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Introduction: Raman spectroscopy and associated imaging techniques are generally non-destructive, and can be used to identify a wide range of minerals and gemstones. It is a vibrational spectroscopy technique and provides information on the molecular vibrational modes of the sample. The volume sampled is generally restricted by the diffraction limit of light, and resolution is limited to about a cubic micron under optimum conditions. Typically spectra are obtained from a sample of five cubic microns or more, depending upon the microscope optics used. The spectra are obtained from the Raman shift measured for the scattered light, which can have a wavelength in the range of UV through to the near Infra-red, for commercial instruments. Glass and water are weak Raman scatterers and spectra from minerals can easily be obtained from samples in air, through glass and / or immersed in water. For materials, which are transparent at the wavelength of the laser being used, confocal measurements can be made to obtain spectra from selected regions inside the mineral sample, thus enabling the characterization of inclusions and artefacts.

We have been investigating the properties of natural sphalerite as a part of an industrially sponsored project. Various sphalerite specimens of known provenance were obtained and these have been investigated using Raman spectroscopy and energy dispersive X-ray (EDX) analysis. Sphalerite is well known for having variable iron and manganese content, which seriously influence the processability of the mineral concentrate. Sphalerite is also an interesting structure for spectroscopic investigation. Stoichiometric sphalerite is cubic close packed in sulfur with half the tetrahedral sites occupied by zinc. It has been suggested that ferric ions occupy octahedral sites in sphalerite [1] whereas it would be expected that species such as ferrous and manganous ions would occupy tetrahedral sites.

Experimental: Raman spectra were obtained using a Renishaw 2000 Raman spectrometer and a 514.5 nm green laser for each sample as received. Small representative pieces of the samples were broken off, set in polyester resin, cut and polished. These specimens were then used for spectroscopy and EDX analysis for the elemental content using the Jeol JXA-840A Electron Probe Analyser.

Results: Raman spectra for sulphide minerals exhibit metal sulphur bands in the region below 500 cm\(^{-1}\). In the case of sphalerite, the main Zn-S band is located near 350 cm\(^{-1}\). The other main region of note in the sphalerite spectrum is that between 600 cm\(^{-1}\) and 700 cm\(^{-1}\) where the S-S vibrations dominate.

In general, low Fe content (below about 2% by weight) sphalerite spectra exhibit bands where expected, though in one case, a shifting of the major Zn-S band occurred and an additional band at 377 cm\(^{-1}\) was observed. This change would not appear to be dependent on the iron as the sample had a low Fe content similar to that of the other sphalerite samples in this group. EDX analysis did not reveal substantial quantities of other elements present in the specimen. The spectral variation could be related to the stoichiometry of specimens, since sphalerite is known to have a variable stoichiometry [2, 3]. We can conclude that the most probable reason for this change was due to differences in the ordering of the atoms within the crystal structure.

Comparison of the high Fe (above 2% by weight) sphalerite spectra with those of the low Fe spectra indicate significant differences, especially in the region between 298 cm\(^{-1}\) and 350 cm\(^{-1}\) where the metal sulphur bands predominate. The intensity of the major Zn-S peak and other bands in this low wavenumber region are reduced and new bands appear in the spectra. The observed increase in intensity of the bands at 298 cm\(^{-1}\) and 330 cm\(^{-1}\) is apparent as the iron content of the sphalerite increases, probably a characteristic of tetrahedral Fe-S coordination. The other major change observed in the Raman spectra with iron content is associated with the suppression of bands in the S-S vibration region of the spectra between 600 cm\(^{-1}\) and 700 cm\(^{-1}\). This decrease, for such low atomic substitution levels, is indicative of the crystal structure nature of the 600 – 700 cm\(^{-1}\) group of Raman bands, and as such the Raman band does not appear to represent simple S-S bond groups.

Conclusion: The Zn-S Raman band for the mineral sphalerite occurs at approximately 350 cm\(^{-1}\) and the position and intensity are sensitive to the extent of iron substitution in the sample. At iron levels above 6% by weight, the 350 cm\(^{-1}\) band is almost completely suppressed. At lower iron contents, this band position shifts to lower wavenumber with reducing iron content. Sharp Raman bands in the region between 600 and 700 wavenumbers are only observed for very low iron sphalerite. Further investigation using a wider selection of well characterized sphalerite samples is proposed.

References: