

TIE-36: Fluorescence of optical glass

1. Introduction

Fluorescence is a molecular phenomenon in which a substance absorbs light at a certain wavelength and almost instantaneously radiates the light at longer wavelength and lower energy. These processes are known as excitation and emission. Many substances both organic and inorganic exhibit some fluorescence.

Other designations for fluorescence are primary fluorescence, or autofluorescence usually used by optical designer and microscopists. In optical application using excitation sources like lamps or lasers the usage of optical material exhibiting fluorescence may decrease the contrast. When indirect fluorescence via fluorochromes or dyes is used in microscopy, the fluorescence of the optical components is generally considered undesirable because it is often the major source of unwanted light in an image.

Fluorescence is mainly generated by point defects like color centers, which are known to be originated by rare earth elements and other critical impurities [1,2,3] in optical glass. The fluorescence behaviour of a glass can be influenced by existing process technology and the use of higher purified raw materials.

Usually qualification tests are performed for initial absorption (also named internal transmission), the induced absorption (laser resistivity, solarisation) [4], and fluorescence [5], for example. Typical light sources applied for these kind of measurements are UV-lasers and high power Mercury, Xenon- or Deuterium-lamps. To get a deeper understanding of the origins of fluorescence the existing metrology has been enhanced to provide fluorescence spectroscopy.

2. Origin of fluorescence in glass

When optical material is exposed to intense light its intensity is partially absorbed. In some cases a luminescence or lighting causes by the irradiation is observed. This luminescence is caused elementary or origin extrinsic respectively (raw material or processing) or by material specific reasons.

The luminescence itself distinguishes by its lifetime or decay time respectively and is described as fluorescence (typically several ns to μ s) or phosphorescence (ms to s range).

The efficiency of energy transfer of the absorption light, known as quantum efficiency, strongly depends on the excitation wavelength or wavelength spectrum. It has a maximum close to the absorption bands and high photon energy respectively.

The fluorescence is in contrast to the non-radiative absorption where the incident light is transferred to a higher energy level and the down conversion to lower energy levels occurs without light emission. This energy is absorbed as phonons (solid state vibrations), as heat or as long living phosphorescence emission as mentioned earlier.

The spectrum of emitted radiation is shifted to longer wavelength compared to excitation wavelength in general.

The observed UV excited fluorescence correlates strongly with the content of UV absorbing ions in the material like rare earth elements, Iron, Zinc or Vanadium [6].

There are two independent origins of fluorescence:

The so-called elementary fluorescence displays the optical absorption and emission of each elementary impurity ions, e.g. rare earth elements and lead Pb^{2+} . These elements absorb and emit nearly independent from the glass matrix.

Optical transitions from the ns^2 -levels ($n=1,2,3,..$), related to SbO_3 , AsO_3 or ZnO , behave in a different way. Here the glass matrix and the processing (oxidation and reduction) have a strong influence on the absorption and emission characteristic.

3. Methods of Characterization

The measurement procedure shown in figure 1 works as follows: On the excitation side a 450 Watt Osram type lamp delivers a broad band radiation spectrum from 200 to 1500 nm with a maximum intensity between 250 and 600 nm. The radiation is spectrally selected and guided to the sample box by a double monochromator system which allows a high noise reduction in order to enable a signal to noise ratio better than 4000. The modular setup of this equipment allows an easy change of the excitation source. On the emission side one can choose between an UV/VIS and an IR-channel.

The UV/VIS detector is a photo multiplier, whereas the IR-detection is based on a germanium detector. Alternatively, pulsed excitation and a corresponding detection are also possible. Besides the intensity of the excitation source, the optimization of the detection efficiency depends on the proper choice of geometry and cut-off filter settings, which are required to have no intrinsic fluorescence at the applied wavelength.

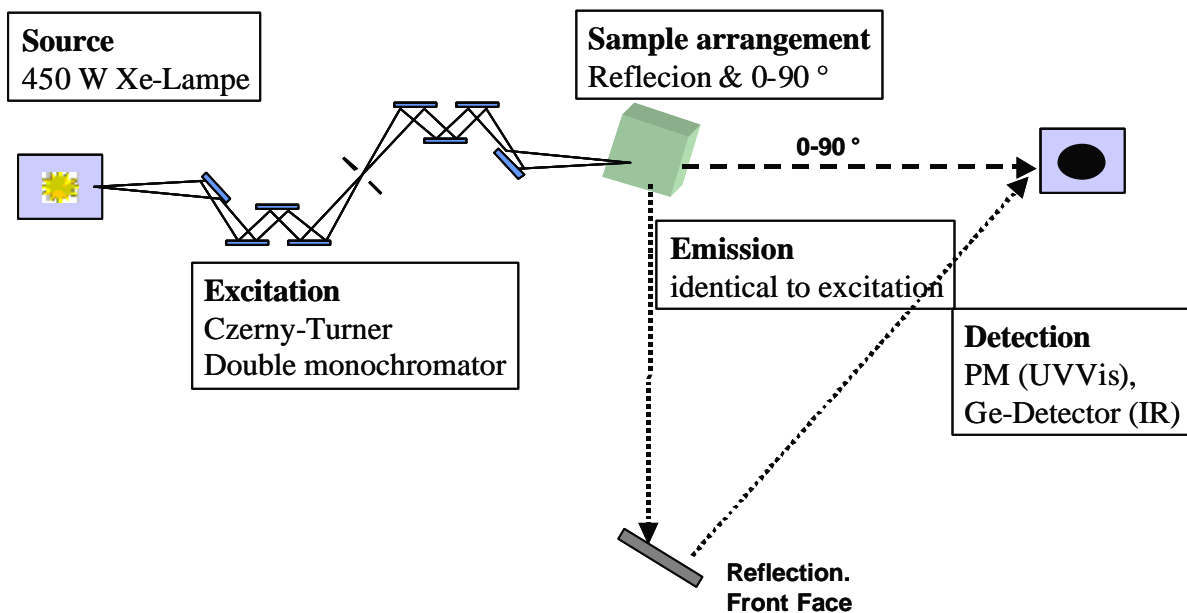


Figure 1: Setup of the fluorescence spectrometer Jobin Yvon Fluorolog 3. The arrangement allows flexibility in geometry and excitation source. Due to the double monochromator concept no filters are required

4. Accuracy of method

For quantitative measurements the grating efficiency has to be evaluated using different types of calibrated standards from Starna (Starna Company (Essex, UK) and BAM (Bundesanstalt für Materialforschung und –prüfung [Berlin, Germany]). The grating consists of 1200 lines/mm and has maximum reflexion efficiency at 420 nm due to blazing of the grooves (fig. 1). For further measurements the spectrometer software allows to correct the original spectrum with a flat line spectrum simultaneously. One has to consider that the numerical correction is most accurate in the range of the maximum sensitivity and decrease with the loss in sensitivity. The sensitivity range defines the detectable wavelength range. This means that emission between 300 and 700 nm can be investigated.

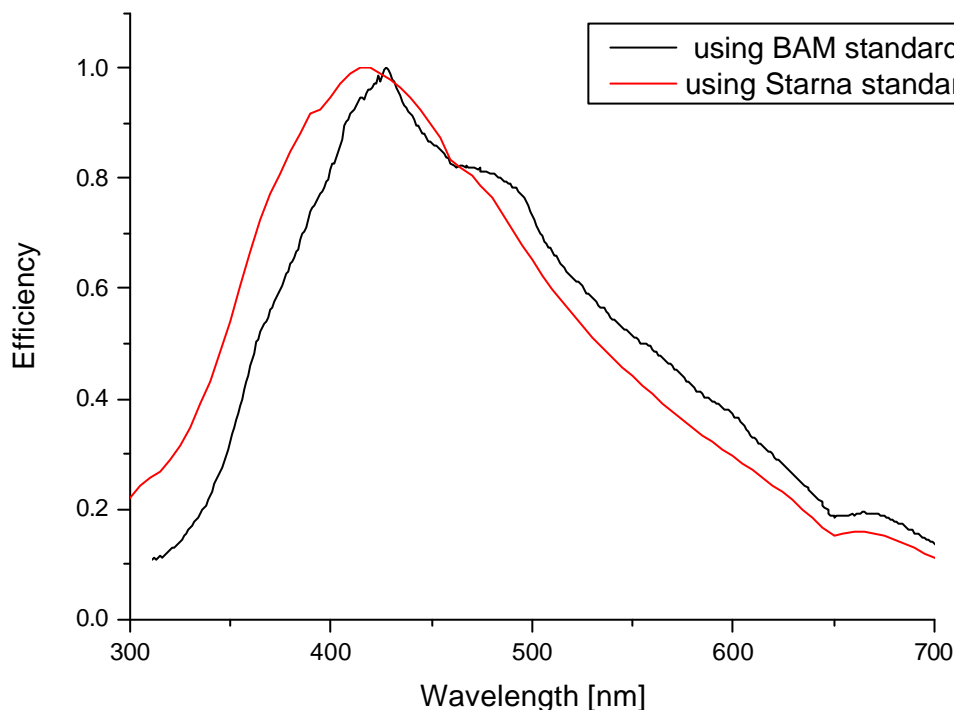


Figure 2: Efficiency for 1200 lines/nm grating and the PM detector. The maximum efficiency is observed for appr. 420 nm.

With this setup emission spectra as well as excitation spectra are obtainable. The emission spectra are taken by keeping the excitation wavelength constant, whereas the excitation spectra are recorded by keeping the emission wavelength constant.

For determination of the wavelength accuracy the emission, excitation and absorption spectra of doped samples have been investigated. In figure 3 these spectra are visualized using about 485 ppm TmF₃ as dopand in CaF₂ crystal. Doped CaF₂ is used because it exhibits a higher light yield compared to optical glass and can therefore be used even for less sensitive fluorescence spectrometers.

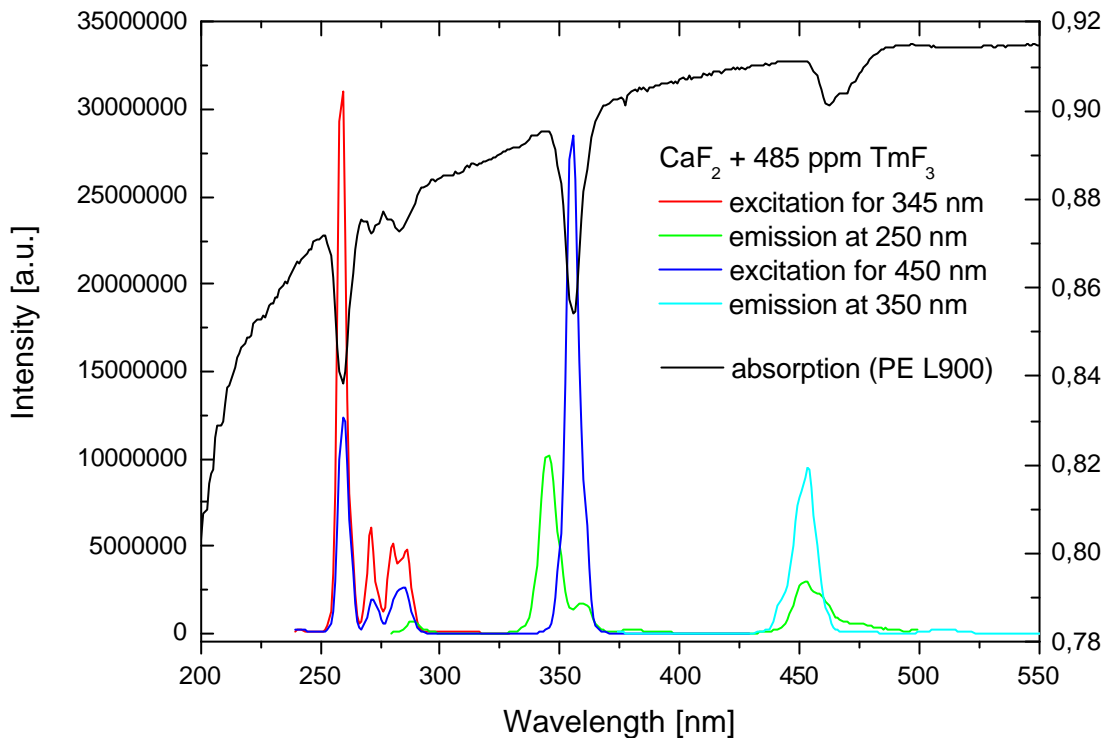


Figure 3: Absorption, excitation and emission spectra of TmF₃ doped CaF₂.

Results have been compared using theoretical and analytical work and data from literature [1-4,6].

The absorption, excitation and emission spectra for this sample have been obtained. It is observed that the peak of absorption and excitation spectra is exactly on the same position and therefore the consistency of absorption and excitation spectrum becomes visible. The emission peaks at 350 and 450 nm are situated on the same position as expected from the literature and known from optical glass when excited with 250 and 350 nm respectively.

The accuracy of the spectrometer has been evaluated using certified standards. In figure 4 the emission spectra of Quinine Sulphate certified by NIST is shown. We observed accuracy better than five percent for the FLUOROLOG 3 spectrometer.

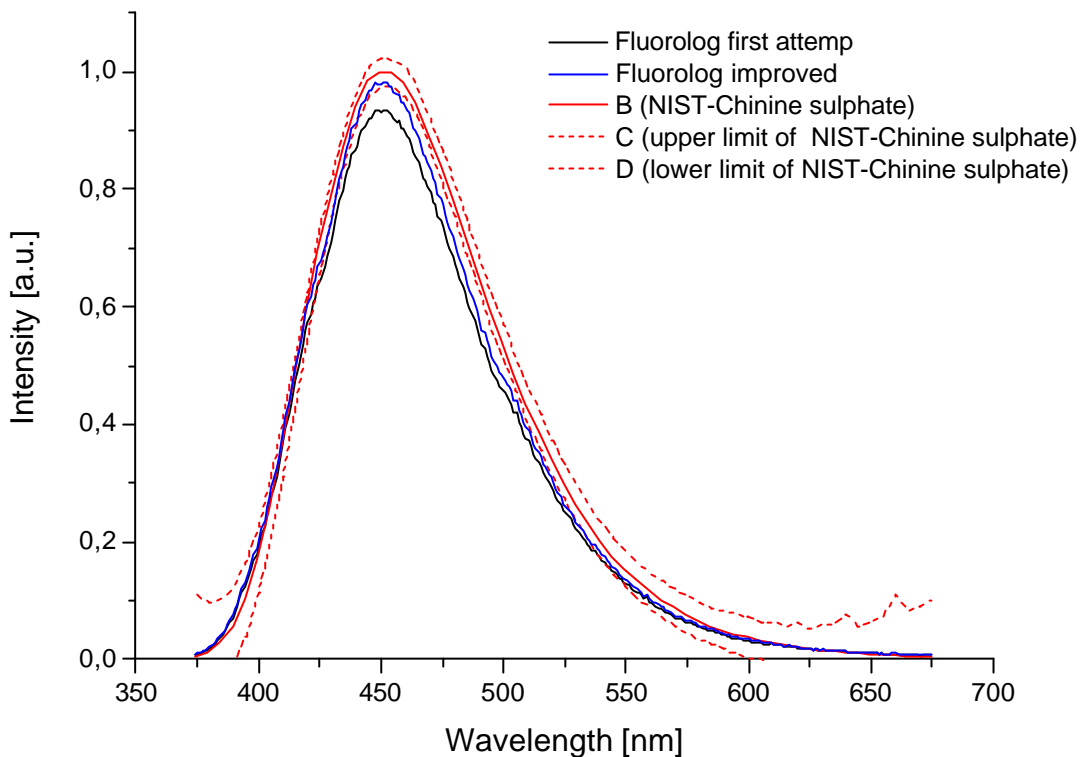


Figure 4: Emission spectrum of NIST certificates fluorophore Quinine Sulphate.

5. Fluorescence results for optical glass

5.1 UV excited fluorescence @365 nm

For quality control of optical glass emission spectra induced by the mercury excitation line at 365 nm are investigated. These results are shown in figure 5a for different glasses using identical setup parameters (slit widths, integration time, detection regime). The emission spectra have typical maxima at 435 and 525 or 670 nm depending on the material composition of each glass type. These features for N-type glasses are mainly driven by the elimination of PbO and As₂O₃ and substitution by Sb₂O₃, or ZnO as reported in [3,4,6].

The most common method to compare the fluorescence of different optical glasses is to integrate the spectrum of each glass and compare the results with a reference glass.

Typical values – shown in figure 5b - ranging from 1 to 5 percents as evaluated from emission curves in figure 5 compared to PbO containing glass SF1.

In principle characteristic fluorescence data were calculated by integrating intensity values of the measured spectrum between 400 nm and 700 nm first. The obtained result is divided by a reference value (SF1 or SF6), which was calculated in the same way.

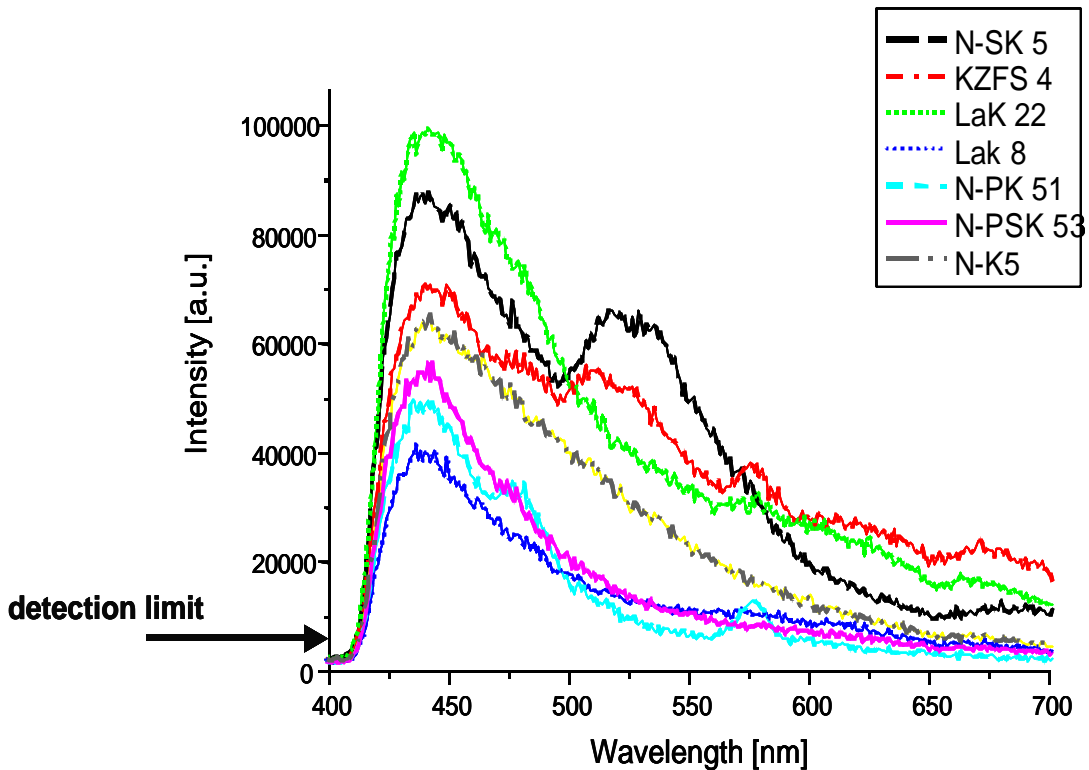


Figure 5a: Emission spectra of low fluorescent optical glasses using 365 nm excitation wavelength and a cut off filter (KV 418)

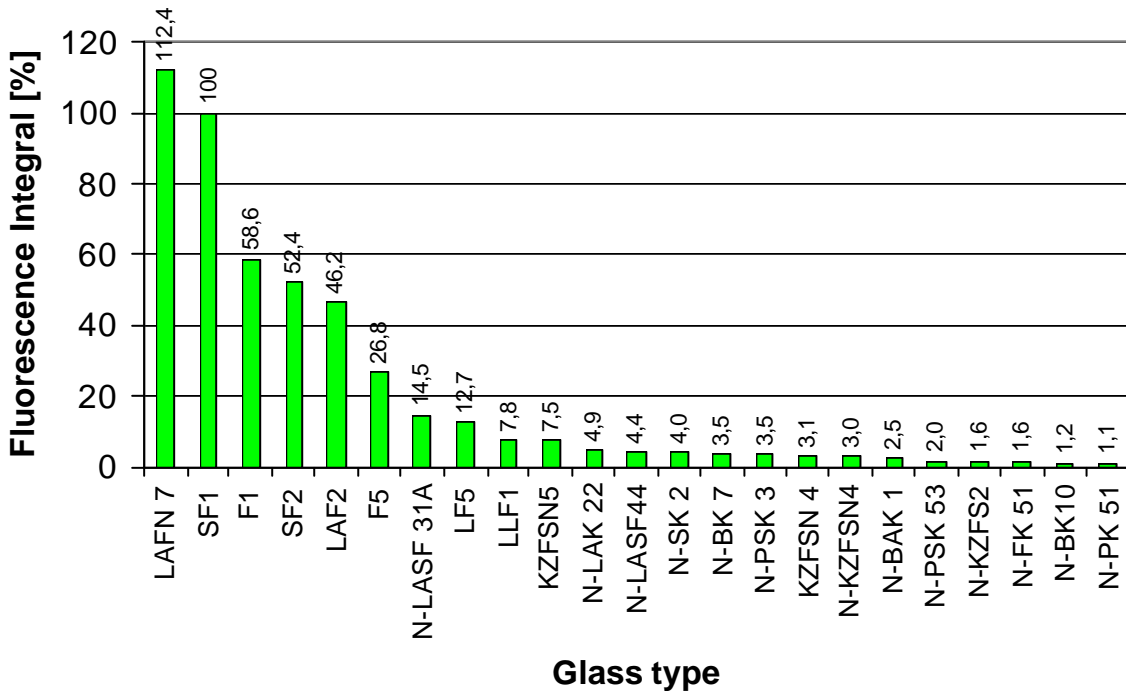


Figure 5b: Typical fluorescence data using 365 nm excitation

A similar type of qualitative evaluation for 365 nm excitation is performed within the Japanese Optical Glass Industrial Standard JOGIS procedure, which is used by Japanese companies [7]. Even for these low fluorescent material, typically used for H-line lithography or fluorescence microscopy, the analytical emission intensity level is still significantly above the detection limit of the spectrometer and offers potential for the characterization of high quality material of the next generation.

The long term and batch-to-batch reproducibility is shown in figure 6 using different samples of N-LASF type glass. It is seen that the variation from batch to batch and the long-term reproducibility is less than 10 percent for the total error. In principle the error can be reduced by working with optimized experimental setup for each glass type, but then the comparison between different glasses is becoming less accurate.

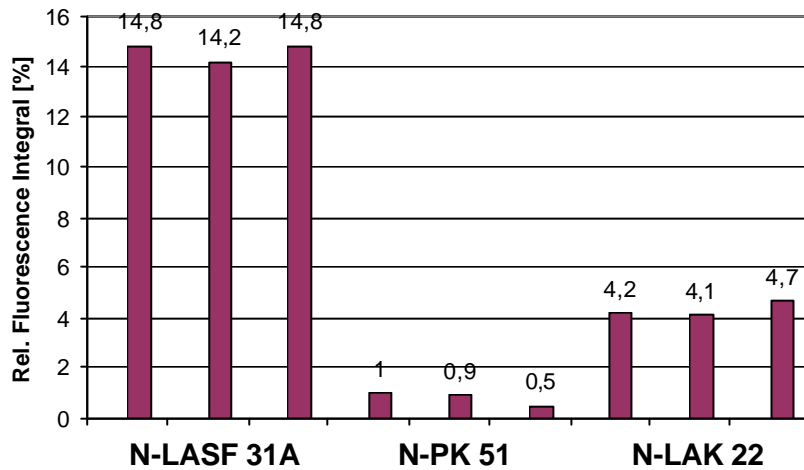


Figure 6a: Fluorescence data using 365 nm excitation obtained from one melt

N-LASF-type error indicator 10 %

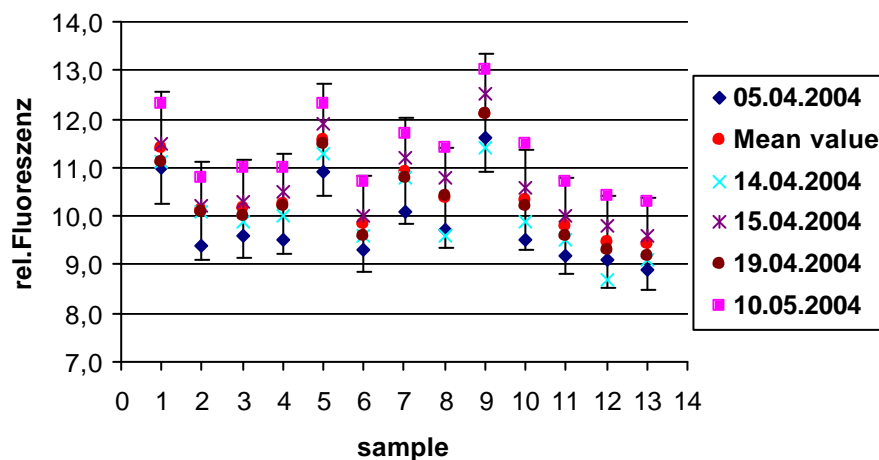


Figure 6b: Typical fluorescence data using 365 nm excitation for various samples of N-LASF type.

5.2 Fluorescence for excitation at 550 nm

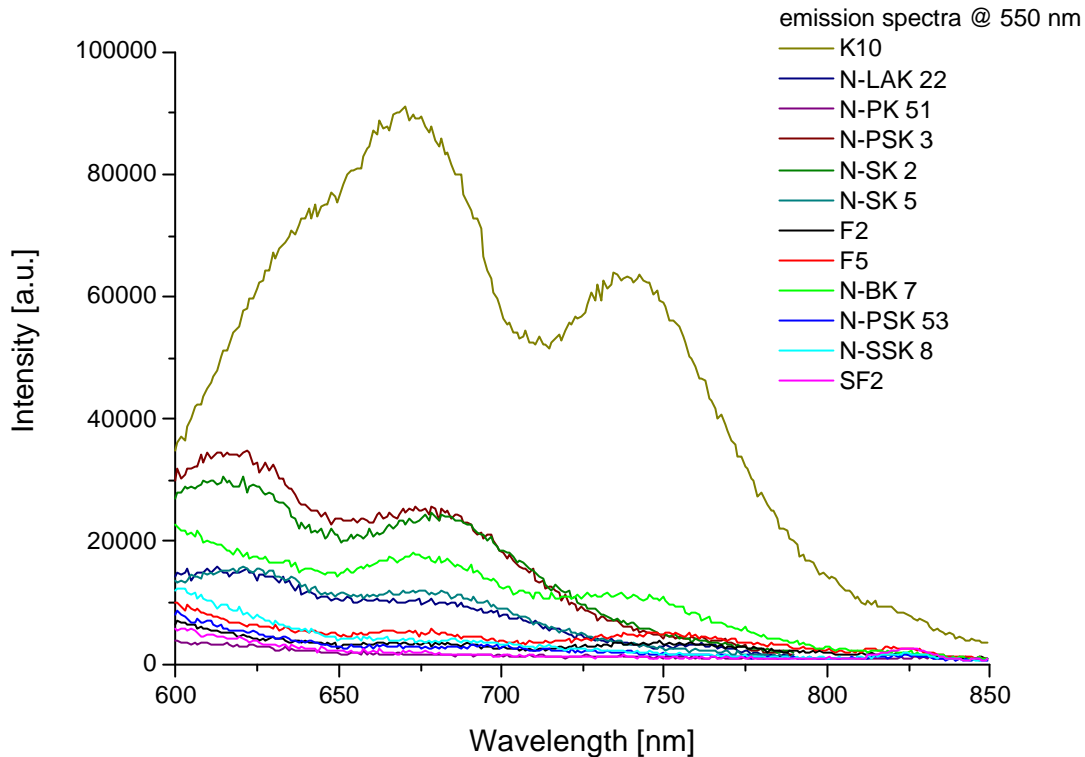


Figure 7: Emission spectra of optical glasses using 550 nm excitation wavelength and without a cut off filter.

Further applications exist besides the 365 nm excitation, e.g. for bioanalytical use where excitation larger 400 nm is adapted [8]. In figure 7 typical emission spectra using 550 nm excitation wavelength are shown for several N-type (low fluorescence at 365 nm excitation due to use of pure raw material) optical glasses. Using the identical experimental setup the shape of the emission profiles are similar, but the measured intensities are different.

It has to be pointed out there is no correlation between the 365 nm and the excitation larger 400 nm as seen in figure 8. There the fluorescence values @365 nm and 550 nm are plotted versus each other. The reason is that the UV excitation/absorption depends mainly on impurities whereas for larger excitation wavelengths respectively lower photon energies, where merely absorption bands are observed, the glass composition is the driver for the fluorescence features [5].

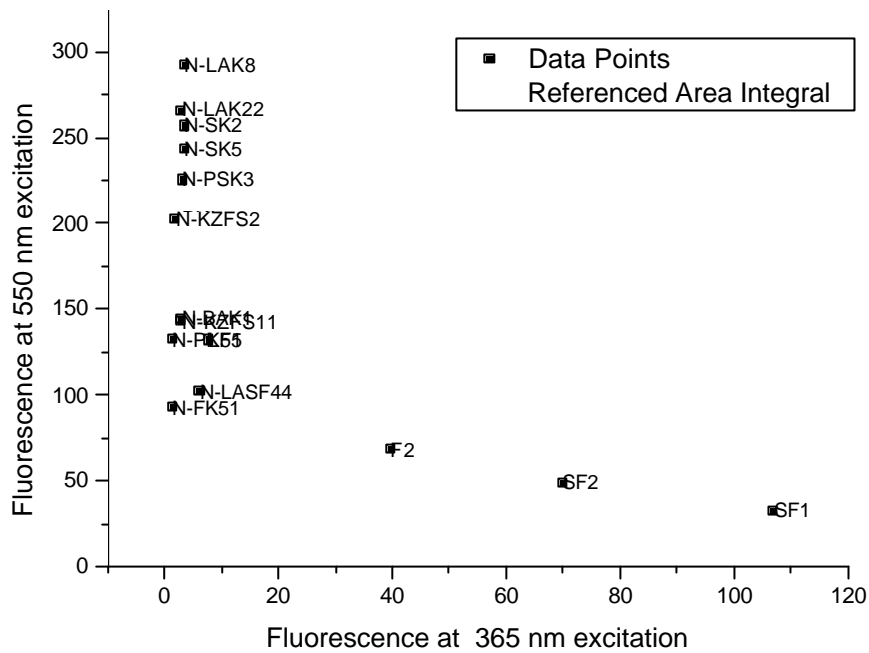


Figure 8: Fluorescence of UV-excited and 550 nm excited optical glass using identical setup (slit widths, no cut-off filter). There is no correlation observable.

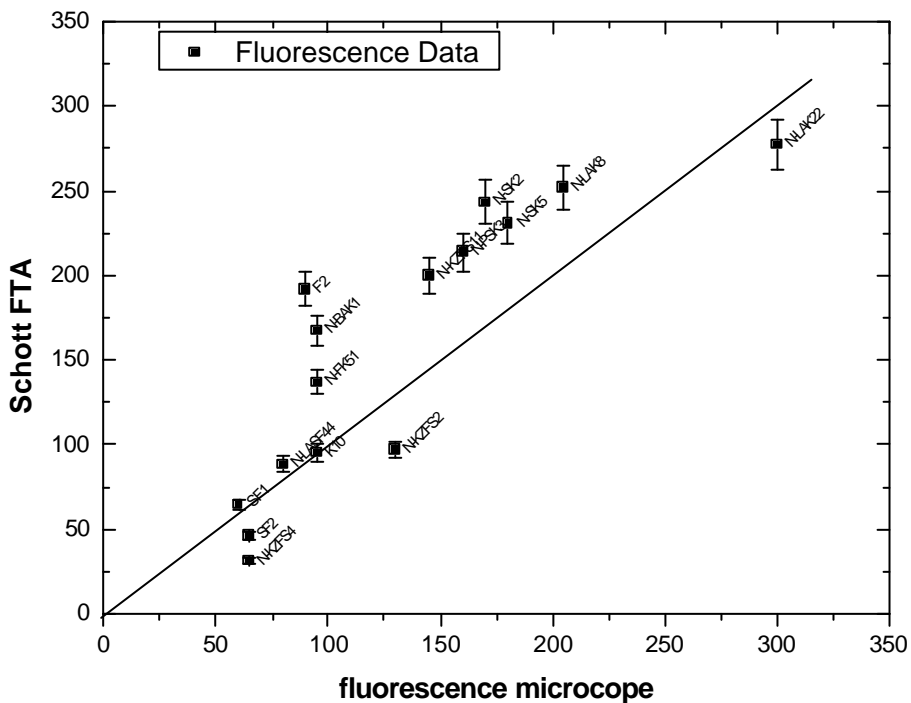


Figure 9: Correlation of spectroscopic and microscopic fluorescence for the red fluorescence

For the application of the optical glass in microscopy and lithography for example the spectroscopic setup has to be very similar to the projected optical design. In figure 9 the correlation of fluorescence data in the red wavelength range of a microscope and the Fluorolog 3 spectrometer are shown. It is clearly seen that a correlation of both detection methods is very feasible.

6. Summary

The characterization of fluorescence for optical glass is available for excitation between 250 and 700 nm with an emission between 300 and 850 nm. Schott is providing data and additional measurements for optical and coloured glass exhibiting low and high intensity levels with an accuracy and reproducibility better than 10 percent. Additionally fluorescence evaluation for specific applications using various set-ups (applications wavelengths, geometries)

7. Literature

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