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Laser-stimulated desorption and damage at polished CaF_2 surfaces irradiated with 532 nm laser light

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Laser-stimulated emission of Ca neutrals from polished CaF_2 (111)-surfaces was studied with a quadrupole mass filter system under UHV conditions. For intensity dependent measurements performed at various spots of the crystal surface a threshold pulse energy could be determined where a sharp decrease in transmitted light intensity occurred. Only for a few measurements this threshold coincided with the ablation threshold (type 1 spots). In most cases, however, the transmission breakdown threshold was found to be distinctly lower than the ablation threshold (type 2 spots). For type 2 spots a weak emission of delayed calcium atoms was observed at the transmission breakdown threshold. Irradiated spots have been examined by optical and scanning electron microscopy. Damage phenomena observed included coloration, cracking along crystal axes, surface erosion and surface melting depending on incident laser intensity. Pronounced differences between type 1 and type 2 spots with respect to laser light entrance and exit surface damage morphology were found.

1. Introduction

The interaction of intense laser radiation with single crystals of alkali and alkaline-earth halides has been extensively studied over the last years [1]. This work has been motivated by both a general interest in the mechanisms of light-solid interaction and a reliable determination and prediction of damage thresholds for IR and UV window materials. Some of the open questions in this field are most apparent when dealing with "real surfaces", i.e. polished crystals as used for optics applications, since in that case many complicated physical processes are introduced by extrinsic defects that locally disturb the geometrical and electronic structure of the perfect crystal [2].

The light–solid interaction mechanisms have been mainly discussed in terms of two different models depending on the quality of the crystal and its surface. For ultra-high purity materials with a perfect crystalline structure multiphoton processes bridging the bandgap have been found to be dominant for bulk absorption [3] while in the presence of absorbing centers an avalanche process is mainly responsible for the transfer of energy to the lattice. In the latter case the primary process of absorption is linear and may result from intrinsic point-defects [4], impurity ions of higher valence or surface contaminations. Also nonlinear light absorption resonantly enhanced by intrinsic surface states has been discussed [5]. In early work by Bloembergen [6] also damage resulting from local electric field enhancement and absorptive effects at cracks, pores and inclusions has been investigated.

Recently, two studies on UV laser ablation from alkaline earth halides and oxides have been published. Kreitschitz et al. [7] investigated the threshold behaviour of alkali earth halide surfaces exposed to pulsed laser irradiation in an *N*-on-1 irradiation mode by desorption measurements while Webb et al. [8] combined desorption studies with an examination of the resulting damage morphology. In a previous study [9] of laser induced desorption from CaF_2 we have shown that the main interaction process is the interaction of the laser light with crystal defects and impurities and particle emission has been observed below the front surface ablation threshold.

For the present study in-situ desorption and transmission measurements have been combined with an ex-situ analysis of laser damage at the entrance as well as the exit surface of the irradiated crystal.

2. Experimental

Polished, UV-grade single crystals supplied by Karl Korth company were mounted in a UHV chamber and

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baked out at 350°C for several hours prior to measurements. Details about surface analysis and preparation have been described in previous work [10].

Samples were irradiated with 532 nm laser light from a frequency doubled Nd:YAG laser system providing a doughnut shaped beam that was focused into a spot of approximately 0.2 mm diameter at the surface. The pulse energy was varied in the range of 1 to 10 mJ/pulse. Due to the poor laser beam profile that additionally contained some hot spots, the incident laser fluence could only be estimated to be in the range of 0.1 to 1 GW/cm^2 for the 7 ns laser pulse. The spatial laser beam profile present in most measurements had a five peak intensity structure resulting in "foot print" like damage structures on multiply irradiated spots. Incident and transmitted light intensity were monitored by a dual probe pyroelectric power meter.

Emitted particles were detected with a quadrupole mass filter equipped with an ionization device for the detection of neutrals [9,10]. Measurements for the present study were partly devoted to the investigation of delayed emission phenomena. To accomplish time-of-flight analysis the output pulses of the mass filter system were processed by a multi-channel-analyzer where each channel collected pulses within a time

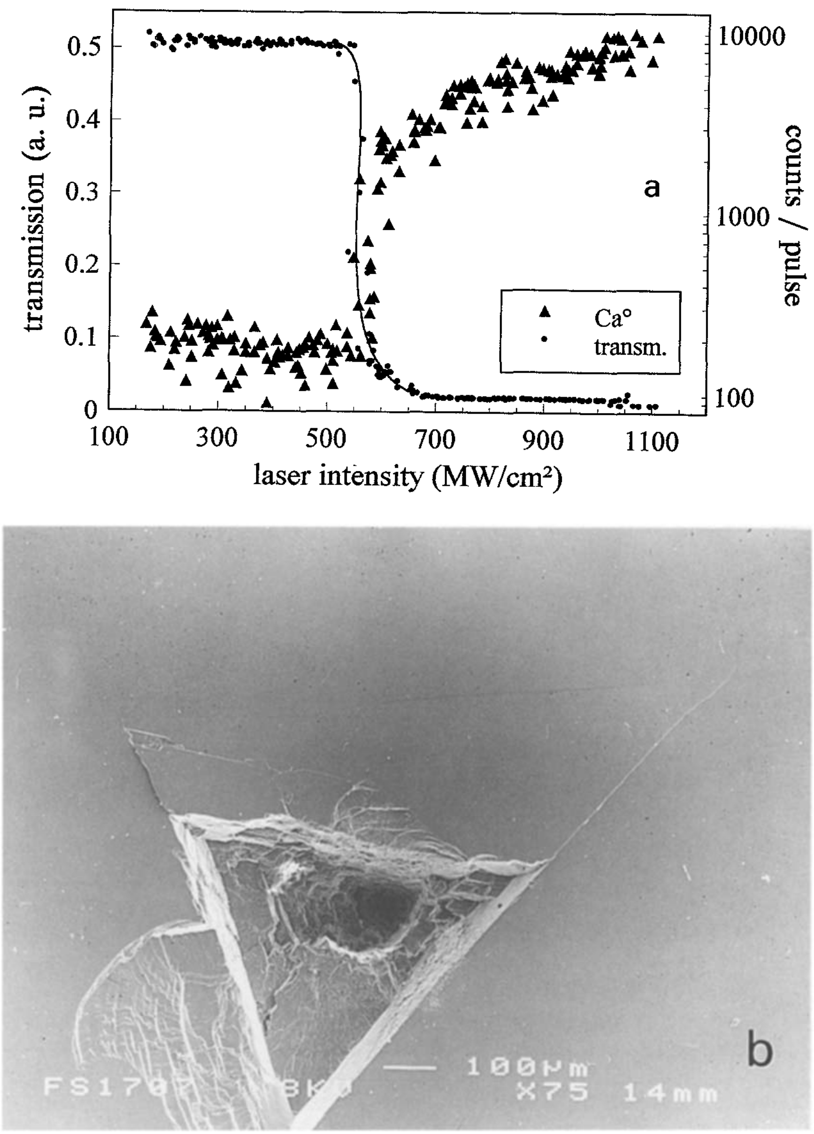

Fig. 1. Type 1 damage spot. (a) Laser-intensity dependent Ca^0 desorption yield and laser light transmission; (b) SEM micrograph of surface damage.

interval of 0.5 ms length at a certain time after the laser pulse. Data was accumulated for about 20 laser pulses with intensities in the region of interest.

3. Results

3.1. Desorption

For a great number of spots the yield of Ca^0 was measured for pulse intensities scanned from 200 to 1100 MW/cm^2, while irradiating the same spot with a total number of approximately 200 shots. Simultaneously, the transmitted laser light intensity was measured for each pulse and recorded as a function of intensity. Typical results for two spots are displayed in Figs. 1a and 2a.

In both measurements the transmitted intensity exhibits a sharp decrease at a certain pulse energy threshold followed by a gradual reduction to the minimum value characteristic for the heavily damaged crystal.

Particle count rates remain at a certain background value up to the ablation threshold intensity characterized by a sharp rise in count rate. The two thresholds, however, coincide (type 1 spots) in Fig. 1a while they

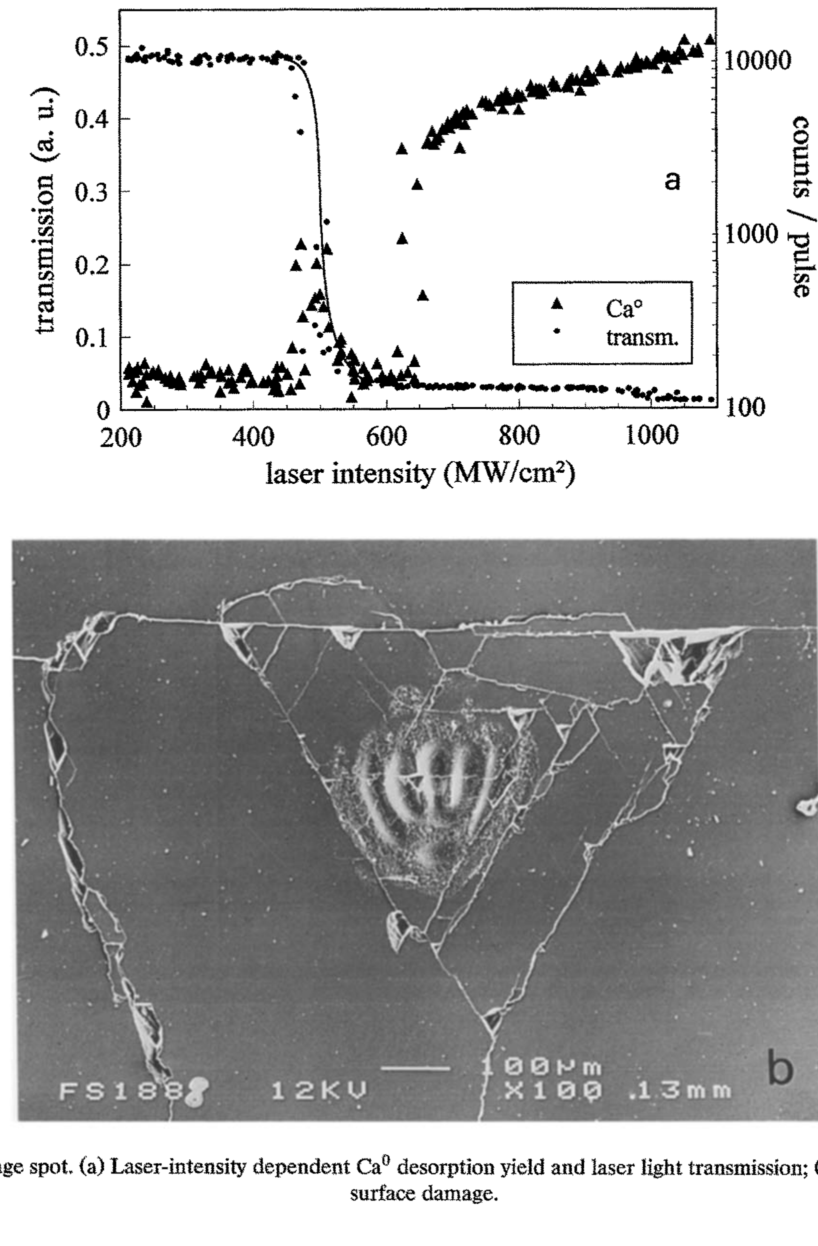

Fig. 2. Type 2 damage spot. (a) Laser-intensity dependent Ca^0 desorption yield and laser light transmission; (b) SEM micrograph of surface damage.

are well separated (type 2 spots) in Fig. 2a. Such a separation was observed for three fourth of the investigated spots. Another particular feature of the latter scans was the delayed emission of Ca^0 in a narrow intensity window around the transmission breakdown threshold.

Since we expected delayed emission from type 2 spots, the events corresponding to the desorption peak were analyzed with respect to their time of arrival at the detector. A typical time-of-flight distribution is shown in Fig. 3b and exhibits a quasi-exponential behaviour with a decay time of 130 ms. No enhanced prompt emission could be found in this and similar scans.

3.2. Damage

The front surface damage morphology resulting from heavy irradiation of the type 1 spot (same spot as Fig 1a) as seen in a scanning electron microscope (SEM) image in Fig. 1b comprises several different ablation and crack phenomena. The most significant damage is the removal of a large triangular piece of material with crack planes oriented along the natural cleavage planes.

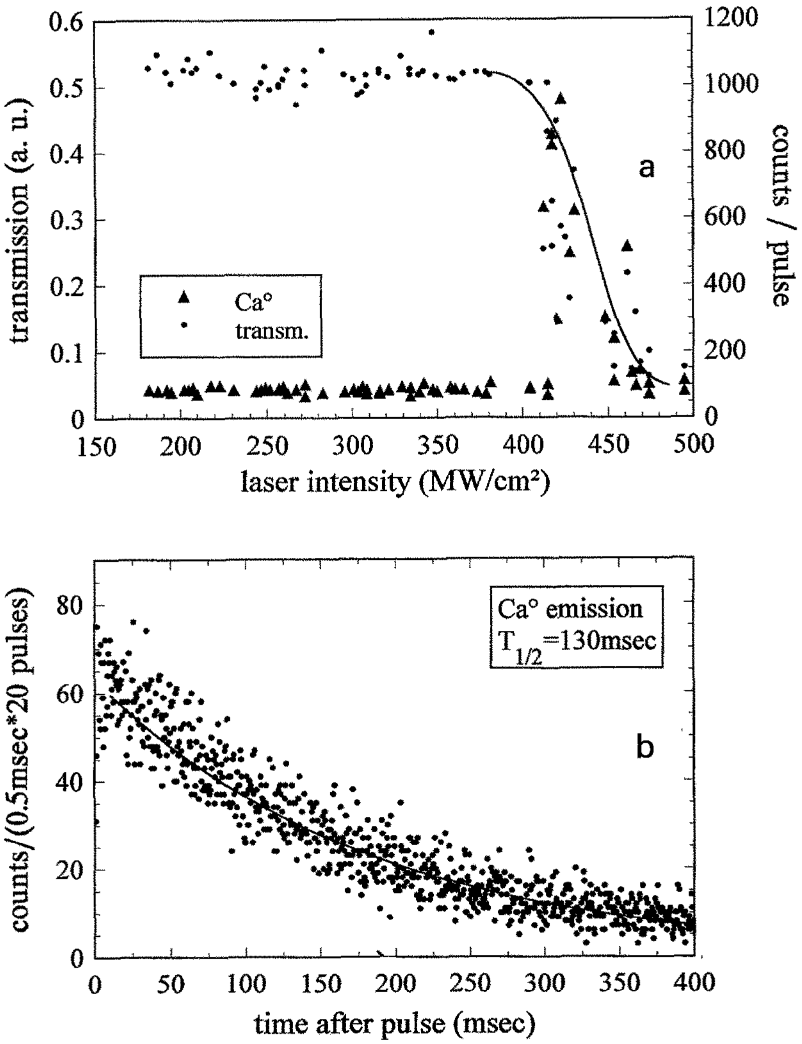

Fig. 3. Type 2 damage spot, irradiated with laser intensities below the ablation threshold. (a) Laser-intensity dependent Ca^0 desorption yield and laser light transmission. (b) Time-of-flight spectrum of the delayed Ca^0 emision signal integrated over 20 pulses in the vicinity of the intensity breakdown threshold.

The strongly localized energy input at hot spots in the laser profile results in the formation of two conical holes of different depth at the bottom of the ablated area. For irradiation with even higher dosages evidence for melting was found from SEM images not displayed here.

The most prominent features in the SEM picture of the type 2 spot (Fig. 2b, same spot as Fig. 2a) are the triangular crack structure extending far beyond the laser beam diameter and the "foot print" structure rendering the laser beam profile. This erosion type structure may be characterized as resulting from an "etching" process resulting in smooth shallow moulds on the surface. It is surrounded by a fine grain ruptured surface pattern in areas of less intense irradiation. High resolution microscopy on these areas reveals that the pattern mostly consists of small plates cut along the cleavage planes. The onset of such damage can be studied in Fig. 4 showing the result of single-shot laser irradiation at an intensity of 950 MW/cm^2. The thickness of the platelets was determined by SEM direct imaging under high specimen tilting to be between 0.3 and 0.4 μm.

No surface damage could be identified in SEM images for the weakly irradiated type 2 spot from the measurement shown in Fig. 3. Damage phenomena of this spot were investigated in detail with the optical microscope by a variation of the focal plane from the front surface to the bulk and exit surface of the specimen. The front surface picture does not display any irradiation induced modification while massive damage is found in the bulk. There, we additionally observed a massive purple coloration in regions of high laser intensity. The exit surface damage takes the form of an irregularly shaped crater surrounded by cracks without much alignment with respect to the crystal axes.

4. Discussion

In summary, four types of damage have been observed: *cracking* along crystal axes and *erosion* at the light entrance surface, the formation of irregularly shaped *craters* at the exit surface as well as bulk *coloration*.

The phenomenology of these observations is well in accordance with damage results on glasses reported by Boling et al. [11]. These authors pointed out that the apparent damage threshold is not only determined by the material, its defects and contaminations but also by the electric field distribution of the incident laser light in the material. Quantitative analysis reveals that there is a considerably large enhancement of field strength inside the material near to the exit surface while this

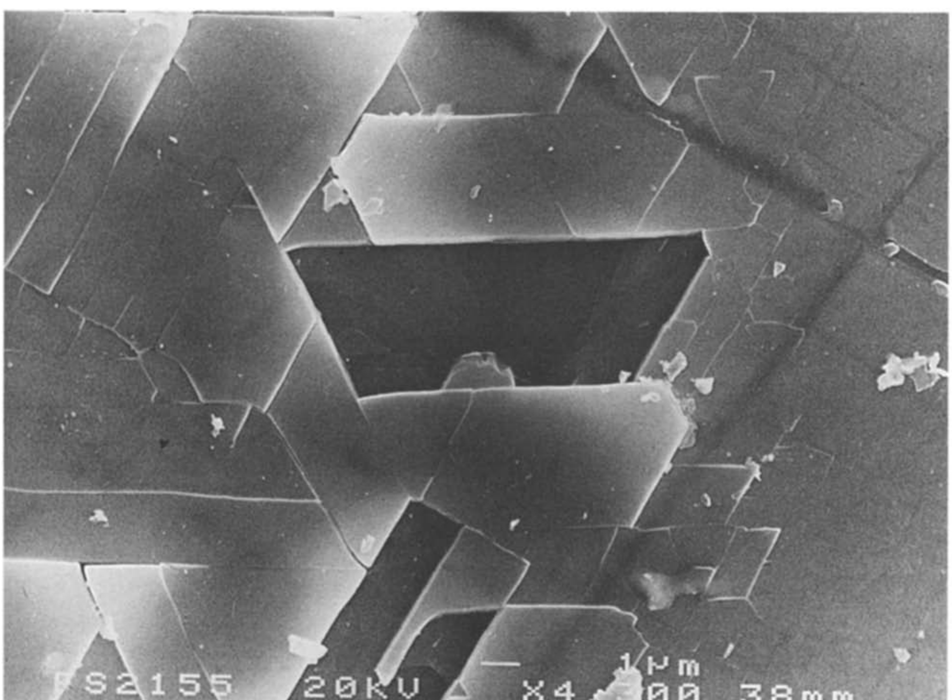

Fig. 4. SEM micrograph of surface damage resulting from single-shot irradiation at 950 MW/cm^2.

enhancement is outside of the entrance surface. Hence, for CaF_2 one would expect a ratio of 3 for the apparent field strength at exit and entrance surface.

In view of their considerations the following speculative model for the laser damage in CaF_2 can be developed. The location of initial damage events is either determined by defects at a specific location or by the hot spots of the damaging laser beam. Damage at the exit surface is more likely due to the electric field enhancement effect. The exit surface crater damage morphology results from an explosion like removal of material initated by strong absorption, heating and thermally induced expansion inside the crystal. At the entrance surface ablation only occurs at very high intensities. For medium intensity irradiation a large fraction of the laser pulse energy will be absorbed by the plasma ignited in front of the surface. The plasma–surface interaction results in the etched structures, however, the entrance surface is also subject to strong mechanical stress due to shock waves launched from the plasma region. This leads to surface cracking what is the predominant feature for low intensity above threshold irradiation. If bulk damage occurs the plasma will be confined to the interior of the crystal and heat up to very high temperatures. The vicinity of such damage sites will be heavily bombarded by energetic electrons and soft X-rays from the plasma. This could readily explain the coloration often present at bulk damage spots.

The origin of the delayed emission of Ca^0 observed for type 2 spots in the vicinity of the transmission breakdown threshold can be explained as an entrance surface desorption resulting from exit surface damage, although, up to now we do not have complete experimental evidence for such a process. The basic observation leading to this assumption is the fact that for all type 2 spots that have not been irradiated with intensities above the second threshold severe exit surface damage was found, however, the entrance surface was not visibly or only slightly crack damaged. Presently we believe that the delayed emission results from particles creeping out of micro-cracks that are generated by shock-waves launched from an exit surface or bulk damage center. Several experiments have been carried out to exclude measuring delayed particles emitted from the back side of the sample (e.g. reduced pump speed yields same results). Furthermore, we regard the emission of F^+ ions at the intensity breakdown threshold of type 2 spots observed in many experiments [10] as strong evidence for a front side emission since ions emitted from the back side will be neutralized immediately when interacting with chamber walls.

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