The crystal chemistry of Fe-bearing sphalerites: An infrared spectroscopic study

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ABSTRACT

Iron substitution into sphalerite, ZnS, has been studied systematically by infrared spectroscopy. A range of natural and synthetic compositions, \((\text{Zn}_n, \text{Fe}_x)\text{S}\), \(0 \leq x \leq 0.24\), were examined. The IR spectrum of pure ZnS contains a single strong absorption band at 320 cm\(^{-1}\). With addition of FeS, the spectra become broader and shoulders appear. For compositions \(x \geq 9\) mol\% FeS, a splitting of the main peak occurs, and the spectra show two absorption maxima at approximately 300 and 315 cm\(^{-1}\), respectively. The observation of such extra features does not correspond to the usual behavior observed in other ternary mixed crystals, where either one-, two-, or mixed-mode behavior is observed. The spectra can be deconvoluted into up to three peaks, main Peaks A and B at around 300 and 315 cm\(^{-1}\), respectively, and a shoulder at around 330 cm\(^{-1}\) (Peak C). The positions and area of the peaks do not change significantly with increasing Fe content. The peak at 315 cm\(^{-1}\) is the main absorption peak of the host ZnS structure, and the peak at 300 cm\(^{-1}\) is an impurity induced mode. An effective linewidth parameter \(\Delta_{\text{corr}}\) was determined by autocorrelation analysis for each spectrum, but there are no obvious trends in the values of \(\Delta_{\text{corr}}\) that can be interpreted in terms of an inhomogeneous distribution of Fe within the sphalerite structure.

Keywords: Fe-bearing sphalerites, infrared spectroscopy, autocorrelation analysis, solid solution

INTRODUCTION

Sphalerite is not only the most important ore of Zn but is also a major source for other metals, including Cd, In, Ge, and Ga. The latter metals, together with Fe and Mn, are known to substitute for Zn in the sphalerite structure, and to form extensive solid solutions. There have been reports of up to 56 mol\% FeS replacing ZnS (Balabin and Urusov 1995; Pattrick et al. 1998), whereas Cd and Mn substitutions only extend to around 14 and 15 mol\%, respectively (Tauson et al. 1977; Maurel 1978; Pattrick et al. 1998). Sphalerite ores commonly contain up to 24 mol\% Fe, and this is of great importance in ore processing, as the flotation behavior of the mineral changes with iron content. Sphalerite is also of considerable interest as a II-VI semiconductor, largely because of its wide band-gap. It can be tuned through the substitution of Zn by paramagnetic ions such as Fe\(^{2+}\), Mn\(^{2+}\), and Co\(^{2+}\), leading to the formation of dilute magnetic systems (Furdyna 1988; Twardowksi 1990).

The extent as well as the mechanism underlying Fe substitution into sphalerite is therefore of great interest both from the point of view of economic geology and of materials technology (Lepetit et al. 2003; Bente and Doering 1993, 1995; Barton and Toulmin 1966; Barton and Bethke 1987; Di Benedetto et al. 2005a, 2005b). Phase equilibrium studies on the Fe-Zn-S system have thus been of considerable importance and early studies include Kullerud (1953), Barton and Kullerud (1958), and Barton and Toulmin (1966). These authors noted the importance of temperature and S fugacity on the extent of solubility. Lepetit et al. (2003) found that the upper solubility limit of Fe in ZnS at 700 °C ranged from 21 mol\%, for a low sulfur fugacity up to as high as 52 mol\% for a high-sulfur fugacity.

If sphalerite is formed in equilibrium with a suitable buffering mineral assemblage such as pyrrhotite and pyrite, then the Fe content can be used as a geothermometer (Scott 1973; Lusk et al. 1993). Several authors, however, have pointed out that great care must be exercised in using this geobarometer because of compositional and textural readjustments in sulfides (Toulmin et al. 1991; Lepetit et al. 2003).

The nature of the substitution of Fe and other cations for Zn in sphalerite has been probed using a wide variety of techniques. The relationship between the cubic unit-cell edge and Fe content was found to be linear by Skinner et al. (1959), but later workers reported non-linear behavior as a function of Fe content above ~10 mol\%, which has been correlated with variable sulfur fugaci-