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Laser damage of alkaline-earth fluorides at 248 nm and the influence of polishing grades

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Abstract

Damage behaviour and thresholds for single 248 nm/14 ns excimer laser pulses have been investigated for single crystals of CaF_2 and BaF_2 with (111) surface orientation. The probe beam deflection technique was applied as a sensitive tool for detecting the onset of single-shot damage. Below the plasma threshold, we observed one- and two-photon absorption for CaF_2 and BaF_2, respectively. When testing the influence of different polishing techniques, we found the lowest thresholds for conventional hard-polish. Advanced methods as ductile machining or chemical polishing lead to a distinct increase in damage threshold up to and even better than what is observed for cleaved surfaces. SEM investigations of irradiated areas show that damage preferably takes place at residual steps or other structural defects.

1. Introduction

Damage resistivity of dielectrics with band gaps much larger than the photon energy is of increasing practical importance. In the development of high-intensity laser systems, e.g., one of the limiting elements is the durability of optical elements. This especially holds in the UV region which is of particular interest for many applications. For example in laser lithography utilizing UV light damage problems become more severe when going to a shorter wavelength. But even for wavelengths as short as 193 nm we have to consider the mechanisms of light absorption for photon energies lower than the optical band gap of the material, as e.g. in case of fluoride. Here, the purity of the crystals plays a determinative role since impurities, point- and structural defects, as well as surface states give rise to occupied states in the band gap [1]. These states may promote single photon absorption [2–4] but unfortunately in most cases their electronic structure is not reliably known. This applies especially for commercial crystals, whereas multiphoton absorption may become important only in ultrapure crystals [5]. However, even in case of commercial crystals, multiphoton absorption can be resonantly enhanced by unoccupied defect states in the band gap and thus gain in importance [2,6]. When the wavelength of the laser light is in the deep UV, two-photon absorption may become possi-

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ble by exciting an electron directly from the valence to the conduction band. For CaF_2 this was shown by measuring the two-photon absorption coefficient for 193 nm laser light [7].

In this contribution we investigate laser induced damage of CaF_2 polished by different techniques. This material is due to its hardness and large band gap of about 12 eV [8,9] a promising candidate for optical components and achromatic multi-lens systems in UV laser optics. Recently we have shown that cleaved surfaces of $CaF_2(111)$ exhibit a remarkably higher laser damage threshold than polished crystals [10,11]. In order to corroborate this observation similar measurements were performed with cleaved and polished $BaF_2(111)$ crystals. They show the same trends, as described in Section 3. These results indicate that the damage behaviour is not only determined by crystal properties but in particular also by surface finishing. Polishing procedures cause severe surface deterioration and evoke structural defects. For standard polishing, e.g., a surface layer of about 0.3 μm thickness consisting of mechanically introduced dislocations was found to have a disordered crystalline structure [12,13]. Those lead to additional electronic states in the band gap and strongly enhance absorption of laser energy.

Advanced polishing techniques like ductile machining [14] or chemical polishing [15] that have been tested successfully on other materials may exhibit damage thresholds similar to those observed for terraces of cleaved surfaces. The main emphasis here is not damage topography, that has been described in detail elsewhere [10,11], but a comparison of these different surface finishings. This was accomplished combining two complementary experimental techniques: the probe beam deflection (PBD) [16] technique for in-situ detection of damage thresholds and scanning electron microscopy (SEM) for a further inspection of laser irradiated crystal areas. Additionally ultraviolet photoemission spectroscopy (UPS) was performed to verify the enrichment of occupied states in the band gap due to polishing.

2. Experimental

Experiments were carried out on cleaved and optically polished UV-grade CaF_2 and BaF_2 single crystals with (111) orientation, purchased from Karl Korth (Kiel). The influence of surface finish was investigated on four different samples of $CaF_2(111)$. Two of them have been hard-polished, the third sample was cleaved and afterwards mechano-chemically polished (at the Max-Planck-Institut für Mikrostrukturphysik in Halle), and the last one was polished (by K. Korth) by moving a sharp diamond point across the surface that penetrates the brittle material to a depth less than about 500 nm, a technique called ductile grinding.

All crystals were irradiated under normal conditions with 14 ns light pulses of 248 nm of an excimer laser with pulse energy densities varying in the range of 0.3 to 40 J/cm^2. In order to avoid incubation effects, i.e. increasing defect concentration during continued irradiation [17], *all measurements were carried out in a single-shot irradiation mode*. A HeNe laser probe beam guided parallel to the surface at a distance of about 3 mm was deflected by acoustic or shock waves. The arrival time of this deflection signal as well as its amplitude were monitored. As a further indication of the damage onset plasma light was measured. Scanning electron microscopy of the irradiated sample was performed using a JEOL field emission SEM 6300F in secondary electron mode. Crystal surfaces were not conductively coated which remarkably enhanced the sensitivity for detection of surface modifications, as described in Ref. [18].

3. Intrinsic crystal properties versus surface modifications

The observation that *cleaved* CaF_2 shows a distinctly higher laser resistivity than *polished* CaF_2 proves that surface quality plays a much more important role for the onset of damage than intrinsic crystal properties. This raises the question whether polishing can produce a sufficiently high density of electronic states in the band gap to distinctly alter the absorption properties of the investigated dielectric materials. This was tested by UPS measurements carried out on polished and cleaved $CaF_2(111)$ crystals. Results are shown in Fig. 1 where two observations can be made for polished surfaces. First, the valence band consisting of 2p electrons of the fluorine ion is substantially broadened and, secondly, an additional peak appears as a shoulder at the right side of the valence band peak. This feature is due to defect states and clearly shows that polishing creates additional occupied states in the band gap that must be attributed to dislocations.

A second set of experiments, also checking the importance of surface quality for the damage onset, was performed with $BaF_2(111)$ crystals. BaF_2 differs from CaF_2 by its smaller band gap (10.5 eV) and its lower hardness due to a reduced surface energy (28 $\mu J/cm^2$ instead of 45 $\mu J/cm^2$) [19]. Also, in contrast to CaF_2, a two-photon absorption becomes possible with the 5 eV photons at the moderate intensities used in our experiments [20,21].

As in the case of CaF_2, samples were sliced into two pieces to obtain a cleaved and a polished surface from the same crystal charge. The results of probe beam deflection measurements on polished $BaF_2(111)$ are displayed in Fig. 2 and show similar trends as for CaF_2 [10,11]. At a fluence of 5 J/cm^2 the deflection amplitude starts to increase significantly (Fig. 2a), but a two-threshold behaviour is not as obvious as for CaF_2. It becomes evident, however, when inspecting Fig. 2b, where the transit time of the deflection signal is plotted. It is found to be constant between 5 J/cm^2 and 12 J/cm^2, indicating an acoustic wave traveling with the speed of sound.

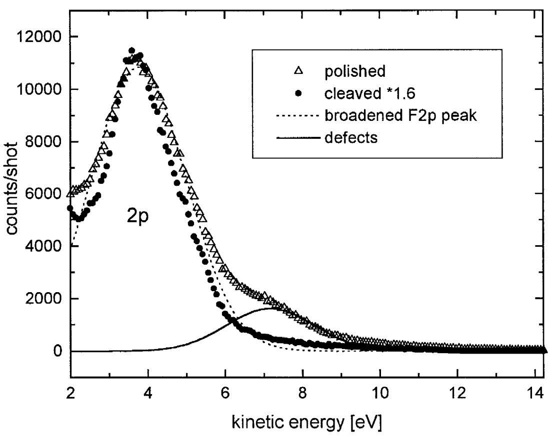

Fig. 1. UPS on cleaved and polished $CaF_2(111)$ measured with 21.2 eV He(I) photons at a temperature of 290°C. The spectra have been scaled to the maximum of the 2p valence band. For the polished surface the valence band is broadened and an additional peak appears.

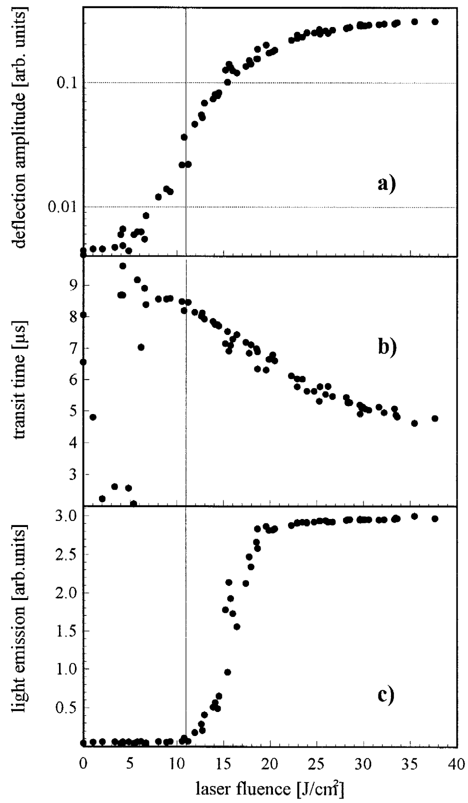

Fig. 2. Single shot damage threshold of *polished* $BaF_2(111)$ surfaces for irradiation with 248 nm/14 ns laser light under normal conditions. Each point represents a new virgin spot on the surface. The amplitude of the probe beam deflection signal is shown in (a), its transit time in (b), and (c) displays the light emission caused by a plasma. The solid line indicates the plasma threshold.

For fluence values greater than 12 J/cm^2 the transit time decreases due to the supersonic velocity of the shock wave generated by the plasma formation. This is further supported by Fig. 2c displaying the light emission from the plasma which also shows a threshold at 12 J/cm^2.

The slope of the signal in the acoustic region in a log–log plot is 2 (Fig. 3a) proving two-photon absorption for BaF_2 in contrast to polished CaF_2, where the subthreshold energy absorption is linear (Fig. 4a). Similar results have been obtained by Eva and Mann [7] in laser-calorimetric measurements, but these authors were not able to distinguish between bulk and surface absorption. To clarify the question whether the two-photon absorption is mainly of in-

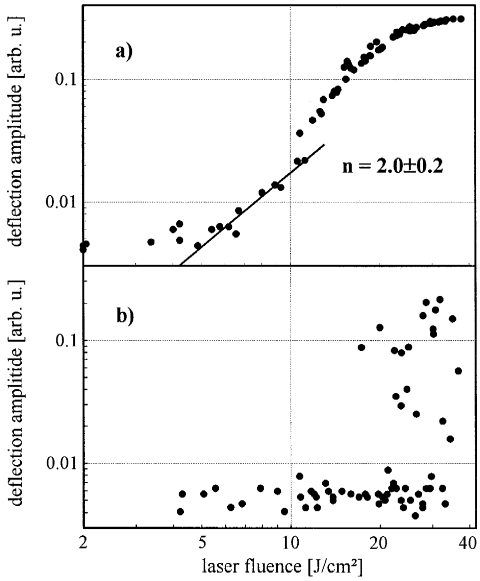

Fig. 3. Amplitudes of the probe beam deflection for (a) polished and (b) cleaved $BaF_2(111)$ surfaces. The slope of the signal in the heating region below the plasma onset is plotted in (a) to indicate the intensity range where two-photon absorption takes place.

trinsic nature this difference is of great importance. Therefore, we also compared polished and cleaved BaF_2. The cleaved crystals have no well-defined damage threshold but they always exhibit a higher resistivity compared to polished ones (Fig. 3b). Similar to CaF_2, damage preferably takes place at steps or edges. These observations and the fact that cleaved crystals exhibit no well defined slope in contrast to polished ones show that the probability of two-photon absorption is enhanced by unoccupied states in the band gap connected with dislocations, which have been introduced by the polishing process. Therefore, despite the differing degree of absorption, surface finish is the most relevant parameter determining the damage threshold.

4. Comparison of different polishing techniques

In the last section we have seen the detrimental effect of polishing on the resistance of dielectrics to high-power laser irradiation. Polishing, however, is essential for the production of optical components, especially curved surfaces. Therefore, damage thresholds of $CaF_2(111)$ crystals processed by applying *new polishing techniques* have been compared with those obtained by traditional methods. In Fig. 4 the dependence of the deflection amplitude on laser fluence is illustrated for the different samples. Each point represents the single-shot response of a virgin surface spot. Fig. 4a and b show crystals, which have been hard polished, the first by K. Korth and the

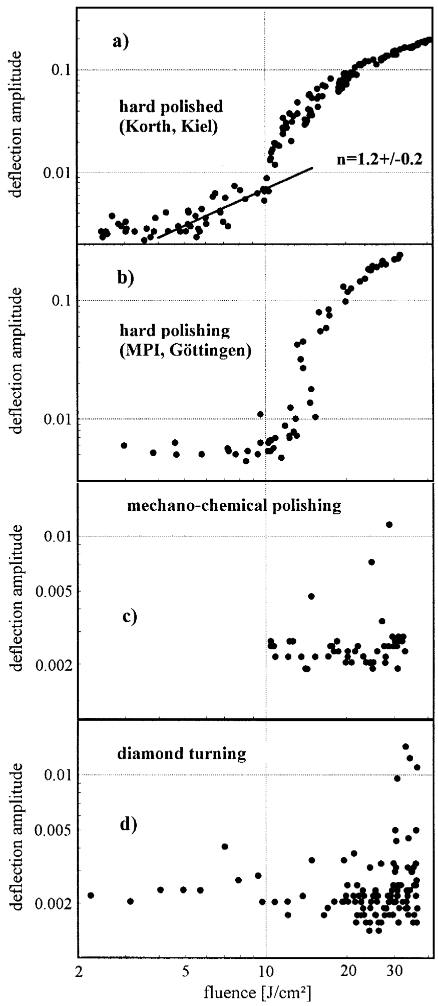

Fig. 4. Deflection signal caused by single-shot irradiation of $CaF_2(111)$ crystals polished by different techniques. In (a) and (b) the samples were hard polished and show a similar damage behaviour. Crystal (c) with a mechano-chemically polished surface as well as the ductile grinded crystal (d) display in general remarkably enhanced damage thresholds distorted by spurious defect spots. However, even at the highest applied fluences their deflection amplitudes are an order of magnitude lower.

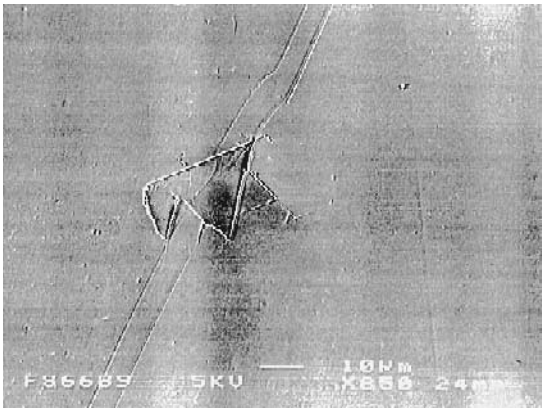

Fig. 5. SEM image of $CaF_2(111)$ irradiated with one laser pulse of 30.1 J/cm^2. The sample was first cleaved and than mechano-chemically polished. The crystal was tilted 45° with respect to the primary electron beam to enhance the topographic contrast. Damage clearly starts at residual steps.

second by the Max-Planck-Institut für biophysikalische Chemie in Göttingen. Both curves show similar trends with the second sample having a slightly higher damage threshold. Completely different results are obtained for the ductile grinded and the mechano-chemically polished crystals as shown in Fig. 4c and d. Most of the irradiated spots do withstand the laser light even at the highest fluences applied. The laser resistivity of these surfaces is as good as on terraces of cleaved samples. Only on a few spots a significant deflection amplitude is detectable which, however, is an order of magnitude lower compared to the signal obtained from surfaces polished by traditional techniques. This indicates very localized damage. To support this interpretation of the low deflection signal, SEM investigations were carried out on mechano-chemically polished crystals. An example is shown in Fig. 5. Obviously, damage occurs only at those parts of the irradiated area where steps of the originally cleaved crystals have not been completely removed by the polishing treatment. Similarly, in the process of ductile grinding periodic grooves remain (not shown here) and constitute preferential absorption sites.

5. Summary and conclusion

Single-shot laser damage of CaF_2 and BaF_2 at 248 nm has been investigated using the probe beam deflection technique. For polished BaF_2 surfaces we observed a two-threshold behaviour similar to that detected for CaF_2 but differences do exist concerning the energy deposition in the fluence region below the plasma onset. This subthreshold absorption occurs via two photons for BaF_2, whereas for CaF_2 it is linear. Polishing strongly enhances this absorption as shown by comparative experiments performed on cleaved BaF_2 surfaces. UPS measurements on CaF_2 revealed the generation of additional states in the band gap due to surface finishing. These are responsible for the observed absorption.

Advanced polishing techniques like chemical polishing or ductile machining have been found to enhance the damage resistivity as compared to traditional methods. Since damage of the chemo-mechanically treated crystal starts at residual steps as indicated by SEM investigations, further improvements may be possible.

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