

structure of the ferroelectric KNO_3 III phase and that CaCO_3 III does not have the KNO_3 IV structure. Neither CaCO_3 II nor CaCO_3 III is aragonite. The CaCO_3 II spectrum has both more and narrower lines than the spectrum of the high-temperature phase of NaNO_3 reported by Chisler,¹⁸ indicating that these phases have different structures.

The CaCO_3 II spectrum would be consistent with a structure with a trigonal lattice and a primitive cell containing one formula unit suggested by x-ray powder patterns if anion orientational disorder or crystal field splitting of otherwise degenerate modes into transversely and longitudinally polarized modes combined with lower than D_{3d} factor group symmetry to make essentially all Raman modes allowed. In this regard, it may be noteworthy that each of the lattice phonon lines in the Raman spectrum of CaCO_3 II, except that at 99 cm^{-1} , is not more than 27 cm^{-1} higher in frequency than a strong infrared or Raman-active phonon of calcite at atmospheric pressure. Such differences in frequency can be attributed to pressure-dependent frequency shifts. The assignment of the lattice phonons of calcite, however, is still incomplete, and it would be premature to make more definite statements about this possible assignment of the CaCO_3 II spectrum at this time. Further study of possible similarities between CaCO_3 II and KNO_3 IV are also suggested by several qualitative similarities of their Raman spectra; and, of course, several other structures not discussed here for lack of data and other reasons also must be considered.

The CaCO_3 III spectra provide fewer clues concerning its possible structures. The splittings of the ν_1 and ν_3 bands suggests that the primitive cell contains at least two and possibly four formula units; available x-ray data are inconclusive in this regard. Although the spectra clearly indicate that CaCO_3 III and aragonite are distinct species, some similarities between their spectra suggest that they may be closely related. The distribution of lattice phonon frequencies, although not the Raman intensities of these polycrystalline and probably preferentially oriented samples, are comparable for these two CaCO_3 phases. In the internal phonon region, the relationship between the CaCO_3 III and the aragonite spectra somewhat parallels that between CaCO_3 II and calcite. This suggests the possibility that CaCO_3 III is a disordered or differently ordered variant of aragonite, although the observation that CaCO_3 II and calcite (but no aragonite) are obtained from CaCO_3 III upon decompression

argues against this. It would be interesting to compare these spectra with the Raman spectrum of vaterite and, of course, to have more detailed x-ray information about these materials. Without more precise structural information about these materials than is available, it is beyond the scope of this work to comment in greater detail about the origins and magnitudes of the frequency shifts of these phonon modes.

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