

WATER TRACES AND CHEMISTRY OF CASSITERITES

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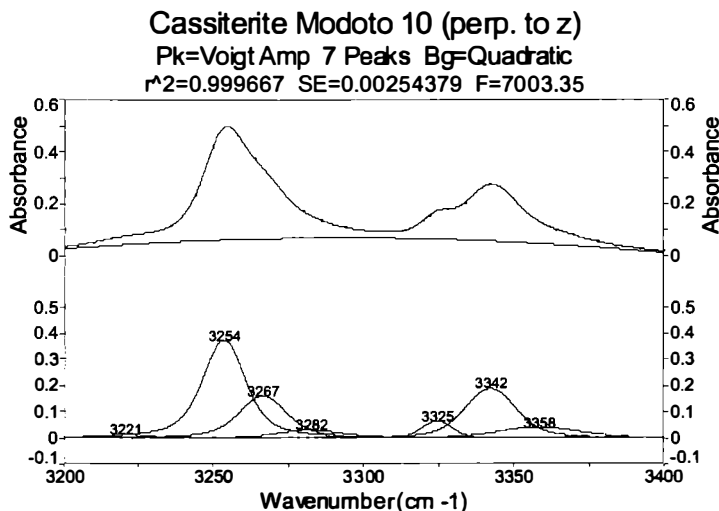
The presence of water (OH groups) in natural cassiterite was originally established by BERAN & ZEMANN [1] on the basis of IR-spectroscopy. Cassiterites are characterized by absorption bands centered in the 3250 and 3350 cm<sup>-1</sup> region.

Our suite of 16 cassiterite samples originate from localities in Czech Republic, Great Britain, Mongolia, Portugal, France, Bolivia, Brazil and Russia. Most of the cassiterites come from greisen (high temperature hydrothermal) deposits (Cínovec, Krupka, Horní Slavkov, Cornwall). A sample from Potosi belongs to the cassiterite-sulphidic deposit of Bolivia type. Cassiterite from Li-pegmatite is represented by a sample from Rožná.

Single-crystal plates cut parallel to the z-axis were used for the IR measurements. Band deconvolution procedure revealed distinct absorption maxima with varying intensities. Generally 2 types of IR absorption spectra were found.

IR spectrum type I is represented by synthetic cassiterites. It is characterized by only one sharp maximum centered at 3255 cm<sup>-1</sup>, with an additional weak band centered at 3265 cm<sup>-1</sup>. Chemically these cassiterites are pure SnO<sub>2</sub>, suggesting that the absorption band at 3255 cm<sup>-1</sup> corresponds to structural OH groups solely coordinated by Sn.

Fig. 1  
Typical polarized IR spectrum type II (E vector perpendicular to z-axis) of a natural cassiterite crystal from Modoto, Mongolia. The result of band deconvolution by the PeakFit 4 program is shown in the lower part of the diagram.



The IR spectrum type II, represented by a natural cassiterite sample from Modoto, shows a very complex absorption pattern with several absorption bands. Most of these bands can also be observed in the spectra of cassiterite samples from other localities. The spectra are characterized by two band groups with maxima centered around 3250 and 3350  $\text{cm}^{-1}$  (Fig. 1). Each band group can be separated in three peaks with different intensities at individual samples:

- The first sharp band maximum at 3254  $\text{cm}^{-1}$  corresponds to that of synthetic cassiterites. An additional band can be observed in the 3219–3224  $\text{cm}^{-1}$  region and a more intense band in the 3265–3270  $\text{cm}^{-1}$  region.
- The second absorption maximum is centered at 3340–3350  $\text{cm}^{-1}$ , two additional bands which are centered at 3324–3327  $\text{cm}^{-1}$  and 3360–3370  $\text{cm}^{-1}$  can be separated.

Most of natural cassiterite crystals, especially from greisens, show under the microscope sharp colour zoning (from colourless over yellow to brown and black-brown with changing intensity). Zoning is often oscillatory, the dark-brown to black zones are typical for marginal parts of the crystals. However, small areas are microscopically homogeneous in colour and were measured by polarized and unpolarized FTIR microspectroscopy. All the measured areas of different colour reveal similar types of absorption spectra (band positions), except the black-brown zone, where the distinct absorption bands differ in intensities.

Extremely strong absorption of the visible light and of the IR-radiation is observed in cassiterite from the Li-pegmatite in Rožná (CZ). Slabs of black-brown colour with a thickness of about 0.5 mm are opaque for visible light, as well as for IR-radiation.

The individual absorption bands of natural cassiterites, especially in the 3320–3370  $\text{cm}^{-1}$  region are probably correlated with OH groups that are coordinated to different trace elements (Ti, Fe, Nb, Ta, W) or cation vacancies. Natural samples are strongly varying in their trace element content. No significant correlation with the striking colour zoning in some of the samples could be observed. Very dark-coloured, nearly opaque cassiterites, rich in Fe, Nb and Ta (several tenths of wt.%) reveal also higher concentrations of OH defects, showing an IR spectrum, characterized by strong absorptions in the 3350  $\text{cm}^{-1}$  region.

Based on the molar OH absorption coefficient for cassiterite, determined to 65 000  $\text{l}\cdot\text{mol}^{-1}\cdot\text{H}_2\text{O}\cdot\text{cm}^{-2}$  by MALDENER ET AL. [2] the calculated analytical water content ranges from about  $2.7\cdot 10^{-4}$  to  $1.9\cdot 10^{-2}$  wt.%. The synthetic samples prepared from melts contain  $\text{H}_2\text{O}$  concentrations of only about  $2.7\text{--}9.5\cdot 10^{-4}$  wt.%. As a general feature samples from hydrothermal occurrences show enhanced  $\text{H}_2\text{O}$  values, ranging from  $3.6\cdot 10^{-3}$  to  $1.9\cdot 10^{-2}$  wt.%.

#### Acknowledgements

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#### References

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