Effects of Pressure on the Chemical Properties of Solid Surfaces. VII. Surface Basicities of Some Compressed Carbonates and Related Compounds

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In order to investigate the effect of the compacting pressure on the surface basicities of solids, experiments were carried out by employing various carbonates, hydroxides, and oxides of alkali metals and alkaline earth metals as samples. That is, compacting pressures ranging from 0 to 15000 kg/cm^2 were applied to these samples, and the changes in the surface basicities were observed using an indicator method. It was observed that the surface basicities of various solid vary on compression. Further, the respective basicity change in cadmium carbonate, calcite, and aragonite could be explained by the change in the surface area of each of these samples. On the other hand, the basicity changes of both strontium carbonate and barium carbonate could be explained thus only with difficulty. From the results of the X-ray-diffraction study and the electron-diffraction study, the changes in the crystal structures of these samples were suspected of causing the basicity changes due to compressions. According to the results of infrared spectroscopic studies, changes in the symmetry around carbonate ions in the sample crystals were considered to be the cause of the basicity changes in strontium cabonate and barium carbonate.

It has been revealed by previous works[1-4] of this laboratory that the surface acidities of various solids including metal sulfates vary on compression. Considering from the conjugate characters of the acid and the base and from the findings in the previous works,[1-4] we can expect the surface basicity of a solid will also vary on compression.

The purpose of the present work is to confirm the above expectation. It will be demonstrated in this paper that the surface basicities of various solids vary on compression. Further, some additional experimental results which serve to explain the change will also be included in this paper.

Experimental

Materials. The following solids served as samples for the qualitative experimental works to disclose the pressure effect on the surface basicity:

Carbonates: $CaCO_3$(calcite), $SrCO_3$, $BaCO_3$, $KHCO_3$, K_2CO_3, $NaCO_3$, $NaCO_3 \cdot H_2O$, $(NH)_4CO_3$
Hydroxides: $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot 8H_2O$
Oxides: BeO, MgO, CaO, ZnO, BaO

They were all obtained commercially as reagent-grade materials, except for the magnesium oxide, which was obtained by pyrolyzing a commercial magnesium hydroxide at 700°C. In addition, the following carbonates served as samples for the quantitative measurements of the basicity change as well as the structural change;

$CaCO_3$(calcite), $CdCO_3$: sodium nitrate structure
$CaCO_3$(aragonite), $SrCO_3$, $BaCO_3$: potassium nitrate structure

These materials were all obtained commercially as reagent-grade materials, except for the aragonite, which was prepared by drying precipitate obtained by mixing an aqueous calcium chloride solution with an aqueous sodium carbonate solution at 90~100°C.

Preparation of the Sample. The compression of the raw materials was carried out by essentially the same procedures as have been described in the preceding papers.[1-4] That is, the material was gently pulverized in an agate mortar, and then about 0.1 g of the powder was packed into the sample room of a piston-cylinder device. A desired pressure, ranging from 0 to 15000 kg/cm^2, was applied to the powder for 10 min at room temperature.[5] After compression, the resulting cylindrical pellet (1—2 mm in height and 6 mm in diameter) was pulverized in a mortar. The pulverized material was subjected to drying in a vacuum over a 1 hr period at room temperature. The resulting dry material served as a sample for a desired experiment.

Surface Basicity. The qualitative effect of pressure on the surface basicity was observed by the following procedures: by manipulation in a dry box, a given amount of the powder of the compressed sample was transferred to a 50 ml conical flask containing 10 ml of purified benzene. Then, several drops of a 0.1% phenolphtalein (pK_a=9.3) solution in benzene were added, and after 1 hr the surface color of the sample was observed. At the same time, a similar observation was carried out by using as uncompressed sample. The difference between the colors of the two samples was then recorded.

The quantitative determination of the surface basicity of the carbonate sample was carried out by employing the following method: by manipulation in a dry box, a given amount (0.05 g) of the sample powder was transferred to each of a a series (usually ten) of 50 ml conical flasks each containing 10 ml of purified benzene. Then enough 1/500 or 1/1000N benzoic acid in benzene was added to each of these ten samples so as to bracket the expected titer. After the samples had then stood for 20 hr. several drops of the indicator solution, *i.e.*, a 0.1% phenolphthalein solution in benzene, were added to each flask. The bracketed titer, *i.e.*, the titer of benzoic acid required to neutralize the surface base, could be determined easily by the observation of the surface color of each sample.

Surface Area. The specific surface area of the carbo-

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[1] Y. Ogino and T. Kawakami, This Bulletin, **38**, 972 (1965).
[2] Y. Ogino, T. Kawakami, and K. Tsurumi, *ibid.*, **39**, 639 (1966).
[3] Y. Ogino, T. Kawakami, and T. Matsuoka, *ibid.*, **39**, 859 (1966).
[4] T. Kawakami, A. Konno, and Y. Ogino, *ibid.*, **44**, 1772 (1971).
[5] Exceptionally, pressure was applied at a temperature of 100°C.

nate samples were evaluted by applying the BET theory to the absorption data of nitrogen at −195°C.

X-ray Diffraction. Powder X-ray diffraction patterns of carbonates which have a potassium nitrate structure were obtained with a Shimadzu GX-1 X-ray Diffractometer. The Cu$K\alpha$ radiation (Ni filter) at 30 KV and 20 mA was used.

Infrared Spectroscopy. The infrared spectra (600—1200 cm^{-1} wave number range) of carbonates which have a potassium nitrate structure were obtained with Perkin-Elmer Model 337 Infrared Spectrophotometer. A Nujol mull technique was employed in every case.

Electron Diffraction. Phtographs of the Debye-Scherrer rings of the strontium carbonate sample and the barium carbonate sample were obtained with an electron-diffraction apparatus (JEM-ADF) attached to a JEOLCO JEN-50 Electron Microscope. The operation was carried out at 50 KV and about 5 μA.

Results

Surface Basicity. The surface colors of the various samples are summarized in Table 1. As can be seen in this table, the compression at 4500 kg/cm^2 resulted in an increase in the surface color for about 2/3 of all the samples. In other words, the surface basicities of these samples increased on compression.

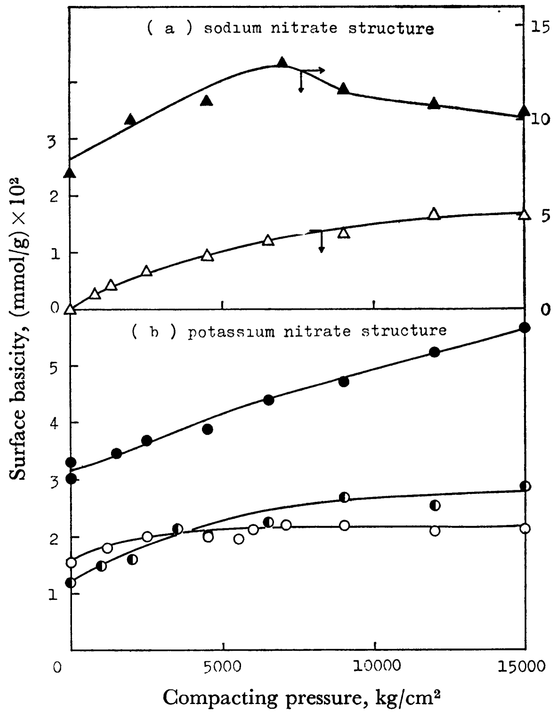

Fig. 1. Relations between the surface basicity and the compacting pressure.
△: $CaCO_3$ (calcite), ▲: $CdCO_3$, ◐: $CaCO_3$ (aragonite), ●: $SrCO_3$, ○: $BaCO_3$

The results of the quantitative determination of the surface basicity are given in Fig. 1 (a, b), wherein the surface basicities of the samples with a sodium nitrate structure as well as the basicities of the samples with a potassium nitrate structure are both expressed as functions of the compacting pressure. As can be seen in this figure, the basicity of every carbonate increased considerably on compression, though the shape of the basicity-*vs.*-pressure curve was different from carbonate to carbonate. For example, the basicity of calcite, whose original basicity was nearly zero, increased monotonously with an increase in the compacting pressure and reached about 1.6×10^{-2} mmol/g at 15000 kg/cm^2. In contrast with this, the pressure-*vs.*-basicity curve for cadmium carbonate had a maximum at a pressure of about 7000 kg/cm^2, and the basicity at this pressure was about twice the original value.

Surface Area. As can be seen in Fig. 2 (a, b),

Table 1. Effect of the compacting pressure on the surface basicities of various solids

Sample	Compacting Pressure 0 kg/cm^2	 4500 kg/cm$_2$	Change of Surface Color$^{a)}$
Na_2CO_3	Slightly violet	violet	++
$Na_2CO_3 \cdot H_2O$	Slightly violet	violet	++
$KHCO_3$	Very slightly pink	pink	++
K_2CO_3	Violet	violet	?
$(NH_4)_2CO_3$	Colorless	colorless	?
$CaCO_3$ (calcite)	Colorless	pink	++
$SrCO_3$	Slightly pink	slightly pink	+
$BaCO_3$	Slightly pink	slightly pink	+
$Mg(OH)_2$	Very slightly pink	slightly pink	++
$Ca(OH)_2$	Red violet	red violet	+
$Sr(OH)_2 \cdot 8H_2O$	Violet	violet	+
$Ba(OH)_2 \cdot 8H_2O$	Slightly violet	slightly violet	++
BeO	Slightly pink	slighly pink	+
MgO	Red violet	red violet	?
CaO	Red violet	red violet	?
ZnO	Slightly pink	slightly pink	?
BaO	Slightly violet	violet	+

(indicator; phenolphthalein (pK_a=9.3))
a) ++; increase, +; slightly increase, ?; uncertain

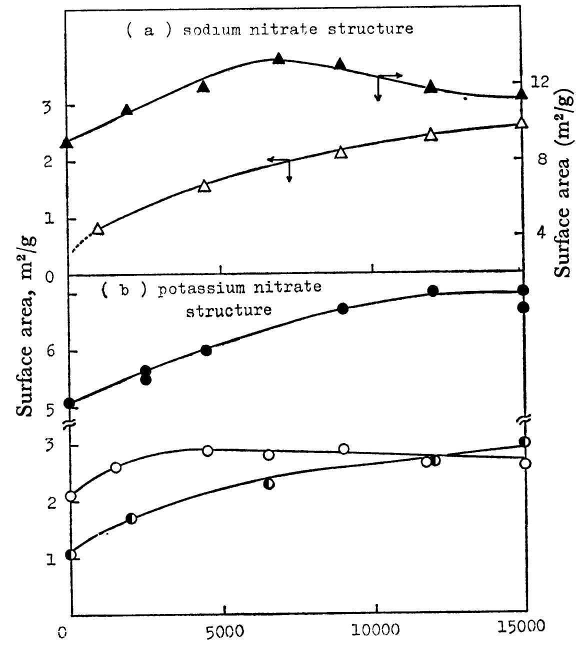

Fig. 2. Relations between the specific surface area and the compacting pressure.
△: $CaCO_3$ (calcite), ▲: $CdCO_3$, ◐: $CaCO_3$ (aragonite), ●: $SrCO_3$, ○: $BaCO_3$

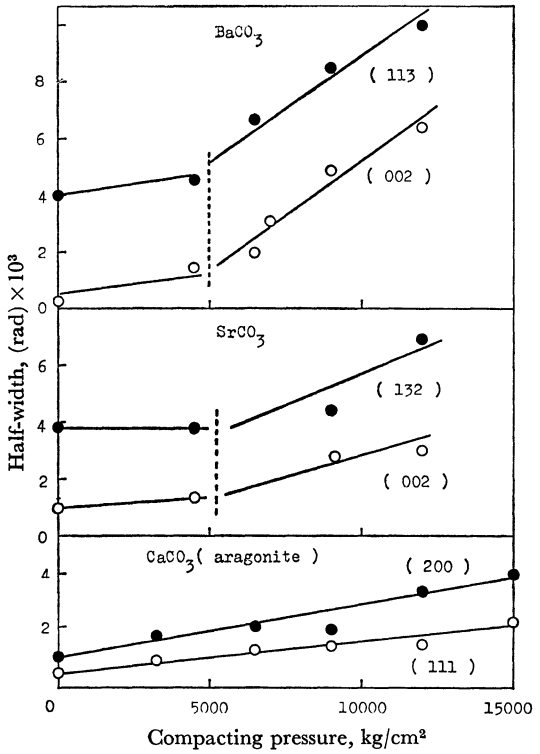

Fig. 3. Relations between the half-widths of the X-ray diffraction peaks and the compacting pressure.

the specific surface areas of every carbonate also varried on compression, though the shape of the surface area-*vs.*-pressure curve was different from carbonate to carbonate.

X-Ray Diffraction. Except for an increase in the halfwidth of the diffraction peak, no appreciable changes in their X-ray diffraction patterns resulted from the compressions of aragonite, strontium carbonate, and barium carbonate. The plots of the half-width against the compacting pressure are given in Fig. 3. Although the evaluation of the lattice distortion by applying Hall's method[6] to the broadening of the X-ray diffraction peaks was not possible, Fig. 3 reveals an interesting aspect of the pressure dependence of the half-width. The half-width of the diffraction peak for aragonite increased monotonously on an increase in the compacting pressure, whereas the half-width of both strontium carbonate and barium carbonate increased abruptly at a compacting pressure of about 5000 kg/cm^2.

Infrared Spectra. Examples of the infrared spectra for the samples with a potassium nitrate structure (aragonite, strontium carbonate, and barium carbonate) are given in Fig. 4. Two absorption bands, expressed as ν_1 and ν_2 in these spectra were assigned to the totally symmetric stretching vibration of the carbonate anion (CO_3^{2-}) and the out-of-plane deformation vibration of the same anion respectively. Further, the intensities[7] of the ν_1 absorptions of both strontium carbonate and barium carbonate were found to diminish at higher compacting pressures, while the intensities of the ν_2 absorptions of these samples varied little.[8] This behavior is depicted in Fig. 5. As can be seen in this figure, the $S\nu_1/S\nu_2$ ratio, where $S\nu_1$ is the intensity of the ν_1 absorption and $S\nu_2$ is the intensity of the ν_2 absorption, diminished pronouncedly at higher compacting pressures than 5000 kg/cm^2. In contrast with the pressure-dependent behaviors of the $S\nu_1/S\nu_2$ ratios

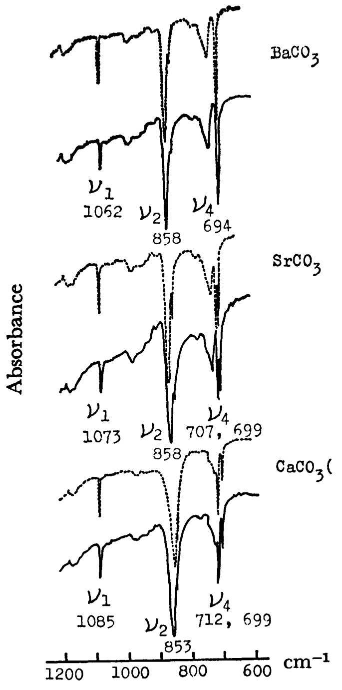

Fig. 4. Infrared spectra for the carbonates having potassium nitrate structure.
……: uncompressed sample, ——: compressed sample (15000 kg/cm^2)

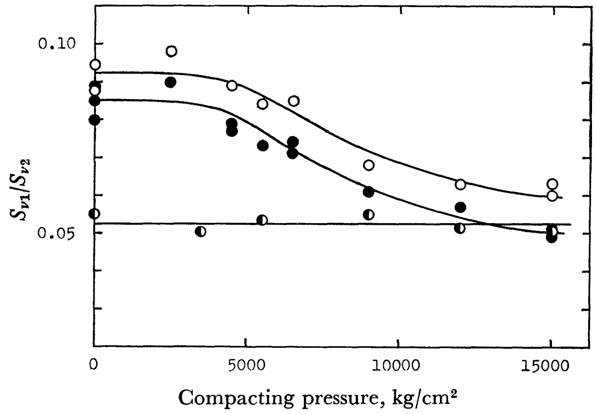

Fig. 5. Relations between $S\nu_1/S\nu_2$ ratios and the compacting pressure.
◐: CaCO$_3$ (aragonite), ●: SrCO$_3$, ○: BaCO$_3$

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6) W. H. Hall, *Proc. Phys. Soc., Ser. A*, **62**, 741 (1949).

7) The absorption intensities were determined from the areas (half-width × peak height/2) of the absorption bands.

8) The intensity of the ν_3 absorption (1450 cm^{-1}), measured by a HCB mull technique, also varied little upon the compression, as is shwon in the next table:

TABLE. S_{ν_4}/S_{ν_3} FOR THE COMPRESSED CARBONATES

Pressure (kg/cm^2)	0	7500	15000
BaCO$_3$	0.06	0.05	0.07
SrCO$_3$	0.05	0.05	0.06
CaCO$_3$ (aragonite)	0.04	0.05	0.04

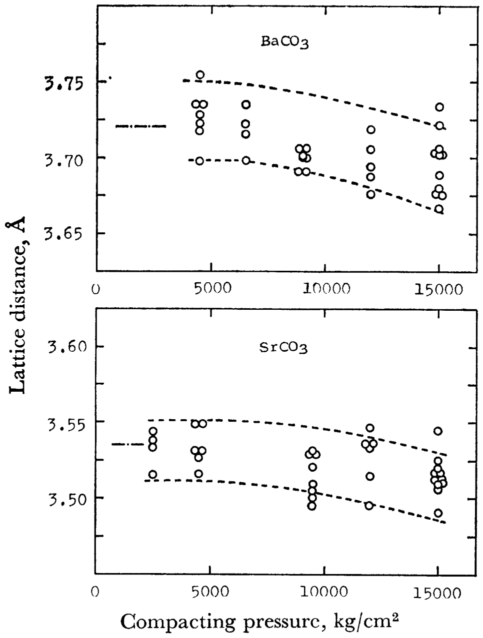

Fig. 6. Relations between the lattice distances for (111) planes of barium carbonate and strontium carbonate samples and the compacting pressure.
—·—: literature value for (111) plane

for strontium carbonate and barium carbonate, the Sv_1/Sv_2 ratio for aragonite was found to be independent of the compacting pressure (Fig. 5).

Electron Diffraction. On the basis of the photographs obtained from the electron-diffraction studies for strontium carbonate and barium carbonate, the lattice distances of the crystals of these samples were calculated. As is illustrated in Fig. 6, the lattice distances for the (111) planes of these samples diminished slightly with the increase in the compacting pressure. Considering the lager scattering of the experimental data shown in Fig. 6, a statistical treatment was applied on the data. The results are given in Table 2. It may be concluded from this table that the decrease in the lattice distance is appreciable.

Table 2. Statistical treatment of the data (the analysis of variance)

	f	$S\times10^6$	ϕ	$V\times10^6$	F_0	F (4.30; 0.05)
$BaCO_3$	pressures	4817	4	1204	3.97*	2.69
	errors	9102	30	303		
$SrCO_3$	pressures	2551	4	638	3.01*	2.69
	errors	6360	30	212		

(f; factor, S; sum of squares, ϕ; degrees of freedom, V; unbiased variance, F_0; observed F)

Discussion

Basicity Change on Compression. As can be seen in Table 1, the present work revealed that the surface basicities of many solid substances vary on compression. Generally speaking, the change in the surface basicity may be caused by the change in the structure of the sample. However, care must be taken to select suitable samples so as to obtain unambiguous structural data for the discussion of the basicity change. It was found by preliminary experiments that carbonates are suitable for this purpose. Thus, only discussions of the basicity changes in carbonates will be described in this paper.

For the sake of simplicity, the basicity changes in calcite and cadmium carbonate will be considered first. By comparing Fig. 1 (a) with Fig. 2 (a), it can easily be understood that the curves representing the basicity *vs.* pressure relations parallel the cruves representing the surface area-*vs.*-pressure relations. Therefore, the changes in the surface areas are supsected of causing the basicity changes in these samples. In fact, as can be seen in Fig. 7 (a), the surface basicity per unit of surface area for each of the two samples was independent of the compacting pressure. This verifies the validity of the suspicion.

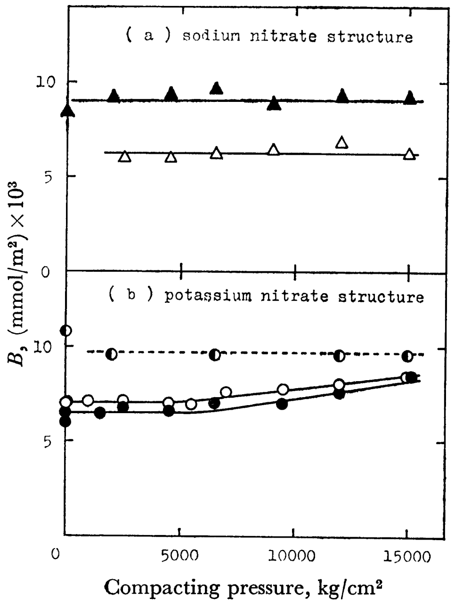

Fig. 7. Relations between B (the basicity per unit of surface area) and the compacting pressure.
△: $CaCO_3$ (calcite), ▲: $CdCO_3$, ◐: $CaCO_3$ (aragonite), ●: $SrCO_3$, ○: $BaCO_3$

In contrast with the above-mentioned simple behavior of the samples with the sodium nitrate structure, the samples with the potassium nitrate structure behaved somewhat complicatedly. That is, as can be seen in Fig. 7 (b), the basicity per unit of surface area of aragonite was found to be independent of the compacting pressure, whereas the surface basicity per unit of surface area of each of the other two samples (strontium carbonate and barium carbonate) showed a pressure dependence. This pressure dependence was small at pressures lower than 5000 kg/cm², but it tended to increase beyond this pressure. In the pressure range of 5000~15000 kg/cm², the pressure dependence was evaluated to be about 30%/1000 kg/cm².

Considering the facts described above, the basicity change in aragonite may be ascribed to the change in the surface area of this sample. That is, the reason for the basicity change in aragonite may be considered to be the same as for that in calcite or in cadmium carbonate. However, the pressure dependences of the surface basicities of both strontium carbonate and barium carbonate can not be attributed to the cahnges in the surface areas. In order to explain the basicity changes in the strontium carbonate and barium carbonate samples, some other factors must be taken into consideration.

Crystal-structure Change upon Compression. The results of the X-ray diffraction study seem to give some information about the basicity changes in strontium carbonate and barium carbonate. As can be seen in Fig. 3, the half-width of the X-ray diffraction peak for each of these samples tended to increase at ~5000 kg/cm^2. The same tendency is observable in Fig. 7 (b), where the change in the basicity per unit of surface area for each of these two samples is depicted. These facts seem to suggest that the deformation of the crystallites resulted in the increases in the number of basic sites on the surfaces of the samples. Further, the electron-diffraction studies in the present work have revealed that the compression resulted in a decrease in the lattice distances ((111) plane) of strontium carbonate and barium carbonate. These facts also suggest the existence of an intimate relation between the respective basicity change of these samples and the deformation of the crystal structure in each of these samples. Unfortunately, however, because of the existence of larger scatterings in the X-ray diffraction data as well as in the electron-diffraction data, further discussions based on the changes in the crystal structure were not possible.

For the purposes of the present discussion, the infrared-absorption data appears to be more useful than the X-ray-diffraction data. That is, by comparing Fig. 5 with Fig. 7 (b), it can easily be seen that a close relation between the basicity change and the change in the $S\nu_1/S\nu_2$ ratio exists. Corresponding to the samll change in the basicity per unit of surface area of the aragonite sample, the $S\nu_1/S\nu_2$ ratio of this sample showed little pressure dependence. This fact supports the previous consideration that the observed basicity change (Fig. 1 (b)) of aragonite must result solely from the change in the surface area. On the other hand, the $S\nu_1/S\nu_2$ ratios of both strontium carbonate and barium carbonate varied considerably on compression, this tendency seems to correspond to the basicity changes in these samples (Fig. 7 (b)). Thus, in Fig. 8, the basicity changes, $B/B_0$9) are plotted against the $S\nu_1/S\nu_2$ ratios. As can be seen in this figure, the B/B_0 *vs.* $S\nu_1/S\nu_2$ relations for both strontium carbonate and barium carbonate can be expressed by a single curve. This fact seems to indicate that the change in the ν_1 vibration of the carbonate ion in these samples is directly related to the basicity change.

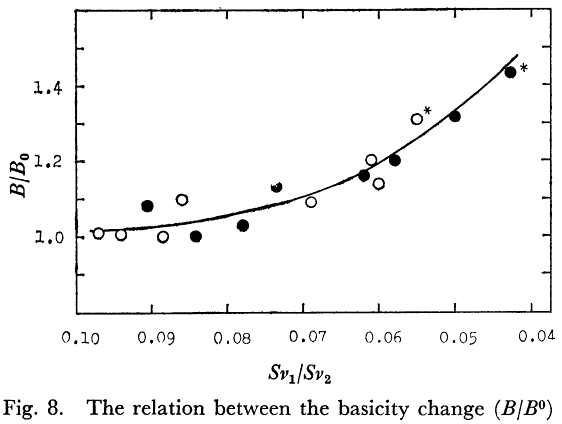

Fig. 8. The relation between the basicity change (B/B^0) and the change in the relative intensity of ν_1 vibration ($S\nu_1/S\nu_2$). ●: $SrCO_3$, ○: $BaCO_3$. (The mark * means the value obtained by using the sample compressed under the pressure of 15000 kg/cm^2 and at a temperature of 100°C.)

Analysis of IR Data. It is known that the ν_1 vibration of the carbonate ion becomes inactive for the infrared absorption when the ion is placed in site of D_{3h}, D_3, or C_{3h} symmetry.10) However, when the site symmetry changes to C_{3v}, C_{2v}, C_3, C_2, or C_s, the ν_1 vibration becomes active for the infrared absorption. The crystal structures of calcium carbonate (aragonite), strontium carbonate, and barium carbonate are of the potassium-nitrate type and belong to the space group D_{16}^{2h}, and the site symmetry is C_s. Therefore, the ν_1 vibration of the carbonate ion becomes active for the infrared absorption. Thus, the observed invariance of the ν_1 absorption spectra of calcium carbonate means either that the original D_{2h} structure of this sample is preserved even in the compressed state or that the original site symmetry varied to C_{3v}, C_3, or C_2. However, few changes in the crystal structure (for example, a change to the calcite structure) were detected from the X-ray-diffraction data and the electron-diffraction data given above. Therefore, the possibility of change in the site symmetry in the calcium carbonate sample may be ignored. Thus, it seems probable to consider that the original crystal structure, D_{2h}, is preserved.

On the contrary, the pressure-dependent behavior of the infrared spectra of both strontium carbonate and

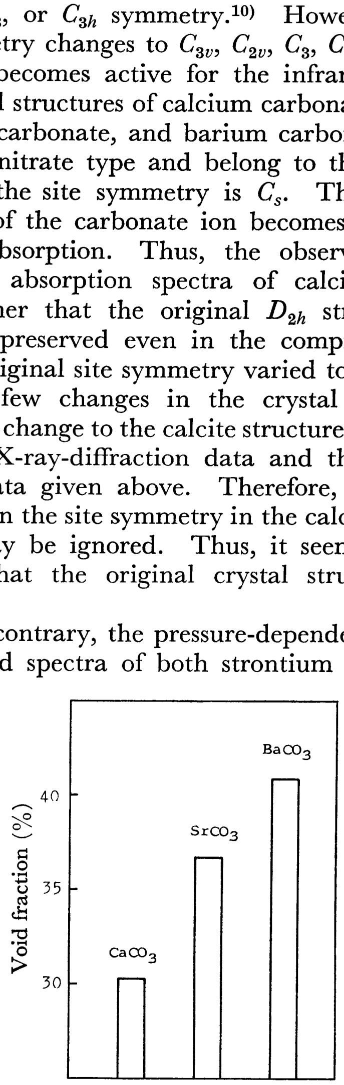

Fig. 9. The void fraction.

The void fractions were approximated by the following equation.

void fraction (%) $=(1-(v/V))\times 100$

v: sum of the volume of metal ions (4π(ionic radius)$^3/3$) and carbonate ions ($3\times 4\pi$(ionic radius of O^{2-})$^3/3$) in a unit cell

V: volume of a unit cell

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9) B_0 was defined as the original basicity per unit of surface area, and B was defined as the basicity per unit of surface area of the compressed sample.

10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons. New York (1970), p. 61.

barium carbonate mean that the original D_{2h} structures of these samples varied on compression to direction where the symmetry of the crystal increases, *i.e.*, from C_s to D_{3h}, D_3, or C_{3h}.

Presumably, the structural changes being considered accompany contractions, for pressure acts to reduce the volume of a sample. As can be seen in Fig. 9, the void fraction of aragonite is considerably smaller than that of strontium carbonate or of barium carbonate. Therefore, it seems reasonable to consider that the smaller void fraction of aragonite hinders the contraction of this sample and that the original D_{2h} structure is preserved in the compressed state. On the contrary, the larger void fractions of strontium carbonate and barium carbonate may provide spaces to be contracted by the compression.[11]

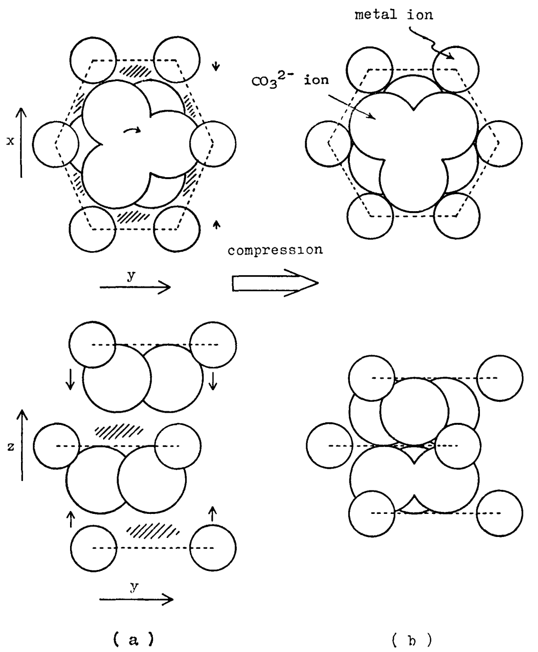
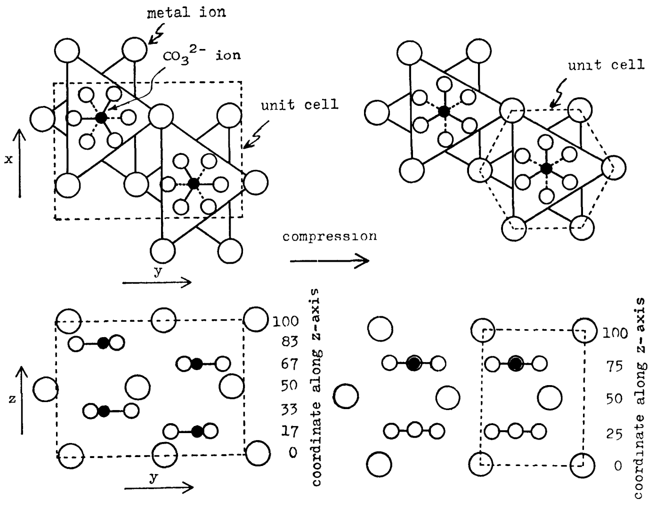


Fig. 10. The expected structural changes of strontium carbonate and barium carbonate due to compression.

The expected structural changes in strontium carbonate and barium carbonate are depicted in Fig. 10. The shaded areas in this figure are the spaces to be contracted by the compression. When these spaces are contracted, the following three changes may occur: (i) the original distorted hexagonal network, which is perpendicular to the z-axis constituted by metal ions, is transformed into a perfect hexagonal network; (ii) around the respective carbon atom, each carbonate ions rotates horizontally (parallel with the xy-plane), 30° from the original position, and (iii) each horizontal plane on which the center of the carbonate ion is located is brought to the hypothetical horizontal plane existing at the center of two nighboring hexagonal networks.

On the basis of the above mentioned discussion, a more precise model for the structural change was



(a) D_2 symmetry (b) D_6 symmetry

Fig. 11. The expected structural change due to compression.

Table 3. Factor group analysis of the crystal having the structure depicted in Fig. 11 (b)

	Number of vibration					Selection rules	
	N	T	T'	R'	n	IR	Raman
A_1	1	0	0	0	1	inactive	active
A_2	4	1	1	1	1	active	inactive
B_1	2	0	1	0	1	inactive	inactive
B_2	3	0	1	1	1	inactive	inactive
E_1	5	1	1	1	2	active	active
E_2	5	0	2	1	2	inactive	active

	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	−1	−1
B_1	1	−1	1	−1	1	−1
B_2	1	−1	1	−1	−1	1
E_1	2	1	−1	−2	0	0
E_2	2	−1	−1	2	0	0
$U_R(p)$	10	0	2	0	4	2
$U_R(s)$	4	0	2	0	2	2
$U_R(s\text{-}v)$	2	0	2	0	2	0
$\pm 1+2\cos\phi_R$	3	2	0	−1	−1	−1
$\chi_R'(N)$	30	0	0	0	−4	−2
$\chi_R'(T)$	3	2	0	−1	−1	−1
$\chi_R'(T')$	9	−2	0	1	−1	−1
$1\pm 2\cos\phi_R$	3	2	0	−1	−1	−1
$\chi_R'(R')$	6	0	0	0	−2	0
$\chi_R'(n)$	12	0	0	0	0	0

a) The usual nomenclatures were used in this table.

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[11] If the compressibility of a solid is proportional to the void fraction, it may be expected that the change in the infrared spectra of barium carbonate will be larger than that of strontium carbonate because the former sample has a larger void fraction. However, the compressibility of a solid is affected by many factors, *i.e.*, the void fraction, the ionic radius, the crystal structure, *etc.*, and is not neceassarily propotional to the void fraction. Therefore, the fact the extents of the changes in the infrared spectra for both samples were nearly equal (Fig. 5) is not always in conflict with the different void fractions of the two carbonate samples. Although the details of the mechanisms of the compression are not clear, the more complete hexagonal structure of the barium carbonate crystal might reduce the degree of the contraction of void. Generally, a crystal of a higher symmetry, *i.e.*, regular cubic or hexagonal, is less compressible than a crystal of lower symmetry.

constructed to give Fig. 11. This figure was used as a basis for the factor group analysis designed to clarify selection rules for the infrared absorption. The results of the conventional-factor group analysis[12] are give in Table 3. This table indicates that both ν_1 vibration of the carbonate ions in the unit cell of the compressed sample (Fig. 11 (b)), which belong to the A_1 and B_1 or B_2 species, are inactive for the infrared absorption. Thus, it became clear that the intensity of the infrared ν_1 absorption diminishes as the symmetry of the sample crystal changes from the original D_{2h} type in the direction of the final D_6 type. The observed pressure-dependent spectral changes of strontium carbonate and barium carbonate may be considered to be examples of such cases as have been described above.

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This paper is a part of a dissertation submitted by one of the authors (Shoe Baba) in partial fulfillment of the requirements for the degree of Doctor of Engineering in Tohoku University.

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12) M. Tsuboi, "Kagaku no Ryoiki (an extra number)," Vol. 32, Nankodo, Tokyo (1961), p. 35.