

LASER INDUCED DEFECT CENTERS IN $\text{Ce}^{3+}:\text{CaF}_2$

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After laser irradiation at 308-nm of a 0.05% $\text{Ce}^{3+}:\text{CaF}_2$ sample, coloration of the crystal was observed due to laser induced defects. These new centers are associated with the cerium ions, and their creation kinetics have been measured. The coloration is photo-reversible, and may be bleached by illumination in the defect center absorption bands.

Cerium ions, when doped into a CaF_2 host, have previously been shown to exhibit photochromic properties.¹ These photochromic centers have been observed when the cerium ions have been reduced to the Ce^{2+} valence state as was done either by an additive coloration process, or by the long term exposure to gamma rays at low temperature.^{2,3} In contrast, the photochromic centers that are produced by irradiation with UV laser light, appear without any prior treatment of the sample. The centers are associated with the Ce^{3+} ions, and are evident after a single 5 nsec laser pulse.

To produce the centers, a 1.3 mm thick, 0.05% $\text{Ce}^{3+}:\text{CaF}_2$ sample was irradiated by 308-nm laser emission from a XeCl excimer laser. The 308-nm light is in near resonance with the lowest $4f \rightarrow 5d$ absorption band of the Ce^{3+} ions. Similar excitation of the sample with 351-nm and 337-nm laser light shows no effect and undoped CaF_2 remains transparent under 308-nm excitation. Also, illumination with 308-nm light from a Xe lamp failed to produce any coloration, even after several hours of exposure.

The absorption spectrum of the photochromic centers is shown in Fig. 1. The absorption bands are broad with peaks at 360 nm, 510 nm, and 800 nm. The sample can be bleached back to its original state by illumination into the absorption bands of the center. This bleaching has been observed with 351-nm, 532-nm, and 633-nm laser light as well as with white light. The centers can also be bleached by the $5d \rightarrow 4f$ luminescence of the Ce^{3+} ions. The centers are very stable at room temperature and they will persist for over a month if the sample is kept in a dark place.

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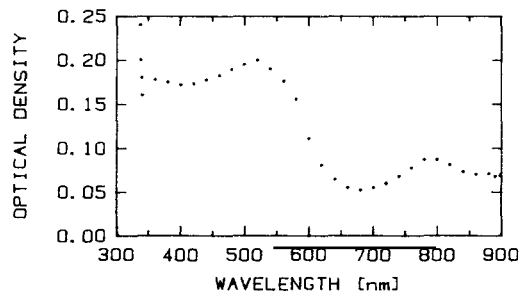


Fig. 1. Absorption spectrum of the laser induced photochromic centers taken with a Cary 14 spectrophotometer

To measure the creation kinetics of these centers, we monitored the absorption coefficient at 633 nm as a function of the number of laser pulses for different intensities of the 308 nm beam. The results of these measurements are summarized in Fig. 2. The change in the absorption coefficient after the first shot shows a linear dependence on the intensity from approximately 2 to 30 MW/cm^2 . However, when the intensity was reduced to 0.1 MW/cm^2 , no absorption was observed even for a large number of laser shots. This seems to indicate that some threshold intensity must be reached before the photochromic centers can be created, and that the creation process may be more complicated than simple one photon absorption.

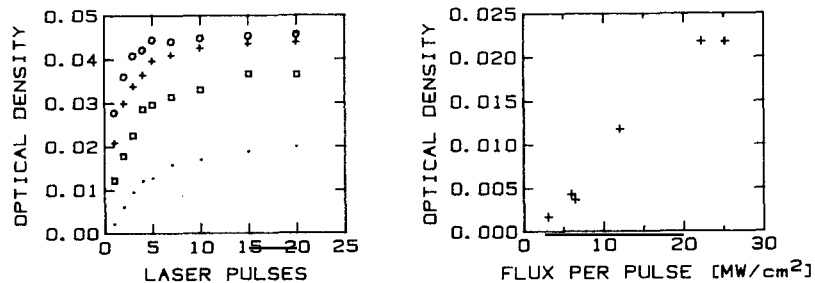


Fig. 2 a) Absorption at 633 nm versus laser shots for different intensities of the 308 nm beam. (intensities in MW/cm^2 are (\cdot)=6; (\square)=12; ($+$)=25; and (\circ)=44). b) Absorption at 633 nm after a single 5 nsec pulse versus the pulse intensity.

One can also see that the absorption coefficient reaches a saturation value which depends on the intensity of the laser light. For intensities below 50

MW/cm^2 , the saturation value of the absorption coefficient has a strong dependence on intensity. But for higher intensities, the dependence is very weak. The saturation process for the absorption coefficient suggests that some flux dependent process limits the number of photochromic centers created.

We have also observed an afterglow phosphorescence associated with the laser induced centers. After irradiation at 308 nm, the sample continues to fluoresce as long as there are photochromic centers present. Their emission spectrum was measured with a half-meter spectrometer and was found to be due to the $5d \rightarrow 4f$ fluorescence of the Ce^{3+} ions. In addition to the luminescence caused by the relaxation of the photochromic centers, there is a much stronger fluorescence due to other transient centers in the crystal. The fluorescence for these centers shows a multi-component decay with an initial lifetime of approximately 5 sec and another component whose lifetime is about 24 sec. The fluorescence can be enhanced by illuminating the sample with visible light while the centers are present. If the sample is bleached by irradiation with 532-nm laser light, the fluorescence disappears.

Although further experiments are needed before a detailed model of these centers can be presented, a number of observations can be made. The creation of the centers involves the excited state of the Ce^{3+} ion. Once the cerium ion is in an excited state, it may autoionize leaving a trapped electron in the crystal, rather than return to its $4f$ ground state by photon emission. While there does seem to be an intensity threshold for the creation of the centers, the production rate appears to be linearly proportional to the intensity beyond the threshold value. The fluorescence experiments indicate a number of different traps are populated after the excitation of the cerium ion by the UV irradiation. All of these centers can relax via the Ce^{3+} excited state and subsequent photon emission. While most of the fluorescence decays in a few minutes, some photon emission persists as long as photochromic centers are present. The phosphorescence can also be enhanced by illumination of the sample with visible light.

In summary, the excitation of a Ce^{3+} ion in a CaF_2 host by illumination with strong laser light can produce optical centers in the crystal with broad absorption bands. The process is photo-reversible and the system can return to the ground state through the excited state of the cerium ions.

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- 2) D.S. McClure and Z.J. Kiss, *J. Chem. Phys.* 39 (1963) 3251.
- 3) Z.J. Kiss and P.N. Yocum, *J. Chem. Phys.* 41 (1964) 1511.