

## **A vibrational spectroscopic study of kernite to 25 GPa: Implications for the high-pressure stability of borate polyhedra**

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### **ABSTRACT**

The Raman and infrared spectra of kernite [Na<sub>2</sub>B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O] have been characterized up to ~25 and 23 GPa, respectively, to explore pressure-induced changes in a structurally novel mineral that contains mixed coordination borate groups (threefold and fourfold), as well as both hydroxyl groups and water molecules. BO<sub>3</sub> and BO<sub>4</sub> vibrational modes are characterized in both the Raman and infrared spectra of kernite, and reassignments of some modes are made based on observed pressure shifts. Under compression to ~25 GPa, kernite undergoes three phase transitions: one initiates near ~2.5 GPa, the second occurs at ~7.0 GPa, and the third near 11.0 GPa. The first transition is characterized by a loss of both a subset of the Na-associated modes and a sharp OH peak, and it is fully reversible. The second transition is characterized by the loss of most of the BO<sub>3</sub> modes, some of the BO<sub>4</sub> modes at ~7 GPa, and further broadening of the H<sub>2</sub>O and OH peaks. This transition is partially reversible on decompression, but the Raman spectra indicate that the high-pressure structure and its reversion products are likely disordered. The third transition is characterized by the loss of most of the Raman and infrared modes, and it is not reversible on decompression. The decompression products from ~25 GPa have markedly different infrared and Raman spectra from the starting material, and appear to involve different bonding environments of boron than are present in the starting materials: thus, pressure treatment of boron-rich materials may generate novel quenchable structures. Notably, the BO<sub>3</sub> groups in kernite are destabilized under compression, with the BO<sub>4</sub> groups appearing to be more stable under compression. This shift in coordination may be endemic among borate glasses and crystalline borates under compression. The coordination conversion (and its products on decompression) is likely to highly depend on the detailed topology of the starting materials. Commonalities and differences between the threefold to fourfold transitions in borate systems relative to those in carbonate systems are presented. Our results, combined with prior shock data, indicate that kernite, which may be representative of low-temperature borate minerals, can persist during impact events with peak shock pressures less than ~33 GPa, and the primary polyborate structural units involved in early ribose stabilization would thus survive most impact conditions.

**Keywords:** Kernite, boron, high pressure, vibrational spectroscopy