Introduction to light spectroscopy: Luminescence

(1) Generalities

The term *luminescence* (originally "luminescence glow") is derived from *lumen* (Latin for light). It describes the ability of minerals and other matter to emit light after being excited with various kinds of energy. This ability is controlled by multiple electronic transitions, whose energy lie in the range of tenth to a few electron volts. Widely simplified, energy input may transform a lattice ion with un-filled electron shells to an excited state, by passing an electron to an energetically higher level. The excited state will eventually decay (with decay times τ ranging from $<10^{-8}$ s to several hours and more). The return of ions from the excited state to the ground state may involve non-radiative transitions (e.g., absorption or emission of lattice vibrations, i.e., phonons) as well as radiative transitions (in particular the emission of light photons). The excitation – (energetic transformation) – emission process, which eventually results in luminescence, is reversible and normally does not cause permanent changes or damage to a mineral sample. Luminescence techniques are therefore (for the most part) non-destructive.

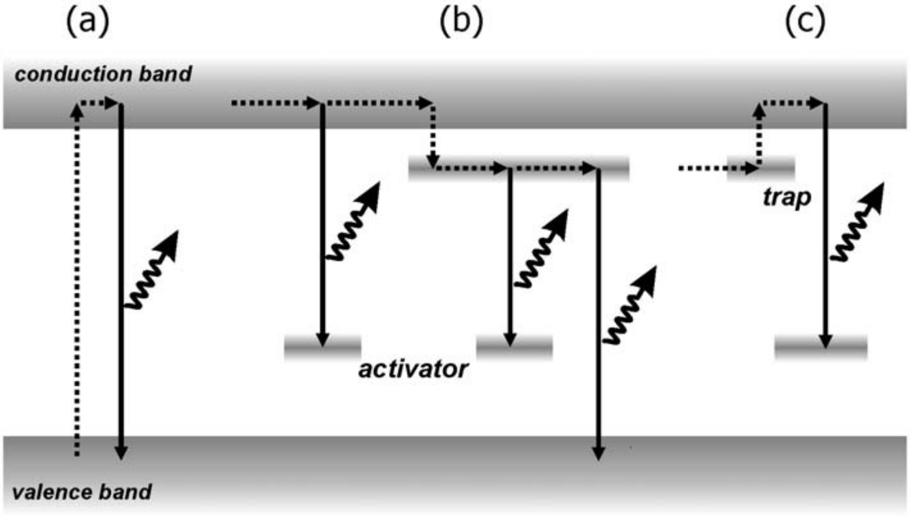

Figure 1: *Simplified sketch of the electronic band structure of an insulator crystal, showing the processes of excitation (dotted), non-radiative energy transfer (dotted), and generation of luminescence (solid, bold).* ***(a)*** *Band-band transition (often referred to as intrinsic luminescence).* ***(b)*** *Various transitions involving electronic levels (so-called activators) within the forbidden band gap.* ***(c)*** *Afterglow luminescence: Stimulated release of an electron from a trap to the conduction band, followed by emissive recombination with an activator. After Krbetschek et al. (1997) and Nasdala et al. (2003), modified.*

There exist several types of luminescence, which are usually classified according to (i) the kinetics of the excitation-emission succession and (ii) the type of excitation. First, to emphasise the fast or slow response of a solid to the energetic excitation, luminescence is subdivided, with a rather arbitrary boundary in between, into *fluorescence* (more or less immediate decay of the excited state; named after the mineral fluorite, CaF_2) and *phosphorescence* (slow decay; named after the white phosphorus). There exists a third, rather rare sub-group, the so-called *afterglow*, which describes emissions after the release of electrons that were trapped elsewhere. The more common differentiation of luminescence types according to the type of the excitation includes *photoluminescence* (PL; light emission of minerals after being irradiated with light photons), *cathodoluminescence* (CL; excited by electrons), X-ray luminescence, triboluminescence (excited by mechanical energy), *chemoluminescence*, and many others. To avoid any confusion, it should be noted that terms such as *thermoluminescence* (TL) and *optically stimulated luminescence* (OSL) do not describe the type of excitation but belong to afterglow-type radioluminescence (excitation by natural irradiation, stimulation of trapped electrons by heating or light).

(2) Interpretation of spectra; applications

The luminescence signal emitted from minerals is in most cases quite complex; it usually consists of several, overlapping bands. Spectral parameters of these bands may provide valuable information on the emitting material and in particular its electron band structure. Emission spectra are, among other factors, controlled by the type of excitation, the excitation energy, and the excited sample volume. There may, therefore, exist widely different luminescence spectra for one and the same sample. Also, intensities of luminescence bands is not necessarily related to the number / concentration of emission centres. The observed intensity may, for instance, be modified appreciably by *sensitising* and *quenching*. Sensitised luminescence summarises emissions that were indirectly excited through different kinds of energy transfer from other ions (so-called sensitisers) to the activator (Marfunin, 1979). *Quenching* (luminescence decay) describes the decrease of the intensity of the emitted light due to simultaneously occurring non-radiative energy transfer processes. There are various quenching processes, including concentration quenching (self quenching; see Fig. 3), quenching by ions with intense charge transfer bands, quenching due to lattice defects, and thermal quenching.

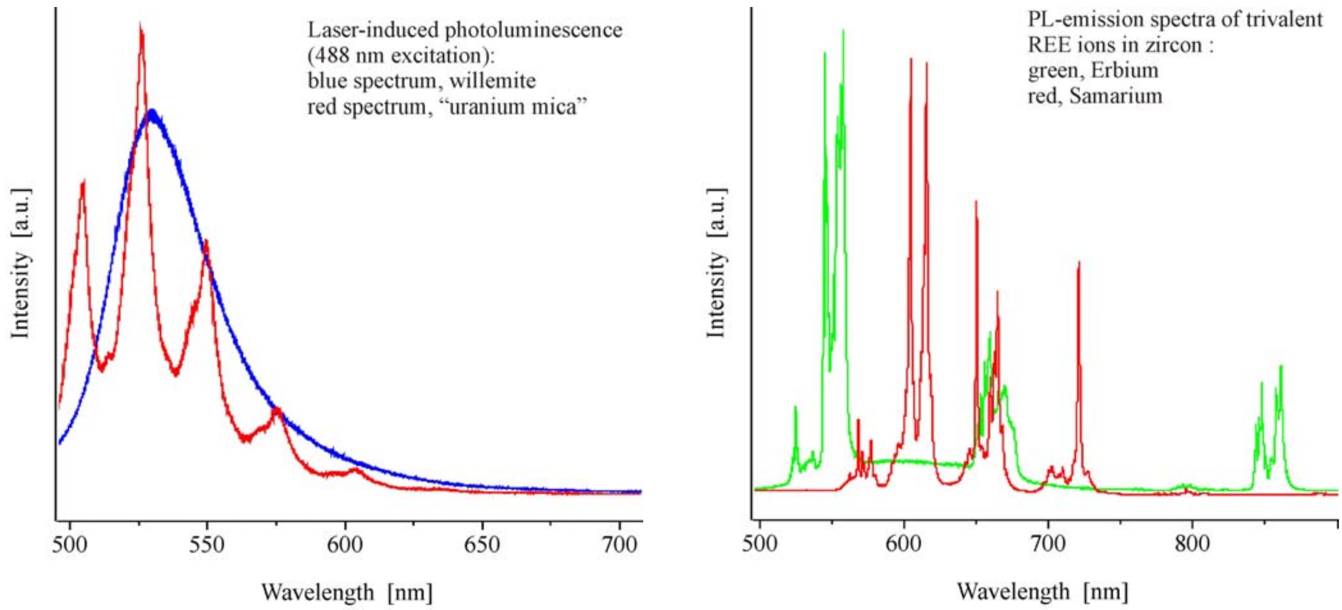

Figure 2: *Examples for luminescence emission spectra of minerals. Left, broad-band emission of* Mn^{2+} *in willemite,* Zn_2SiO_4*, and* $(UO_2)^{2+}$ *in autunite. Right, groups of narrow emission bands (resulting from crystal-field splitting) of two rare earth element centres in zircon,* $ZrSiO_4$*.*

Luminescence techniques have become most powerful for various kinds of studies in the Earth sciences. First, luminescence spectra allow the rapid, non-destructive identification of minerals. They are also most sensitive tools to study trace element-related centres, especially ions with *3d* (as for instance Mn^{2+} in carbonates or Cr^{3+} in various coloured gemstones) or *4f* electronic structure (for instance REEs in accessory minerals, see Fig. 2). Spectral parameters do not only include information on the ionic species and its concentration but also on valence state and occupied crystallographic site. Finally, luminescence spectra have been shown to be most sensitive to order-disorder phenomena, which is for instance used to study amorphization and recrystallization processes, such as metamictization or devitrification of nuclear waste glasses.

In addition to single analyses, the luminescence emission is often used to generate images or colour-coded maps (see "hyperspectral imaging" or mapping in more recent publications). Data processing to generate maps includes the advantage of spectral treatment (the lateral distribution of virtually any spectral parameter can be studied) whereas direct images have the advantage of being obtained in short times. Both techniques are successfully applied to study internal textures of minerals.

Applications cover virtually all fields of the Earth sciences, ranging from gemmology and art history over petrology (reconstruction of milieu conditions during growth and alteration), geochemistry, and technical applications such as mineral sorting or evaluation of synthetic growth products. The afterglow-type luminescence techniques are increasingly used to date sediments or artefacts. For a detailed list of applications see the literature references below. Most of these applications use the special advantages of the technique, which include the ability to analyze samples non-destructively on and mostly without the need for special sample preparation, on a micron-scale.

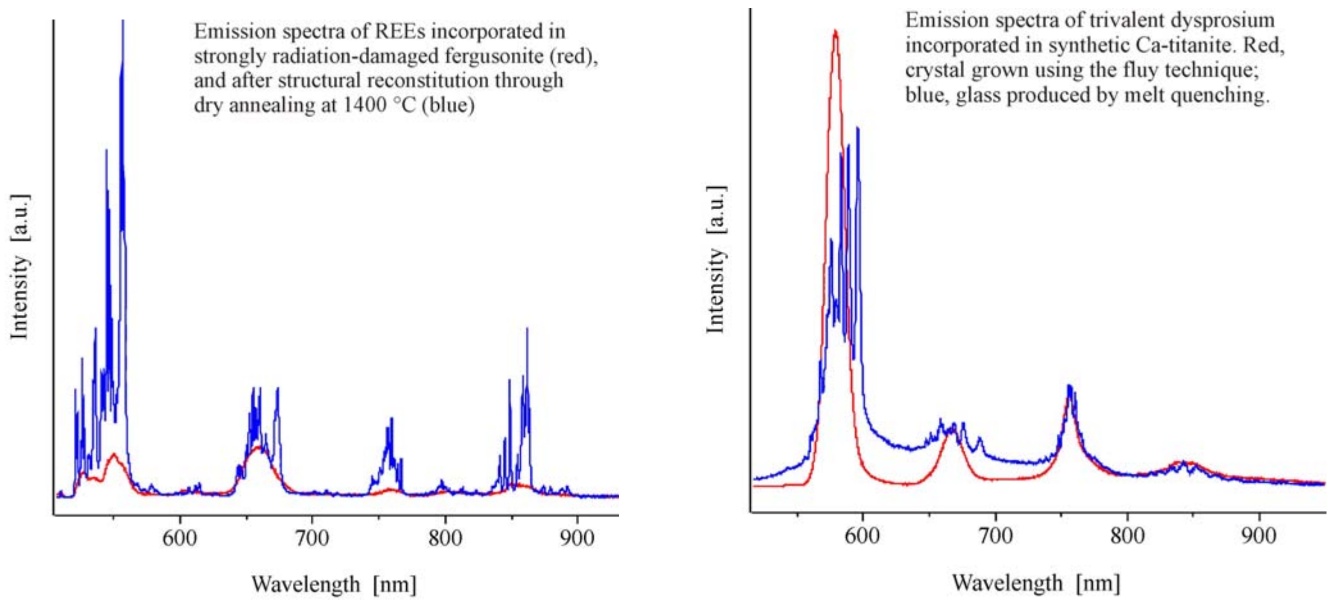

Figure 3: *Two examples for strong crystal field effects on emission centres. Left, radiation-damaged and recrystallized fergusonite (see Ruschel et al., 2008); right, crystalline and glassy titanite. In both cases it can be seen that the crystal-field splitting of transitions is lost if the REEs are incorporated in an amorphous host. Here, transitions are observed as broad bands (red spectra) whereas their counterparts in spectra of the crystalline analogs show a fine structure that is sensitive to the host lattice.*

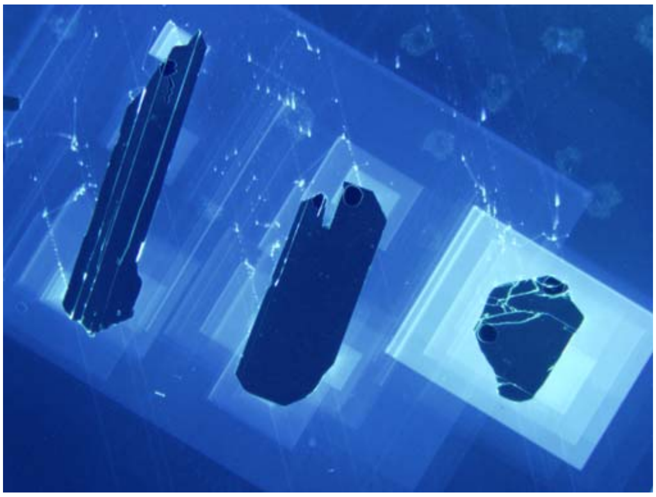

Figure 4: *Luminescence image of an araldite epoxy mount with embedded $CePO_4$ crystals, after imaging in a scanning electron microscope. Surficial electron beam damage of the epoxy has resulted in an increase of the defect luminescence; scanned areas are therefore seen as bright rectangles.*

Literature:

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