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Structure of vaterite and infrared spectra

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Auszug

Zwei Strukturvorschläge für Vaterit wurden mit Hilfe der Infrarot-Spektroskopie überprüft. Im Strukturvorschlag von MEVER (1959) hat das Carbonat-Ion die Punktsymmetrie C_s , im Strukturvorschlag von KAMHI (1963) die Punktsymmetrie C_{2v} . Die beobachteten Infrarotspektren sind charakterisiert durch die Anregung und Aufspaltung von v_1 und durch die Aufspaltung von v_3 , was die Annahme der C_{2v} -Punktsymmetrie stützt.

Abstract

Two structural propositions of vaterite are examined using infrared spectroscopy. The carbonate ion has C_s -site symmetry in the structure presented by MEYER (1959), but C_{2v} according to KAMHI (1963). Observed infrared spectra are characterized by (1) the activation and splitting of v_1 and (2) the splitting of v_3 , which support C_{2v} symmetry.

Introduction

It was by MEYER (1959) and KAMHI (1963) that the structure of vaterite (CaCO₃) was determined by x-ray methods. MEYER reported an orthorhombic cell with the dimensions a = 4.13, b = 7.15, c = 8.48 Å, space group $Pnma - V_h^{16}$, whereas KAMHI found a hexagonal cell with the dimensions a = 4.13, c = 8.49 Å, space group $P6_3/mmc - D_{6h}^4$. MEYER's structure is fairly consistent with KAMHI's in its unit-cell dimensions, but not in its atomic positions, especially in the site symmetry of the carbonate ion.

Many workers such as NAKAMOTO *et al.* (1957), GATEHOUSE *et al.* (1958), ADLER and KERR (1963) examined the infrared spectra of a number of carbonate compounds and showed the spectral differences related to differences in the site symmetry of the carbonate ion. These may give us further knowledge to the vaterite structure.

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Experimental

Preparation

The vaterite sample used in this work was prepared as follows; a 3M solution of CaCl₂ in 50 ml of water and 1M solution of Na₂CO₃ in 450 ml of water, both preheated at 30 °C, were mixed simultaneously in a beaker and stirred for 30 minutes at 30 °C. The product was washed rapidly with water and ethylalcohol, and then dried in a desiccator with P₂O₅ (INOUE *et al.*, 1962).

X-ray powder data

An x-ray powder pattern was taken using the Rigaku Denki x-ray diffractometer (CuK α radiation).

Infrared absorption measurements

The infrared spectra were obtained by a Nihon Bunko IR-G spectrometer through the spectral range 4000 to 400 cm⁻¹. The KBr disk method was employed.

Results and discussions

X-ray diffraction

The observed x-ray intensity is compared with the calculated ones in the Table 1. The calculation is based on the equation $I(hkl) = LP \cdot j \cdot |F(hkl)|^2$, j multiplicity factor. Atomic positions are referred

	MEYER				KAMHI		this paper		MEYER			KAMNI		this paper
h k l	đ	Ic	h	k 1	đ	I c	Io	h k l	đ	1 c	h k l	đ	I.c	I D
002	4.240	6	0	02	4.245	6	7	133	1.667	< 1				
101	3.713	7						222	1.648	22	202	1,648	31	30
1 1 0	3.576	35	Ð	10	3.577	65	59	140	1.640	< 1				
1 1 1	3.295	71	1	0 1	3.296	117	86	213	1.624	< 1				
1 1 2	2.734	100	1	02	2.735	100	100	141	1.611	< 1				
120	2.703	< 1						105	1.569	< 1				
121	2.575	< 1						2 3 0	1.561	< 1				
103	2,333	< 1						231	1.535	< 1	105	1.534	< 1	< 1
1 2 2	2.279	< 1						115	1.532	1				
1 1 3	2.218	17	1	03	2,219	3	2	142	1.530	< 1				
004	2.120	5	0	04	2,122	7	6	2 2 3	1.511	< 1	203	1,512	2	< 1
200	2,065	53	1	10	2,065	73	63	204	1.479	1	114	1,480	7	< 1
131	2,006	< 1	1	11	2,007	< 1	< 1	232	1.465	< 1				
210	1.984	< 1						214	1.449	< 1				
1 2 3	1.954	< 1						1 2 5	1.437	< 1				
2 1 1	1.932	< 1						1 4 3	1.419	< 1				
202	1.857	35	1	12	1.857	29	29	006	1.413	< 1	006	1.415	< 1	
114	1.824	h 4	1	04	1.825	65	53	224	1.367	11	204	1.368	11	1
212	1.797	< 1						2 3 3	1,366	< 1				
220	1.788	3	9	ου	1.788	5	3	301	1.359	< 1				
221	1.750	10	2	01	1.750	1	< 1	310	1.352	1	120	1.352	3	< 1
124	1.668	< 1	1.	13	1.668	< 1	< 1	240	1.351	1				

Table 1. Observed and calculated intensity of vaterite

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below. There is no considerable difference between MEYER's and KAMHI's x-ray powder data except for the 101 reflection in MEYER's results.

Site symmetry

Atomic positions and site symmetries are:

Atomic positions

Site symmetries

In the structure presented by MEYER:

Ca :	(4a)				C_i
C :	(4c)	with $x = 0.67$,	z = 0.157		C_s
O(1)	: (4c)	with $x = 0.67$,	z = 0.471		C_s
O(2)	: (8d)	with $x = 0.67$,	y = 0.118,	z = 0.0	C_i

In the structure by KAMHI:

Ca: $(2a)$		D_{3d}
C: $(6h)$ with $x = 0.29$		C_{2v}
O(1): (6h) with $x = 0.12$		C_{2v}
O(2): (12k) with $x = 0.38$,	z = 0.12	C_s

where two carbon atoms are randomely distributed over six positions and six oxygen atoms over eighteen positions. From the atomic positions and the site symmetries mentioned above, the site symmetries of the carbon and the carbonate ion of vaterite are derived and shown in Table 2. Those of calcite and aragonite are listed in the same table for reference.

Table 2. Site symmetries of carbon and carbonate ion in CaCO₃ polymorphs

	Vate	erite	Cl-l-it-	Anamita	
	(MEYER)	(Камні)	Calcite	Aragonite	
с	C_i	D_{3d}	C_{3i}	C _s	
CO_3	C_s	C_{2v}	D_3	C_{s}	

Infrared spectra

The infrared spectrum of vaterite is shown in Fig. 1, and compared to these of the two other polymorphs, calcite and aragonite. The wave numbers are listed in Table 3. The characteristic features of the infrared spectrum of vaterite are:

1. the activation and splitting of v_1 ,

2. the splitting of v_3 ,

3. the appearance of satellites near the fundamental v_2 .

The details of both 1 and 3 are shown in Fig. 2.



Fig. 1. Infrared absorption spectra of vaterite, aragonite and calcite

Table 3. Infrared spectra of CaCO3 polymorphs

	v_3	v_1	v_2	v_4	
Vaterite Aragonite Calcite	1490, 1420 1475 1430	1085, 1070 1080	870, 850, 830 855, 840 870, 845	750 cm ⁻¹ 715, 700 715	



Fig. 2. Detailed infrared spectra of v_1 and v_2 in vaterite

The ideal carbonate ion has the internal symmetry $D_{3\hbar}$. However, if the site symmetry is considered, $D_{3\hbar}$ is lowered to D_3 in calcite and to C_s in aragonite, while in vaterite it is lowered to C_s (MEYER's model) and to C_{2v} (KAMHI's) respectively. Correlation between $D_{3\hbar}$, D_3 , C_{2v} and C_s is shown in Table 4 (WILSON *et al.*, 1955; NAKAMOTO *et al.*, 1957). We can expect from this table that in both symmetries,

	D _{3h}	D_3	C2v	C_s	assignment
v ₁	A'_1	A_1	$A_1(\mathrm{I})$	A'(I)	symmetric stretching
v_2	$A_{2}^{\tilde{\prime}\prime}(1)$	$A_2(\mathbf{I})$	$B_1(\mathbf{I})$	$A^{\prime\prime}(\mathbf{I})$	out-of-plane bending
ν_3	$E'(\mathbf{I})$	$E(\mathbf{I})$	$A_1(\mathbf{I}) + B_2(\mathbf{I})$	$A'(\mathbf{I}) + A'(\mathbf{I})$	asymmetric stretching
v_4	$E'(\mathbf{I})$	$E(\mathbf{I})$	$A_1(\mathrm{I}) + B_2(\mathrm{I})$	$A'(\mathbf{I}) + A'(\mathbf{I})$	in-plane bending

Table 4. Correlation between D_{3h} , D_3 , C_{2v} and C_s

(I): infrared active.

Compound		Sym- metry	v ₃	<i>v</i> 1	v_2	v4
Free CO ₃	1	D_{3h}	1415		879	680
CaCO ₃ (calcite)	1	D_3	1430		874	710
[Co(NH ₃) ₆]ClCO ₃	1	D_3	13901370		868	688
CaCO ₃ (aragonite)	1	C_s	1470	1080	855	710, 696
BaCO ₃	2	C_s	1435	1062	860	694
$(Ce, La) (CO_3) F$	2	C_{s}	1443	1086	868	728
$Na_2Ca(CO_3)_2 \cdot 2H_2O$	2	C_{2v}	1488, 1414	1068	869	712-699
$[Co(NH_3)_5CO_3]Br$	1	C_{2v}	1450, 1370	1070	848	750
[Co(NH ₃) ₄ CO ₃]Cl	1	C_{2v}	1592, 1255	1025	837	752
$Na_2[Cu(CO_3)_2] \cdot 3H_2O$	3	C_{2v}	1529, 1326	1066, 1050	850	755
$\mathrm{K}_{2}[\mathrm{Co}(\mathrm{CO}_{3})_{2}] \cdot 4\mathrm{H}_{2}\mathrm{O}$	3	C_{2v}	1338	1082, 1049	884	799, 766
$\mathrm{K}_{3}[\mathrm{Co}(\mathrm{CO}_{3})_{3}] \cdot \mathbf{3H}_{2}\mathrm{O}$	3	C_{2v}	1527, 1330	1080, 1037	851	809
$[Co(NH_3)_6][Co(CO_3)_3]$	3	C_{2v}	1523, 1285	1073, 1031	889	738
[Co(NH ₃) ₅ CO ₃]Cl	3	C_{2v}	1493, 1297	1057, 1043	873, 848	738

Table 5. Infrared spectra of carbonate compounds

¹ NAKAMOTO et al. (1957), ² ADLER and KERR (1963), ³ GATEHOUSE et al. (1958).

the v_1 mode is activated and the degeneracies of both v_3 and v_4 are resolved, but we can not distinguish C_{2v} from C_s in this point. Their distinction, however, is possible experimentally. The infrared spectra data of carbonate compounds presented by NAKAMOTO *et al.* (1957), GATEHOUSE *et al.* (1958) and ADLER and KERR (1963) are shown in Table 5. The r_1 activation is easily seen in both C_s and C_{2v} site symmetries, though, in addition, C_{2v} symmetry has frequently a characteristic splitting of r_1 . The resolution of both r_3 and r_4 is not complete in C_s symmetry, while that of r_3 is complete in C_{2v} symmetry. The frequent absence of r_3 and r_4 doublets in C_s symmetry has been explained by ADLER and KERR (1963) as caused by accidental degeneracy, which may also explain the absence of r_4 doublet in C_{2v} symmetry. The satellites near the fundamental r_2 in vaterite may be due to the coupling of the out-of-plane bending as in aragonite (DECIUS, 1955, 1963). The features in infrared spectrum of vaterite shown in Fig. 1 and Table 3 are fairely consistent with that of C_{2v} symmetry, but not with C_s . Therefore we conclude that the site symmetry of the carbonate ion in vaterite is C_{2v} , which may confirm the structure presented by KAMHI.

References

- H. H. ADLER and P. F. KERR (1963), Infrared spectra, symmetry and structure relations of some carbonate minerals. Amer. Mineral. 48, 839-853.
- J. C. DECIUS (1955), Coupling of the out-of-plane bending mode in nitrates and carbonates of the aragonite structure. J. Chem. Physics 23, 1290--1294.
- J. C. DECIUS (1963), The effect of intermolecular forces upon the vibrations of molecules in the crystalline ion in aragonite minerals. Proc. Roy. Soc. [London] [A] 275, 295-309.
- B. M. GATEHOUSE, S. E. LIVINGSTONE and R. S. NYHOLM (1958), The infrared spectra of some simple and complex carbonates. J. Chem. Soc. 3137-3142.
- Y. INOUE, G. HASHIZUME, Y. KANAZI and Y. ISHII (1962), X-ray diffraction of the reaction products in CaCl₂-Na₂CO₃ system. J. Chem. Soc. Japan 83, 777-782 [in Japanese].
- S. R. KAMHI (1963), On the structure of vaterite, CaCO₃. Acta Crystallogr. 16, 770-772.
- H. J. MEYER (1959), Über Vaterit und seine Struktur. Angew. Chemie 71, 678-679.
- K. NAKAMOTO, J. FUJITA, S. TANAKA and M. KOBAYASHI (1957), Infrared spectra of metallic complexes IV. Comparison of the infrared spectra of unidentate and bidentate metallic complexes. J. Amer. Chem. Soc. 79, 4904-4908.
- E. B. WILSON, J. C. DECIUS and P. C. CROSS (1955), Molecular vibrations; the theory of infrared and Raman vibrational spectra. McGraw-Hill, New York; p. 333-340.

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