Luminescence- and reflection spectroscopy for automatic classification of various minerals

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Abstract Fundamental studies for sensor based sorting on several industrially relevant minerals and a lead containing glass sample are presented. The examined minerals were: Talc, Magnesite, Calcite, Fluorite, Scheelite and Chalcedony. The methods of investigation were UV-VIS-NIR reflection spectrometry between 200 - 2500 nm and UV induced solid state fluorescence measurements with excitation between 200 - 380 nm and emission detection between 400 - 900 nm. A common quenching mechanism for UV-induced fluorescence is discussed. Artefacts and sources of error for solid state luminescence measurements are mentioned.

1 Introduction

Sensor based sorting is a growing area of beneficiation of secondary and primary resources. There are several optical properties that can be used to obtain discriminators for different material classes [1]. An overview was given in literature and is reproduced in Table 1.1. This contribution will only cover UV-VIS-NIR reflection spectroscopy and UV excited fluorescence of minerals and glasses. Those two types of spectra often show features, which can be used for sorting purposes. UV-induced fluorescence is an optical property, which is not so well established for optical sorting until now. However, light induced fluorescence in minerals is known since the time of the ancient Greek philosophers. The first

records of mineral fluorescence go back to writings by Herodotus, Aristotle, Theophrastus, Strabo and Pliny. It was defined as a glow of non-thermal origin. A. Magnus described the thermoluminescence of heated diamond in 1280. From 17th to 19th century many observations on natural phosphors were made. First scientific contributions to luminescence were made by G. Stokes (1852), E. Becquerel (1859) and E. Wiedeman (1888) who proposed the term "luminescence" and gave a definition [2]. The most important contributions on mineral fluorescence in 20th and 21th century were made by Marfunin [3, 4], Gorobets and Rogojine [5] and Gaft et al [6]. A good introduction to the field of luminescent inorganic materials is provided from Jüstel et al [7]. First results in the area of mineral sorting via UV induced fluorescence were published last year in the framework of a cooperation of the R & D department of Binder + Co, Austria, the Chair of Mineral Processing at the Montanuniversität Leoben, Austria, and the Institute of Physical and Theoretical Chemistry at the Graz University of Technology, Austria [8]. The sorting of lead containing glasses by UV induced fluorescence is a process which is already established by Binder + Co since a few years and the fundamental processes are well understood [9]. In general UV-VIS reflection spectra of solids consist of electronic transitions of transition- and rare-earth metal ions having unfilled d- and f-electronic shells, respectively, and can be interpreted using quantum mechanical models like ligand field theory, Tanabe-Sugano and configuration coordinate diagrams [10]. These electronic transitions occur between 200 and 800 nm. In the NIR range between 800 and 2500 nm combinations and overtones of fundamental vibrations of functional groups in minerals can be observed and are interpreted using the harmonic oscillator model. Slight deviations between calculated and observed energies for these overtones are expected because of the anharmonicity of the vibrations. Energies for the fundamental vibrations used to calculate of overtones and combinations can be found in the literature [11]. For the interpretation of solid state luminescence an understanding of the luminescence mechanisms is required. For a radiative transition an electron has to be in an excited state, from which it relaxes to its ground state under emission of a photon. Phosphors consist of a crystalline host lattice or a supercooled melt (for glasses). A host lattice always carries defects and impurity ions. These defects are highly important for luminescent processes. Non-radiative vibrational transitions, which only generate heat

Table 21.1: Optical properties used for mineral sorting [1].

Radiation	Sensor Technology	Material property	Sorter application
Gamma-radiation	radiometry	natural gamma radiation	radioactive ores
X-Ray	XRT (X-ray transmission)	atomic density	base and heavy metal ores, precious metal ores, industrial minerals, coal, diamonds, scrap metals
X-Ray	XRF (R-ray fluorescence)	visible fluorescence under X-rays	diamonds
UV-VIS	Color (CCD color camera)	reflection, absorption, transmission	base metal ores, precious metal ores, industrial minerals, diamonds, glass
VIS-NIR	Photometry	monochromatic reflection, absorption	base metal ores, industrial minerals, plastic, paper, cardboard
NIR	NIR-sensors (semiconductors)	reflection, absorption	base metal ores, industrial minerals, plastic, paper, cardboard
IR	Infrared cameras	heat conductivity, heat dissipation	base metal sulfide ores, precious metal ores, industrial minerals, graphite, coal
Radio waves and AC	Electromagnetic sensor	conductivity, permeability	base metal sulfide ores, scrap metals

UV = ultraviolett; VIS = visible light; NIR = near infrared light, IR = infrared, AC = alternating current

instead of light, are competing with radiative transitions. Luminescence processes are subdivided according to the life time of the excited state. The threshold is 10^{-8} s to distinguish between short-time fluorescence and long-time phosphorescence.

A systematization of luminescent minerals was made by Gorobets and Rogojine in 2001, it provides a system of hierarchical order in three levels, which allows predictions of luminescence centers in minerals with known formula and structure [5]. A luminescent mineral has to satisfy the following three conditions [12]:

1. A suitable type of crystal lattice favorable for emission centers is formed.
2. The content of photoluminescent centers is high enough (usually $> 0,01$ w%)
3. The amount of iron or other quenchers is small enough (around $0,5 - 1$ w%). Iron is a principal quenching element in nature.

A subdivision of luminescence into five types is possible: **1) Center luminescence** is generated by an optical center, e.g., a transition metal ion like Mn^{2+}, a rare-earth ion like Eu^{2+} or a s^2-ion like Pb^{2+}. **2) Charge-Transfer luminescence** where a transition takes place between electronic states of different ions, e.g., in WO_4^{2-}, MoO_4^{2-}, VO_4^{2-} ,, NbO_4^{2-} and TaO_4^{2-}. **3) Luminescence involving impurity levels** for semiconductors with certain dopants e.g. Mg^{2+} or Si^{4+} in GaN or defects. **4) Persistent luminescence**, where energy is stored in the host lattice by trapping free charge carriers. **5) Sensitization of Luminescent Centers** where an energy transfer from a non-luminescent ion to an activator takes place [7].

From a technologists point of view the features in a reflection spectrum are simply the sum of all possible features of the materials components. For luminescence spectra, however, more effects concerning the composition and interactions of components are possible. Notably, concentration quenching, inner filtering and energy transfer can occur. Concentration quenching means that, e.g., for a lead containing glass the luminescence intensity increases with the lead content up to a certain concentration and decreases again for higher lead concentrations. Fortunately those samples can be detected by their UV-cut off or reflection properties. The UV cut-off process is implemented in glass sorting systems by Binder + Co [13].

2 Experimental setup

2.1 Sample preparation

All samples were cut with a cutting machine (Einhell, BT-TC 600 Blue) mounted with a diamond circular saw (Baier's Enkel, cutting wheel F2). Then the samples were wet polished with diamond abrasive paper. The examined powders were used as received from the supplier. Powder samples were measured in the powder sample holder with a Quartz-glass window provided from Perkin Elmer.

2.2 Reflection measurements

The reflection measurements were carried out using a Lambda 950 Reflection spectrometer from Perkin Elmer. A 150 mm integrating spectralon-sphere with a double detector system (photomultiplier tube and an InGaAs-semiconductor detector) was used. Data recording was made using the UV-WinLab Software from Perkin Elmer. Automatic spectralon correction was performed by the software.

2.3 Luminescence measurements

The luminescence measurements were carried out using a LS 55 luminescence spectrometer from Perkin Elmer mounted with a red sensitive photomultiplier tube R955 from Hamamatsu. All samples were clamped into the measurement chamber with the original solid sample holder from Perkin Elmer.

All spectra were recorded with the BL-Studio from Biolight. All spectra were automatically excitation corrected via the internal Rhodamin6G standard. The spectra were not corrected for detector sensitivity and can be regarded as technical spectra.

3 Results and discussion

3.1 Reflection measurements

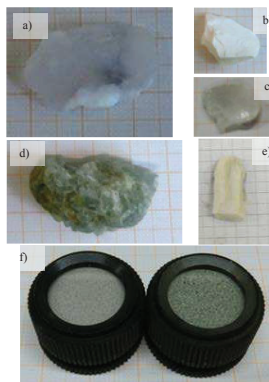The examined sample set is depicted in Fig. 21.1.

Figure 21.1: Sample set for reflection measurements: a) Chalcedony, b) Magnesite, c) Calcite, d) Fluorite, e) Talc, f) Scheelite ore, g) Scheelite tailings [14].

The reflection spectra of Talc, Calcite, Fluorite and Magnesite are given together with the assignment of their spectral features as representative examples (see Fig. 21.2). For sorting applications the setting of discriminators is desired. The absolute reflectance of the mineral samples depends strongly on the positioning, surface condition, etc. To get rid of such artefacts the first and second derivatives can be calculated and compared.

The original data and the derivatives are shown in Fig. 21.3. The data depicted in Fig. 21.3 allow decisions about proper optical configurations of sensor based sorters. It is not only necessary to find spectral features, which allow the distinguishing of several mineral classes. It is also of interest to increase recognition efficiency and speed, which is often achieved by sensor fusion. This means that several recognition systems are linked together, e.g., shape analysis via CCD and NIR-sensors. Economic reasons and sensor-stability make detection systems in the VIS-range more desirable then NIR systems.
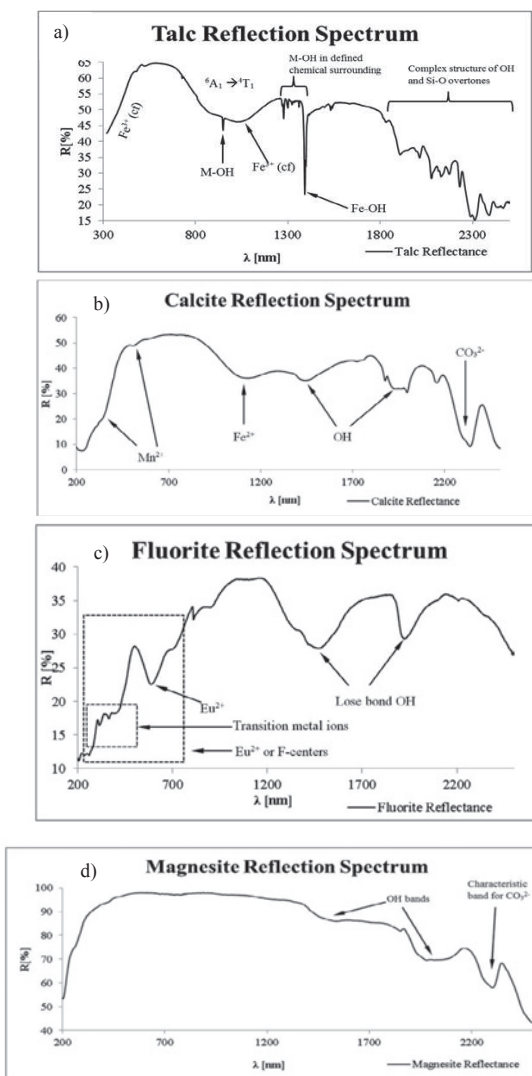
Figure 21.2: Interpretation of reflection spectra for a) Talc, b) Calcite, c) Fluorite, d) Magnesite [14].
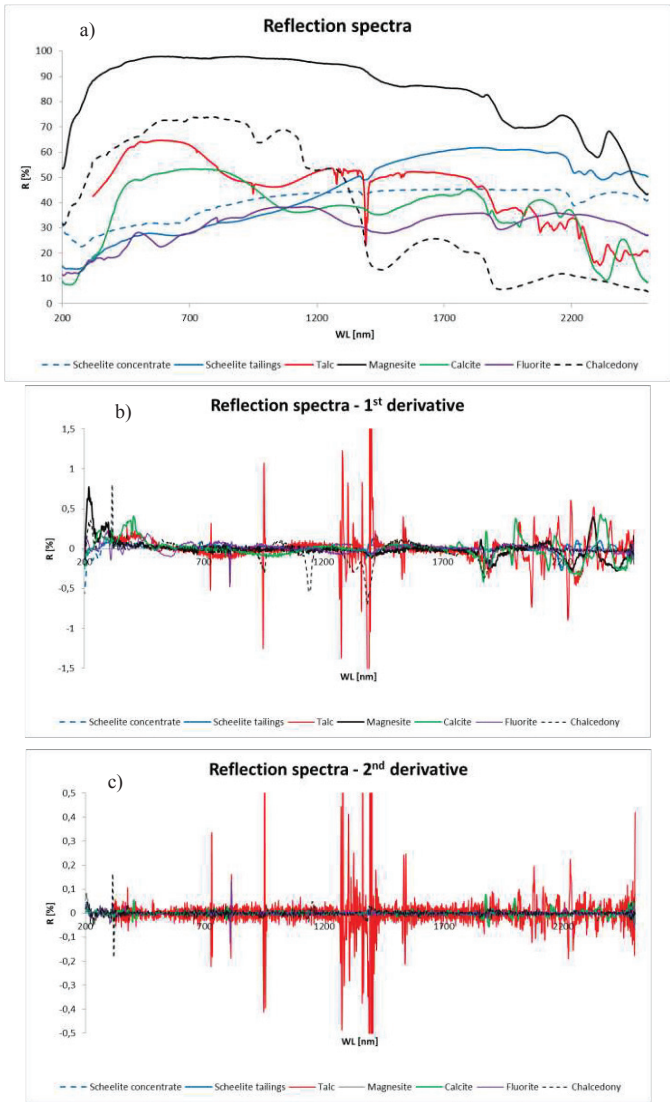
Figure 21.3: Reflection spectra a) original data, b) 1st derivative, c) 2nd derivative [14].

In nearly every NIR-spectrum of industrial minerals more or less sharp water-features around 1400 nm and 1900 nm and a decrease of the reflection intensity towards 2500 nm can be observed. The gaseous water molecule shows a symmetric OH-stretch at 2738 nm and an asymmetric stretch vibration around 2663 nm. The H-O-H bending mode is located in the MIR around 6270 nm. When a mineral contains a certain amount of water, both features at 1400 nm (overtone of the OH-stretches) and 1900 (combinations of H-O-H bend and OH-stretches) nm are present. When there is no water in or on a mineral no 1900 nm band will occur and a 1400 nm feature indicates only hydroxyl. A hydroxyl moiety has only a stretching mode, whose energy is highly dependent on its bonding partner. In minerals this stretching can be found between 2670 - 3450 nm. Since an OH can occur on multiple crystallographic sites and is usually attached to a metal ion, there can be a combination of metal-OH bend and OH stretch around 2200 - 2300 nm. For the carbonate group doublet-features around 2500 - 2550 nm and 2300 - 2350 nm are expected. Three weaker bands are reported around 2120 - 2160 nm and 1850 - 1870 nm. In general the energy and thereby the position in the spectrum of OH-moieties and CO_3-groups is very dependent on the group they are attached to [15]. As a rule of the thumb for OH-group features it could be said, that the lower the degree of freedom of an OH-moiety in a crystal, the sharper the peak which is observed. For loosely bond OH-groups or capillary water or surface water broad features are to be expected.

3.2 Luminescence measurements

The Scheelite concentrate- and tailing-samples were obtained from an industrial flotation process of an Austrian supplier. A piece of poly-crystalline silicon from the semiconductor industry was used as a blank standard for the measurements.

The LS 55 has a pulsed Xe-flash lamp as excitation source. The pulsation of the source is coupled to the line frequency and has a full width at half maximum of 10^{-6} s. It was necessary to adjust the pulse to pause ratio so that the pause did not fall into a time slot were the sample was still emitting photons. This would have caused erroneous dark current compensation of the PMT. The measurement logic of the LS 55 is depicted in Fig. 21.4.
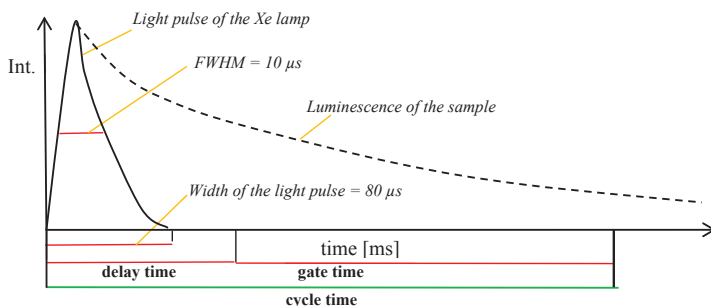
Figure 21.4: Measurement logic of the LS 55 (not to scale) [14].

The monochromator system of the LS 55 consists of a grid monochromator in the excitation channel and a grid monochromator in the emission channel. So artefacts from second and third order diffraction of excitation light and short wave luminescence are to be expected. To get rid of these artefacts additional cut off filters were used in the emission channel. An example for the second order biased emission spectra are given in Fig. 21.5.

Since the system has a two monochromators and a light source that provides illumination from a range of 200 – 400 nm, emission spectra and excitation spectra can be recorded. This makes the device more versatile than a device that works with laser excitation. A confinement of the LS 55 is that the minimal delay time after an excitation pulse is 0.01 ms. Thus decay time measurements for many of the short-lived activators are not possible.

In general excitation and absorption spectra give similar information of the material. But for samples which are not transparent to UV radiation, e.g., certain glasses the UV cut-off of the host material can conceal the excitation of an activator. In such cases the excitation spectrum reveals the absorption of the activator, while the absorption of the host material itself can be found by standard absorption/transmission measurements.

The investigated samples are depicted under daylight as well as under UV light in Fig. 21.6. The luminescence spectra for the samples
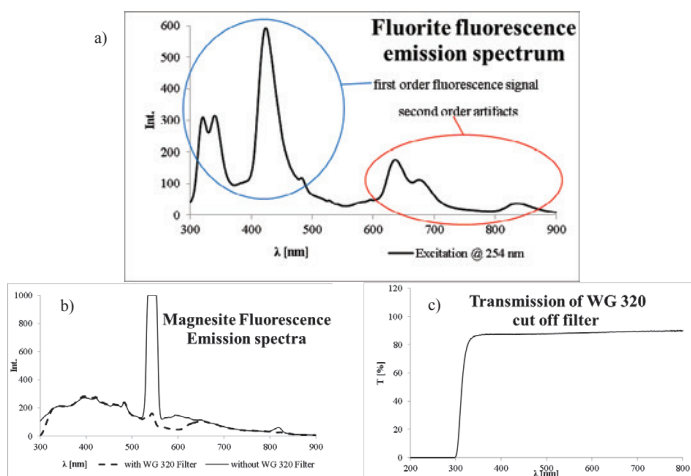
Figure 21.5: Spectra biased by second order artefacts a) a Fluorite Emission spectrum, b) a Magnesite emission spectrum after 266 nm excitation with and without a proper filter, c) transmission characteristic of the filter used [14].

are depicted in Fig. 21.7. In Fig. 21.7 the comment "fluorescence" and "phosphorescence" are linked to the settings of the spectrofluorimeter. "Fluorescence" is used for short-term luminescence measurements and "Phosphorescence" is used for long-term luminescence measurements.

When nothing is known about a sample the 3D-plot option in the software can used to automatically record several emission spectra for different excitation wave lengths. An example for a 3 dimensional plot for the Calcite sample is presented in Fig. 21.8. Unfortunately this measurement technique is more time consuming, than the traditional 2-dimensional measurements.

The Fluorite-Emission at 400 nm is assigned to traces of Eu^{2+}, the most common activator, which can be found in Fluorite. The green colour of the Fluorite sample indicates traces of Sm^{2+}, Dy^{2+} or Tm^{2+}, which could be responsible for the double peak feature between 300 - 400nm. The Fluorite system is frequently a multi-activator system, which has been extensively studied. Fluorites with Sm^{2+}, Dy^{2+}, Tm^{2+}, Nd^{3+}, Er^{3+}, Tm^{3+} and Ho^{3+} were used as laser materials [16].
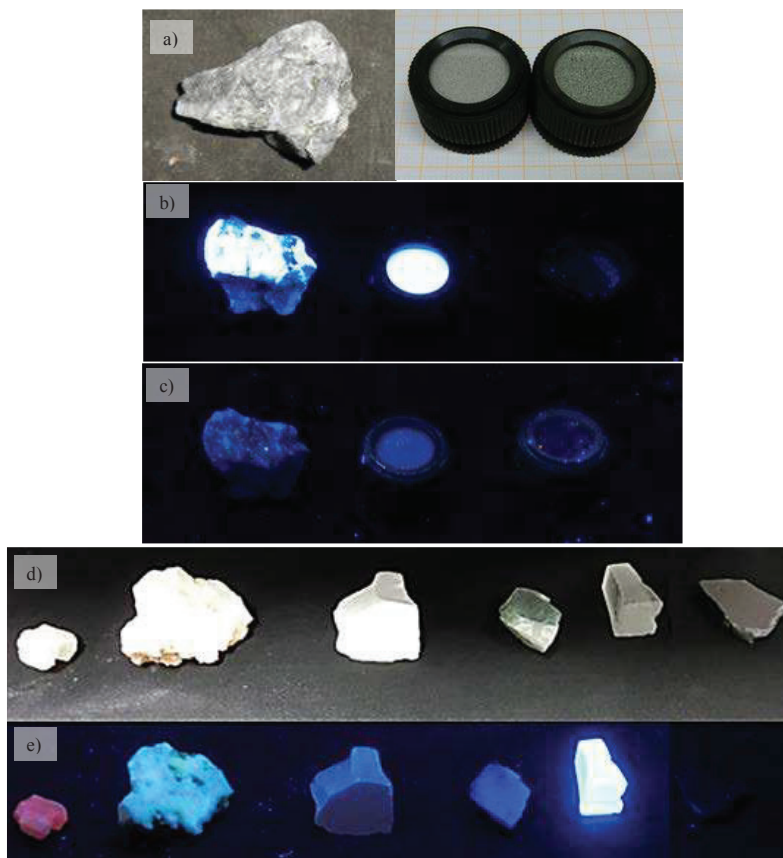
Figure 21.6: Sample set for luminescence measurements: a) a piece of Scheel-
ite ore, Scheelite concentrate, Scheelite tailing (left to right) in daylight, b) same
samples under 254 nm light, c) same samples under 366 nm, d) Calcite, Chal-
cedony, Magnesite, Fluorite, lead containing glass and highly pure silicon (left
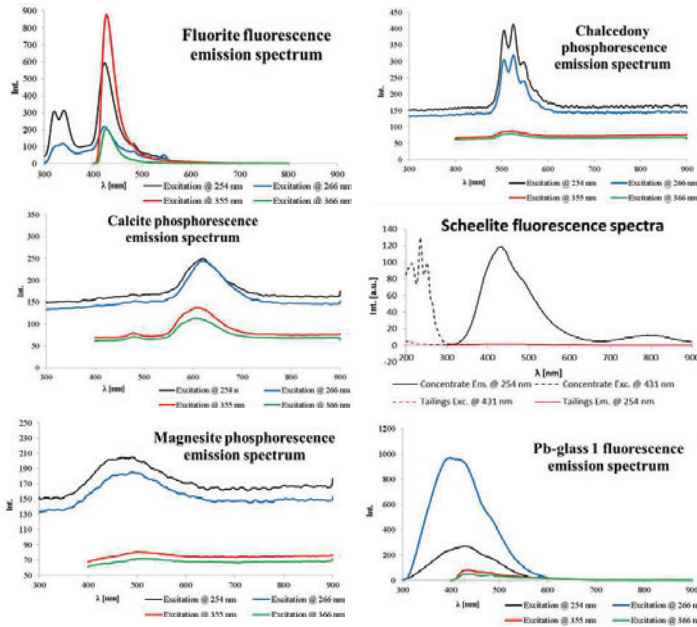to right) in daylight, e) same samples under 254 nm illumination [14].

Figure 21.7: Emission spectra for the mineral and glass samples [14].

The Chalcedony sample shows a feature in the green region of the VIS between 500 - 600 nm that is characteristic for traces of Uranyl, UO_2^{2+}. This group is responsible for the green, yellow and orange colours of Uranium minerals. The characteristic structure in the emission spectrum is due to vibronic transitions of this molecule [17].

The red glow of the Calcite sample can be assigned to traces of Mn^{2+}. The emission is generated by a d $\rightarrow$ d transition with the term symbols $^4A_{1g} \rightarrow \, ^6A_{1g}$. The optical properties of Mn^{2+} are highly dependent on its environment. For example in solution it appears colorless, in $CaCO_3$ it yields red fluorescence and in Zn_2SiO_4:Mn^{2+} it causes green emission [5, 18].

The intensive white glow of Scheelite is related to a charge transfer-transition in the tungstate group, therefore an intrinsic fluorescence of the mineral is encountered. The charge transfer involves a transition

of electrons from the oxygen ions to the empty d levels of the tungsten ion and backwards [19]. The bluish luminescence of Magnesite may be caused by oxygen around the carbonate-groups [20].

The intensive short-lived luminescence of the lead glass sample is caused by the s^2-ion Pb^{2+}. The luminescence is due to the lone pair $ns^2 \leftarrow ns^1np^1$ transition [19].
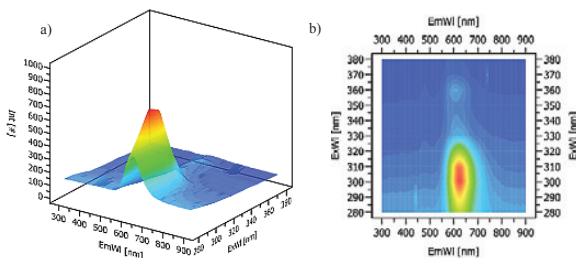

Figure 21.8: 3-D emission spectrum at different excitation wavelengths for the Calcite sample a) side view, b) top view [14].

As it was stated in the introduction iron is a common fluorescence quencher that can be found in many minerals. This is of special interest for the chalcedony sample. Many Chalcedony samples are coated by a brownish skin which is in many cases iron-oxide (see Fig. 21.9). The comparison of reflection spectra (see Fig. 21.10) of the brownish skin and the break planes shows that the brown part absorbs in the UV-VIS-range of the spectrum.

Figure 21.9: Chalcedony sample with brownish skin: a) under daylight, b) under 254 nm illumination and c) under 366 nm illumination.

This "quenching" by iron is an absorption process that is related to a charge transfer transition of Fe^{3+}, whose absorption maxima lays in the UV region and stretches far into the VIS range. Charge transfer quenching can also occur with Fe^{2+}, Co^{2+} and Ni^{3+} ions, but is not so strongly

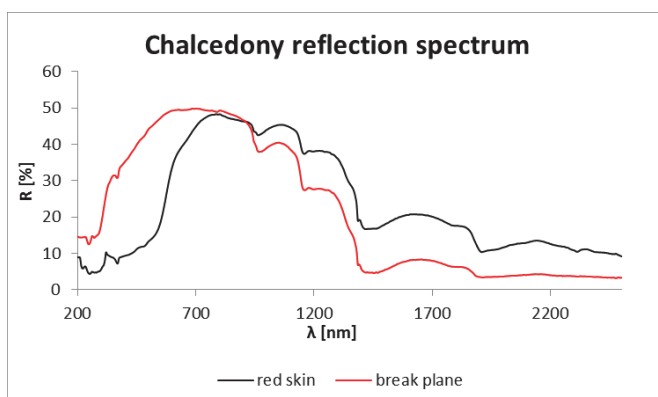**Chalcedony reflection spectrum**

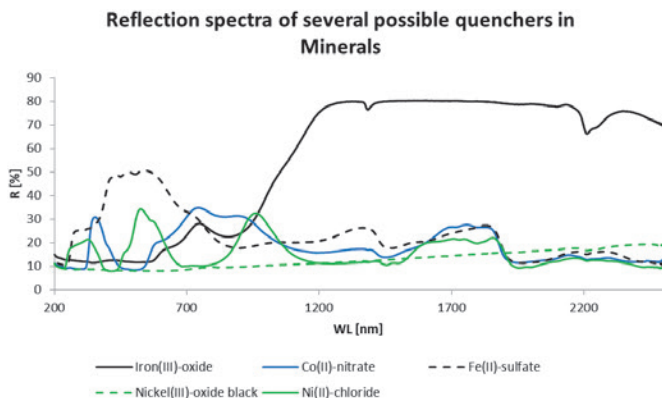**Figure 21.10:** Reflection spectra of the red skin of Chalcedony and its breaking planes.

Figure 21.11: Reflection spectra of possible quenchers in minerals.

observed as with Fe^{3+}. The Fe^{3+} content in a material drastically reduces the glow of every activator in a crystal [21]. To verify that the strong absorption in the VIS range of the Chalcedony skin is due to Fe^{3+} the reflection spectra of some pure transition metal compounds were investigated (see Fig. 21.11). All the examined compounds were of analytical grade.

In fact, the Fe^{3+} absorption covers the whole VIS range and corroborates the statement that it seems to be the most important and strongest quencher encountered in naturally occurring minerals.

4 Conclusion

Like all samples that come from nature and are not manufactured in a laboratory minerals have many impurities, dopants and trace contaminations. Often these traces are responsible for distinct features in fluorescence and reflection spectra. For fundamental studies for sensor based sorting of minerals, glasses and other materials an investigation of samples from an actual deposit is necessary. The decision which sensor system, what type of optics and/or sensor fusion should be used is based on efficiency and economic considerations. It could be shown, that with the presented methods distinguishing between different material classes and interpretation of spectral features is possible.

Acknowledgements

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