

Crystal chemistry of arsenian pyrites: A Raman spectroscopic study

HE ZHANG^{1,2}, GUJIE QIAN², YUANFENG CAI^{1,†}, CHRISTOPHER GIBSON^{3,4}, AND ALLAN PRING^{2,*}

¹State Key Laboratory of Mineral Deposit Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

²College of Science and Engineering, Flinders University, Adelaide, South Australia 5042, Australia

³Flinders Microscopy and Microanalysis, College of Science and Engineering, Flinders University, Bedford Park, South Australia 5042, Australia

⁴Flinders Institute for Nanoscale Science and Technology, College of Science and Engineering, Flinders University, Bedford Park, South Australia 5042, Australia

ABSTRACT

A Raman spectroscopic study on the nature of As-S substitution in natural arsenian pyrite [Fe(S,As)₂] 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_g (344 cm⁻¹), A_g (379 cm⁻¹), and T_g(3) (432 cm⁻¹). 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_g 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