THE AMERICAN MINERALOGIST, VOL. 55, MAY-JUNE, 1970

HIGH PRESSURE MID-INFRARED STUDIES OF CALCIUM CARBONATE

S. DAVID CIFRULAK,[1] *Mellon Institute of Carnegie-Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213.*

ABSTRACT

The infrared analysis of calcite to pressures of 61 kbar, obtained by means of a high-pressure diamond cell equipped with type II diamond anvils, has shown spectroscopicly that a new high pressure polymorph of calcium carbonate is produced at pressures above 30 kbars having a "vaterite-type" structure.

INTRODUCTION

In this study, variations in the carbonate site symmetry due to pressure have been found to alter the calcite absorption spectra. These changes have led us to certain inferences regarding the ionic symmetry of calcite as a function of pressure.

Terminology. The point group notations used to identify molecular and site symmetries are the usual sets described by Herzberg (1945).

The *internal* symmetry of the molecules is established by the configuration of nuclei comprising the molecule. In the carbonate ion, the positions of the single carbon and three oxygen atoms determine this symmetry.

The *site* symmetry of the molecule is defined by the arrangement of any molecular ion and extramolecular nuclei to which it is bonded. It is, therefore, a function both of the symmetry of the molecule and its external environment.

For example, the ideal carbonate ion has the *internal* symmetry D_3h. However, if neighboring calcium atoms are also considered as in calcite. the *site* symmetry elements which define the configuration of one carbon, three oxygen and six calcium atoms are no longer D_3h, but D_3. Similarly for the aragonite structure, the divalent metallic ions provide still different site symmetry for the carbonate ion. In this case, the site symmetry for aragonite is Cs.

Site symmetry of the $CaCO_3$ polymorphs. Examination of the site symmetries of the various known calcium carbonate polymorphs substantiates the above.

Calcite. The carbonate ion has a site symmetry of D_3 which results in three infrared active bands and one infrared inactive band.

---

[1] Present address: USS Chemicals, Neville Island, Pennsylvania 15225.

Mode or Vibration	Wave Number	IR Activity
ν_1=sym. str.	1097 cm^{-1}	inactive
ν_2=out-of-plane bend	879 cm^{-1}	active
ν_3=antisym. str.	1432 cm^{-1}	doubly degenerate[a]
ν_4=in-plane bend	714 cm^{-1}	doubly degenerate[a]

[a] *i.e.*, each under certain symmetry conditions may split into two distinct vibrations of different frequency.

Weir, *et al.* (1959) propose that degenerate lattice frequencies of translational or rotational origin may interact with the degenerate fundamentals to produce a splitting or doubling. They observe a reversible splitting of the ν_3 and a less apparent splitting of the ν_4 fundamentals at pressures less than 30 kbar. At these pressures, the ν_1 fundamental is observed and increases in intensity as pressure is applied. This suggests a deviation of the D_3 site symmetry selection rules; although, optically a change of phase is not observed.

Aragonite. Its carbonate ions have a C_2 site symmetry. Hence, six internal frequencies of the ion are now permitted in the infrared: the degeneracy is removed from ν_3 and ν_4, ν_1 becomes active, and ν_2 should remain unchanged. It is well to note that no changes are observed in aragonite by Weir, *et al.*, below 30 kbar.

Vaterite. This polymorph is reported to have a hexagonal unit cell containing two or more molecules per unit cell. However, structural details of the unit cell have not been established so far as can be ascertained. Therefore, the expected spectrum cannot be predicted.

All vaterite spectra obtained thus far agree with those previously published (Weir and Lippincott, 1961; Baron, 1959; Sterzel and Chorinsky, 1968). Comparison of the vaterite data with that of the calcite and aragonite types shows that the stretching force constant and out-of-plane bending constant are essentially unchanged. However, the in-plane constant has increased in vaterite.

	Calcite	*Aragonite*	*Vaterite*
ν_1	—	1087	1090
ν_2	881	866	850–878
ν_3	1432	1430–1550	1450
ν_4	712	715–703	741–747

Weir and Lippincott (1961) suggest this marked change in the in-plane bending constant is indicative of repulsion between oxygen atoms in the plane of the ion if the analysis of the effects of different types of