

Crystal-chemical effects of heat treatment on Mg-dominant tourmalines

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We present a detailed study of thermally driven oxidation of Fe in the structure of Mg-dominant tourmaline. High-temperature changes were evidenced using ⁵⁷Fe Mössbauer, infrared, and optical absorption spectroscopy, and electron microprobe. Tourmaline samples were thermally treated in air at temperature of 700, 800 and 900°C.

Heat experiments were performed on the following samples: (1) dravite from Yunnan, China (CHD) forms euhedral brown thick prismatic crystals, with pyramidal faces, 2-3 cm in size; (2) schorlitic-dravite from Rubeho Mts., Tanzania (TSCH) forms black thin prismatic crystals, with pyramidal faces, up to 2 cm long; (3) Cr-bearing fluor-uvite from Mere-lani Hills, Tanzania (TUV) forms anhedral black thick prismatic crystals, with pyramidal faces up to 1,5 cm in size. After the heat treatment, no apparent visual changes were observed.

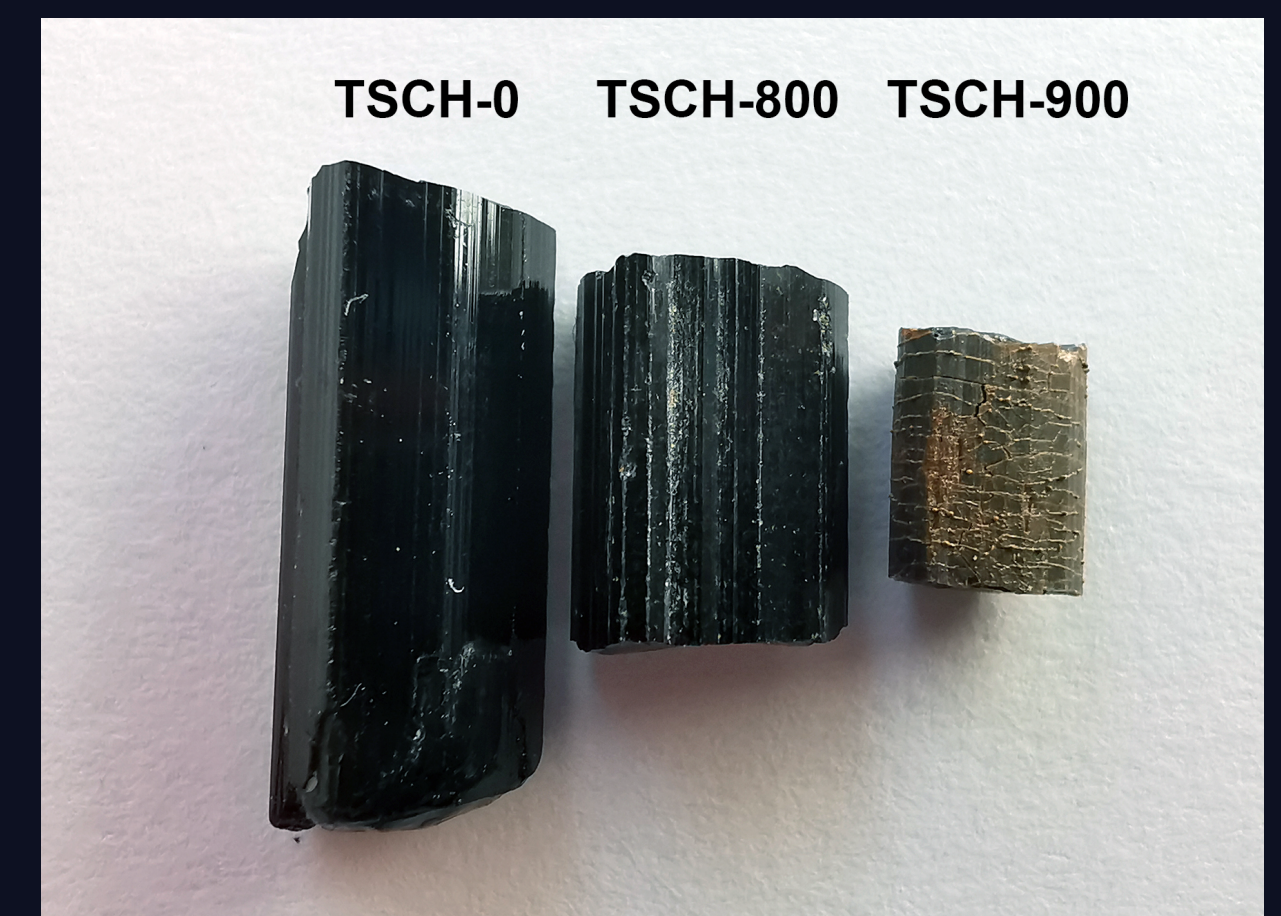
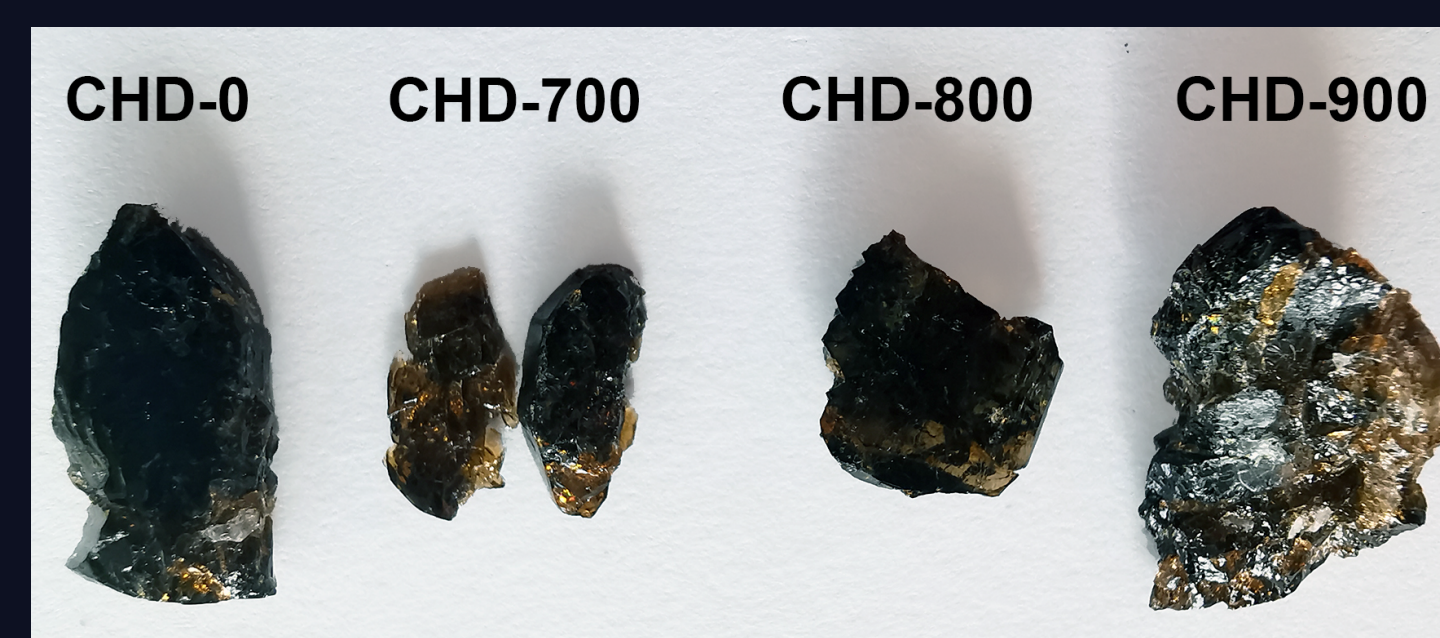
According to their chemical composition analysed by electron microprobe, all samples are Mg dominant, but with variable X_{Mg} (Mg/(Mg+Fe)). The TSCH sample schorlitic dravite from Tanzania with X_{Mg} of 0.5-0.8. CHD sample is Mg-dominant dravite with X_{Mg} > 0.9. The TUV sample Cr-bearing fluor-uvite (up to Cr 0.095 apfu) with X_{Mg} > 0.99.

Mössbauer spectroscopy was planned to use for determination of Fe charge and its changes after the heat treatment but only the TSCH sample had sufficient Fe content for analysis. Tourmaline heated at 700°C did not show any change in Fe oxidation state, but Fe oxidized to trivalent at 800°C and 900°C.

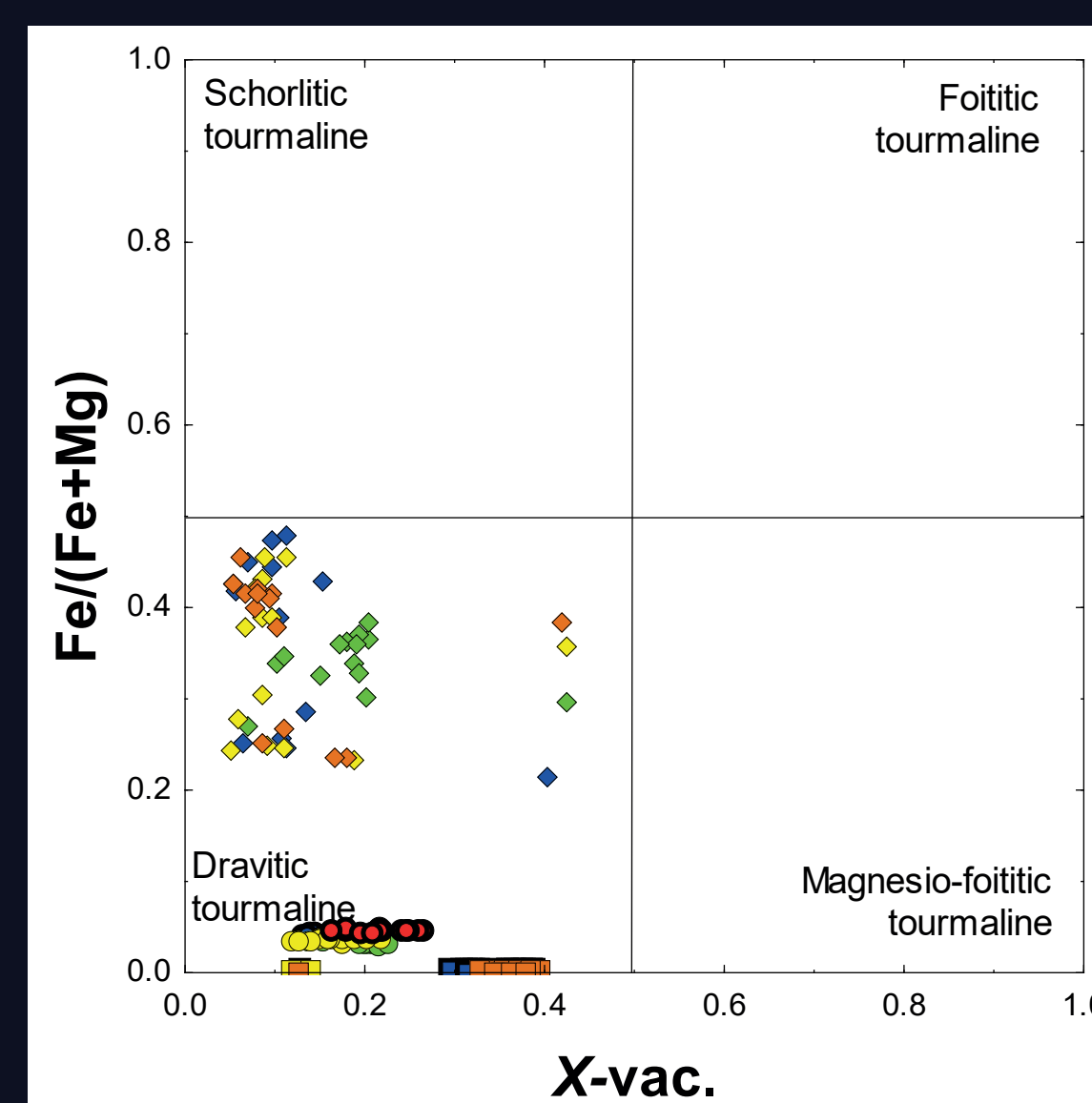
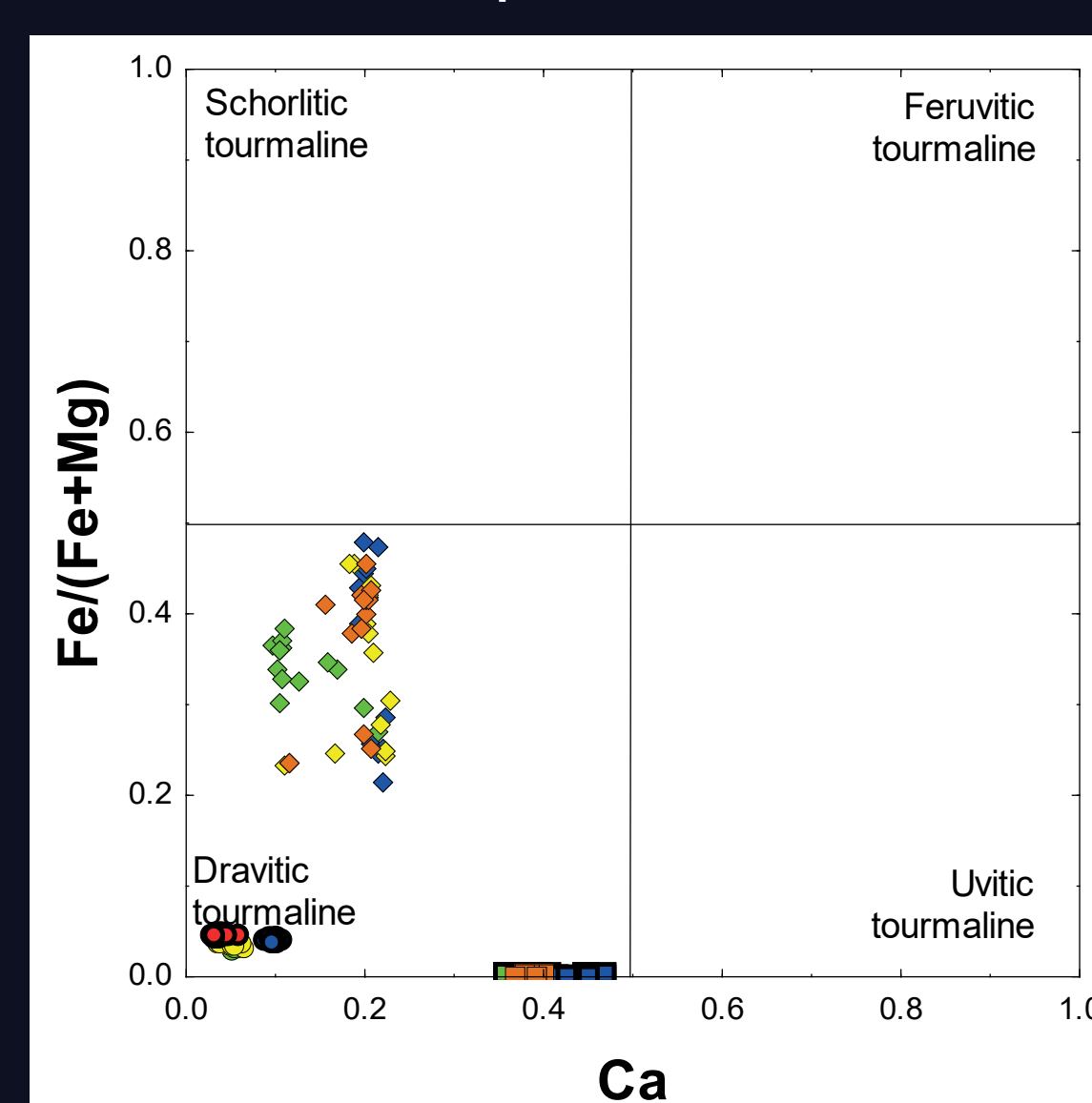
The influence of the possible cation oxidation on the OH groups bonded at the edges of YO₆ octahedra was determined by Raman and FTIR spectroscopy. TSCH and CHD samples show decrease in absorbance of OH bands which indicates deprotonization and Fe oxidation present. TUV sample does not show any significant decrease in absorbance. This suggests that no oxidation could take a place due to a very low Fe, Mn and V content and Cr cannot oxidize at normal atmosphere.

Optical absorption spectroscopy was used to illustrate possible oxidation of the transition metals. In the samples with at least some Fe content – CHD and TSCH – Fe oxidation was indicated by change of absorption bands. However, all changes in the optical spectra happened in the NIR region, therefore, original brown and black colour did not change. Almost Fe-free TUV sample with Cr as dominant chromophore displayed no significant changes in optical spectra.

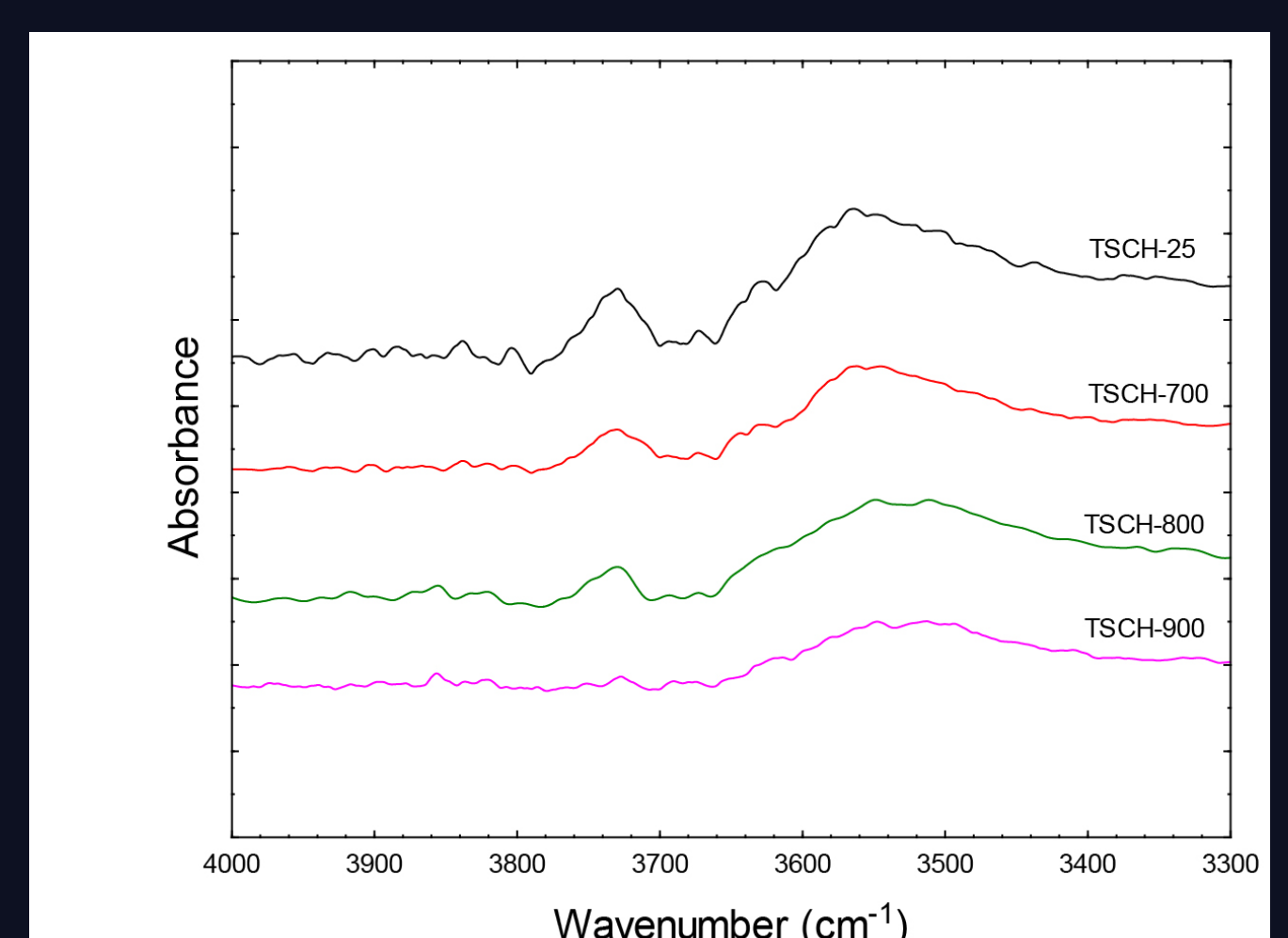
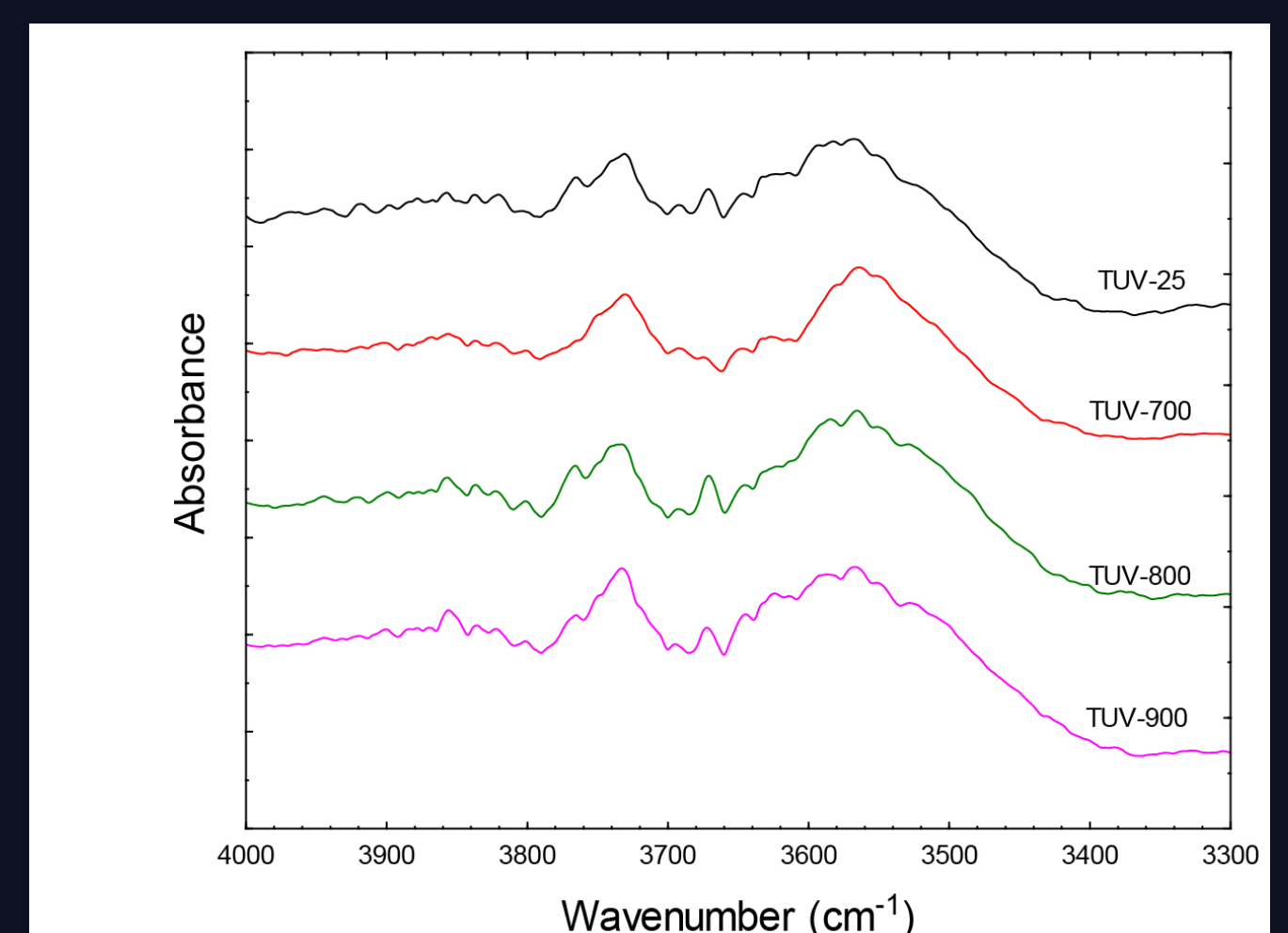
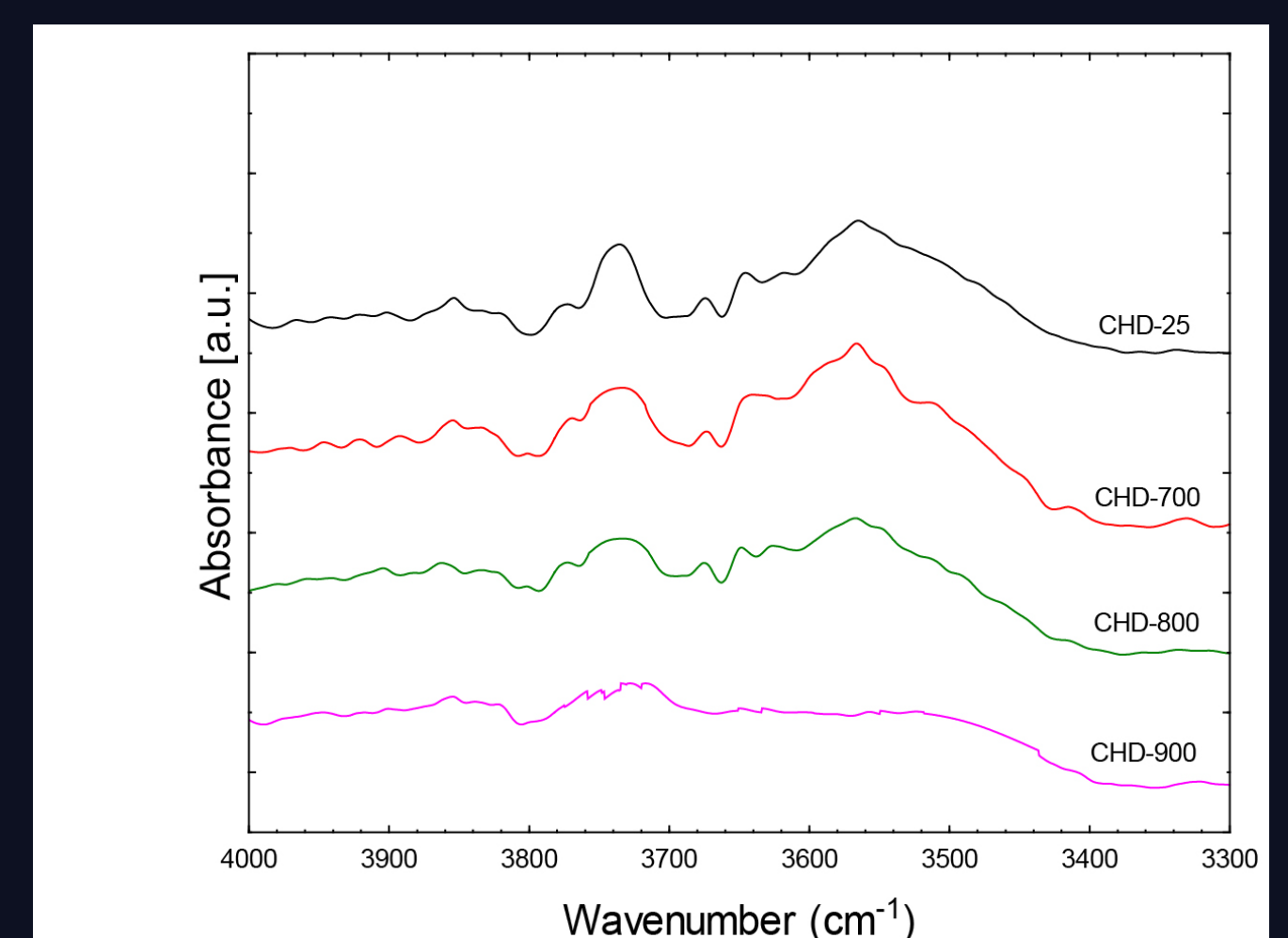
Studied samples



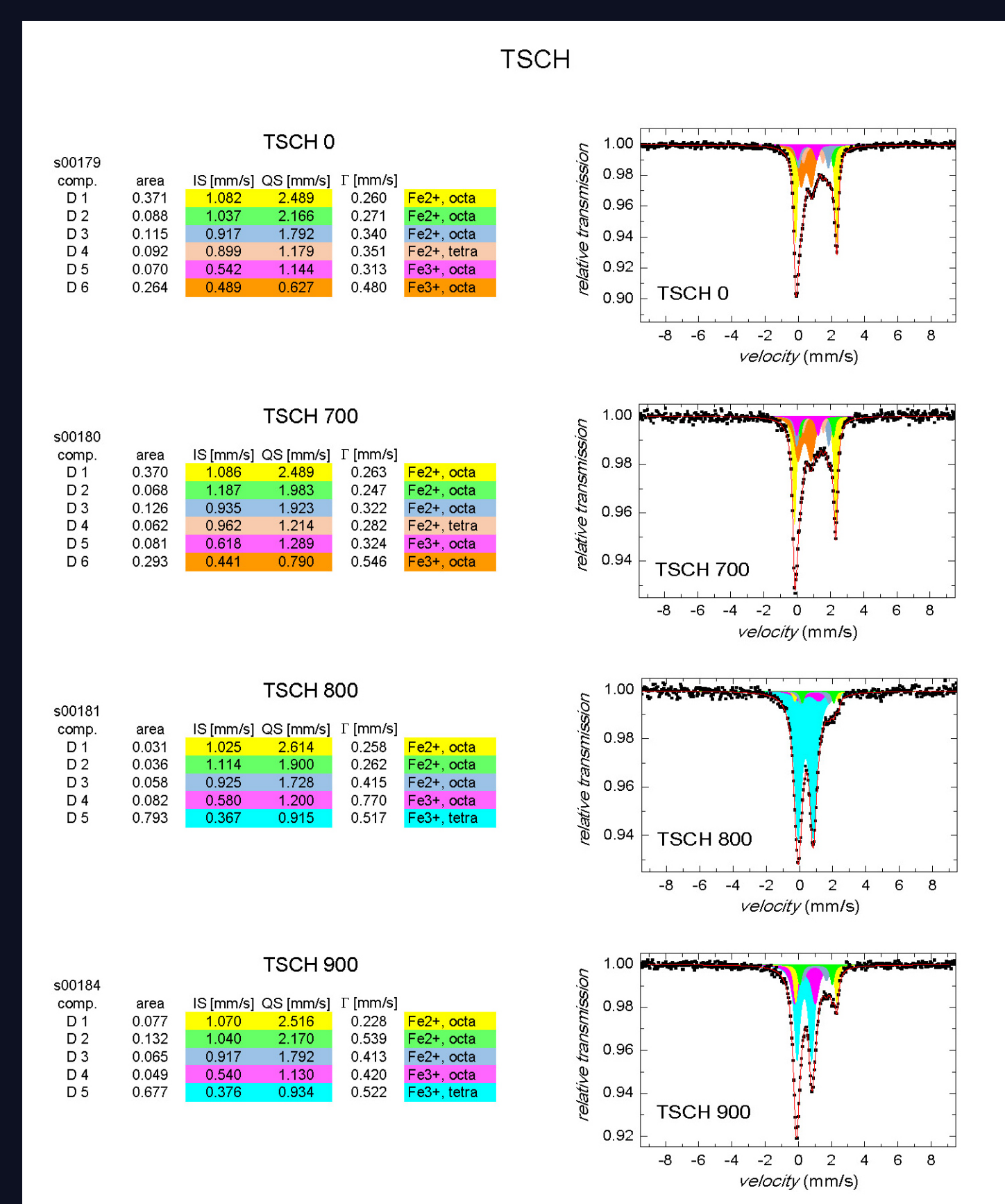
Electron microprobe



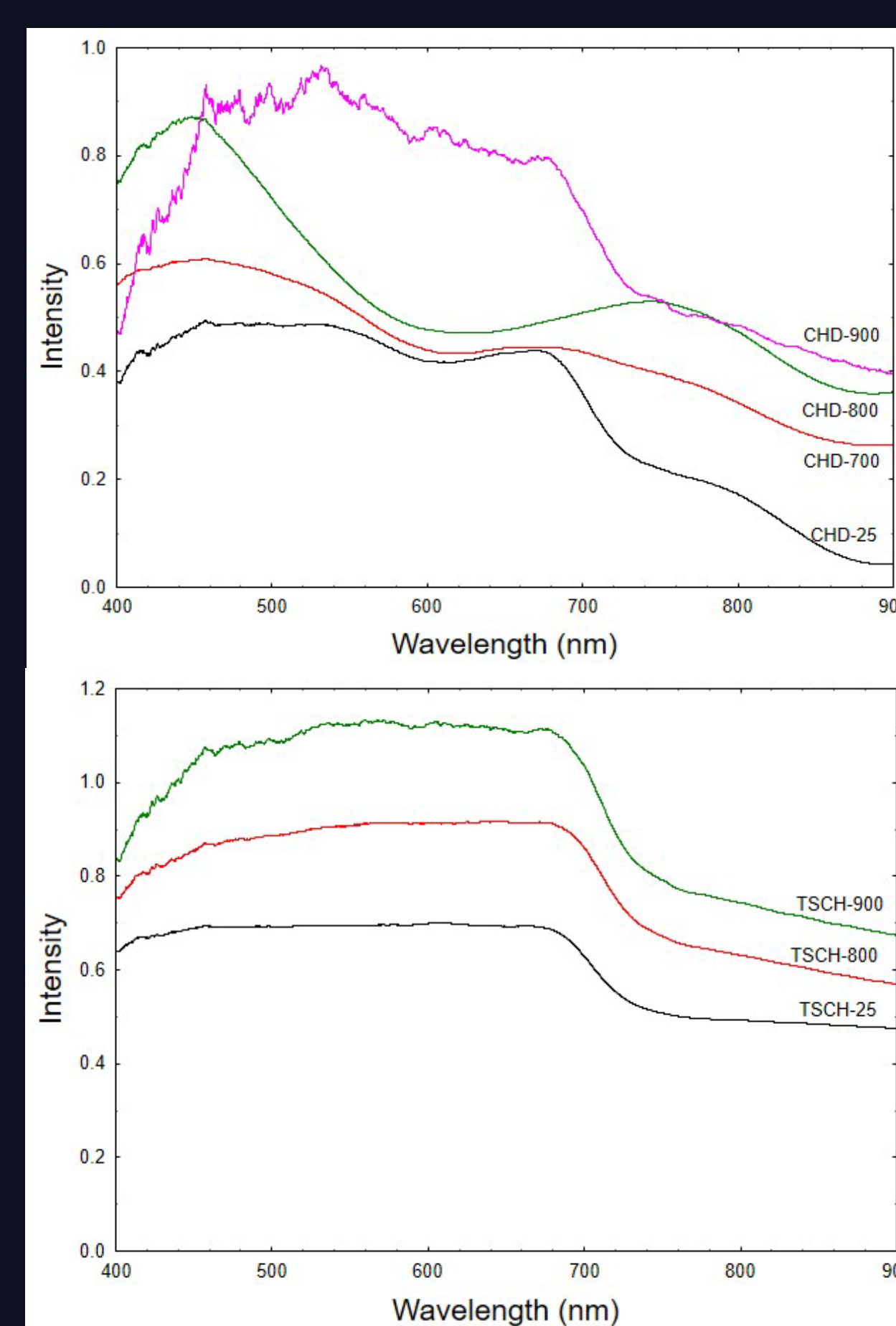
FTIR spectroscopy



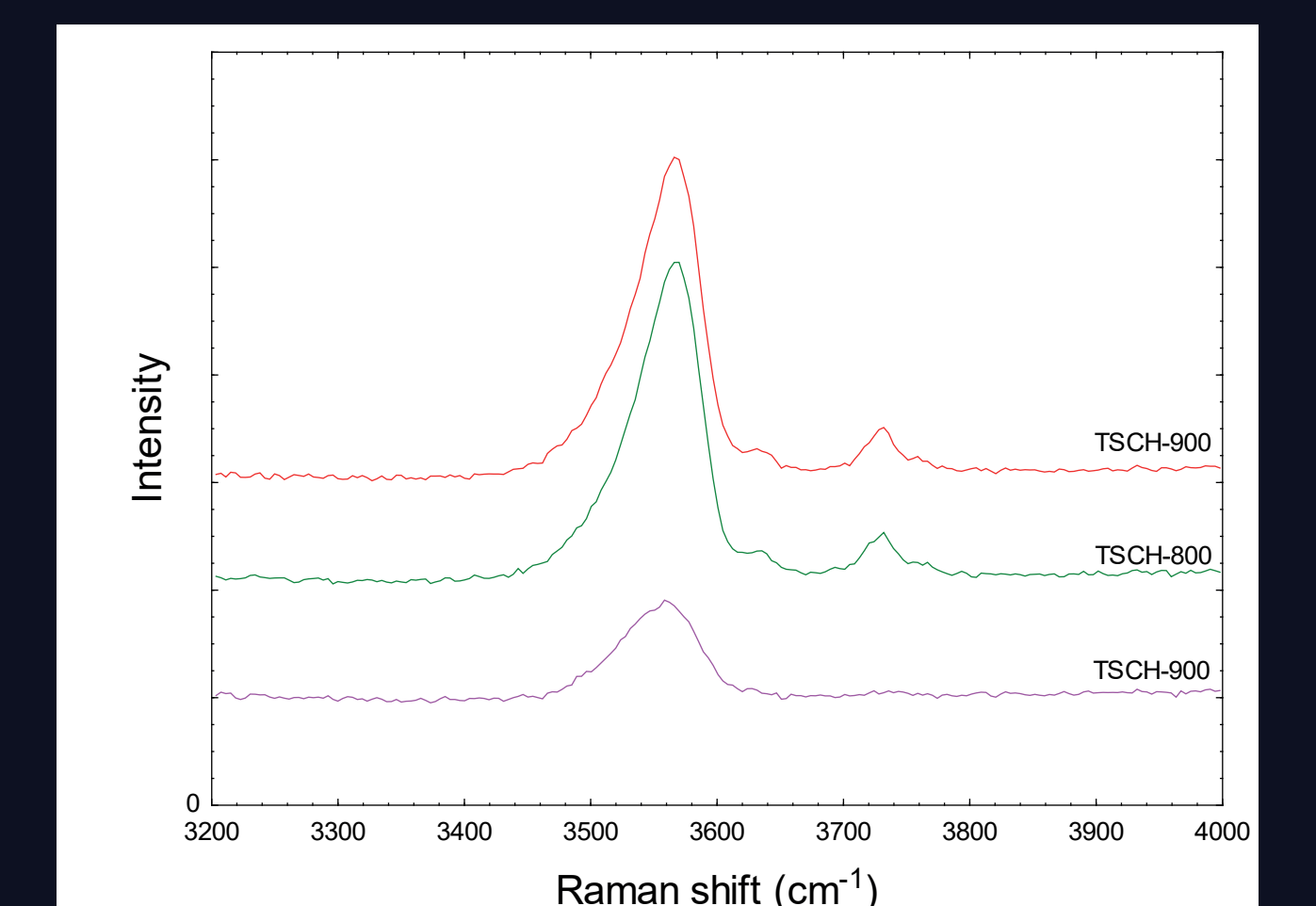
Mössbauer spectroscopy



Optical absorption spectroscopy



Raman spectroscopy



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