

Influence of surface defects on Raman spectra of ore minerals

Eugen Libowitzky, Andreas Bechtold, Patrick Friesl, Lydia Oberwandling, Markus Wildner
Institut für Mineralogie und Kristallographie, Universität Wien, Austria

Surface defects caused by classical mechanical (e.g. diamond) polishing of ore mineral sections may lead to severe artifacts, such as anomalous optical anisotropy effects in cubic ore minerals (e.g. pyrite, spinels, cuprite), and loss of crystallinity evidenced by back-scattered electron diffraction experiments (Libowitzky, 1994a,b,c). In the present study a number of ore minerals were investigated by confocal micro-Raman spectroscopy to identify possible spectral artifacts from diamond-polished surfaces in comparison to spectra from untreated or carefully alkaline silica-prepared samples.

Experiments were performed on a Renishaw RM1000 confocal micro-Raman system with laser excitation at 488, 514.5, 632.8, 785 nm (~ 20 mW each). Samples consisted of common cubic opaque minerals, i.e. pyrite and related (aurostibite, sperrylite, gersdorffite, cobaltite), cuprite, magnetite, chromite, nickel-skutterudite, pentlandite, fahlore, sphalerite, and in addition some non-cubic samples, i.e. marcasite and related (löllingite, arsenopyrite).

Four observations are characteristic: (1) Untreated samples (natural crystal faces, cleaved or broken surfaces) and samples with a careful alkaline silica polish show Raman spectra with rather sharp, comparably intense and well discernable bands. For example, in pyrite two strong bands appear at 343 and 379 cm^{-1} with narrow peak shapes (FWHM only slightly above the spectral resolution of the Raman system). In contrast, mechanically polished ore mineral samples reveal broadened Raman bands with decreased amplitudes and even shifted band positions. For example, on pyrite (100) faces the two strong bands are shifted to 354 and 388 cm^{-1} and their peak widths are more than doubled (488 nm excitation). (2) Crystal orientation appears important, e.g. the shift on (111) pyrite faces is considerably less than on (100) faces. (3) The effect is more dramatic in Raman spectra excited with the blue laser than in those excited with the (infra)red laser. (4) Artifacts are (almost) absent in case of samples that are not strongly absorbing such as sphalerite, fahlore, spinels, cuprite.

According to the observations above, defects induced by mechanical polishing occur only in a very thin surface layer, probably to a depth of only tens of nm. Therefore, the deformed surface layers cause artifacts preferably in reflected visible light, e.g. anomalous optical anisotropy in ore minerals and distortion of their Raman spectra (blue worse than red). The effect is negligible at longer wavelengths, e.g. in IR reflectance spectra, and in samples with only weak absorption, because in these cases a larger sample depth and consequently a larger sample volume are probed in comparison to the extremely thin surface layers.

It is emphasized that mechanical sample preparation leads to surface defects that may result in spectral artifacts. Hence, quantitative data obtained from Raman spectroscopy may be distorted (e.g. Pačevski et al., 2008), and even sample identification may be hampered.

References:

- Libowitzky E. (1994a), *Physics and Chemistry of Minerals*, 21, 97-103.
- Libowitzky E. (1994b), *European Journal of Mineralogy*, 6, 187-194.
- Libowitzky E. (1994c), *Canadian Mineralogist*, 32, 353-358.
- Pačevski A., Libowitzky E., Živković P., Dimitrijević R., Cvetković L. (2008), *Canadian Mineralogist*, 46, 249-261.