

## Crystal chemistry of arsenian pyrites: A Raman spectroscopic study

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### ABSTRACT

A Raman spectroscopic study on the nature of As-S substitution in natural arsenian pyrite [Fe(S,As)<sub>2</sub>] is presented, covering a compositional range of 0.01–4.6 at% As. Three Raman-active modes were identified in the Raman spectrum of a nearly pure pyrite: E<sub>g</sub> (344 cm<sup>-1</sup>), A<sub>g</sub> (379 cm<sup>-1</sup>), and T<sub>g</sub>(3) (432 cm<sup>-1</sup>). The Raman vibrational modes exhibit one-mode behavior, and the wavenumbers of optical modes vary approximately linearly with As content, correlating with the change in bond constants with increasing substitution of As for S. The linewidth of the A<sub>g</sub> mode increases with increasing As substitution, which may be attributed to the increase in lattice strain associated with the substitution of As for S. This study provides experimental evidence for As-induced structural evolution of pyrite from being stable to metastable before decomposing into other phases. Our results, together with those of another Raman study of arsenian pyrite whose As substitution is more complex, indicate that one cannot use Raman band shifts to determine As content, but for a given As content, can characterize the nature of As substitution, i.e., As for S or As for Fe or both.

**Keywords:** Arsenian pyrite, Raman spectroscopy, solid solution, structural defect