

Study of the defect in the CaF₂ materials via a laser-induced fluorescence measurement

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Abstract. Analysis of defects in optical materials is crucial for their applicability in cutting-edge optical components. Since calcium fluoride (CaF₂) is highly regarded for optical applications, understanding the nature of defects within CaF₂ is particularly significant. These defects have been conventionally identified through absorption and photoluminescence (PL) emission studies. In this work, we investigate the defects by measuring laser-induced fluorescence (LIF) spectra over a long irradiation. By decomposing the PL spectrum into multiple Gaussian PL bands, we identify the defects within the CaF₂ material. The measurement of irradiation-induced PL can be rationalized by the stabilization of F-centers via the formation of M-centers. PL mapping has been also studied to study the potential link between the surface oxygen contamination of CaF₂ samples and polishing techniques.

1 Introduction

Calcium fluoride (CaF₂) holds significant importance in optical applications, commonly utilized in the fabrication of optical components such as lenses and window materials for lithography. However, this material is characterized by several intrinsic defects including F-centres and M-centres or traces of impurities of various elements, referred to as extrinsic defects [1].

These defects, which can be also induced by the different polishing procedures, lead to optical absorption and photoluminescence (PL) in UV and visible regions, restricting the optical quality of the CaF₂ materials. Another mechanism of defect formation is CaF₂ exposure to UV laser light, which leads to enhanced PL emission from the material, denoted as laser-induced fluorescence (LIF). LIF has been previously studied with the observation of the influence of Na on the formation and stabilization of color centers in CaF₂ [2].

In this work, we report on an observation of LIF in CaF₂ with properties highly different from the previous reports. We studied the phenomenon on two samples prepared using different polishing procedures. Subsequently, by fitting the LIF spectra with multiple Gaussian emission bands, we discuss and identify the different defects within the CaF₂ samples. Additionally, we rationalized our results by the formation of M-centers. Finally, we discuss the effect of the polishing procedure on oxygen surface contamination by mapping the PL over the samples.

2 Results and discussions

2.1. Laser-induced fluorescence spectra

Figures 1(a) and 2(a) represent the LIF spectra of two CaF₂ samples under continuous laser illumination at 257 nm, i.e. 4.82 eV (215 fs pulse length, 100 kHz rep. rate, 3 μJ/pulse). The samples (Knight Optical substrates, 25mm diameter, 3mm thickness standard grade) were polished by a continuous pitch polishing technique using two different polishing agents: ceria (CeO₂) and diamond.

The LIF spectra of both samples displayed different PL bands with peaks at approx. 2.5, 2.75 and 2.9 eV. Furthermore, these spectra exhibited broader features at both high and low energies, indicating the presence of additional bands. Therefore, we applied fit via multiple Gaussian functions. To reach a reliable result, we fitted mutually all spectra measured over long-time irradiation.

We present here only the fit of the initial and the final measurements of PL spectra for Samples 1 and 2 – see Figures 1 and 2, respectively. In both figures, the experimental spectra are represented by a solid black line, and the theoretical fit (solid red line) was obtained as a sum of multiple Gaussian bands (blue dashed lines).

The fit revealed six PL bands with their maxima located at 2.1 eV, 2.5 eV, 2.78 eV, 2.95 eV, 3.2 eV, and 3.5 eV. According to Ref. [1,3], the emission bands observed in CaF₂ samples at 2.95 and 2.1 eV were identified as F-center and M-center, respectively.

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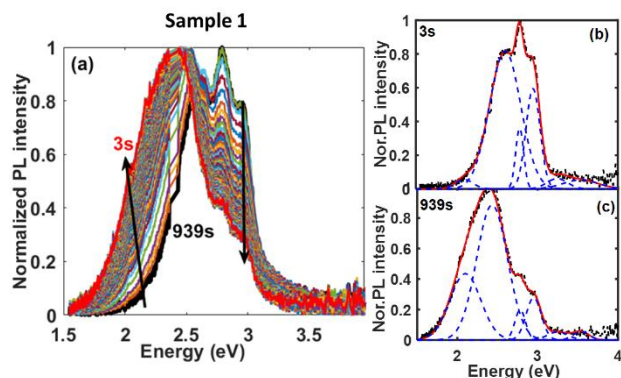


Fig. 1. (a) Normalized LIF spectra for Sample 1 of CaF₂, polished using the pitch polishing method using ceria (CeO₂) water-based polishing slurry, excited at 4.82 eV and detected at long irradiation. (b) and (c): Normalized LIF spectra for the first at 3s and last measurements at 939s, respectively.

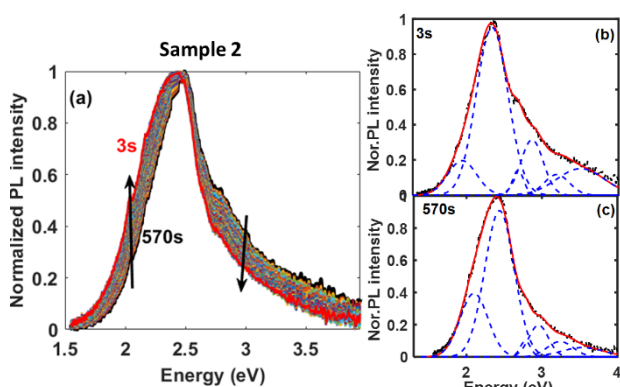


Fig. 2. (a) Normalized LIF spectra for Sample 2 of CaF₂, polished using the pitch polishing method using diamond water-based polishing slurry, excited at 4.82 eV and detected at long irradiation. (b) and (c): Normalized LIF spectra for the first at 3s and last measurements at 570s, respectively.

The fluorescence intensity behaviour of the F and M-centers in both samples showed similar signs – see Fig. 3. We observed that PL ascribed to the F-center in CaF₂ decreased over long laser irradiation while the PL of the M-center increased. Yet, it is worth noting that the exact rate of changes and their saturation for longer irradiation time were different for different spots.

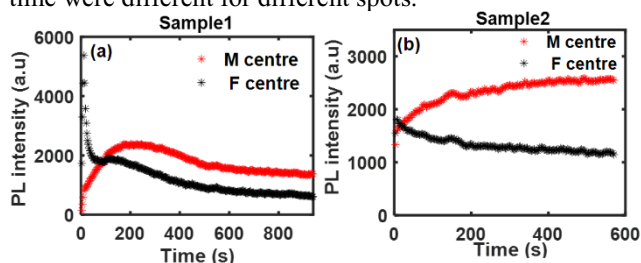


Fig.3. Variation with time of the fluorescence intensity of the F and M-centers: (a) Sample 1 and (b) Sample 2.

This can be explained by the self-stabilization of the F-centers [2, 4]. Over irradiation, two F centers self-stabilize by forming an M-center. This leads to a reduction in F-center concentration and, therefore, a decrease in their fluorescence intensity. While, the concentration of M-centers increases, leading to an increase in their fluorescence intensity.

2.3 Photoluminescence mapping

CaF₂ suffers also from the presence of other defects. Common is the presence of oxygen, which can be located on the surface or in bulk. The presence of oxygen in the bulk can be assigned to the PL emission band located at 2.78 eV. However, the oxygen on the surface emits at 2.5 eV [1, 5]. These oxygen surface defects were confirmed by measuring the Raman spectra for both CaF₂ samples. Since we used two different polishing slurries, the concentration of surface defects may vary. To check this effect, we compare the PL maps of oxygen surface defect between the two CaF₂ samples, as represented in Figure 3 (a) and (b).

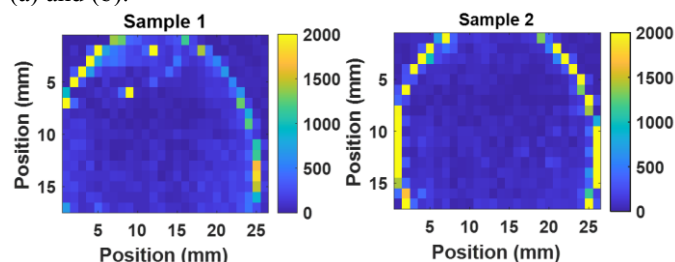


Fig. 3. PL maps of the oxygen surface defect for Sample 1 (a) and Sample 2 (b). Note that the color scale was adjusted to show PL from the sample center, while unpolished facets are saturated.

Surface oxygen PL mapping indicates that Sample 1, polished with a ceria slurry, exhibits locally higher oxygen contamination (see the upper sample part) than Sample 2, which was polished with diamond. This suggests that ceria is more prone to induce oxygen contamination in the CaF₂ polishing procedure. Moreover, we note that both samples exhibited strong emission along their facets on edges and adjacent areas. This likely stemmed from the difficulty of polishing these areas compared to the flat surfaces.

3 Conclusion

In this work, we used the laser-induced fluorescence measurement to study the defects in CaF₂, polished using different polishing agents' ceria and diamond. The measurement provides and identifies the different defects involved in the materials and also takes a look at the stabilization of the F and M centres. By mapping the PL of the samples, we reveal that surface oxygen contamination is improved by using diamond as a polishing agent.

References

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