

Characterization of a New SO_4^{2-} -Stabilized Phase of BaCO_3

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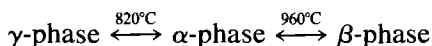
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The structure and composition of a new SO_4^{2-} -stabilized phase of barium carbonate, $\delta\text{-BaCO}_3$, have been characterized. Fine crystalline powder of $\delta\text{-BaCO}_3$ was prepared from BaCO_3 with a few mole% of BaSO_4 by heating at above 820°C and quenching into liquid nitrogen. The SO_4^{2-} -stabilized $\delta\text{-BaCO}_3$ has the chemical composition $\text{Ba}(\text{CO}_3)_{1-x}(\text{SO}_4)_x$ with x ranging from 0 to 0.1 and is gradually decomposed into aragonite-type $\gamma\text{-BaCO}_3$ and BaSO_4 in the presence of water at room temperature. The X-ray powder pattern of the substance was interpreted with the use of an automatic indexing computer program. The crystal data for $\delta\text{-Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$ are monoclinic, $P2_1/m$, $a = 6.913(3)$, $b = 5.295(1)$, $c = 4.545(1)$ Å, $\beta = 107.89(3)^\circ$, $Z = 2$, $D_x = 4.21$ g/cm³. A proposed structural model for $\delta\text{-BaCO}_3$ in this paper has a close relation to a high-pressure metastable structure of calcium carbonate, $\text{CaCO}_3(\text{II})$.

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1. Introduction

It is well known that BaCO_3 has three kinds of polymorphs, γ -phase with aragonite structure, α -phase with calcite structure, and β -phase with a cubic structure (1). The thermal stability of the three phases is

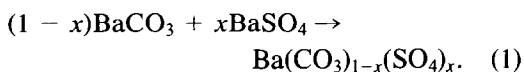


Among these three phases, α - and β -phase are unquenchable and cannot be obtained at room temperature even if they are quenched into liquid nitrogen. Only γ -phase is stable at room temperature.

One of the authors (T.S.) has found a new metastable crystalline phase of BaCO_3 , 0022-4596/87 \$3.00

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named δ -phase, obtained by heating a mixture of $\gamma\text{-BaCO}_3$ and a few mole% of sulfate or chromate (such as BaSO_4 or SrCrO_4) near the γ - α phase transition temperature and quenching into liquid nitrogen (2, 3). The new δ -phase changes easily to γ -phase by reaction with water or by reheating to about 700°C in air. The structural stability of δ -phase is considered to be caused by a partial anion substitution of CO_3^{2-} in the host lattice by SO_4^{2-} or CrO_4^{2-} with larger ionic size, in the following way:



This paper describes the chemical analysis of the SO_4^{2-} solubility limit in Eq. (1) and

the crystal structure analysis by an X-ray powder diffraction method.

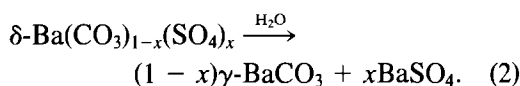
2. Experimental

2.1. Sample Preparation

BaCO_3 (Rare Metallic Co., Japan, 99.99% purity) and BaSO_4 (Merck's reagent) were weighed to desired compositions and mixed homogeneously for 1 hr with an agate mortar and pestle. The mixed powder was heated at 820°C for 30 min and rapidly quenched into liquid nitrogen.

2.2. Chemical Analysis

The SO_4^{2-} -stabilized δ -phase is decomposed into BaSO_4 and BaCO_3 in the presence of water as follows:



Among the products, $\gamma\text{-BaCO}_3$ dissolves into dilute acid solution while BaSO_4 is generally insoluble and forms extremely fine particles (60 nm) (3). These fine BaSO_4 particles become soluble when a strong acidic cation exchange resin coexists in solution. Thus, the amount of BaSO_4 in δ -phase was analyzed by the following procedure: (1) The calcined sample (100–150 mg) and 4.0 g of H-resin (Dowex 50W-X4) were suspended together in 3 ml of 1 M HCl aq. solution. (2) The suspension was filtered and the residue washed with 450 ml of distilled water. (3) The filtrate was adjusted to 500 ml in a volumetric flask with water. (4) The amount of SO_4^{2-} in the filtrate was measured using ion chromatography (Dionex Model 10).

The calcined specimen contains unreacted BaSO_4 particles in addition to fine δ particles when the starting amount of BaSO_4 exceeds the solubility limit in Eq. (1). These unreacted BaSO_4 particles became so large (400 nm) (3) during the calci-

nation that their solubility in the acidic suspension with H-resin was negligible in comparison with that of the fine BaSO_4 formed by Eq. (2). Thus, the presence of the unreacted BaSO_4 presented little problem to the chemical analysis of the SO_4^{2-} concentration in δ -phase.

2.3. Crystal Structure Analysis

Powder X-ray diffraction data of $\delta\text{-Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$ were obtained by a diffractometer (Philips PW1700) with graphite monochromated CuK_α radiation. Step scanning technique was employed with a step size of 0.02° and a fixed counting time of 10 sec in the 2θ range 4°–100°. Peak positions were calculated by the digital filter method (4). Correction for the systematic angular error was carried out using Si powder as the external standard. Visser's indexing program (5), which is based on Ito's method (6) applicable to all crystal systems, was used to find the unit cell of δ -phase. After eliminating several weak peaks assigned to the γ -phase, the remaining 31 peaks in the range 4–57° were used as the input data of the program. All peaks were indexed with a monoclinic cell, resulting in a figure of merit (FOM) of 32.8. The FOM is defined as $Q_{\text{obs}}(2\theta)/[2 \times \Delta Q \times N]$, where $Q_{\text{obs}}(n)$ is $d^* \times 10^4$ of the n th line, ΔQ is the mean difference between Q_{obs} and Q_{calc} , and N is the number of possible lines in the measured angular range (7). The FOM value obtained in the calculation indicates that the monoclinic unit cell is acceptable. The lattice constants were refined with a least-squares procedure using RLC3 in the UNICS program system (8). Peaks corresponding to $0k0$ reflections with $k = \text{odd}$ were systematically absent. Thus, the space group of δ -phase was limited to centrosymmetric $P2_1/m$ and noncentrosymmetric $P2_1$, assuming monoclinic symmetry. Comparing the unit cell volume of δ -phase to that of γ -phase, it was found that the

former contained two BaCO_3 molecules in a unit cell.

The structure factors and the subsequent powder diffraction intensities were calculated using the program POWD10 (9) on the basis of a structural model of δ -phase described later. The contribution of SO_4^{2-} was not included for the structure factor calculation, since the site occupancy of SO_4^{2-} is only 10% and the X-ray scattering powers of SO_4^{2-} and CO_3^{2-} are regarded as almost the same in comparison with that of Ba^{2+} in the first approximation. Isotropic temperature factors B , expressed in terms of $\exp(-B(\sin \theta/\lambda)^2)$, were assumed as 1.0 for Ba and O atoms and 0.5 for C. Atomic scattering factors for Ba, C, and O atoms and the dispersion correction factors for Ba atom were taken from "International Tables for X-Ray Crystallography" (10).

3. Results and Discussion

3.1. Chemical Composition

Figure 1 shows the relation between the amount of BaSO_4 substituted in the δ lattice and that added in the starting mixture. All BaSO_4 added in the range of 0–10 mole% can be perfectly exchanged with BaCO_3 , but for more than 10 mole%, unreacted

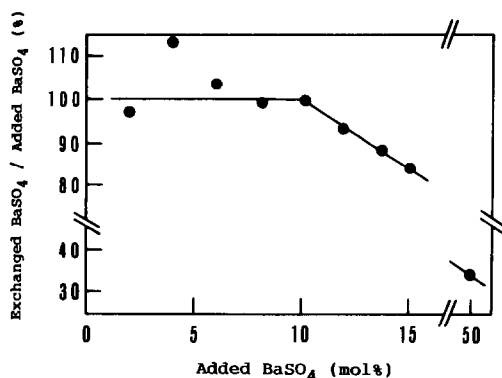


FIG. 1. Plots of BaSO_4 solubility (exchanged BaSO_4 /added BaSO_4) (%) against added BaSO_4 (mole%).

TABLE I
CRYSTAL DATA FOR $\delta\text{-Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$

Crystal system	Monoclinic
Space group	$P2_1/m$
Cell dimensions	$a = 6.913(3) \text{ \AA}$ $b = 5.295(1) \text{ \AA}$ $c = 4.545(1) \text{ \AA}$ $\beta = 107.89(3)^\circ$
Z	2
D_x	4.21 g/cm ³

BaSO_4 was found. Therefore, the maximum amount of substituted BaSO_4 is considered to be 10 mole%, that is, $\text{Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$.

3.2. Crystal Structure

Crystal data for $\delta\text{-Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$ are given in Table I. A typical X-ray diffraction pattern of the substance is given in Fig. 2. The crystal data for selected polymorphs of BaCO_3 and CaCO_3 are given in Table II for comparison. The structure of $\delta\text{-BaCO}_3$ is closely related to that of $\text{CaCO}_3(\text{II})$ (11), a high-pressure metastable phase of calcium carbonate. The β angles of $\delta\text{-BaCO}_3$ and $\text{CaCO}_3(\text{II})$ are the same within a standard deviation. The a , b , and c axes of $\delta\text{-BaCO}_3$ essentially correspond to a , b , and $c/2$ of $\text{CaCO}_3(\text{II})$, respectively, though their lengths are slightly different because of the size effect of cations with different ionic radii. If we assume the positional disorder of CO_3^{2-} group, the structure of $\delta\text{-BaCO}_3$ can be derived from that of $\text{CaCO}_3(\text{II})$ as illustrated in Fig. 3. By shifting the Ca and C atoms to place them on the plane $y = 0.25$ and 0.75 and arranging the CO_3^{2-} groups in the disordered state as shown in the figure, the c -glide plane in the $\text{CaCO}_3(\text{II})$ structure becomes the mirror plane at $y = 0.25$ and 0.75 and the c axis becomes halved. Accordingly, the space group of the structure changes from $P2_1/c$ to $P2_1/m$, which corresponds to one of the two possible space groups of $\delta\text{-BaCO}_3$ determined by the powder X-ray analysis. The positional param-

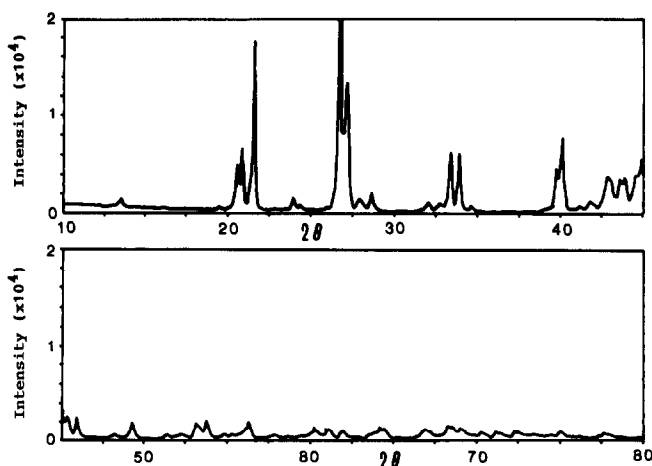


FIG. 2. Powder X-ray diffraction pattern ($\text{CuK}\alpha$) of $\delta\text{-Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$.

ters of atoms for the proposed structural model are listed in Table III. Observed and calculated peak intensities and interplanar spacings of $\delta\text{-Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$ are given in Table IV. Peak intensities calculated on the

proposed model agreed well with the observed ones except for a few. Thus, the model is considered to be basically correct.

The structure of $\alpha\text{-BaCO}_3$ at above 820°C has the halved c axis and the space group

TABLE II
CRYSTAL DATA FOR SELECTED BARIUM AND CALCIUM CARBONATES

Crystal system	BaCO_3	CaCO_3
Cubic	$\beta\text{-BaCO}_3^a$ $a = 6.96 \text{ \AA}$ (960°C) $Z = 4, Fm\bar{3}m$	—
Rhombohedral	$\alpha\text{-BaCO}_3^a$ $a = 5.205, c = 10.55 \text{ \AA}$ (830°C) $Z = 3, R\bar{3}m$	Calcite ^b $a = 4.990, c = 17.002 \text{ \AA}$ $Z = 6, R\bar{3}c$
Orthorhombic	$\gamma\text{-BaCO}_3^c$ (witherite) $a = 5.314, b = 8.904, c = 6.430 \text{ \AA}$ $Z = 4, Pmcn$	Aragonite ^b $a = 4.94, b = 7.94, c = 5.72 \text{ \AA}$ $Z = 4, Pmcn$
Monoclinic	$\delta\text{-BaCO}_3^d$ $a = 6.913, b = 5.295, c = 4.545 \text{ \AA}$ $\beta = 107.89^\circ$ $Z = 2, P2_1/m$	$\text{CaCO}_3(\text{II})^e$ $a = 6.334, b = 4.984, c = 8.033 \text{ \AA}$ $\beta = 107.9^\circ$ $Z = 4, P2_1/c$

^a From Lander (1).

^b From Megaw (12).

^c From Swanson and Fuyat (13).

^d Present study.

^e From Merrill and Bassett (11).

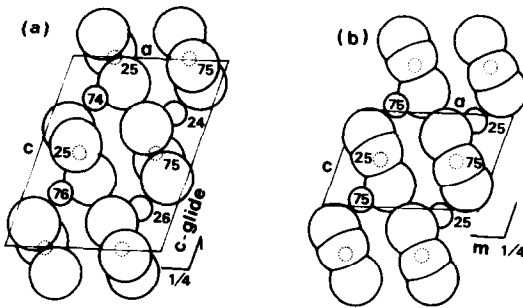


Fig. 3. The crystal structure of (a) $\text{CaCO}_3(\text{II})$ (Merrill and Bassett, 11) and the proposed model of (b) $\delta\text{-BaCO}_3$, viewed along the b axis. Large, medium, and small circles represent oxygen, calcium (or barium), and carbon atoms, respectively.

$R\bar{3}m$ in comparison with the normal $R\bar{3}c$ calcite-type structure, which has been ascribed to the free rotation of CO_3^{2-} group around their triad axes (14). Thus, the structural change from α - to δ -phase can be described by assuming that the free rotation of CO_3^{2-} group is suddenly frozen in on quick cooling and that the resultant positional disorder of CO_3^{2-} group is introduced in the low-temperature form. In conclusion, it is strongly suggested that the metastable δ -phase quenched from $\alpha\text{-BaCO}_3$ at high temperatures has a structure closely related to that of the high-pressure metastable $\text{CaCO}_3(\text{II})$ except that the CO_3^{2-} groups are in a disordered state.

TABLE III
POSITIONAL PARAMETERS FOR $\delta\text{-BaCO}_3$
STRUCTURAL MODEL

Atom	Multiplicity ^a	x	y	z
Ba	0.5	0.234	0.75	0.934
C	0.5	0.260	0.25	0.508
O(1)	0.5	0.380	0.156	0.774
O(2)	0.5	0.134	0.088	0.262
O(3)	0.5	0.221	0.490	0.434

^a Symmetry operations: x, y, z ; $\bar{x}, \frac{1}{2} + y, \bar{z}$; $\bar{x}, \bar{y}, \bar{z}$; $x, \frac{1}{2} - y, z$.

TABLE IV
OBSERVED AND CALCULATED INTERPLANAR
SPACINGS AND INTENSITIES OF THE X-RAY
DIFFRACTION PATTERN OF $\delta\text{-Ba}(\text{CO}_3)_{0.9}(\text{SO}_4)_{0.1}$

$h k l$	d_{obs}	d_{calc}	I_{obs}	I_{calc}
1 0 0	6.5559	6.5785	3	2
0 0 1	4.3168	4.3254	18	35
1 0 -1	4.2554	4.2653	24	26
1 1 0	4.1169	4.1247	70	73
0 1 1	3.3462	3.3497	} 100	10
1 1 -1		3.3216		100
2 0 0	3.2838	3.2893	50	52
1 0 1	3.1907	3.1920	5	5
2 0 -1	3.1180	3.1205	7	8
2 1 0	2.7926	2.7940	5	3
1 1 1	2.7339	2.7337	3	31
2 1 -1	2.6862	2.6883	24	2
0 2 0	2.6446	2.6473	23	18
1 2 0	2.4553	2.4559	<1	<1
1 0 -2	2.2716	2.2720	17	8
0 2 1	2.2543	2.2580	} 33	24
3 0 -1		2.2551		<1
3 0 3	2.1932	2.1928	2	2
0 0 2	2.1633	2.1627	4	4
2 1 1	2.1107	2.1095	20	8
1 1 -2	2.0878	2.0879	6	13
3 1 -1	2.0756	2.0747	12	29
2 2 0	2.0615	2.0623	13	18
1 2 1	2.0373	2.0377	13	8
2 2 -1	2.0197	2.0187	20	20
0 1 2	2.0013	2.0021	8	9
2 1 -2	1.9767	1.9782	12	7
1 0 2	1.8888	1.8895	2	7
3 0 -2	1.8507	1.8499	7	2
1 1 2	1.7796	1.7796	1	5
1 2 -2	1.7232	1.7241	} 9	4
4 0 -1		1.7231		4
1 3 0	1.7038	1.7046	11	12
0 2 2	1.6761	1.6748	2	5
3 1 1	1.6620	1.6624	} 1	6
2 2 -2		1.6608		6
0 3 1	1.6348	1.6341	} 7	1
1 3 -1		1.6301		8
2 0 2	1.5949	1.5960	2	2
4 1 0	1.5708	1.5706	1	1
2 3 0	1.5560	1.5552	1	1

Acknowledgment

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