

Spectroscopic and X-ray diffraction investigation of the behavior of hanksite and tychite at high pressures, and a model for the compressibility of sulfate minerals

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ABSTRACT

The rare evaporite minerals hanksite, $\text{Na}_{22}\text{K}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl}$, and tychite, $\text{Na}_6\text{Mg}_2(\text{CO}_3)_4(\text{SO}_4)$, are excellent case studies for the high-pressure behavior of ionic groups since their structures combine ionic complexity and high symmetry (hexagonal $P6_3/m$ and cubic $Fd\bar{3}$, respectively). Here we investigate the structure and compressibility of hanksite up to 20 GPa in the diamond-anvil cell using Raman spectroscopy and X-ray diffraction and of tychite up to 17 GPa in the diamond cell using X-ray diffraction and first-principles modeling. At ambient pressure, the Raman spectrum of hanksite has a single sulfate ν_1 frequency at 992 cm^{-1} with a lower-frequency shoulder. As pressure is increased, this mode splits into two distinct peaks, which arise from two distinct local environments for the sulfate tetrahedra within the hanksite structure. Below 10 GPa, the mode Grüneisen parameter of the dominant sulfate ν_1 frequency is 0.27(1); the mode Grüneisen parameter of the lower frequency shoulder is 0.199(7). X-ray diffraction data of hanksite indicate a 5% volume drop between 8–10 GPa with no apparent change of symmetry. A Birch-Murnaghan fit to the data below 8 GPa yields an isothermal bulk modulus of 66(1) GPa for hanksite and 85(1) GPa for tychite, with K' fixed at 4.

Keywords: High pressure, X-ray diffraction, Raman spectroscopy, evaporite salt, sulfate, carbonate