesized samples/mol ratio
0	25	0	1.03
25	25	11.7	1.04
50	25	29.3	1.04
70	25	51.3	1.04
70	above 97	62.9	1.03
80	above 97	75.5	1.05
100	above 97	100	1.06

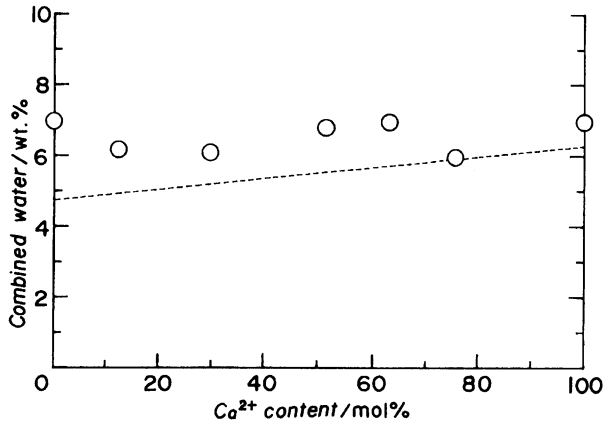

Fig. 6. Change in combined water in the synthesized samples incorporated with Ca^{2+}. ○: observed value, ---: Theoretical value for $(Ca_x, Sr_{1-x})\ SO_4 \cdot 1/2H_2O$.

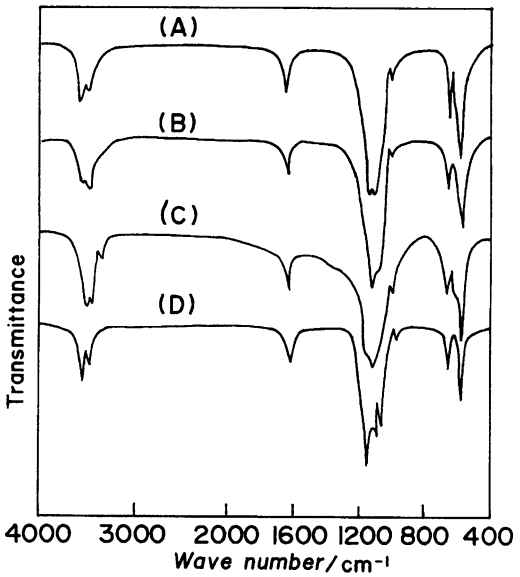

Fig. 7. IR spectra of the synthesized samples. (A): Ca^{2+} mixing ratio in original soln; 0 mol% (at 25 °C), (B): 70 mol% (above 97 °C), (C): 100 mol% (above 97 °C), (D): β-$CaSO_4 \cdot 1/2H_2O$ (calcined gypsum) for control.

The IR spectra of the new products (as shown in (A) and (B) in Fig. 7) are similar to that of $CaSO_4 \cdot 1/2H_2O$, suggesting that the former would have water crystals of the same type as the latter.

The absorption bands by H_2O molecules in both $CaSO_4 \cdot 1/2H_2O$ samples (one was synthesized at 97 °C in the present investigation ((C) in Fig. 7), and the other was calcined gypsum ((D) in Fig. 7)) were observed at 3611, 3556, and 1618 cm^{-1}. To the contrary, the new product in the $SrSO_4$–H_2O system gave 3592, 3533, and 1631 cm^{-1}, which indicates a shifting to a lower wave number for the stretching vibration, and to a higher wave number for a deformation vibration. The samples containing Ca^{2+} of 25—70 mol% gave absorption bands at wave numbers between the two ((A) and (C)).

The hydrogen bond distance in the new product in the $SrSO_4$–H_2O system and $CaSO_4 \cdot 1/2H_2O$ were calculated using a method by Nakamoto,[9] along with the data of the 3592 cm^{-1} peak for $SrSO_4 \cdot 1/2H_2O$ and 3611 cm^{-1} for $CaSO_4 \cdot 1/2H_2O$, to be 2.90 and 3.30 Å respectively. This means a stronger hydrogen bond of the former than the latter.

Lattice Constants. The lattice constants of a pure sample of the new product for the $SrSO_4$–H_2O system were determined on the basis of the data of the JCPDS 24-1068, hexagonal crystal system description

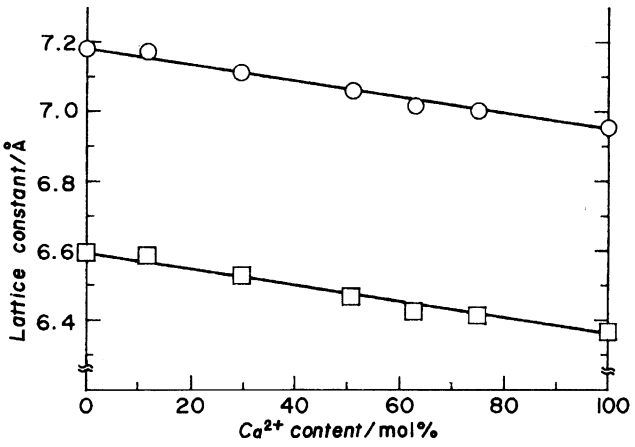

Fig. 8. Change in lattice paramater of solid solution of $CaSO_4 \cdot 1/2H_2O$–$SrSO_4 \cdot 1/2H_2O$ (hexagonal system). ○: a-axis, □: c-axis.

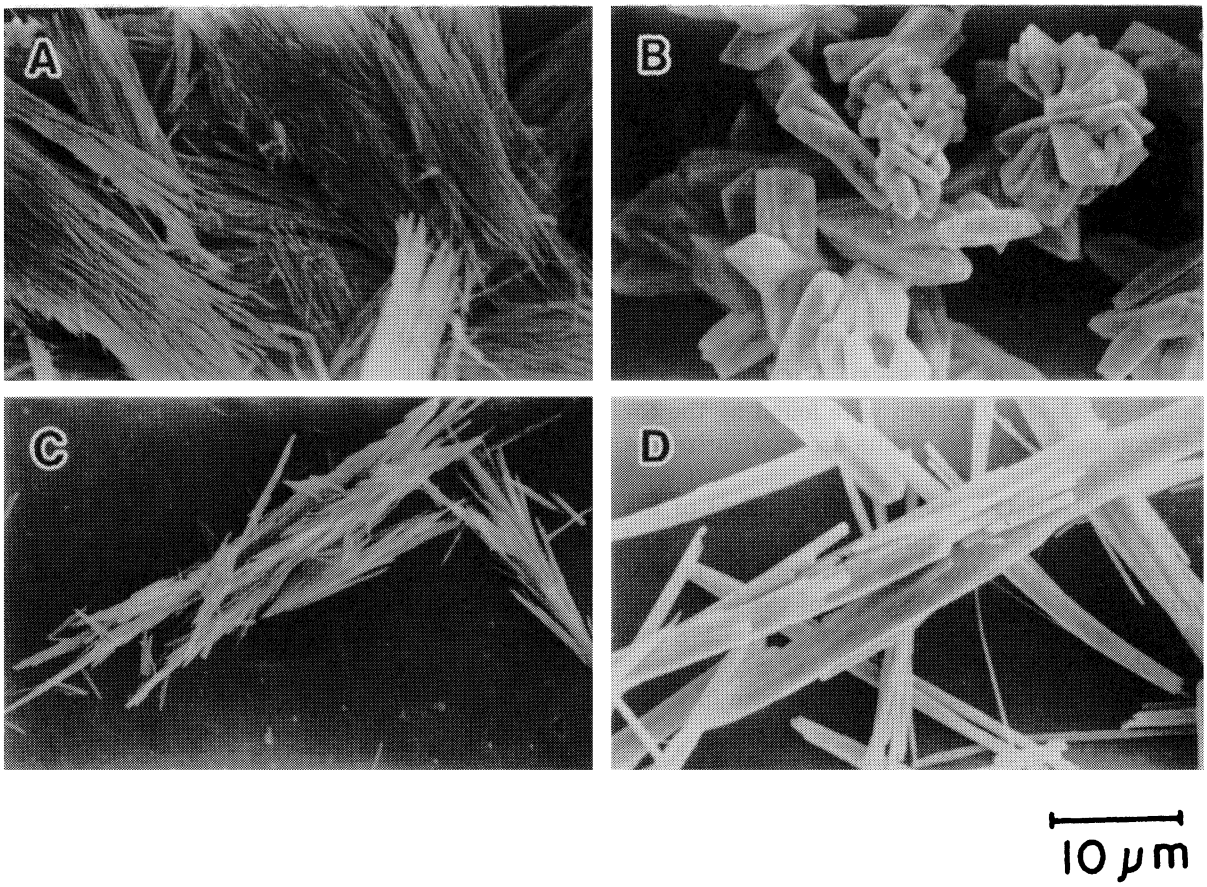

Fig. 9. SEM photographs of the synthesized samples. A : sample 10 min after precipitation ($SrSO_4 \cdot 1/2H_2O$), B : sample 120 min after precipitation (anhydrous $SrSO_4$), C : sample of containing 29.3 mol% of Ca^{2+}, D : sample of containing 62.9 mol% of Ca^{2+}.

for $CaSO_4 \cdot 1/2H_2O$. The results showed that lattice constants of $a=7.178$ and $c=6.589$ Å were obtained. The observed and theoretical value of d for each diffraction pattern nearly coincided with each other, as shown in Table 2. Based on these results, together with those of the TG-DTA and IR spectra, the new product in the $SrSO_4$–H_2O system was considered to be metastable strontium sulfate hemihydrate, $SrSO_4 \cdot 1/2H_2O$, and has a similar crystal structure to that of $CaSO_4 \cdot 1/2H_2O$.

Likewise, the lattice constants of the new products for the $CaSO_4$–$SrSO_4$–H_2O system were determined, the results of which are shown in Fig. 8 in terms of the Ca^{2+} content. Since the ion radii of Sr^{2+} is larger than that of Ca^{2+}, the lattice constants of $SrSO_4 \cdot 1/2H_2O$ give larger values. As can be seen in Fig. 8, the lattice constants of both the a-axis and b-axis shrink linearly as the Ca^{2+} content increases. The axial ratio of a/c for all samples is approximately 1.09, indicating the same degree of change for both axes, which means that Vegard's rule holds for those samples prepared in the $CaSO_4$–$SrSO_4$–H_2O system.

It was thus considered that the new products containing different amounts of Ca^{2+} in the $CaSO_4$–$SrSO_4$–H_2O system are a complete series of solid solutions of $CaSO_4 \cdot 1/2H_2O$ and $SrSO_4 \cdot 1/2H_2O$.

Table 2. X-Ray Powder Diffraction Data for the New Products of the $SrSO_4$–H_2O System

hkl	I/I_0	d,obsd/Å	d,calcd/Å
100	30	6.251	6.216
101	4	4.518	4.522
110	58	3.598	3.589
200	100	3.116	3.108
102	36	2.916	2.911
112	5	2.429	2.427
210	8	2.353	2.350
211	28	2.214	2.213
301	9	1.977	1.977
212	28	1.915	1.913
220	10	1.798	1.794
302	10	1.756	1.754
310	16	1.726	1.724

Observation by SEM. An example of the crystal shape of the prepared samples is shown in Fig. 9. As can be seen in Fig. 9(A) for the $SrSO_4$–H_2O system, strontium sulfate hemihydrate having a fibrous shape with a size of 0.1—0.2 μm×8—15 μm was produced during the initial period of reaction, and then converted with

time to anhydrous $SrSO_4$ having the shape shown in Fig. 9(B).

The prepared sample containing 29.3 mol% of Ca^{2+} for the $CaSO_4$–$SrSO_4$–H_2O system (Fig. 9(C)) has a sector form made by congregation of needle-like crystal with a size of 0.4—0.6 μm×4—12 μm. The sample synthesized at high temperature with a Ca^{2+} content of 62.9 mol% (Fig. 9(D)) is of prismatic shape with a size of 1—4 μm×20—100 μm. Generally, the particle size seems to become larger as the Ca^{2+} content increases.

Conclusion

The new products for the $SrSO_4$–H_2O system and the $CaSO_4$–$SrSO_4$–H_2O system were found by the coprecipitation method. The results are summarized as follows;

For the $SrSO_4$–H_2O system, $SrSO_4 \cdot 1/2H_2O$ of the metastable form is formed during the initial period of the coprecipitation reaction. It has a similar crystal structure to that of $CaSO_4 \cdot 1/2H_2O$ of the hexagonal crystal system, having lattice constants of $a=7.178$ and $c=6.589$ Å. Although it is stable in the dry state, it converts to anhydrous $SrSO_4$ of a stable form in water with time.

For the $CaSO_4$–$SrSO_4$–H_2O system, a series of new products which give similar X-ray diffraction patterns to those of $SrSO_4 \cdot 1/2H_2O$ and have wide-ranging Ca^{2+}/Sr^{2+} ratios are formed. The new product was found to be a complete series of solid solutions of $CaSO_4 \cdot 1/2H_2O$ and $SrSO_4 \cdot 1/2H_2O$; it is unstable in water, and converts with time to stable anhydrous $SrSO_4$ and $CaSO_4 \cdot 2H_2O$.

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