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On the Crystal Structures of the High-temperature Forms of Strontium and Barium Carbonate and Structurally Related Compounds

K. O. STRØMME

Department of Chemistry, Blindern, Oslo 3, Norway

The crystal structures of the orientationally disordered rhombohedral and cubic high-temperature phases of strontium and barium carbonate are discussed. Approximate values of the configurational entropies are calculated from structural models of the disordered phases and compared with entropy changes observed in the corresponding phase transitions, involving changes in orientational disorder. The structure of the rhombohedral phases is probably more complex than the kind of model proposed previously for disordered rhombohedral phases such as $NaNO_3$-I, in accordance with observations made on other disordered structures.

Calcium, strontium and barium carbonate belong to a structural family,[1] the members of which transform into structurally closely related, disordered rhombohedral or cubic phases at higher temperatures.[1] Structural models have previously been proposed for both kinds of high-temperature phase.[2,3] These were used as basis in the present configurational entropy calculations to be discussed in the next two sections. The oxygen positions can hardly be obtained from standard X-ray or neutron diffraction data because of the strong positional overlap and the small number of observable reflections,[4] *etc.*

Crystallographic data for the room and high-temperature forms of barium and strontium carbonate are shown along with calorimetric data in Table 1.[4–8] Some of the high-temperature data were measured at elevated CO_2-pressures to avoid dissociation of the salt. The room temperature phases are of the ordered aragonite-type [8] (KNO_3-II). Crystal data for $SrCO_3$-I, stable above 1413 °C,[7] are not known. The phase is probably isostructural with the face-centered, cubic form of $BaCO_3$.[7]

The heat of transition in solid calcium carbonate and the unit cell dimensions of the rhombohedral high-temperature phase of this compound have not been measured, probably because of experimental difficulties due to dissociation of the salt. The transition temperature is reported to be 970 °C.[9]

On the structure of the rhombohedral phases. Average atomic positions and the shortest, statistical intermolecular distances based on standard calcite- and aragonite-like O-positions [2] in space group $R\bar{3}m$ of the rhombohedral phases, are listed in Table 2.

The metal-oxygen contact distances are somewhat shorter than the sum of the ionic radius reported for barium or strontium,[12] and the oxygen contact radius of 1.40 Å.[12] Two of the listed, inequivalent O—O distances implied statistically, are considerably shorter than the normal O—O contact distance of 2.80 Å in the case of $SrCO_3$, while only one such distance is found in the other case. Assuming the corresponding relative positions of the carbonate groups to be inaccessible and assigning a common probability to the remaining, accessible configurations for simplicity, approximate configurational entropy values were derived as outlined for $NaNO_3$-I [2] and others. The results are shown plotted in Fig. 1, a and b. The fraction of anions occupying the two types of position is not known. The III→II

Table 1. (a) Crystallographic and (b) calorimetric data for strontium and barium carbonate.

	$SrCO_3$	$BaCO_3$
(a) Crystallographic data [a]		
Orthorhombic (III); 4 molec./cell		
a (r.t.)	5.08 Å	5.30 Å
b (r.t)	8.36	8.88
c (r.t.)	6.00	6.42
Rhombohedral (II); 3 molec./cell		
a_{hex}	5.092 (920 °C)	5.205 (830 °C)
c_{hex}	9.53 (920 °C)	10.55 (830 °C)
a_{hex} [b]	5.106 (965 °C)	
c_{hex} [b]	9.516 (965 °C)	
Cubic face centered; 4 molec./cell		
a [c]		6.96 (960 °C)
(b) Calorimetric data [d]		
ΔH(III→II) (kcal/mol)	4.70	4.49
t(III→II) (°C)	924	806
	930 [e]	779 [e]
	912 [f]	803 [f]
ΔH(II→I) (cal/mol)	800 [g]	730
t(II→I) (°C)	1413 [g]	968
		976 [f]

[a] Data from Ref. 4, if not otherwise stated. [b] Ref. 5. [c] Super-cooled sample. [d] Data from Ref. 6, if not otherwise stated. [e] Ref. 8. [f] Ref. 4. [g] Ref. 7.

entropy changes [ΔS(III→II)] obtained for $SrCO_3$ and $BaCO_3$ from Table 1, are 3.94 and 4.17 cal/mol K, respectively. Configurational changes are generally found to predominate in order-disorder transitions,[13,14] The rather large discrepancy between observed and calculated entropy terms (Fig. 1) indicates therefore that the configurational entropy of the rhombohedral phases is probably actually considerably greater than the maximum values indicated in Fig. 1, a and b. This may be achieved by assuming additional equilibrium orientations of the anions to be accessible in the rhombohedral phases. Similar findings were also obtained for $AgNO_3$-I [15] and $RbNO_3$-II,[3] in which cases possible alternative positions were actually discussed.

The structure of the face-centred cubic phase. The II→I transition resembles the II→I transition in $RbNO_3$.[3] The entropy changes are small. The values obtained for $SrCO_3$ and $BaCO_3$ from Table 1, are 0.42 and 0.55 cal/mol K, respectively which are close to the ΔS(II→I) values of 0.42 [14] and 0.55 (0.01) cal/mol K [16] available for $RbNO_3$ (e.s.d. in parentheses). The hexagonal unit cell axes of $BaCO_3$ change from $a=5.205$ Å and $c=10.55$ Å in phase II to $a=4.921$ Å and $c=12.06$ Å in phase I (Table 1) at the experimental temperatures, respectively. The hexagonal c-axis thus increases, whereas the a and b axes decrease in the transition, as obtained for $RbNO_3$. The molecular volume changes from 82.5 Å^3 in phase II to 84.3 Å^3 in phase I, *i.e.* only by 2.2 %.

Phase I is probably isostructural [1,7] with $RbNO_3$-I.[3] The carbonate groups are accordingly assumed to be centred about the

Table 2. (a) Average atomic positions and (b) statistical intermolecular distances in phase II according to space group $R\bar{3}m$.[2] Hexagonal unit cell dimensions from Table 1.[4] $d(C-O)=1.285$ Å (ass.) [10,11] in planar carbonate group. Metal ions in $(00\frac{1}{2})$ *etc.*[2] Molecular three-fold axes along hexagonal *c*-axes.

(a)	Calcite-type positions (C)	Aragonite-type positions (A)
$SrCO_3$	Carbon: $x=y=z=0$ Oxygen: $x=0.252$, $y=z=0$	$x=y=0$, $z=z$ (oxygen) $x=2y=0.291$, $z=0.031$ (0.004)
$BaCO_3$	Carbon: $x=y=z=0$ Oxygen: $x=0.247$, $y=z=0$	$x=y=0$, $z=z$ (oxygen) $x=2y=0.285$, $z=0.026$ (0.004)

z_A is calculated on the assumption that the $Me-O_A$ contact distance $=Me-O_C$ contact distance. Assuming roughly an error of 0.03 Å in the $Me-O_A$ contact distance leads to the estimated errors in the parentheses. Errors in unit cell dimensions and the CO bond length expected to be small and are ignored.

(b) Atomic positions	$SrCO_3$ Distance (Å) (920 °C)	$BaCO_3$ Distance (Å) (830 °C)
$O_C(x\ 0\ 0)-Me(2/3\ 1/3-1/6)$	2.505	2.662
$O_A(x\ \frac{1}{2}\ x\ z)-Me(2/3\ 1/3-1/6)$	» (0.030) (ass.)	» (0.030) (ass.)
$O_A(x\ \frac{1}{2}\ x\ z)-Me(1/3\ 2/3\ 1/6)$	2.86 (0.02)	3.00 (0.02)
$O_C(x\ 0\ 0)-O_C(1-x,0,0)$	2.52	2.63
$O_C(x\ 0\ 0)-O_C(2/3-x,1/3-x,1/3)$	3.26	3.60
$O_C(x\ 0\ 0)-O_A(2/3-x,1/3-\frac{1}{2}x,1/3-z)$	3.00 (0.04)	3.36 (0.04)
$O_A(x\ \frac{1}{2}\ x\ z)-O_C(1-x,0,0)$	2.785 (0.004)	2.892 (0.004)
$O_A(x\ \frac{1}{2}\ x\ z)-O_A(2/3-x,1/3-x,1/3-z)$	2.61 (0.06)	3.00 (0.06)
$O_A(x\ \frac{1}{2}\ x\ z)-O_A(1-\frac{1}{2}x,\ \frac{1}{2}x,\ z)$	2.87 (0)	2.98 (0)

three-fold axes (space diagonals) in either calcite and/or aragonite-type equilibrium positions.[3] There are statistically 8 positions of each kind per anion. Each oxygen atom makes close contact with two metal ions when the anion is in a calcite-type position, whereas one short distance and two intermediate metal-oxygen separations are formed for each O atom when an aragonite-like orientation is occupied. Average atomic positions and statistical intermolecular distances based on space group $Fm3m$ are listed for $BaCO_3$-I in Table 3. The metal-oxygen contact distance is somewhat larger than the corresponding values obtained for $BaCO_3$-II. A complete set of inequivalent O—O distances less than 2.80 Å is also contained in Table 3 together with some equivalent O—O distances. The corresponding number of statistical anion positions less than 2.80 Å from a given anion in either the calcite- or aragonite-like orientation [2] are listed as a function of associated lattice site in Table 4.

These relative positions of two and two carbonate groups were assumed to be blocked in the subsequent configurational entropy calculation, while the remaining, accessible configurations were assigned a common weight factor. The approximate entropy values, Fig. 1, c, were obtained as outlined for $RbNO_3$,[3] using the information contained in Table 4. Comparison of graph b and c, Fig. 1, indicates that $S_c(I)$ is considerably higher than $S_c(II)+\Delta S(II\rightarrow I)$. $\Delta S(II\rightarrow I)$ is given above and $Sc(II)$ denotes the configurational entropy corresponding to the simple calcite- and aragonite-type positional disorder [2] discussed in the preceding section. (The change $x_A(II)\sim 0.6$ to $x_A(I)\sim 1$ is seen to produce a relatively small configurational entropy change. This implies that calcite-like orientations are practically blocked in phase I but not in II, which seems unreasonable in view of the structural resemblance of the two phases.) It appears therefore, in agreement with the result of the

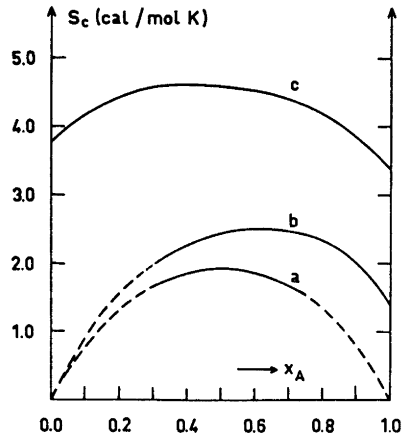

Fig. 1. Calculated configurational entropy values derived from calcite- and aragonite-like anion disorder,[2,3] as a function of average fraction, x_A, of molecules in argaonite-type positions. Molecular threefold axes aligned along the three-fold axes of either the rhombohedral or cubic lattice. Broken lines are used when the computed values are more uncertain because of the computational approximations involved. (Nearly) zero configurational entropy is evident from mere inspection of structural model, however.
a: $SrCO_3$-II, b: $BaCO_3$-II and c: $BaCO_3$-I.

preceding section, that the actual configurational entropy of phase II is probably considerably higher than that based on the simple calcite- and aragonite-type positional disorder. A similar way of showing this holds probably also for $SrCO_3$. An alternative explanation of the indicated discrepancies is difficult to see.

Possible, additional equilibrium positions of the anions in the rhombohedral phases. Fig. 2, a shows the two types of average equilibrium anion orientation proposed previously for $NaNO_3$-I and others and used in the preceding configurational entropy analysis of the rhombohedral phases. Possible, additional average equilibrium positions of the anions are indicated in Fig. 2, b. $BaCO_3$-II is used as model. The arrangement of positive ions in Fig. 2, b is somewhat contracted in the vertical direction in the paper plane and somewhat lengthened in the direction perpendicular to this plane compared with the rhombohedral arrangement of the positive ions in Fig. 2, a. The aragonite-like position in Fig. 2, b may be adjusted by translation in the mirror plane and rotated about an axis perpendicular to

Table 3. (a) Average atomic positions and (b) intermolecular statistical distances in $BaCO_3$-I according to space group $Fm3m$. $a=6.96$ Å (Table 1).[4] $d(C-O)=1.285$ Å (ass.)[10,11] in planar carbonate group. Metal ions in $(\frac{1}{2}00)$ *etc.*[3] Threefold axis of anion, centred about the origin, along the [111]-direction.

(a) Calcite-type positions (C)	Aragonite-type positions (A)
Carbon: $x=y=z=0$	$x=y=z=-0.019$ (0.004)
Oxygen: $x=0$, $y=-z=-0.130(5)$	$x=y=-0.094(0.004)$, $z=0.132(0.004)$

z_A is calculated on the assumption that the Me$-O_A$ contact distance=Me$-O_C$ contact distance. Assuming roughly an error 0.03 Å in the Me$-O_A$ contact distance leads to the estimated errors in the parentheses. Errors in the a-axis and the C$-$O bond length expected to be relatively small and are ignored.

(b) Atomic positions	Distance (Å) (960 °C)
$O_C(0\ \bar{z}\ z)-Me(0\ 0\ \frac{1}{2})$	2.727
$O_A(x\ x\ z)-Me(0\ 0\ \frac{1}{2})$	2.727 (0.030) (ass.)
$O_A(x\ x\ z)-Me(-\frac{1}{2}\ 0\ 0)$	3.04 (0.03)
$O_C(0\ \bar{z}\ z)-O_C(0,-\frac{1}{2}+z,\frac{1}{2}-z)$	2.35
$O_C(0\ \bar{z}\ z)-O_A(x,-\frac{1}{2}+z,\frac{1}{2}+x)$	2.61 (0.03)
$O_C(0\ \bar{z}\ z)-O_A(-x,-\frac{1}{2}+z,\frac{1}{2}+x)$	2.61 (0.03)
$O_C(0\ \bar{z}\ z)-O_A(x,-\frac{1}{2}-x,\frac{1}{2}-z)$	2.61 (0.03)
$O_C(0\ \bar{z}\ z)-O_A(-x,-\frac{1}{2}-x,\frac{1}{2}-z)$	2.61 (0.03)
$O_A(x\ x\ z)-O_A(-\frac{1}{2}+z,x,\frac{1}{2}+x)$	2.69 (0.04)
$O_A(x\ x\ z)-O_A(x,-\frac{1}{2}-x,\frac{1}{2}-z)$	2.72 (0.04)

Table 4. The number of calcite (C)- and aragonite (A)-type anion positions at neighbour sites, L, less than 2.80 Å from a central anion, S, in either the calcite- or aragonite-type position defined in Table 3, which contains the necessary information for the present derivation along with the molecular and space group symmetry.

		L lattice site:											
S	L	$(\frac{1}{2}\frac{1}{2}0)$	$(0\frac{1}{2}\frac{1}{2})$	$(\frac{1}{2}0\frac{1}{2})$	$(\frac{1}{2}\bar{\frac{1}{2}}0)$	$(0\frac{1}{2}\bar{\frac{1}{2}})$	$(\bar{\frac{1}{2}}0\frac{1}{2})$	$(\bar{\frac{1}{2}}\frac{1}{2}0)$	$(0\bar{\frac{1}{2}}\frac{1}{2})$	$(\frac{1}{2}0\bar{\frac{1}{2}})$	$(\bar{\frac{1}{2}}\bar{\frac{1}{2}}0)$	$(0\bar{\frac{1}{2}}\bar{\frac{1}{2}})$	$(\bar{\frac{1}{2}}0\bar{\frac{1}{2}})$
C	C				1	1	1						
C	A				4	4	4						
A	C				1	1	1				1	1	1
A	A				1	1	1				1	1	1

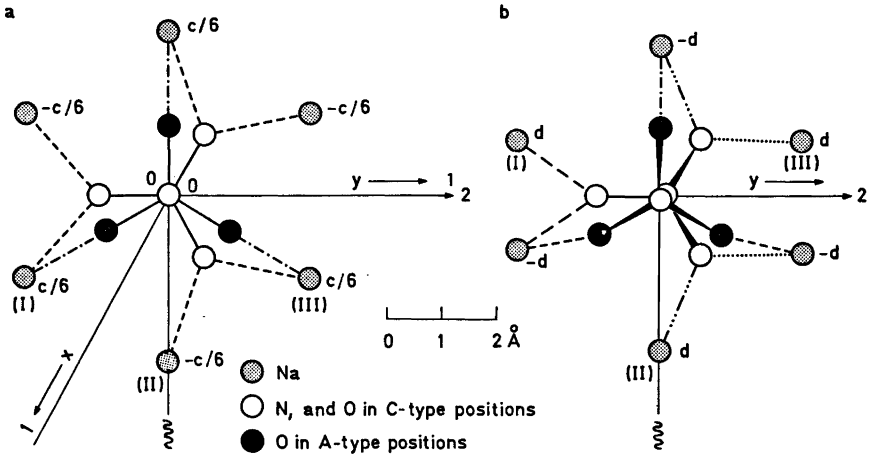

Fig. 2. Orientational disorder in the rhombohedral phases. Crystal and molecular data for $BaCO_3$-II are used. Hexagonal indexing.
a. The arrangement of positive ions in the rhombohedral phase, as viewed along the hexagonal c-axis. One of the two standard aragonite (A)- and one of the two standard calcite (C)-type anion orientations [2] used in the preceding calculations are also shown. Molecular threefold axes along the threefold axes of the lattice.
b. The corresponding arrangement of positive ions as viewed perpendicular to the plane containing the positive ions denoted by (I), (II) and (III) in Fig. 2, a. The hexagonal c-axis, in the symmetry plane, makes an angle of 113.1° with the (downwards) normal to the plane of (I), (II) and (III), as compared with 109°28′ for a cubic crystal. Distance from origin to plane containing (I), (II) and (III), $d=2.07$ Å, compared with $c/6=1.76$ Å (Fig. 2, a). An *alternative* "calcite-like" and an alternative "aragonite-like" anion positions are indicated. A symmetry plane of the latter grouping coincide with a symmetry plane of the space groups ($R\bar{3}m$), while a two-fold axis of the former position coincides with a two-fold axis of the space group. Two orientations of each kind are obtained through the operation of the space group symmetry elements shown.

this plane ("three degrees of freedom" as compared with one for the A-type positions in Fig. 2, a), while the calcite-like position may be translated along and rotated about the two-fold axis "two degrees of freedom,, as compared to none for the C-type position in Fig. 2, a). Three oxygen-metal contacts of lengths similar to the metal-oxygen contacts in Fig. 2, a, are obtained by a small adjustment of the A-like position in Fig. 2, b from a position where the carbonate group is parallell with the plane of these three nearest neighbour metal ions at the same distance as in Fig. 2, a, and the C atom is situated on the normal to this plane through the inversion centre (origin). Similarly, four short and two somewhat longer metal-oxygen positions, for instance, may be obtained by adjusting the

C-like position in Fig. 2, b. (The latter kind of position may seem to be somewhat less probable than the former.) Two and two of the intermolecular metal-oxygen distances (except one) are crystallographically equivalent, as indicated in Fig. 2, b.

Three equivalent configurations of the Fig. 2, b-type are obtained through the operation of the three-fold symmetry axis. There are altogether six anion positions of each kind shown in Fig. 2, b. On transforming to the cubic phase, the Fig. 2, b-type configurations change with relatively small positional adjustments into the Fig. 2, a-type, which become representative of the cubic structure, showing the two kinds of anion orientation mentioned in the preceding section. The anion positions shown in Fig. 2, a and b are thus rather closely related to those of the cubic phase.

Obviously, simple spatial considerations as used in the present section are by themselves only indicative of actual equilibrium positions, which will ultimately have to be confirmed in other ways. On the other hand, the anion positions shown in Fig. 2 appear to be the only kinds of orientation that satisfy reasonably well general, qualitative, spatial requirements necessary to define an anion-orientationel potential minimum in a given frame of positive ions. Furthermore, arguments in favour of an extended model of disorder have already been advanced for the rhombohedral phase. Thus a relatively small number of anions in either or both kinds of molecular orientation shown in Fig. 2, b is required in addition to those in Fig. 2, a-type positions to remove the previously mentioned discrepancies between observed transition and calculated configurational entropy values.

Inspection shows further that Fig. 2, b-type anion positions may also represent (permanent or temporary) equilibrium positions bounded by potential barriers in the rhombohedral phases of $SrCO_3$, $RbNO_3$, $AgNO_3$ and KNO_3. The need of additional orientational disorder has previously been stressed for $SrCO_3$-II, $RbNO_3$-II [8] and $AgNO_3$-I.[15] Some additional configurational disorder may similarly be possible in KNO_3-I, but probably not in $NaNO_3$-I, considering the differences between the transition and configurational entropy data quoted for these compounds.[2,17]

REFERENCES

1. Muller, O. and Roy, R. *The Major Ternary Structural Families*, Springer, New York 1974.
2. Strømme, K. O. *Acta Chem. Scand. 23* (1969) 1616.
3. Strømme, K. O. *Acta Chem. Scand. 25* (1971) 211.
4. Lander, J. J. *J. Chem. Phys. 17* (1949) 892.
5. Moreau, R. *Bull. Soc. Franc. Mineral. Crist. 87* (1964) 547.
6. Kelley, K. K. *Bull. 584, Bureau of Mines* (1960) 23 and 180.
7. Baker, E. H. *J. Chem. Soc.* (1962) 2525.
8. Rapoport, E. and Pistorius, C. W. F. T. *J. Geophys. Res. 12* (1967) 6353.
9. Boeke, H. E. *Neues Jahrb. Mineral, Geol. und Paläontologie 1* (1912) 91.
10. Felty, E. J. *Diss. Abstr. 24* (1964) 4423.
11. Chessin, H., Hamilton, W. C. and Post, B. *Acta Crystallogr. 18* (1965) 689.
12. Slater, J. C. *J. Chem. Phys. 41* (1964) 3199.
13. Darmon, I. and Brot, C. *Molecular Crystals 2* (1967) 301.
14. Newns, D. M. and Staveley, L. A. K. *Chem. Revs. 66* (1966) 267.
15. Strømme, K. O. *Acta Chem. Scand. 24* (1970) 1477.
16. Strømme, K. O. *Unpublished results.*
17. Strømme, K. O. *Acta Chem. Scand. 23* (1969) 1625.