Calcium fluoride for ArF laser lithography – characterization by in situ transmission and LIF measurements

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ABSTRACT

An experimental setup was established for *in situ* transmission and laser induced fluorescence (LIF) measurements of CaF_2 at 193 nm laser irradiation. The known rapid damage process in CaF_2 upon ArF laser irradiation is shown to terminate for all tested samples within $3{\cdot}10^4$ laser pulses for the applied fluences. Furthermore, it is demonstrated that for typical application values the fluence dependent transmission (FDT) at the end of the rapid damage process is independent of the irradiation history and determined by the specific crystal quality.

From the lifetimes and signal strengths of different present fluorescence bands the excitation and recording conditions for LIF investigations are derived. The results of laser induced fluorescence measurements at 193 nm excitation make evident that certain impurities or defects are responsible for the different transmission properties even of high purity CaF_2 crystals. Comparing transmission and LIF data a quantitative correlation was found between selected emission bands and ArF laser stability of CaF_2 material.

Keywords: Laser induced fluorescence, UV optical material, CaF_2, color centers, optical properties, 193 nm

1. INTRODUCTION

Crystalline calcium fluoride is one of the key materials for 193 nm lithography and is used for laser optics, beam delivery system optics and some of the lenses. Beside the excellent transmission properties at 193 nm CaF_2, in contrast to fused silica, does not show compaction or rarefaction upon excimer laser irradiation. However, even in pure CaF_2 samples, the application of DUV laser pulses can cause a considerable transmission decrease in the material. Therefore, in order to enhance the yield of high quality material it is necessary to clarify the effects of different impurities or defects in CaF_2 on the durability against DUV laser irradiation.

The laser induced fluorescence (LIF) and fluence dependent transmission of CaF_2 are characteristic properties of the material that depends on its purity. Recently, some work was done to investigate the excimer laser induced excitation and annealing mechanisms of specific impurities like sodium or yttrium upon ArF laser irradiation[1,2]. Furthermore, it has been shown[3,4] that apart from the intrinsic CaF_2 fluorescence due to the relaxation of self-trapped excitons (STE) there are several other emission bands which are caused by trace impurities or structural defects. However, these reports mainly give an overview of detected emission bands but do not analyze their impact on the material's performance during laser irradiation. Recently, Mann *et al.*[5] pointed out, that in high purity CaF_2 material just the intrinsic STE fluorescence is present because the trace impurity levels are below the detection limit. The study of a large variety of samples only came up with a very weak correlation between the strength of the STE fluorescence signals and the different absorption properties upon ArF laser irradiation.

In this work, excitation and recording conditions for LIF investigations of CaF_2 are established which allow the detection of defects and impurities even in CaF_2 material of highest quality. A large variety of CaF_2 single crystals are

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investigated by LIF and transmission measurements and quantitative correlations between certain emission bands and their influence on the ArF laser hardness are discussed.

2. EXPERIMENTAL SETUP

All investigations have been carried out at room temperature using an ArF excimer laser (LPX 240, Lambda Physik) and a nitrogen purged experimental setup. The laser beam was shaped by an aperture in front of the sample to a cross section of 15 x 5 mm^2. The size of the studied CaF_2 samples was 25 x 25 x 100 mm^3.
In-situ transmission measurements were carried out at a repetition rate of 60 Hz and fluences H_i (i = 1...3) ≤ 10 mJ/cm^2. Each sample was irradiated with the same fluence sequence $H_1 \rightarrow H_2 \rightarrow H_3 \rightarrow H_1$ with $H_1 < H_2 < H_3$. 30,000 laser pulses have been applied at each fluence. The pulse energies in front of and behind the investigated samples were registered by fast pyroelectric detectors (PE-25H, OPHIR Ltd.) which are calibrated against a NIST traceable standard for 193 nm.

For the laser induced fluorescence measurements the samples were pre-irradiated for 3 min at 10 mJ/cm^2 and a repetition rate of 50 Hz to assure the end of the rapid damage process for the applied fluence. Then the repetition rate was switched to 10 Hz at constant fluence. The fluorescence light from the sample was guided by an optical fiber onto the grating spectrometer (grating: 150 lines/mm). An intensified, gated optical multichannel analyzer (OMA) system (Roper Scientific) served for detection. The laser scattering was shielded from the detection system by using an interference filter with high 193 nm suppression, which was placed in front of the fiber entrance. In order to cover a large wavelength range for the fluorescence emission two spectra at different center wavelengths of the grating were recorded. Thus, a wavelength range from about 190 nm to 800 nm could be investigated. To enhance the signal-to-noise ratio and to diminish the fluctuation of the luminescence intensity due to the fluctuation of the laser pulse energy 100 consecutive laser pulses are used for excitation and the corresponding LIF signals were accumulated to record one fluorescence spectrum.

3. RESULTS AND DISCUSSION

3.1 TRANSMISSIONMEASUREMENTS

A typical transmission course of CaF_2 (thickness: 100 mm) upon ArF excimer laser irradiation is given in figure 1. For the first three fluences $H_1 < H_2 < H_3$ the known rapid damage process occurs and after a certain number of laser pulses the transmission reaches a constant value depending on the applied fluence. Switching the fluence back to the level H_1 results in a laser induced recovery terminating at the same transmission value as for the first application of H_1. This makes evident that the fluence dependent transmission value is independent of the actual irradiation history of the sample. For all investigated samples and fluences an irradiation of 30,000 laser pulses was sufficient to achieve the constant transmission. The measurement accuracy for all investigated fluences was better than ± 0.2 %.

Looking at the transmission values versus fluence for all samples a linear relation can be used in a good approximation in the applied fluence range. Whereas the analysis of the fluence dependent transmission measurements indicates in principle the same behavior for all investigated samples with the number of laser pulses, the obtained transmission decrease with increasing fluence can vary by a factor of up to four (fig. 2). Since the achieved slope |dT/dH| is one characteristic property for CaF_2 it is used for the separation into different qualities. However, to raise the yield of highest qualities it is necessary to understand the origin of the different slope values. In our opinion the behavior shown in fig. 2 is due to different impurities or defects within the CaF_2 crystals. Therefore, substance selective, background free investigations are carried out using laser induced fluorescence at 193 nm excitation.

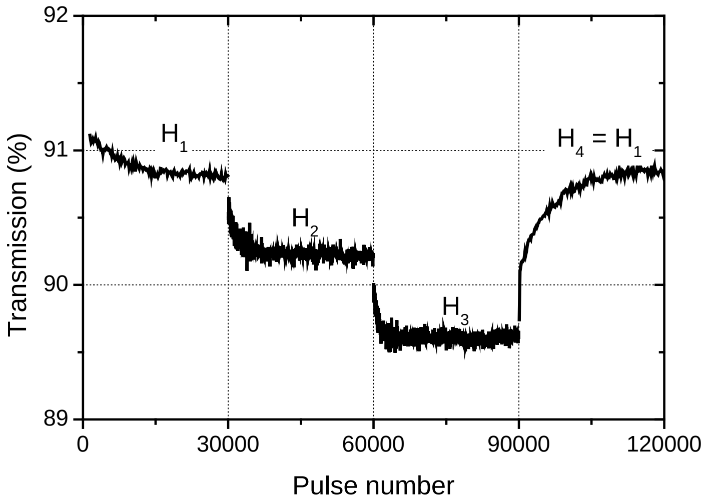

Figure 1: Typical transmission course of high quality CaF_2 samples (thickness: 100 mm) upon ArF laser irradiation showing the rapid damage process for fluences H_i and the laser induced transmission recovery when switching the fluence back to H_1.

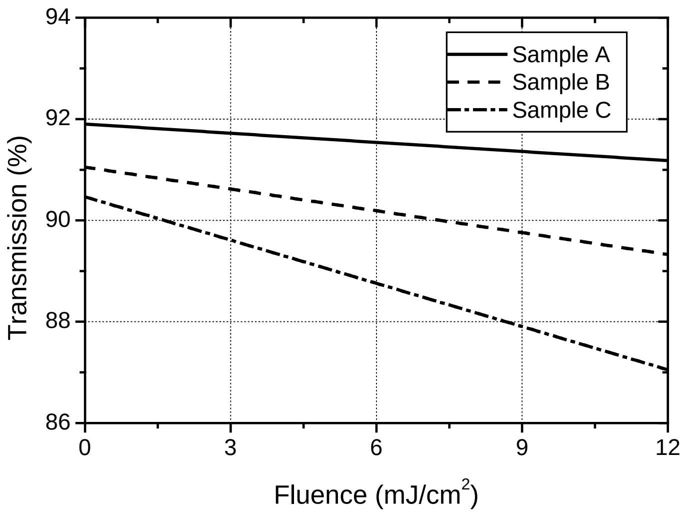

Figure 2: Different slopes for the linear relation between transmission and fluence of CaF_2 samples (thickness: 100 mm)

3.2 LIF MEASUREMENTS

Before starting the actual LIF measurements the first task was the determination of appropriate recording conditions to detect weak and short living LIF signals caused by very small amounts of possible defects or impurities like rare earth ions in high purity CaF_2 crystals. Therefore, first measurements were carried out to obtain fluorescence decay characteristics for all present emission bands. These data were achieved by increasing the delay time between the laser pulse and the start of the LIF measurement at a constant value for the recording duration (gate width). For example, the results and the extrapolated values for the corresponding fluorescence lifetime of two emission bands are given in figures 3a and b. For the known intrinsic fluorescence (fig. 3a) at around 278 nm due to the relaxation of self-trapped excitons (STE) a lifetime of about 1.1 µs was found which is in very good agreement to previously published data[4]. Figure 3b shows the fluorescence decay of a emission band found at around 740 nm with a much shorter lifetime of less than 20 ns. The origin of this emission is still to clarify.

An overview of the fluorescence lifetimes for all investigated laser induced emission bands is given in table 1. Two groups can be identified, one having very small values of less than 100 ns and another showing values in the some 100 nanoseconds to microsecond range. From these data it turned out in the experiments that a recording time (gate width) of only 50 ns starting at the end of the excimer laser pulse in the sample is the most appropriate way to detect most of the emission bands in table 1 with only one setup of the intensified, gated optical multichannel analyzer (OMA) system. To avoid the recording of Rayleigh scattered laser light, an interference filter with high 193 nm suppression was placed in front of the entrance of the fiber which guides the fluorescence light onto the entrance slit of the spectrometer. It was proved that the interference filter itself did not show any luminescence due to the Rayleigh scattered laser light.

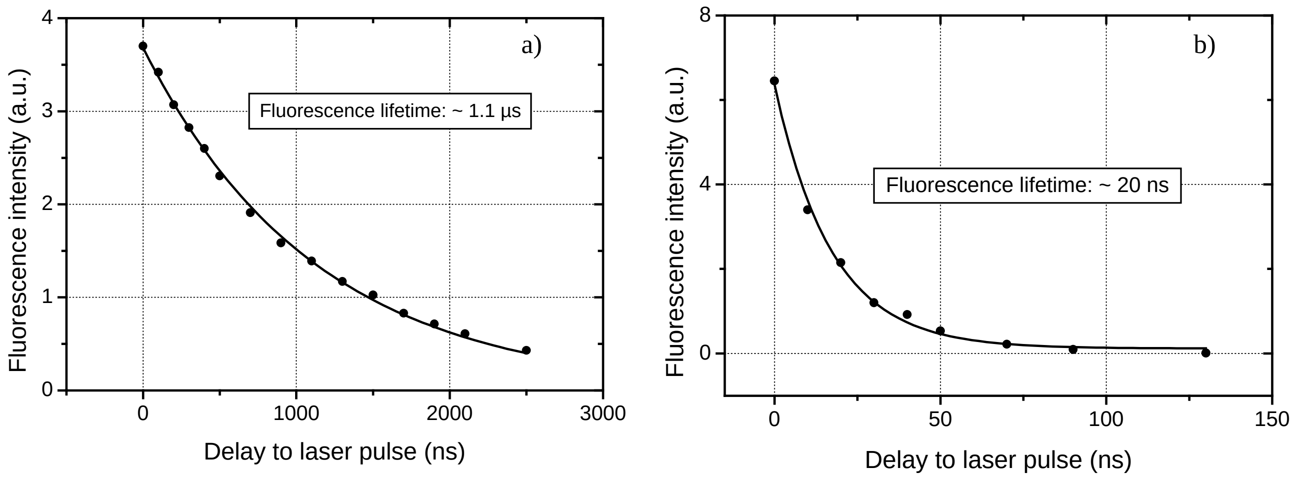

Figure 3: Fluorescence decay and corresponding fluorescence lifetime of a) the intrinsic STE fluorescence at about 278 nm and b) a fluorescence centered at around 740 nm

Emission band (nm)	Fluorescence lifetime (ns)
278	1100
313 + 333	35
420	685
450	60
500	360
580	< 20
740	< 20

Table 1: Experimentally detected laser induced emission bands in CaF_2 and corresponding fluorescence lifetimes.

3.3 CORRELATION BETWEEN TRANSMISSION AND LIF

In order to correlate particular fluorescence emissions to the transmission properties of CaF_2 a large number of samples were selected by LIF measurements which exhibit only the intrinsic STE fluorescence or in addition one of the remaining emission bands shown in table 1. Apart from the intrinsic LIF groups of samples showing the double peak at 313 nm and 333 nm or the emission bands at 450 nm, 580 nm and 740 nm were chosen and analyzed with respect to their laser induced transmission behavior. Correlations were investigated between the LIF properties and the slope |dT/dH| of the fluence dependent transmission and the extrapolated transmission value for zero fluence T_0, respectively. Whereas the slope |dT/dH| is principally a measure for the nonlinear bulk absorption the value T_0 consists of the linear bulk absorption, the surface absorption and the bulk and surface scattering.

3.3.1 SELF TRAPPED EXCITON (STE) FLUORESCENCE

A typical LIF spectrum of CaF_2 samples which only consists of the material independent self trapped exciton (STE) emission band at around 278 nm is given in figure 4a. For these samples the concentrations of defects or impurities resulting in possible additional emission bands shown in table 1 are below the detection limit of our LIF recording system. The results of the transmission measurements (fig. 4b) indicate that all investigated samples show very similar low values for the slope |dT/dH| and, generally, very high extrapolated values for the T_0.

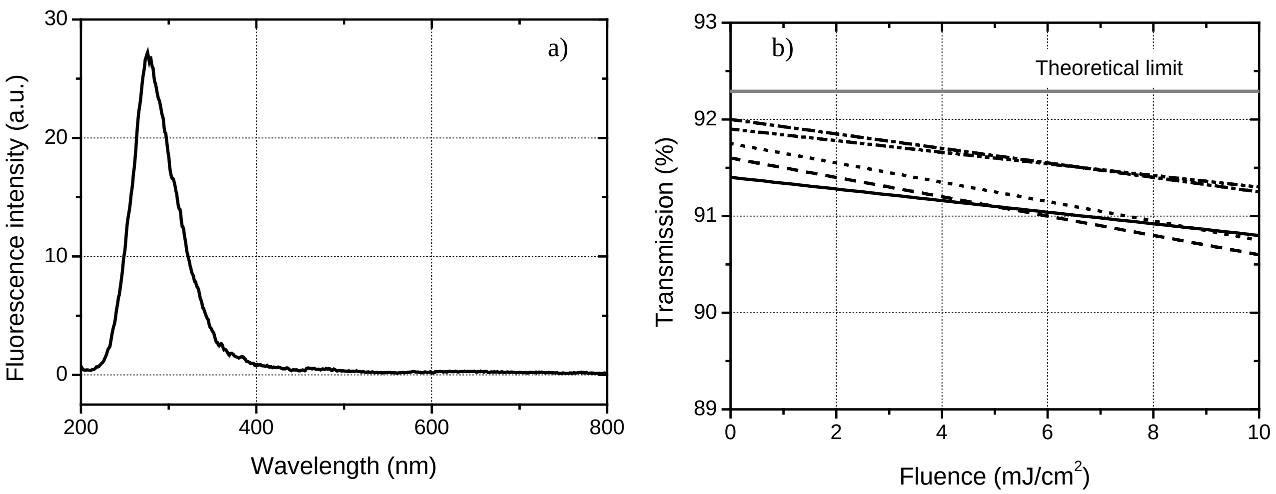

Figure 4: a) Typical LIF spectrum of CaF_2 samples showing only the STE emission band at around 278 nm and b) corresponding fluence dependent transmission data for 5 CaF_2 samples (thickness: 100 mm).

Since a two photon absorption process is the origin of the self trapped exciton emission[4] the still recognizable differences in the T_0 values are supposed to result from different surface absorption or scattering of the samples. The obtained transmission data for this particular group of CaF_2 samples can be considered as the best available with respect to the applied laser parameters.

3.3.2 FLUORESCENCE AT 313 NM AND 333 NM

Figure 5a presents a typical LIF spectrum for CaF_2 samples showing, in addition to the STE fluorescence, two emission bands at around 313 nm and 333 nm, respectively. Comparing the peak positions, FWHM and the fluorescence lifetimes (table 1) with literature[4,6-7] it can be presumed that the two emission bands are a doublet band due to Ce^{3+} in CaF_2. From the results of the fluence dependent transmission measurements (5 samples in fig. 5b) it can be concluded that the presence of the fluorescence bands at 313 nm and 333 nm virtually does not influence the material's quality upon ArF laser irradiation. Compared to the samples from the previous chapter the values for the slope |dT/dH|, indicating the strength of non-linear absorption processes upon ArF laser irradiation, practically remain constant. This result implies that both emissions occur by means of one-photon absorption processes which agrees with the results of Mizuguchi *et al*[4]. It appears from fig. 5b that the slight differences in the T_0 values of the investigated samples can not be correlated to the impurity or defect concentration determined by the strength of the corresponding fluorescence signal. From that we conclude, that similar to the samples showing only the STE emission, different surface absorption or scattering behavior is the main reason for the differing values of T_0.

The results of the transmission measurements show that the presence of the double emission band at 313 nm and 333 nm has no influence on the material's quality upon ArF laser irradiation.

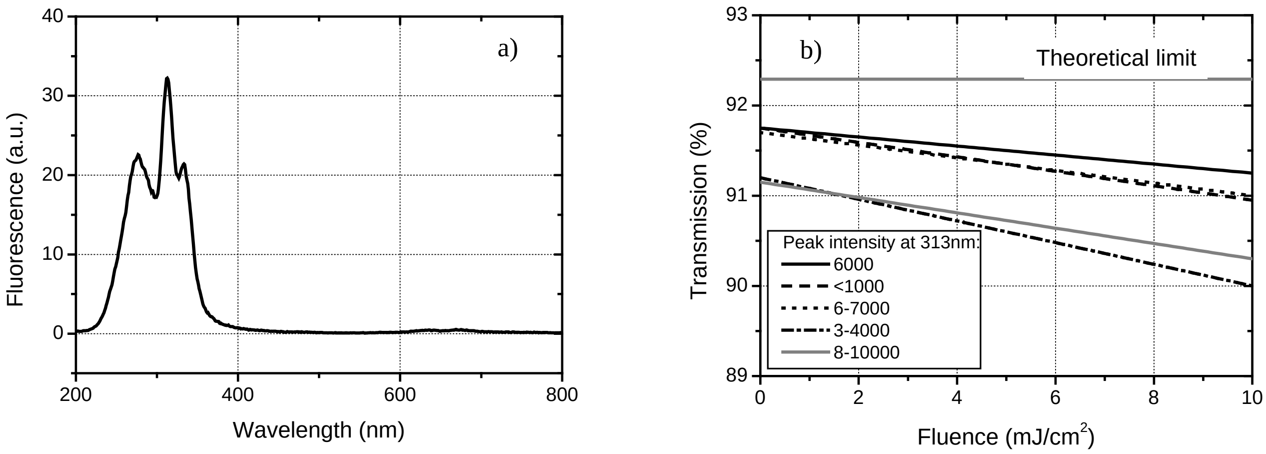

Figure 5: a) Typical LIF spectrum of CaF_2 samples showing, apart from the STE emission, a doublet band at around 313 nm and 333 nm and b) corresponding fluence dependent transmission data for 5 CaF_2 samples (thickness: 100 mm) with different peak intensities of the doublet band.

3.3.3 FLUORESCENCE AT AROUND 580 NM

Some of the investigated CaF_2 samples reveal an laser induced emission band centered at around 580 nm (fig. 6a) which to our best knowledge has not been investigated so far. The origin of this emission is still not known and needs to be clarified. However, the results of the fluence dependent transmission measurements (fig. 6b) of 5 CaF_2 samples with similar 580 nm peak intensity demonstrate that, compared to the samples discussed above, the presence of the 580 nm emission has a large impact of the slope |dT/dH| and no detectable influence on the extrapolated values of T_0. The increase of the slope |dT/dH| by almost a factor of two allows the supposition that a non-linear absorption process is the origin of the fluorescence at 580 nm. Therefore, the presence of the 580 nm emission band puts limitations on the use of this type of CaF_2 especially in high laser fluence applications.

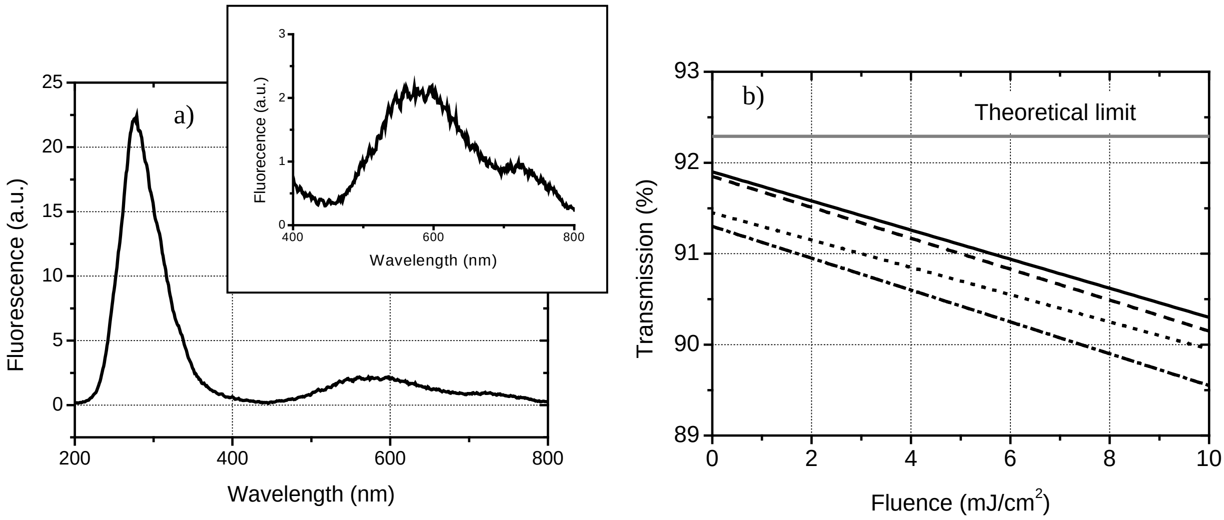

Figure 6: a) Typical LIF spectrum of CaF_2 samples showing, apart from the STE emission, an emission at around 580 nm and b) corresponding fluence dependent transmission data for 5 CaF_2 samples (thickness: 100 mm) with similar peak intensities of the 580 nm fluorescence.

3.3.4 FLUORESCENCE AT AROUND 740 NM

Another group of CaF_2 material was found to exhibit a laser induced fluorescence centered at around 740 nm. A typical LIF spectrum is shown in fig. 7a. To our best knowledge this fluorescence has not been identified and investigated so far in studies about UV/DUV laser induced fluorescence of CaF_2. It, however, appeared in our transmission measurements that the presence of this type of fluorescence has the strongest impact of all investigated LIF bands on the slope |dT/dH|. For the investigated samples (fig. 7b) it can be estimated that the value for |dT/dH| increases by a factor of about 3 to 4 compared to the best available CaF_2.

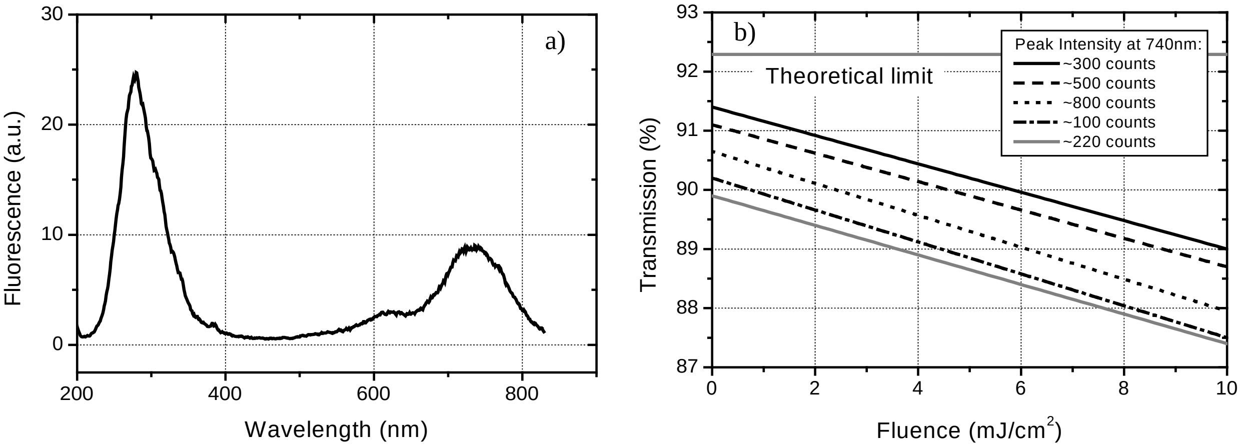

Figure 7: a) Typical LIF spectrum of CaF_2 samples showing, apart from the STE emission, an emission at around 740 nm and b) corresponding fluence dependent transmission data for 5 CaF_2 samples (thickness: 100 mm) with different peak intensities of the 740 nm fluorescence.

Thus, like for the 580 nm emission, a non-linear absorption process is assumed to be the origin of this fluorescence and, even stronger than for the 580 nm emission, this puts limitations on this type of CaF_2 material especially for high laser fluence applications. Additionally, the extrapolated values for T_0 are slightly lower for the investigated samples than for the those in the previous chapters. However, no correlation is found between T_0 and the peak intensity of the 740 nm emission. Therefore, again we suppose that different contributions of surface absorption or scattering are the main reason for the differing values of T_0.

3.3.5 FLUORESCENCE AT AROUND 450 NM

Some of the CaF_2 samples revealed an intense blue fluorescence upon ArF laser irradiation corresponding to an emission peak at around 450 nm (fig. 8a). The presence of this fluorescence is accompanied with a drastic change in the transmission properties of the samples as shown in fig. 8b. The most obvious feature is the significant decrease of the extrapolated values for T_0 compared to all other investigated CaF_2 samples. Since there is barely a correlation between the values T_0 and the peak intensity at 450 nm it can be supposed that evidently a strong increase of scattering is correlated with the occurrence of the 450 nm emission. In addition, the slope |dT/dH| increases compared to the best CaF_2 material in our studies. From the results of the transmission measurements we can conclude that CaF_2 material showing a laser induced fluorescence at 450 nm can hardly be used as the optical material for ArF excimer laser lithography.

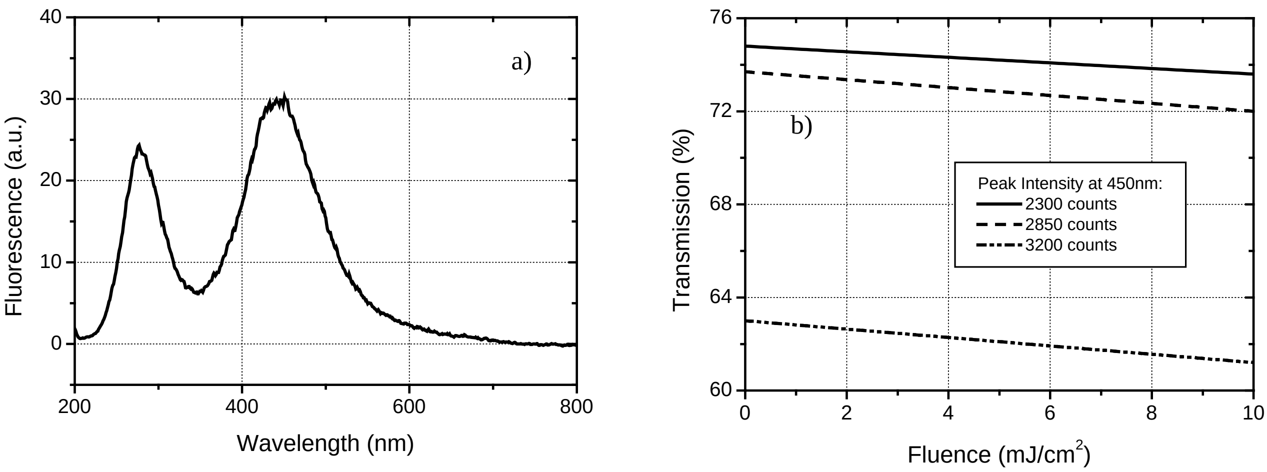

Figure 8: a) Typical LIF spectrum of CaF_2 samples showing, apart from the STE emission, an emission at around 450 nm and b) corresponding fluence dependent transmission data for 3 CaF_2 samples (thickness: 100 mm) with different peak intensities of the 450 nm fluorescence.

4. SUMMARY

Precise transmission measurements of a large number of high purity CaF_2 samples using a particular fluence sequence have demonstrated that the well known fluence dependent stationary transmission value is independent of the irradiation history. It was further found that for all samples and applied fluences a pulse number of 30,000 was sufficient to reach the stationary transmission value. Transmission measurements have also shown that even for the high purity CaF_2 the decrease of the transmission with increasing laser fluence can differ by almost a factor of 4 which is important especially for high laser fluence applications.

In order to distinguish between CaF_2 samples with different fluence dependent transmission behavior a setup for laser induced fluorescence (LIF) measurements was applied. From the measured fluorescence lifetimes of common laser induced emissions in CaF_2 appropriate registration conditions were derived to quickly detect most of the important emission bands even for CaF_2 samples of highest purity. In contrast to previously published data[5] the results of the LIF measurements made evident that the presence of particular fluorescence bands is correlated with a particular behavior of CaF_2 during fluence dependent transmission measurements. Except from the intrinsic self-trapped exciton fluorescence 4 common fluorescence bands have been investigated more detailed. It could be demonstrated that the occurrence of a doublet band at 313 nm and 333 nm has no influence on the material's quality upon ArF laser irradiation. In contrast to this doublet band emissions at around 580 nm and 740 nm show a strong impact especially on the slope |dT/dH| of the fluence dependent transmission. Therefore, this CaF_2 material might cause problems due to unwanted laser induced absorption when operating in high fluence applications. The most critical fluorescence found in the experiments is an emission with its maximum at around 450 nm. The presence of this emission is correlated with a strong decrease of the transmission even for very low fluences, probably due to an associated building up of scattering. Therefore, the origin needs to be clarified and it is strongly recommended to avoid this type of laser induced fluorescence for high quality CaF_2 for ArF laser lithography.

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