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 \([\text{Fe}(S,\text{As})_2]\) 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: Arsenic pyrite, Raman spectroscopy, solid solution, structural defect

INTRODUCTION

Arsenian pyrite \([\text{Fe}(S,\text{As})_2]\) is defined as pyrite containing anywhere from several parts per million to ~19 wt% arsenic (e.g., Abratis et al. 2004; Qian et al. 2013; Reich and Becker 2006), and this substitution is commonly associated with the presence of economically important metals such as Au, Co, Ni, Ag, Cu, etc. (Deditius et al. 2014; Large et al. 2014; Reich et al. 2005, 2013). Understanding the crystal chemistry of arsenian pyrite can help design strategies to control the release of toxic metal(loid)s, explore the enrichment mechanism of valuable metals, and optimize the methods of mining and smelting of metal(loid)s, explore the enrichment mechanism of valuable metals, and optimize the methods of mining and smelting of metal(loid)s. Each S is bonded to 3 Fe ions and a S in the disulfide ion (S\(^{2-}\)) as AsS\(^{2-}\) pairs (e.g., Cook and Chryssoulis 1990; Deditius et al. 2008, 2011; Deditius and Reich 2016; Filimonova et al. 2020; Fleet et al. 1993; Merkulova et al. 2019; Reich et al. 2005; Reich and Becker 2006; Simon et al. 1999a, 1999b). Central to this issue is the nature of As incorporation and its effect on the pyrite structure. The pyrite structure is derived from the NaCl structure with Fe in the Na position in a face-centered array while the Cl ion position is replaced by the disulfide ion, with the orientation of the S-S bond aligned with the body diagonal of the cell, but such that the symmetry is lowered from \(Fm\overline{3}m\) to \(Pm\overline{3}\) (Fig. 1). This results in Fe\(_s\) octahedra with the corners linked by the S\(^{2-}\) ions. Each S is bonded to 3 Fe ions and a S in a tetrahedral arrangement. The Fe-S and S-S bond lengths are 2.262 and 2.177 Å, respectively (Brostigen et al. 1969; Vaughan and Craig 1978). Five Raman active modes (\(A_g+E_g+3T_g\)) are predicated for pyrite based on a group theory analysis of the lattice vibrations, with these modes involving only the movements of the S ions (Mernagh and Trudu 1993; Sourisseau et al. 1991; Vogt et al. 1983). Arsenic can substitute for S in the disulfide ion or Fe in the octahedral site. Fe-S-As (at%) ternary diagram can be used to identify the nature of substitutions of As for either Fe or S for a series of compositional data from a sample; with As\(^{3+}\)-pyrite and As\(^{4+}\)-pyrite trends being parallel to the As-Fe and As-S joins, respectively (Deditius et al. 2008; Liang et al. 2013) (Fig. 2).

A suite of experimental studies that include secondary ionization mass spectrometry (SIMS), electron microprobe analyzer (EMPA), X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) have confirmed that As\(^{5+}\) substitutes for S\(^{2-}\) in the disulfide ion (S\(^{2-}\)) as AsS\(^{2-}\) pairs (e.g., Cook and Chryssoulis 1990; Deditius et al. 2008; Fleet and Mumin 1997; Fleet et al. 1993; Manceau et al. 2020; Reich et al. 2005; Savage et al. 2000; Simon et al. 1999a). In contrast, a few studies have indicated that As can also substitute Fe in pyrite as either As\(^{3+}\) (Deditius et al. 2008) based on the XPS analysis or As\(^{2+}\) (Qian et al. 2013) based on the XPS and XANES analyses. The different valence states of As in arsenian pyrite have been linked to the physiochemical conditions of pyrite formation, with oxidizing and reducing conditions forming As\(^{3+}\)-pyrite and As\(^{4+}\)-pyrite, respectively (Deditius et al. 2008; Kesler et al. 2011). In addition, arsenic is identified as clusters (As\(^{n}\)) in amorphous Fe-As-S nanoparticles (~50 nm in diameter) in pyrite (Deditius et al. 2009).

The anionic As\(^{3+}\) substitution into pyrite causes the breaking of S-S bonds and hence point defects in pyrite (Fleet and Mumin 1997). An expansion of the unit cell of As\(^{4+}\)-pyrite relative to the