CRYSTAL STRUCTURE OF THE SERIES OF BARIUM AND STRONTIUM CARBONATES*

J. M. Cork and S. L. Gerhard, *University of Michigan.*

Abstract

Using the powder method a study was made of the effect upon the lattice constants of barium carbonate by the addition of definite molecular fractions of strontium carbonate. The mixtures examined were of two kinds: (a) mechanical and (b) precipitated. In the former case each component shows its own definite pattern while in the latter only a single intermediate pattern is observed obeying approximately the additive law of Vegard. The effect of heating the pure and mixed carbonates during *x*-ray exposures was investigated. Spectrometer measurements upon natural witherite crystals together with powder pattern measurements on barium carbonate indicate that the previously reported dimensions of the unit orthorhombic cell must be somewhat modified.

The extensive use of various forms of alkaline earth compounds on surfaces employed in electron emission makes any information regarding their crystal structure of interest.

Speculation regarding the lattice constants of barium and strontium carbonates as well as of other carbonates possessing the aragonite type of structure was carried out by Huggins.[1] His results were based upon the axial ratio values given by Groth, together with the value of the density and the assumption that there were two molecules associated with each unit orthorhombic cell.

From measurements of diffraction patterns, using the powdered crystal method, Wilson[2] reported values of the lattice constants quite different from those recorded by Huggins. These were based upon a unit orthorhombic cell containing four molecules, and a space group assignment of $2D_i-16$ (Q_k^{16}) as found by Wyckoff[3] for the related mineral aragonite.

In the present investigation the object was three-fold: (a) to determine as precisely as possible the dimensions of the unit cell of the primary substance, barium carbonate; (b) to show how this is modified by the addition of another constituent, strontium carbonate, in varying amounts, (c) to observe any difference when the added constituent is introduced by different methods.

---

* This investigation was undertaken at the request and with the financial assistance of the Grigsby-Grunow Co., Chicago, Ill.

[1] M. Huggins, *Phys. Rev.*, **19**, p. 354, 1922.

[2] T. A. Wilson, *Phys. Rev.*, **31**, p. 305, 1928.

[3] R. W. C. Wyckoff, *Amer. Jour. of Scien.*, vol. **9**, p. 145.

POWDER METHOD

Using the Hull-Debye-Scherrer method employing molybdenum K_α x-radiation, diffraction patterns were obtained for mixtures of barium and strontium carbonates of varying compositions. These mixtures were of two kinds: (a) mechanical, produced by mixing pure barium carbonate and pure strontium carbonate in the desired proportions, and (b) precipitated, formed either by passing carbon dioxide into a solution containing definite parts by weight of strontium and barium hydroxides, or by adding sodium carbonate to a solution of strontium and barium nitrates in the desired proportions.

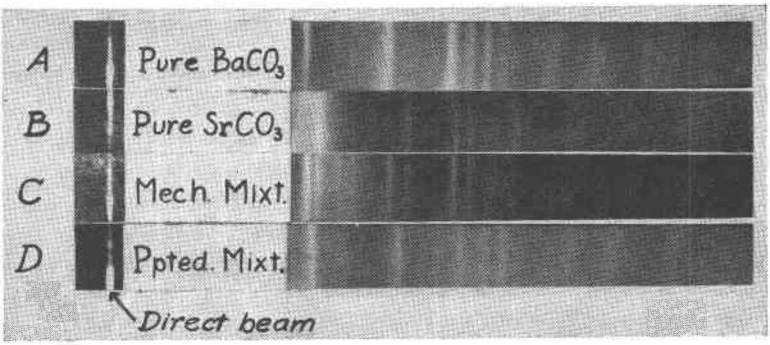

FIG. 1.

The following three types of mountings were employed for the samples under investigation: (a) thin-walled glass capillary tubes, (b) coating on thin nickel wires, (c) thin sheet behind an added fine brass slit. In every case the specimen was mixed with some other crystalline substance such as potassium chloride, sodium chloride, or nickel oxide, in order to have known reference lines in measuring the films.

Typical diffraction patterns obtained for the pure barium and strontium carbonates are shown in A and B, Fig. 1. It is readily observed that the patterns are of the same nature except that the $SrCO_3$ pattern is displaced more toward larger angles from the direct beam than the $BaCO_3$ pattern, because of the smaller dimensions of the unit orthorhombic cell for strontium carbonate.

C and D in Fig. 1 illustrate the result obtained with mechanical and precipitated mixtures of equal amounts of barium and strontium carbonates. In the former case both barium and strontium patterns are clearly present while in the latter case only a single intermediate pattern is observed. Single definite patterns of this sort were observed for every precipitated mixture, its position with respect to the parent patterns being determined solely by the molecular fractions of the components present. This shows clearly that the metallic barium atoms in the carbonate lattice are replacable by strontium atoms with a slight accompanying decrease in lattice dimensions or vice versa.

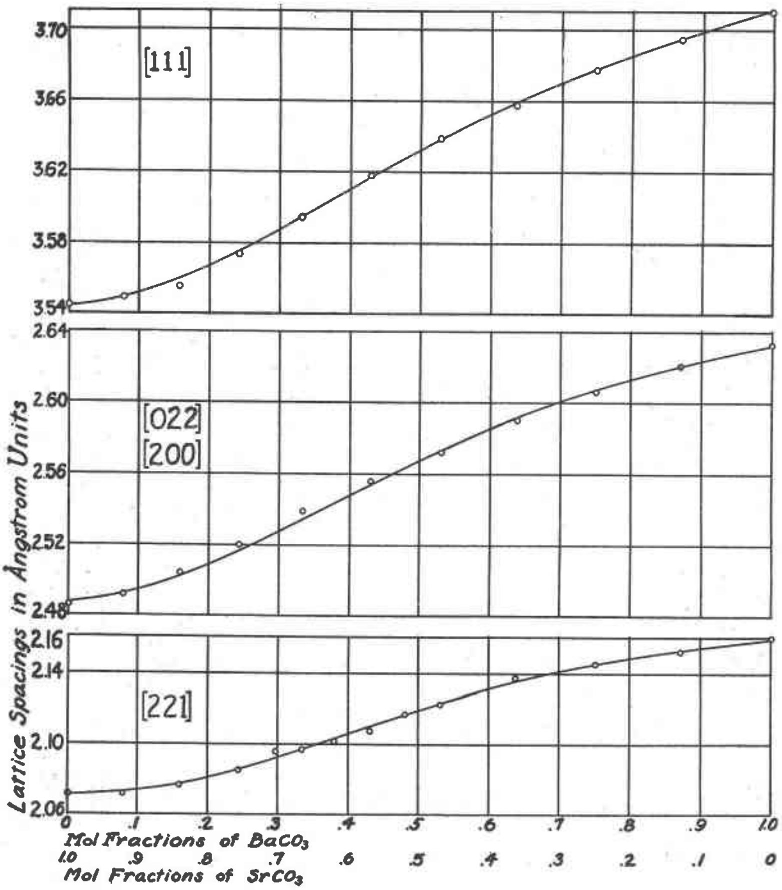

FIG. 2.

The variation in the lattice dimensions with varying molecular fractions of constituents is shown in Fig. 2 for a few of the principal lines in the diffraction patterns. These lines for the precipitated mixtures are in general as sharp as those for the pure substances. It is remarkable that a replacement of one atom of every one hundred barium atoms in the barium carbonate structure by a strontium atom should produce a general contraction of the whole lattice with no loss of definiteness in the diffracted line. The curves of Fig. 2 differ from straight lines only at each end, thus exhibiting a slight deviation from the 'additive' law of Vegard.[4]

Temperature Effect

The effect of heating the mixtures on nickel wires during the x-ray exposure was investigated. Specimens of the precipitated type containing equal parts of strontium and barium carbonates, as well as others of the pure substances were investigated in this way. Each was maintained during the exposure at a constant high temperature perhaps slightly above 1000°C. While this heating was carried out in the presence of air and would be thereby somewhat affected, it is quite probable that the major changes so observed would represent those occurring in the activation of the filaments of radio tubes. Certain results of these tests may be summarized as follows:

(a) In pure barium carbonate no change in structure occurred but simply an enlargement of the lattice by temperature expansion.

(b) In pure strontium carbonate a definite transformation took place in which the strontium carbonate changed into strontium oxide.

(c) In the precipitated mixture of equal parts, diffraction patterns were observed of lines whose origin was not determined, besides those of barium carbonate, strontium oxide and nickel oxide.

Spectrometer Method

To evaluate precisely the lattice constants of a crystal, the powder method is hardly satisfactory. When large single crystals are obtainable the spectrometer yields results of much greater precision.

Natural barium carbonate crystals known as witherite are readily obtained. As the result of twinning these crystals are pseudohexagonal in form. The pyramidal faces have the Miller indices $\{111\}$ and give nearly perfect x-ray reflections.

---

[4] Vegard, *Zeit. für Krist.*, **67**, p. 239, 1928.

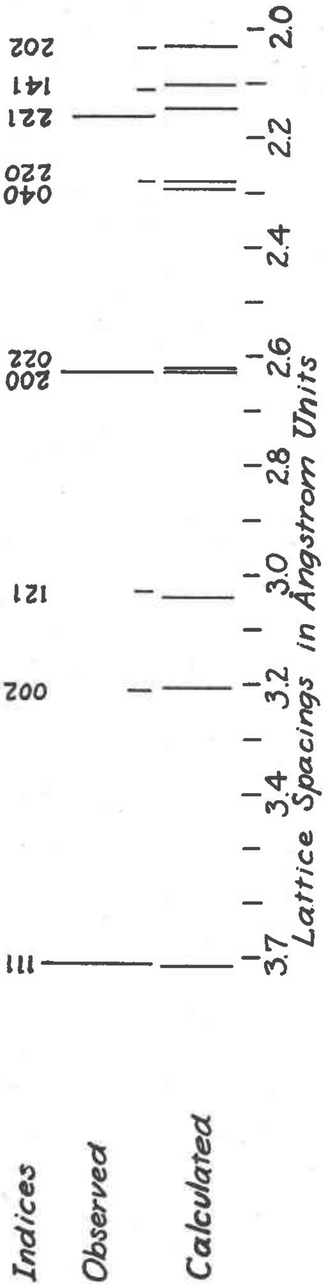
Indices
Observed
Calculated
Lattice Spacings in Ångstrom Units
3.7
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
111
002
121
200
022
040
220
221
141
202

FIG. 3.

Using a Siegbahn vacuum spectrograph with copper K radiation a determination of the interplanar distance for this face was carried out. In this investigation the method employed in precision wave-length measurement was used, that is, crystal and plate were each rotated so as to give on the same plate in almost coincident positions the lines taken on each side of the direct beam. Using the Siegbahn values for the wave-lengths of the copper lines, a value for d_{111} of 3.7178 Ångstroms was obtained.

TABLE I

Plane Set	Wilson's Values	Observed Powder Lines	Present Values
100	5.252	——	5.256
010	8.828	——	9.172
001	6.544	——	6.412
——	——	——	——
111	3.717	3.71	3.717^8
002	3.272	3.21	3.206
121	3.003	3.03	3.040
022	2.629	2.63	2.627
200	2.626		2.628
220	2.257	2.28	2.280
040	2.207		2.293
221	2.134	2.16	2.149
141	1.942	2.11	2.102
202	2.084	2.03^5	2.033
Volume of Unit Cell	303.4		309.1
Density	4.320		4.245

The axial ratio for barium carbonate given by Growth is: $a:b:c=0.5949:1:0.7413$. This axial ratio together with the above measurement on the {111} face would demand the following values for the edges of the unit orthorhombic cell: 5.2556, 8.8345, and 6.5490 ÅU. The dimensions of the unit cell given by Wilson were: 5.252, 8.828, and 6.544 Å.U., in excellent agreement with the above. Now, while these values satisfy the Groth ratio and give the observed {111} spacing, it is still not possible by using them to obtain an agreement between the calculated values for other principal spacings and observed lines in the powder diffraction pattern. While as mentioned above the powder method is incapable of yielding the utmost accuracy, still it should not differ from the true values by more than one, or at most two, hundredths of an Ångstrom unit. Table 1 shows the observed values of the first eight principal lines, together with the values as calculated from the above lattice constants. The discrepancy is too great to be permissible.

In order to check this further spectrometer measurements were made upon the {001} plane. This plane was obtained from a natural crystal by grinding it normal to the *c*-axis in which case the three components of the trilling act together. Spectrometer measurements on this set of planes gave a value 6.412 Å.U., which would yield very satisfactorily the second line in the diffraction pattern, namely 3.21 Ångstroms.

Due to the intergrowth of the three components direct measurements were not obtained for the {100} and {010} planes. These were assigned such values that when they were combined with the above spectrometer measurements best agreement with the principal powder lines was obtained. These values together with the computed spacings for the principal planes are shown in column four, Table 1, and in Fig. 3. For smaller spacings there are so many possible lines that agreement between the observed and either calculated set is within the experimental limit.