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Crystallographic Data for New Phases in the $CaSO_3$–H_2O System

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Among the three modifications of calcium sulfite hemihydrate, two of them, hexagonal β-$CaSO_3 \cdot 1/2H_2O$ with a rhombohedral lattice and γ-$CaSO_3 \cdot 1/2H_2O$ with a simple triangular hexagonal lattice, were found in the authors' recent work.[1] By heating α- and/or γ-hemihydrate at 330—360 °C in a nitrogen atmosphere, the orthorhombic anhydrate α-$CaSO_3$ was formed, with lattice constants of 6.472, 15.93, and 23.44 Å for *a*, *b*, and *c* respectively, while the body-centered tetragonal anhydrate β-$CaSO_3$, with lattice constants of 15.68 and 19.44 Å for *a* and *c* respectively, was formed by heating the β-hemihydrate. The dehydration of three hemihydrates and the hydration of two anhydrates were discussed. The phase relationships in the $CaSO_3$–H_2O system were summarized as follows:

$$\alpha\text{-}CaSO_3 \cdot 1/2H_2O \underset{\text{Hydration (30 °C)}}{\overset{\text{Dehydration (360 °C)}}{\rightleftarrows}} \alpha\text{-}CaSO_3 + 1/2H_2O;$$

$$\beta\text{-}CaSO_3 \cdot 1/2H_2O \underset{\text{Hydration (30 °C)}}{\overset{\text{Dehydration (340 °C)}}{\rightleftarrows}} \beta\text{-}CaSO_3 + 1/2H_2O;$$

$$\gamma\text{-}CaSO_3 \cdot 1/2H_2O \xrightarrow{\text{Dehydration (330 °C)}} \alpha\text{-}CaSO_3 + 1/2H_2O;$$

$$\gamma\text{-}CaSO_3 \cdot 1/2H_2O \xrightarrow{\text{Transformation (in water at 20 °C)}}$$

$$\beta\text{-}CaSO_3 \cdot 1/2H_2O \xrightarrow{\text{Transformation (in water at 20 °C)}} \alpha\text{-}CaSO_3 \cdot 1/2H_2O.$$

Calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$) is useful as an architectural material since it has a high thermal stability and a low water solubility in comparison with calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). A large amount of the hemihydrate has been produced by the milky-lime process for the desulfurization of flue gas. The hemihydrate has also attracted some attention as an inorganic filler in a plastic composite. The present authors have undertaken several fundamental and applied experiments[1–5] on the hemihydrate for use as industrial material.

In the $CaSO_3$–H_2O system, five compounds have been reported: $CaSO_3 \cdot 4H_2O$;[6] $CaSO_3 \cdot 2H_2O$;[7–10] $CaSO_3 \cdot H_2O$;[11] $CaSO_3 \cdot 1/2H_2O$;[12–16] and $CaSO_3$.[16–18] However, the phase relationships in the $CaSO_3$–H_2O system have not yet been established. The existence of di- and monohydrates has, though, been disproved. The tetrahydrate is known to exist at low temperatures below 4 °C and to be converted into hemihydrate instantly at room temperature. Although several papers on the X-ray diffraction data of the hemi- and anhydrates in the $CaSO_3$–H_2O system have been published,[12–18] they are not consistent with each other.

In recent years, the present authors have found three modifications of the hemihydrate, formed by passing SO_2 through a suspension of $Ca(OH)_2$.[1] The present work was undertaken in order to elucidate the crystallographic data of anhydrate formed by the thermal dehydration of the hemihydrate and to establish the phase relationships in the $CaSO_3$–H_2O system.

Experimental

Preparation of Samples. The chemical composition of the guaranteed reagent used, $Ca(OH)_2$, was 74.9% CaO and 24.1% H_2O. The purity of the SO_2 used was 99.98%, judging from the results of gas chromatography. The three modifications of calcium sulfite hemihydrate were prepared by passing dried and decarboxylated SO_2 through a suspension of 2% $Ca(OH)_2$. After finishing the reaction at pH 6—8, the precipitate was filtered and rinsed with water, methanol, and acetone.

Table 1. Synthesis of calcium sulfite hemihydrate

Conditions	A	B	C
$Ca(OH)_2$ in milky lime/%[a]	2	2	2
Flow speed of SO_2/cm³ min	10	10	100
Temperature/°C	20	80	95

a) 4.1 g $Ca(OH)_2$/200 cm³ H_2O.

Table 1 shows the synthesis conditions of the hemihydrate. The composition of the products under the conditions A, B, and C was 43.1—43.2% CaO, 49.0—49.2% SO_2, 0.5—0.6% SO_3, and 6.86—7.13% H_2O. These values were sufficiently close to the calculated values for $CaSO_3 \cdot 1/2H_2O$ (43.4% CaO, 49.6% SO_2, 7.00% H_2O). The hemihydrates, A—C, were dehydrated at 330—360 °C in a nitrogen atmosphere and then kept them for 1 h to convert in order to the anhydrates. In order to avoid the oxidation and moisture absorption of the products, they were kept in a vacuum desiccator with silica gel.

Measurements. The samples were analyzed by means of the X-ray diffraction method, thermal analysis (micro TG-DTA), infrared spectroscopy, and the scanning-microscope technique. The X-ray diffraction measurement of the samples was made by the use of a Rigaku Denki 2001 diffractometer using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å), with high-purity silicon ($d = 3.138$ Å) as the internal standard. The X-ray diffraction data were obtained as the average values from 15—20 samples of a hemihydrate or an anhydrate. The chemical analyses were made as has been described previously.[3]

Results and Discussion

Identification of the New Phases of Calcium Sulfite Hemihydrate. In the previous paper,[1] three modifications of hemihydrate were reported in detail. The conventional orthorhombic hemihydrate was prepared under the A synthesis conditions in Table 1, the new phase I, with the known phase as part of a mixture, was formed under the B conditions, and the new phase II, including the former two phases, was formed as a mixture under the C conditions. Unfortunately, these new phases could not be distinguished as a single phase. In the previous paper, the above new phases were called Phase I and Phase II as a matter of convenience. In this paper, these three modifications of hemihydrate are named α-$CaSO_3\cdot 1/2H_2O$ (orthorhombic system), β-$CaSO_3\cdot 1/2H_2O$ as Phase I, and γ-$CaSO_3\cdot 1/2H_2O$ as Phase II.

Table 2 lists the crystallographic data for the three modifications. The orthorhombic hemihydrate reported by Waerstad *et al.*[15] will be called α-$CaSO_3\cdot 1/2H_2O$ hereafter.

New Phases of Anhydrous Calcium Sulfite. The dehydrated products of the hemihydrates obtained under the A, B, and C preparing conditions will here-

TABLE 2. CRYSTALLOGRAPHIC DATA FOR THREE MODIFICATIONS OF CALCIUM SULFITE HEMIHYDRATE

α-$CaSO_3\cdot 1/2H_2O$ (Orthorhombic system)			
d_{obsd}/Å	d_{calcd}/Å	*h k l*	I/I_0
5.556	5.549	0 1 1	70
5.346	5.338	0 2 0	80
4.826	4.830	1 1 1	10
3.806	3.802	1 2 1	83
3.159	3.156	2 2 1	100
3.121	3.121	0 3 1	20
2.966	2.974	1 3 1	33
2.820	2.817	3 1 1	27
2.671	2.670	1 2 2	46
2.626	2.633	2 3 1	62
	2.625	2 1 2	
2.456	2.452	4 0 0	10
2.377	2.394	1 4 1	3
2.345	2.344	2 4 0	6
2.262	2.257	3 3 1	5
2.241	2.243	4 1 1	8
2.206	2.205	2 4 1	25
2.151	2.155	2 3 2	16
2.125	2.122	0 1 3	13
2.112	2.115	3 2 2	3
	2.114	1 0 3	
2.064	2.062	0 4 2	43
2.011	2.018	1 4 2	3
1.959	1.957	4 0 2	30
1.952	1.948	2 1 3	22
1.929	1.928	4 3 1	7
1.849	1.849	5 1 1	47
	1.850	0 3 3	
1.813	1.818	1 3 3	10
1.807	1.800	4 4 0	25
1.780	1.780	3 1 3	7
1.743	1.744	3 4 2	6
1.677	1.677	2 5 2	16
1.620	1.624	0 0 4	20
1.586	1.585	6 0 1	6
1.581	1.584	1 1 4	6
1.520	1.520	6 2 1	5
1.486	1.487	2 6 2	6
1.476	1.477	4 3 3	10
1.425	1.421	5 4 2	14
1.252	1.252	1 2 5	5

a=9.809 Å, b=10.68 Å, c=6.496 Å.

β-$CaSO_3\cdot 1/2H_2O$ (Hexagonal system, rhombohedral lattice)				
d_{obsd}/Å	d_{calcd}/Å	*h k l**	*h k l***	I/I_0
4.270±0.002	4.270	2 2 2	2 0 $\bar{2}$	54
3.408±0.017	3.425	0 2 4	2 2 0	100
3.220±0.008	3.228	1 4 0	2 1 $\bar{3}$	68
3.100±0.011	3.107	2 3 2	3 1 $\bar{2}$	78
3.020±0.012	3.026	0 1 5	2 2 1	34
2.868±0.015	2.853	2 0 5	3 1 1	49
2.847±0.003	2.846	3 3 0	3 0 $\bar{3}$	74
2.740±0.005	2·735	1 4 3	3 2 $\bar{2}$	27
2.182±0.004	2.184	1 0 7	3 2 2	29
1.870±0.003	1.870	2 0 8	4 2 2	41
1.767±0.003	1.770	0 5 7	4 4 $\bar{1}$	31
1.704±0.003	1.701	5 4 4	6 1 $\bar{3}$	18
1.658±0.003	1.657	6 4 2	6 0 $\bar{4}$	21
1.605±0.009	1.614	2 8 0	4 2 $\bar{6}$	17
1.495±0.002	1.495	3 8 1	5 2 $\bar{6}$	12
1.452±0.002	1.451	9 2 1	7 $\bar{2}$ $\bar{4}$	10

*h k l**: Hexagonal indices, *h k l***: rhombohedral indices a=17.08 Å, c=15.46 Å, a_R=11.13 Å, α=100.3°.

γ-$CaSO_3\cdot 1/2H_2O$ (Hexagonal system, simple triangular lattice)			
d_{obsd}/Å	d_{calcd}/Å	*h k l*	I/I_0
5.867±0.038	5.865	1 0 0	6
4.345±0.015	4.346	1 0 2	51
3.474±0.011	3.475	1 0 3	65
3.382±0.007	3.386	1 1 0	100
3.275±0.007	3.276	1 1 1	74
3.004±0.007	3.000	1 1 2	38
2.933±0.009	2.933	2 0 0	22
2.100±0.003	2.097	1 2 2	20
2.024±0.002	2.024	1 0 6	13
1.942±0.002	1.940	2 0 5	55
1.689±0.004	1.693	2 2 0	20
1.685±0.002	1.684	1 2 5	23
1.611±0.003	1.614	1 3 1	18
1.273±0.001	1.274	1 4 1	13

a=6.773 Å, c=12.94 Å.

Table 3. COMPOSITIONS OF ANHYDROUS CALCIUM SULFITE

Sample	Composition (%)				Mole ratio	
	CaO	SO_2	SO_3	Total	SO_2/CaO	SO_3/CaO
A′	46.3	52.6	0.7	99.6	0.994	0.011
B′	46.4	52.7	0.7	99.8	0.994	0.010
C′	46.4	52.8	0.6	99.8	0.996	0.009
Calcd	46.7	53.3	—	100	1.00	—

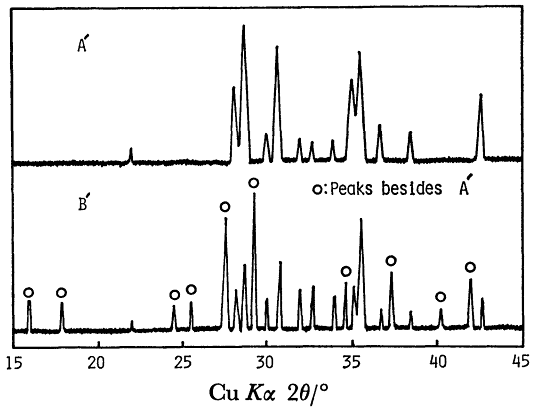

Fig. 1. X-Ray diffraction patterns of anhydrous calcium sulfite.

after be called A′, B′, and C′ respectively. The composition of A′—C′ is shown in Table 3. All of the dehydrated products can be identified as anhydrates. Figure 1 shows the X-ray diffraction patterns for the A′ and B′ anhydrates. The C′ anhydrate gave a pattern identical with that of B′. The X-ray diffraction pattern for A′ agreed generally with that reported by Lutz *et al.*,18) but it showed many additional diffraction peaks. The X-ray diffraction patterns of B′ and C′ contained peaks identical with those observed on A′, but gave many diffraction peaks which were not observed on A′. Therefore, the existence of two modifications in an anhydrate may be inferred from both the chemical analysis and X-ray diffraction.

Though X-ray diffraction data on anhydrous calcium sulfite have been presented by several investigators,16–18) their crystallographic information has not yet been published. On the basis of these X-ray diffraction results, obtained with a high accuracy, the crystallographic analysis was carried out by using Hull-Davey's graph19–20) and a microcomputer. The crystallographic data for two modifications of the anhydrate are shown in Table 4. Thus, it was proved that A′ belonged to an orthorhombic system with $a=6.472$ Å, $b=15.93$ Å, and $c=23.44$ Å. This phase is named α-$CaSO_3$ in this paper. On the other hand, it was found that B′ and C′ existed as mixtures of α-$CaSO_3$ and another anhydrous phase. In fact, this new phase was found to have a body-centered tetragonal lattice with $a=15.68$ Å, and $c=19.44$ Å. This phase is named β-$CaSO_3$. The X-ray diffraction pattern for the mixture of α- and β-anhydrates agreed generally with that reported by Matsuzaki et al.17)

Table 4. CRYSTALLOGRAPHIC DATA FOR TWO MODIFICATIONS OF ANHYDROUS CALCIUM SULFITE

α-$CaSO_3$ (Orthorhombic system)					
d_{obsd}/Å	d_{calcd}/Å	h	k	l	I/I_0
4.044±0.013	4.044	1	3	1	9
3.169±0.003	3.171	2	1	0	54
3.117±0.003	3.119	2	0	2	100
2.980±0.006	2.974	1	0	7	17
2.920±0.004	2.923	1	1	7	83
2.803±0.005	2.800	0	5	4	15
2.740±0.004	2.744	2	3	1	13
2.639±0.002	2.639	0	6	1	13
2.560±0.002	2.561	1	4	6	59
2.533±0.002	2.531	1	2	8	80
2.453±0.003	2.456	2	4	2	24
2.345±0.003	2.344	1	6	3	20
2.123±0.002	2.124	1	2	10	47
1.923±0.002	1.925	1	5	9	34
1.887±0.002	1.886	0	8	4	16
1.820±0.002	1.820	1	2	12	15
1.765±0.002	1.765	0	9	1	15
1.665±0.002	1.665	0	5	12	9
1.634±0.002	1.633	0	7	10	8
1.572±0.002	1.571	4	2	2	10
1.472±0.001	1.472	4	4	3	13
1.455±0.001	1.455	0	8	11	8
1.403±0.001	1.403	1	11	2	8
1.344±0.002	1.344	1	1	17	10
1.309±0.001	1.309	0	12	3	7
1.280±0.001	1.281	2	8	12	10

$a=6.472$ Å, $b=15.93$ Å, $c=23.44$ Å.

β-$CaSO_3$ (Tetragonal system, body-centered lattice)					
d_{obsd}/Å	d_{calcd}/Å	h	k	l	I/I_0
5.560±0.021	5.544	2	2	0	20
4.947±0.019	4.959	1	3	0	20
3.642±0.009	3.636	0	4	2	17
3.500±0.007	3.506	2	4	0	20
3.240±0.005	3.240	0	0	6	86
3.054±0.004	3.051	0	4	4	100
2.589±0.003	2.592	3	5	2	31
2.411±0.003	2.408	4	4	4	43
2.243±0.003	2.243	1	4	7	14
2.149±0.002	2.148	1	6	5	37
1.996±0.001	1.997	5	6	1	23
1.962±0.002	1.960	0	8	0	23
1.546±0.002	1.546	4	9	3	17
1.525±0.001	1.525	2	7	9	11
1.492±0.001	1.492	6	8	4	11
1.386±0.001	1.386	8	8	0	11
1.362±0.002	1.362	7	9	2	11

$a=15.68$ Å, $c=19.44$ Å.

Phase Relationships in the $CaSO_3$–H_2O System. It was confirmed that three modifications in hemihydrates and two modifications in anhydrates existed. In order to elucidate the mutual relationships of these five phases,

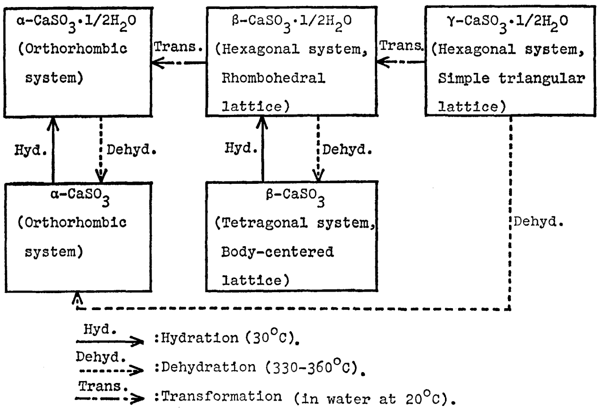

Fig. 2. Phase relationships in the system $CaSO_3$–H_2O.

the phase changes on hydration and dehydration in the $CaSO_3$–H_2O system were traced by means of X-ray diffraction, thermal analysis, and infrared spectroscopy. The phase relationships are summarized in Fig. 2.

The α-$CaSO_3$ anhydrate (orthorhombic system) was formed by the dehydration of both α-$CaSO_3 \cdot 1/2H_2O$ (orthorhombic system) and γ-$CaSO_3 \cdot 1/2H_2O$ (hexagonal system, simple triangular lattice). The β-$CaSO_3$ anhydrate (tetragonal system, body-centered lattice) was formed by the dehydration of β-$CaSO_3 \cdot 1/2H_2O$ (hexagonal system, rhombohedral lattice). When these anhydrates were hydrated in water, α-$CaSO_3$ changed to α-$CaSO_3 \cdot 1/2H_2O$ and β-$CaSO_3$ changed to β-$CaSO_3 \cdot 1/2H_2O$. These results suggest that there were reversible reactions among these phases. In addition, when β- and γ-$CaSO_3 \cdot 1/2H_2O$ were immersed in water, β-$CaSO_3 \cdot 1/2H_2O$ was converted to α-$CaSO_3 \cdot 1/2H_2O$, and γ-$CaSO_3 \cdot 1/2H_2O$ was finally converted to α-$CaSO_3 \cdot 1/2H_2O$ through β-$CaSO_3 \cdot 1/2H_2O$.

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