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Nanosecond UV laser damage and ablation from fluoride crystals polished by different techniques

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Abstract. Ablation thresholds and damage behavior of cleaved and polished surfaces of CaF_2, BaF_2, LiF and MgF_2 subjected to single-shot irradiation with 248 nm/14 ns laser pulses have been investigated using the photoacoustic mirage technique and scanning electron microscopy. For CaF_2, standard polishing yields an ablation threshold of typically 20 J/cm^2. When the surface is polished chemo-mechanically, the threshold can be raised to 43 J/cm^2, while polishing by diamond turning leads to intermediate values around 30 J/cm^2. Cleaved surfaces possess no well-defined damage threshold. When comparing different fluoride surfaces prepared by diamond turning it is found that the damage resistivity roughly scales with the band gap. We find an ablation threshold of 40 J/cm^2 for diamond turned LiF while the MgF_2 surface can withstand a fluence of more than 60 J/cm^2 without damage. The damage topography of conventionally polished surfaces shows flaky ablation across the laser-heated area with cracks along the cleavage planes. No ablation is observed in the case of chemo- mechanical polishing; only a few cracks appear. Diamond turned surfaces show small optical absorption but mostly cracks and ablation of flakes and, in some cases, severe damage in the form of craters larger than the irradiated area. The origin of such different damage behavior is discussed.

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Laser damage and ablation of transparent dielectrics has been an important area of study for many years [1–4]. Among the materials used in optical applications, CaF_2 plays a prominent role in handling excimer laser radiation, specifically in advanced UV-laser lithography where optical elements have to meet highest standards with respect to both optical quality and damage resistivity [5]. The latter has been investigated for CaF_2 in particular with 248 nm – a wavelength today used in laser lithography – and was found to depend sensitively on the surface quality, i.e., extrinsic defects created by surface preparation. Therefore, all our measurements are carried out in a 1-on-1 irradiation mode which is most suitable for the study of defect related absorption [6]. This, however, will not apply to future studies in the deep ultraviolet (e.g., at 193 nm) spectral region where extrinsic defects play a minor role; instead the emphasis will be on the investigation of intrinsic defects and incubation phenomena studied by multi-shot experiments.

In our previous studies at 248 nm we measured the da mage and ablation behavior of conventionally polished CaF_2 (111) surfaces [7, 8] and presented a first comparison with surfaces prepared by advanced polishing techniques [9]. Scanning electron microscopy (SEM) was utilized for surveying irradiated spots and characterizing their damage topography [10]. In the present work we extend our studies to other fluoride materials and investigate ablation thresholds and damage features of samples treated with *advanced polishing techniques.* We elucidate the mechanisms of damage and ablation effective for each type of polish and compare the laser damage resistivities of different fluoride surfaces prepared by diamond turning. The ultimate goal is to explore possibilities for further increasing the laser damage resistivity and to find the best combination of material and polish for practical applications in high power laser applications.

1 Experiment

Three types of differently polished and cleaved (111)-surfaces of highest purity fluoride single crystals of CaF_2, BaF_2, LiF and MgF_2 have been investigated. We studied samples polished by conventional techniques using diamond grit, surfaces processed by diamond turning [11], and surfaces prepared by chemo-mechanical polishing [12] in combination with subsequent ion milling. The results are compared with the damage behavior of surfaces cleaved under normal conditions. All surfaces were irradiated with 248 nm/14 ns laser pulses and their response was detected by the photoacoustic mirage technique, described in detail elsewhere [13, 14]. In short, an acoustic wave travelling with the speed of sound is generated when the surface is heated above the ambient

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temperature. At higher fluences, once a plasma is formed, a supersonic shockwave develops for which speed and amplitude increase with increasing fluence.

Amplitude and arrival time of the mirage signal, the transmission of the sample, as well as plasma light emission were monitored as a function of the incident laser fluence. Here, we only discuss signal amplitudes which reveal sufficient information about pre-damage heating and the onset of ablation. Typical examples for CaF_2 are shown in Fig. 1. All data points are produced by single laser shots, i.e., each fluence value was obtained with one laser pulse directed at a new surface spot (1-on-1). We deliberately avoided measurements of multi-shot (n-on-1) damage since multi-shot results turned out to be hard to reproduce and difficult to interpret. Independent of surface treatment, no signal was detectable at fluences below 10 J/cm^2. When increasing the fluence, we observe a weak increase of the acoustic amplitude between 10–20 J/cm^2 for the standard polish (Fig. 1a) and 20–40 J/cm^2 for the advanced polish (Fig. 1c). The onset of ablation is marked by a sharp increase in amplitude, generated by the shock wave. This ablation threshold is well defined for samples A and C, somewhat fuzzy for the diamond turned surface (Fig. 1b), and non-existent in case of the cleaved surface (Fig. 1d). The reason for the latter is the varying density and quality of steps within the spot size (100 μm diameter) when moving the laser beam across the surface. We have reason to believe that damage starts at steps.

Scanning electron microscopy (SEM) recorded in secondary electron mode was used as a complementary experimental technique which allows visual inspection of the damage topography produced by high fluences. Sensitivity to surface charging also renders SEM capable of detecting minute material modifications even at the lowest applied fluences [10, 15]. We made an effort to establish a correlation between the acoustic signals and the actual surface modifications generated by the laser shots.

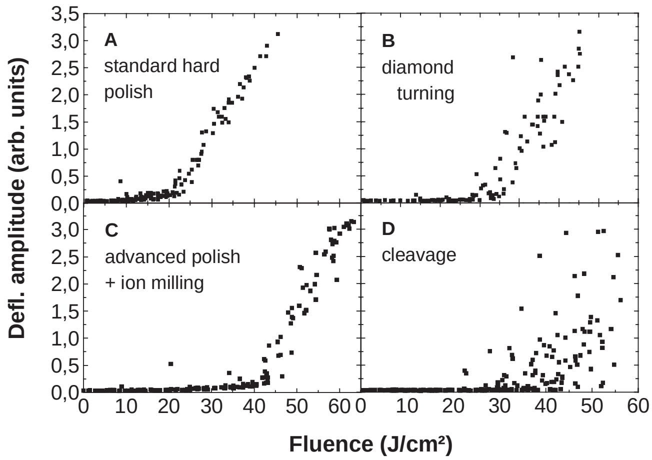

Fig. 1a–d. Fluence dependence of the photoacoustic signal amplitude for differently prepared (111) surfaces of CaF_2 crystals. **a** conventional standard polish; **b** surface prepared by diamond turning; **c** chemo-mechanical polish; **d** cleaved surface

2 Results and discussion

Comparison of the acoustic data for all CaF_2 samples with different polish in Fig. 1 shows a dramatic dependence of the threshold behavior on surface preparation. In Fig. 2 the damage topographies are shown for each polishing type after irradiating them with specific fluences stated in the figure caption. Albeit sold as an optical grade crystal, the surface polished by standard techniques showed the lowest ablation threshold of 20 J/cm^2 (see Fig. 1a). Below this value, surface heating occurs, which we attribute to absorption of light by surface defects introduced by the polishing procedure. The SEM image in Fig. 2a recorded above the damage threshold consists, inside the spot, of long cracks along (111) cleavage planes and massive removal of large flakes. In contrast, we notice at the periphery a high density of short cracks and no ablation. The reason is different thermoelastic forces acting inside and at the edge of the laser spot. Since we worked with a top hat laser profile, heating is fairly homogeneous across the spot. Hence, inside exists a strong *vertical* temperature gradient, but the lateral one is negligible. By exceeding the thermoelastic stress limit, the *vertical* gradient causes rupture at a certain depth parallel to the surface [8], leading to ablation of flakes. At the periphery of the spot, on the other hand, the strong *lateral* temperature gradient generates shear stress along the surface, which is responsible for the high density of short ranged microcracks discernible at the periphery [7, 8].

A significant increase of the damage threshold can be achieved by diamond turning. We observe a well defined damage threshold around 28 J/cm^2 (Fig. 1b), about 40% higher than the one for the conventional polish. For diamond turned polish we notice no apparent surface heating below the threshold. The scatter of the data above the threshold indicates that damage seems to start rather localized and differs significantly from spot to spot. SEM inspection in Fig. 2b exhibits large scale damage inside the spot but a surprisingly sharp boundary without any lateral cracks. The central damage pattern is reminiscent of the one in Fig. 2a, which means

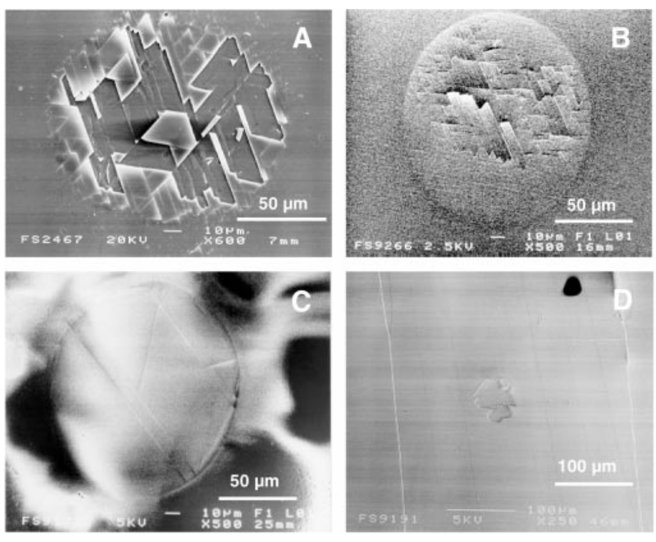

Fig. 2a–d. SEM images of damage topographies of CaF_2(111) surfaces irradiated with the following fluences: **a** 27.6 J/cm^2 at the conventional standard polish; **b** 30 J/cm^2 at the diamond turned surface; **c** 57.7 J/cm^2 at the chemo-mechanically polished surface; **d** 46 J/cm^2 at the terrace area of a cleaved surface

that damage still originates from the *vertical* temperature gradient. Missing cracks at the periphery, on the other hand, indicate that the high pressure applied during the turning procedure has produced a thin amorphous layer with little optical absorption in which no oriented lateral cracks can develop under thermoelastic stress.

The chemo-mechanical polishing technique led to the highest ablation threshold at a fluence value around 43 J/cm^2 (Fig. 1c). A number of SEM investigations with this sample revealed that mostly defects not removed by the polishing process initiate the damage. Interestingly, the overall damage behavior is different compared to the two previous cases. It is characterized by only a few straight fracture lines across the laser spot (Fig. 2c). No material removal could be observed even at the highest applied fluences reaching up to 60 J/cm^2, which raises the question why shock waves are observed in Fig. 1c. We believe those are produced by violent crack formation, seen as fracture lines in the SEM image in Fig. 2c, which seem to originate near the edge of the laser spot. In contrast to conventionally polished surfaces where damage starts at the place of highest vertical temperature gradient, here the highest lateral temperature gradient seems to trigger the cracks. Although there is a slight increase of the acoustic signal below threshold (Fig. 1c), absorption inside the spot in Fig. 2c seems to be significantly reduced, indicating a low concentration of surface defects. As a consequence, vertical stress is too weak to overcome the thermoelastic stress limit.

Contrary to polished surfaces, the acoustic mirage signal of the cleaved surface does not reveal a well defined damage threshold (see Fig. 1d). Instead, over a wide fluence range we find a random distribution of acoustic amplitudes ranging from values close to the noise level to very high signals. Some spots remain undamaged even above 40 J/cm^2. This large scatter of the acoustic data is caused by the step density inside the laser spot. Cleavage steps are easily damaged while terraces are rather radiation resistant due to their low concentration of structural defects and absorption centers [16]. A rare example of a damage spot on a terrace is displayed in Fig. 2d. As can be seen from the length scale, in this case the laser spot was fortuitously placed on a terrace between two steps. The fluence was 46 J/cm^2 which obviously lies above the damage threshold of terraces. The source of this type of damage is not clear but most likely structural defects like dislocations give rise to the initial light absorption.

Results shown in Figs.3 to 5 have all been obtained on diamond turned surfaces. The aim of these investigations was to compare the damage and ablation behaviour of different fluoride materials and to explore some peculiarities of the diamond turning technique. The synopsis of mirage amplitudes shown in Fig. 3 reveals that the damage threshold roughly scales with the UV transparency limit of the respective material that is in turn related to its band gap. For BaF_2, CaF_2 and LiF with UV cut-offs of 150, 130 and 120 nm [17] we find ablation thresholds of about 12, 30 and 40 J/cm^2, respectively. For MgF_2 the ablation threshold is not well defined, but there is hardly any ablation below 50 J/cm^2 and the material having a transparency limit of 110 nm [17] also fits into the series. This scaling behaviour can well be understood by recalling that light energy deposition leading to detrimental effects solely occurs in the form of linear absorption by states

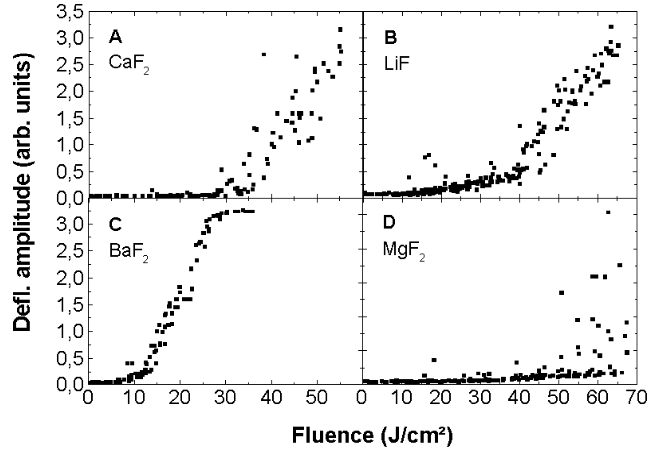

Fig. 3. Fluence dependence of the photoacoustic signal amplitude for different fluoride crystals polished by diamond turning

tailing from the top of the valence band far into the band gap [6]. Hence, for the same surface preparation, the density of occupied states high in the band gap allowing linear absorption of 5 eV photons into the conduction band is smaller for very wide band gap materials compared to that of crystals with a smaller band gap.

As is evident from Fig. 3d, a MgF_2 surface may at certain spots withstand a fluence of more than 65 J/cm^2 without ablation and Fig. 4d shows that there is no crack damage at 54 J/cm^2. We attribute this exceptional behaviour of MgF_2 to the fact that the ablation process is not only determined by the optical absorption but also by the thermoelastic stability of the laser-heated surface region. We speculate that the process of diamond turning does not introduce many absorbing defects into the surface but produces high mechanical stress causing damage in the form of dislocations and microcracks. This interpretation is also supported by other observa-

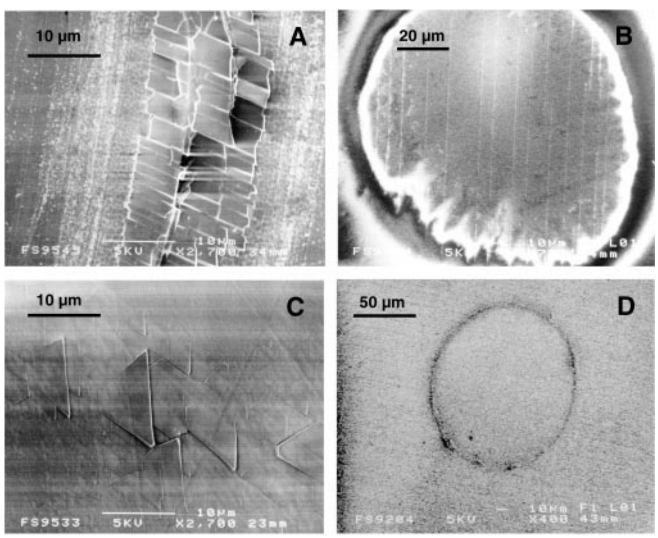

Fig. 4a–d. SEM images of damage topographies of fluoride surfaces polished by diamond turning and irradiated with the following fluences: **a** CaF_2 – 36 J/cm^2; **b** LiF – 50.4 J/cm^2; **c** BaF_2 – 12.6 J/cm^2; **d** MgF_2 – 54 J/cm^2. The laser spot diameter is 100 µm in all cases. Notice the magnified scale in a and c

tions. A comparison of mirage results from diamond turned and chemo-mechanically polished CaF_2 surfaces (Fig. 1b and 1c) reveals, for example, that the ablation threshold of the diamond turned surface is lower than that of the chemo-mechanically polished surface despite the higher absorption in the sub-threshold region observed for the latter. A careful inspection of irradiated spots as shown in Fig. 4 reveals that damage on diamond turned surfaces is often rather localized and associated with specific structural defects created during machining the surface. Examples are the lined-up facet structure in Fig. 4a and the minute tiles in Fig. 4b.

Figure5 demonstrates that such local deficiencies may, in fact, be a severe limitation for the use of diamond turned surfaces in high laser power applications. This SEM survey micrograph displays a series of irradiations on CaF_2 at various fluences where the irradiated spots are clearly marked by the bright circles often inside a larger halo. As will be elsewhere, the darker surrounding halos are charged features resulting from ejecta re-condensed at the surface, with a larger halo diameter produced by a higher laser fluence. Massive catastrophic damage in form of deep, irregularly shaped craters extending far beyond the irradiated area is observed for a great number of spots. Such type of damage has been observed only at very rare occasions in measurements on surfaces subjected to other types of preparation. The structure of these damaged spots, as revealed by SEM imaging with higher resolution, strongly indicates that they originate from well localized defect centers. It is interesting to notice that in Fig. 5 catastrophic damage is not correlated with the halo diameter, i.e., with the incident fluence. This is either due to local light absorption or mechanical weakening. We regard the irregular shape of the craters as a strong indication that in the case of diamond turned surfaces the defects are not light absorbing centers but surface and sub-surface structural damage created by the mechanical impact during machining. We speculate that the fracture strength in a surface region is reduced by micro-cracks surrounded by dislocations and even moderate heating is sufficient to initiate cracks that easily propagate along pathways pre-defined by the machining damage.

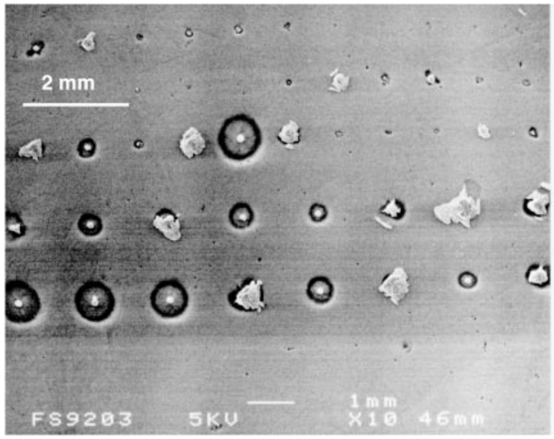

Fig. 5. SEM overview image of damage topographies of diamond turned CaF_2(111) surface irradiated with the fluences in range from 18.3 to 55.3 J/cm^2. *White spots* represent surface damage, *dark halos* originate from recondensed plasma debris

In a second set of experiments we compared the damage and ablation behaviour of diamond turned surfaces of CaF_2, BaF_2, LiF and MgF_2. It was found that the ablation threshold roughly scales with the UV cut-off limit of the respective material. However, MgF_2 exhibits an ablation behaviour distinctly different from that of the other materials insofar as there is large scatter in the data and an ablation threshold cannot be well defined. It was found that certain spots of this material can withstand fluences large than 65 J/cm^2 without ablation. It is concluded that in the case of MgF_2 damage and ablation are very much determined by local surface imperfections similar to the findings for cleaved fluoride surfaces. It has been demonstrated that local defects are generally a problem for diamond turned surfaces and may constitute a severe limitation for their use in high power laser applications.

3 Summary

We have compared single-shot damage produced by 248 nm/ 14 ns laser pulses on differently polished and cleaved CaF_2 (111) surfaces. Large differences were found between the laser resistivity of conventionally polished, diamond turned, and chemo-mechanically polished surfaces, and those prepared by cleavage. Conventionally polished surfaces exhibit the lowest thresholds, chemo-mechanically polished ones the highest. The resistivity of diamond turned surfaces comes out in between. The fluence threshold for damage on a terrace was derived from an SEM image and found to be comparable to the one for a chemo-mechanically polished surface, indicating that this type of polish is superior. SEM also revealed different topographic damage features for the different polishing techniques. For the chemo-mechanically polished surface no ablation could be detected for fluences up to about 60 J/cm^2; damage only resulted in cracks across the laser spot. The other two polishing techniques produced surfaces that could be damaged by fluences between 20 and 30 J/cm^2 with ablation starting in the center of the spot.

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