Strong Reduction of Laser Produced Damage in Sapphire and Ruby by Doping with TiO_2

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The selfdestruction of the ruby crystal which limits the output of a ruby laser in Q-switch operation to some 100 MW/cm^2 has been observed by various workers [1, 2], but has not been previously explained. Therefore it appeared important to us to investigate the damage produced in ruby and sapphire under the action of a well defined external laser radiation [3, 4].

The beam of a Q-switched ruby laser (peak power 50 MW/cm^2, pulse width 20 nsec) was focused by a lens ($f = 4$ cm) inside the crystal under investigation. The damage threshold was defined as the intensity of the parallel unfocused beam at which the resultant damage was just observable under a microscope. In some experiments the damage threshold was also detected by measuring the intensity of the light scattered at 90°, which increased by an order of magnitude at the threshold, or by the abrupt appearance of ultrasonic waves.

The hardness of all crystals (measured by the Vickers method) was approximately the same and hence the great variation of the measured threshold values could not be due to this parameter. Also stimulated Brillouin scattering can be eliminated as a cause for damage since stimulated Brillouin scattering could not be detected in any crystal at any power level.

However, experiments with a series of 8 Verneuil-grown sapphires, different only by their varying TiO_2 concentration in the starting powder, showed a clear relation between the damage threshold and the TiO_2 doping: An increase of the threshold by a factor of 45 with increasing TiO_2 concentration was measured as displayed in Fig. 1. The optimum doping is 80 ppm in the starting material. All crystals represented in Fig. 1 had been annealed simultaneously before the experiment.

During annealing most of the TiO_2 diffuses to the outer surface of the crystal causing the TiO_2 concentration in the interior to be substantially reduced after annealing. In accordance with this fact the annealing of 12 weakly doped (10 ppm) sapphires caused a drop of the threshold by a factor between 40 and 60 without exception.

A decrease of the TiO_2 concentration also causes a shift of the UV-absorption tail towards shorter wavelengths. This dependence (Fig. 2) was well confirmed by measuring the transmission of 5 crystals with varying TiO_2 concentration. Using these same crystals, the damage threshold was also measured. Fig. 2 also shows the relation between the damage threshold and the UV-absorption of these crystals. A higher treshold manifests itself in a shift of the UV-absorption tail towards longer wavelengths. This shift of the UV-absorption tail to longer wavelengths with increasing TiO_2 concentration was observed also in laser rubies (0.05% Cr_2O_3) and here again, the shift of the UV-absorption tail to longer wavelengths was accompanied by an increase of the damage threshold. It should be pointed out, that the absorption and scattering of *visible* light were quite independent of the damage threshold.

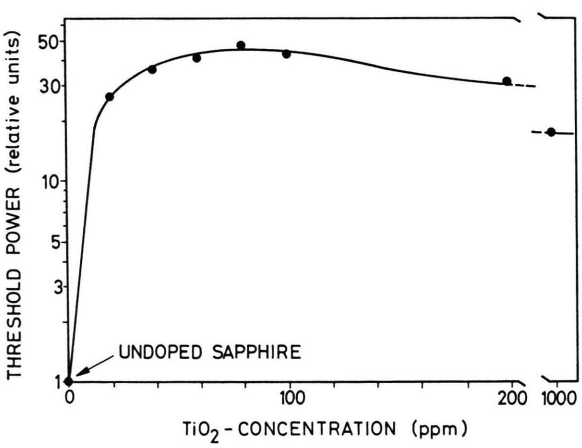

Fig. 1. Threshold power for damage in eight sapphire crystals grown with varying TiO_2 concentration in the starting material. All crystals were annealed simultaneously after growth.

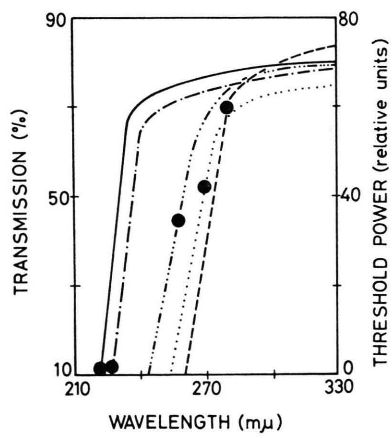

Fig. 2. The curves show the shift of the UV-absorption tail towards longer wavelengths for five sapphires of equal length (3.5 cm) with increasing TiO_2 concentration. The black dots represent the threshold power for damage of each crystal.

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The mechanism of destruction may be as follows. Electrons are lifted from the valence band into the conduction band by multiphoton processes. These conduction electrons are rapidly gaining enough energy in the intense laser beam to create further conduction electrons resulting finally in an electron avalanche which produces the damage. The existence of such a hot electron gas should manifest itself above the damage threshold by the emission of a broadband continuum which we have, in fact, observed between 400 and 800 mμ [5].

The incorporation of titanium in sapphire may prevent a development of the damaging electron avalanche in the following way: Ti probably replaces Al forming an acceptor state. Judging from the titanium induced strong UV-absorption at long wavelengths, the energy of this acceptor state appears to be situated several eV below the conduction band of the host crystal [6]. The presence of such low lying electron traps could effectively prevent the creation of conduction electrons in the host crystal, and thereby increase the damage threshold as observed.

The relation between UV-absorption and damage threshold provides a nondestructive method to select sapphires and rubies with a high damage threshold. Ruby crystals selected by this method showed increased operational lifetime and output when used as active elements in a Q-switched laser.

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The Electrical Conductivity of Solid and Molten Silver Iodide

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Several measurements of the electrical conductivity of molten and solid silver iodide were performed about 50 years ago [1–4]. The difference between the obtained results is more than 15%, and since little is known about the reliability of the difference investigations [5], we decided to remeasure the electrical conductivity of solid and molten silver iodide.

Some years ago we measured the thermoelectric power of molten silver iodide [6] and from the reproducibility of the results, we concluded that molten silver iodide is stable both in air and argon atmosphere up to at least 650 °C.

The conductivity cells were made of pure quartz [7] and the electrodes of bright platinum. Attempts were also made with silver electrodes, but no reproducible results were obtained. The conductivity was measured both in air and argon atmosphere, with cell constants of about 200 and 2000 cm^{-1}. The difference in the two runs was less than 0.2%. The used salt was of reagent quality (Hopkin & Williams) and was used without further purification.

The obtained specific electrical conductivities are given in Table 1 and are in excellent agreement with those obtained by Tubandt and Lorenz [3] both for the solid and for the melt (Fig. 1). The maximal difference is only 0.6%.

t (°C)	$\mathcal{H}$ (ohm^{-1} cm^{-1})	t (°C)	$\mathcal{H}$ (ohm^{-1} cm^{-1})
706.0	2.490	552.2	2.606
694.8	2.480	545.4	2.628
678.8	2.470	532.0	2.610
664.8	2.464	513.0	2.571
648.0	2.453	503.8	2.552
640.8	2.447	486.8	2.506
631.2	2.439	476.5	2.486
611.5	2.422	414.8	2.327
600.5	2.416	403.4	2.293
596.2	2.407	393.0	2.260
591.5	2.404	371.5	2.199
590.2	2.404	360.6	2.166
577.5	2.394	347.0	2.123
576.5	2.391	336.8	2.087
569.8	2.389	276.6	1.868
565.8	2.383	267.8	1.832
564.5	2.380	254.8	1.778
562.0	2.380	222.5	1.643
559.8	2.383		
554.8	2.499		

Table 1. The specific electrical conductivity of solid and molten silver iodide.

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