

Molecules in the SiO₂-clathrate melanophlogite: A single-crystal Raman study

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ABSTRACT

A Raman spectroscopic investigation of the SiO₂-clathrate melanophlogite was undertaken to investigate the enclathrated molecules. The Raman spectra show the presence of N₂, CO₂, and CH₄ molecules based on the observation of their normal stretching modes. An analysis of the spectra, together with single-crystal X-ray results (Gies 1983), demonstrates that the molecules are located in structural cages. Most of the CH₄ is partitioned into the smaller nearly spherical [5¹²] cage, while CO₂ and N₂ prefer the larger more oblate [5¹²6²] cage. The difference in wavenumber for their stretching modes between room temperature and 4 K is minimal. There are also only small differences between the wavenumbers of the modes of the enclathrated molecules and those they possess in the free, gaseous state. The molecules are orientationally disordered in the cavities and they have weak dispersion interactions with the SiO₂ framework. Although the energetic states of the molecules are only slightly modified by being enclathrated, subtle interactions between molecule and framework are necessary to stabilize the clathrate phase. The properties and behavior of single, quasi-free molecules occurring in the cavities of beryl and cordierite are compared to the situation in melanophlogite.