Introduction to light spectroscopy: Optical absorption spectroscopy

(1) Generalities

The main aim of optical absorption spectroscopy is to probe electronic transitions between states of different energy. Such transitions can be excited by electromagnetic waves with energies ranging from ~40,000 to 4,000 cm^{-1} (i.e. ~250 to 2,500 nm). This spectral range does not only cover the visible part of the spectrum (VIS) but also the and near infrared (NIR) and ultraviolet (UV). In materials most relevant for geoscientists, the interactions comprise intraelectronic transitions of 3*d* and 4*f* electrons ("crystal field transitions"), interelectronic transitions between closely neighbouring metal ions ("intervalence charge transfer", IVCT) or between cations and their coordinating ligands ("ligand–metal charge transfer", LMCT), transitions of electron or hole point defects ("colour centres") and inter or intra band-gap transitions in (undoped or doped) insulators and semiconductors.

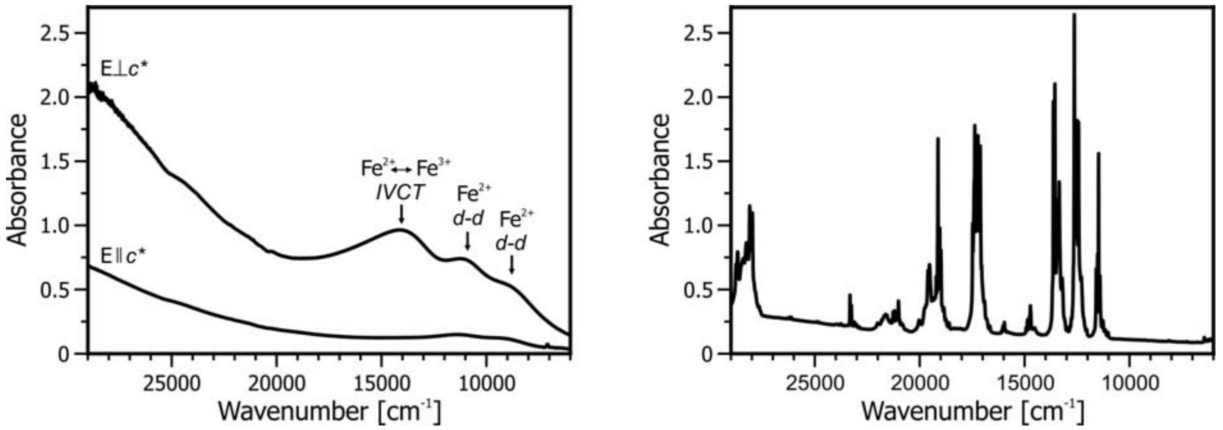

Figure 1: *Examples for optical absorption spectra of minerals. Left, polarised optical absorption spectrum of chlorite* $(\underline{Fe},Mg,Al)_6[(Si,Al)_4O_{10}](OH)_8$*, showing broad absorption bands of* Fe^{2+}*–*Fe^{3+} *intervalence charge transfer and* Fe^{2+} *d-electron crystal field transitions. Right, optical absorption spectrum of synthetic neodymium-doped monazite (*$CePO_4$*:Nd) showing very narrow bands caused by the 4f ion* Nd^{3+}*.*

(2) Sample requirements and measurements

In principle, samples can either be solid, liquid or gaseous (however, the latter two are less often investigated in earth sciences). Measurements can be performed on powdered samples or single crystals in transmitted or reflected light mode. The most comprehensive information can be obtained on appropriately oriented, surficially polished single crystals using polarised light. When using a microscope attached to the spectrometer, sample size can be as small as ~20 µm.

(3) Applications

By using optical absorption spectroscopy, it is possible to investigate the origin of visually perceived colouration and pleochroism. Furthermore, measurements provide qualitative information on the valence state and the coordination number of transition metal ions in measured samples. For example species relevant for earth sciences like Fe^{2+}/Fe^{3+} or Mn^{2+}/Mn^{3+}, which cannot easily be distinguished by other techniques, are characterised by very different absorption features. In some cases, optical absorption spectroscopy can prove the presence of very small amounts of "impurity" ions: It is – for example – possible to deduce the presence of nonformular Fe^{3+} in a number of Mg/Fe^{2+}-minerals by observing typical Fe^{2+}–Fe^{3+} IVCT bands. In this case, polarised spectra may even provide information on the location of the ions. A quantitative treatment of spectra is able to provide crystal chemical information of the local environment of absorbing species: e.g. coordination number, site symmetry, interatomic distances, electronic structure and bonding character.

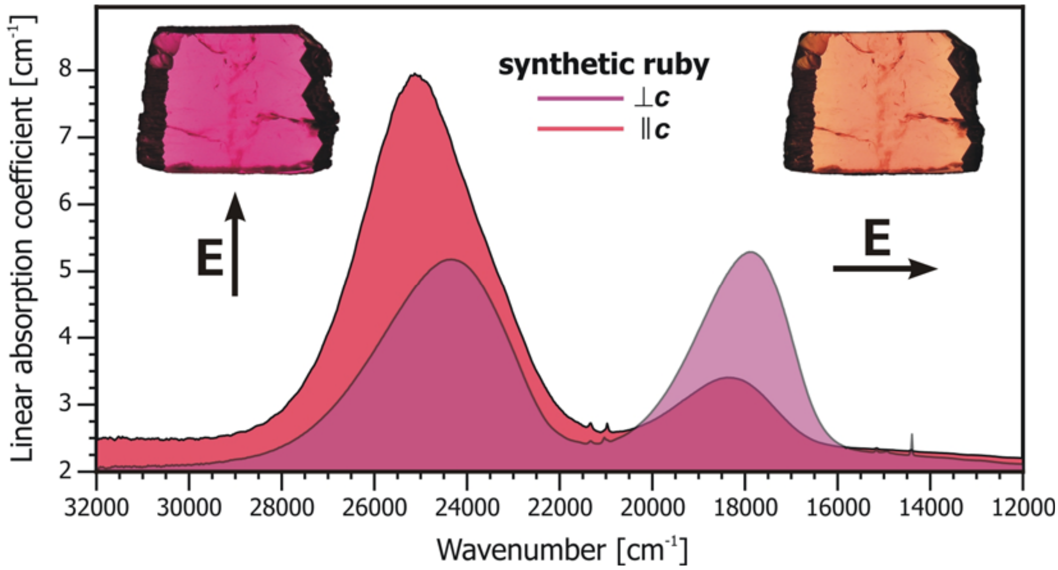

Figure 2: *By recording polarised optical absorption spectra, the pleochroism of synthetic ruby (Al_2O_3:Cr) can be explained by the orientational dependence of Cr^{3+} crystal field band intensities (modified from Wildner et al., 2004).*

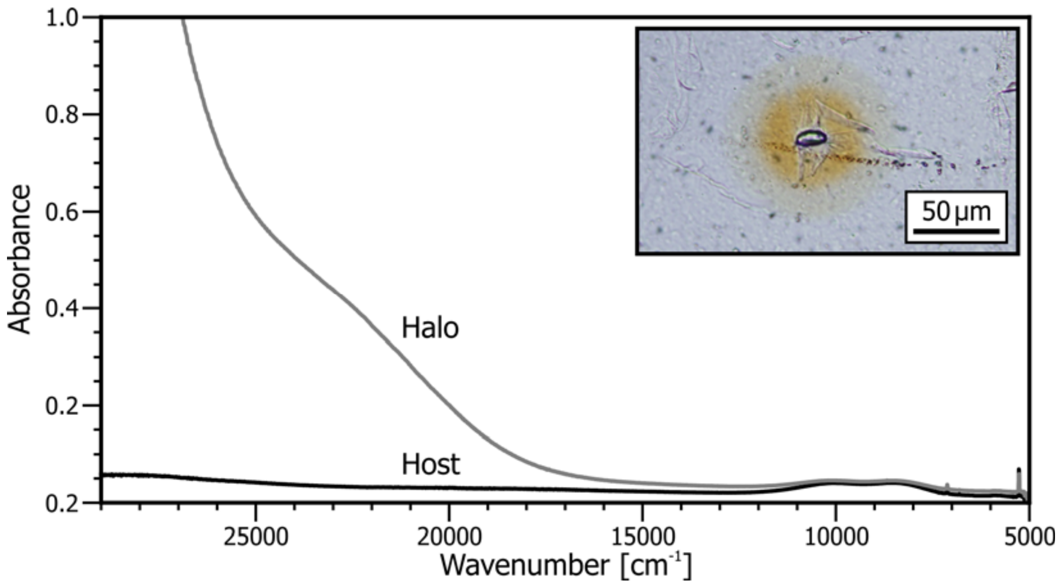

Figure 3: *Polarised (E//c) optical absorption spectra of a radiohalo in cordierite from Madagascar reveal that the changed colour is caused by a strong increase of absorption of high energy light (most probably due to colour centres).*

Recommended literature for further reading:

Burns, R.G. (1993): Mineralogical applications of crystal field theory. Cambridge University Press, Cambridge, 551 p.

Lehmann, G. (1978): Farben von Mineralen und ihre Ursachen. *Fortschritte der Mineralogie*, **56**, 172-252.

Lever, A.B.P. (1984): Inorganic electronic spectroscopy. 864 p., Elsevier, Amsterdam u.a.

Wildner, M., Andrut, M. and Rudowicz, C.Z. (2004): Optical absorption spectroscopy in geosciences. Part I: Basic concepts od crystal field theory. In: Spectroscopic methods in mineralogy (Beran, A. and Libowitzky, E., eds.), EMU Notes in Mineralogy, 6, European Mineralogical Union, pp. 93–143.