DAMAGES IN V_2O_5 SINGLE CRYSTALS DUE TO LASER LIGHT

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The present paper describes our investigations into the optical stability of V_2O_5 single crystals. The energy threshold of surface demage was determined for single crystal plates of (010) orientation in the case of burst mode and *Q*-switched laser light. The interpretation for a possible mechanism of damaging is suggested.

Introduction

The development and use of lasers of increasing power made necessary to solve the problem of optical stability of the optical elements, meters of energy and power, *i.e.* to know the energy and power density at wich damages in the material occur. Most of the publications concerning this problem deal with transparent dielectrics [1—6]; considerably fewer papers are concerned with damaging of semicorductors [7—11]. The conclusions drawn from experimental results are manifold and often contradictory.

Based on the results obtained hitherto, the mechanisms of damaging can be grouped into several classes. In some cases the mechanical damages are attributed to acoustic (hyperacoustic) phonons due to forced MANDELSTAM—BRILLOUIN scattering [12—14]. According to another conception, melting and damaging is caused by intensive energy accumulation due to one and mutiphoton absorption [15]. Strong light absorption caused by surface defects and inhomogeneities of the material may also lead to damaging [16-17]. Thermal stresses due to light absorption, and ensuing shock waves may also cause damaging of the material [5].

The aim of our present work was to study the resistance against ruby laser light on vanadium pentoxide single crystal plates of (010) orientation V_2O_5 crystallizes in the rhombie system and forms optically anisotropic, birefringent biaxial crystals. From optical transmission measurements, its band gap width was found to be 2.3—2.4 eV [18]. Electrically V_2O_5 is an n-type impurity semiconductor of comparatively high thermoelectric force. In its conductivity, vanadium ions of valencies different from (lower then) the basic valency, and oxygen vacancies, both acting as donor centres, play a role.

From the V_2O_5 single crystal produced, crystal plates of different thickness and (010) orientation can be comparatively easily split off. The thickness of the crystal plates used in our experiments varied between 50 and 400 μ. The lustrous plane-parallel plates were visibly inhomogeneous owing to air inclusions formed during crystal growth.

The laser beams used for damaging were perpendicular to the samples of (010) orientation.

Experimental method

In our investigations the light transmit of V_2O_5 single crystals was measured as a function of the intensity of the incident laser light beam. The energy density at wich a sharp plasma flash was observed due to interaction of the incident laser beam with the crystal was considered as threshold for damaging the V_2O_5. The plasma flash was observed through a HELIOS—44 (LOMO) objective at the moment of the impact of the laser pulse. The plasma discharge was always accompanied by mechanical damage of the V_2O_5 surface. It is to be noted that, according to our experience, observation with unaided eye was sufficient for perceiving the plasma flashes.

The diagram of the experimental arrangement used for the measurements is shown in Fig. 1.

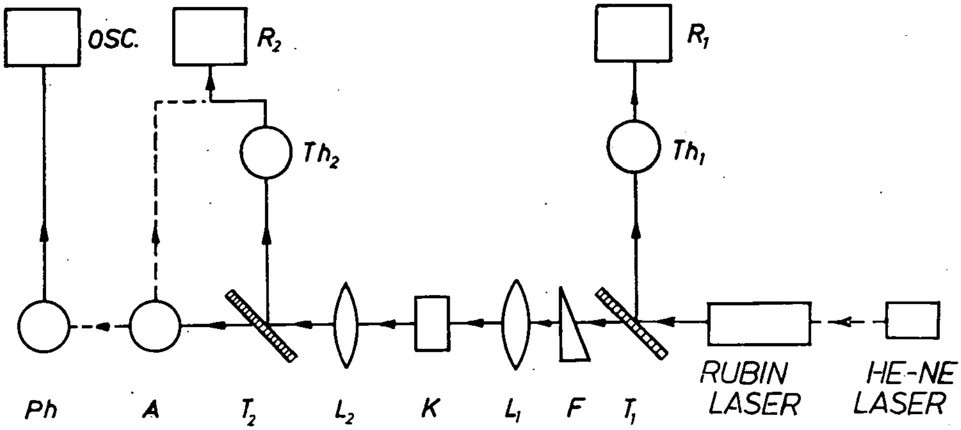

Fig. 1. Experimental arrangement: T_1, T_2: beam splitters; *F:* grey wedge; L_1, L_2: lenses; *K:* sample; Th_1, Th_2: thermoelements; R_1, R_2: compensographs; *A:* calibrated calorimeter; *Ph:* photocell; *OSC:* broad-band oscilloscope

A 0.5 mW CW He—Ne laser served to adjust the light path. A ZEISS ruby laser was used as beam source. The active element of the laser was a ruby rod doped with 0.05% Cr. The laser source was used in burst mode and *Q*-switched mode. For measuring the energy, part of the incident and transmitted energy was split off by the parallel glass plates T_1 and T_2, to reach the thermoelements Th_1 and Th_2. The thermovoltages of the thermoelements were recorded by the micrographs R_1 and R_2 type BD-5.The rise time $\tau = 0.7$ s of KIPP & ZONEN the micrographs was much less then the cooling constant $\tau = 60$—80 s; therefore the peak value of the micrograph signals could be considered to be proportional to the light energy absorbed by the thermoelements. The thermoelements were calibrated with the energy meters denoted by *A* in Fig. 1, developed in our institute.

The calibration curve of the thermoelements is shown in Fig. 2.

The two thermoelements were calibrated with respect to each other for both modes of operation. The intensity of the light incident on the sample was controlled by the calibrated grey wedge *F*. The glass lenses L_1 and L_2 ($f_1 = f_2 = 120$ mm) served for focussing and rendering parallel the laser beams.

For the area of the light spot, $3.6 \cdot 10^{-5}$ cm^2 was obtained on the basis of the known formula. The mean duration of the pulse was determined with the photocell *Ph* (TUNGSRAM type CV-90) and the broad-band oscilloscope *OSC* (UNITRA type OS-701). On the basis of our measurements the duration of the pulses was calculated to be 0.8 ms for the burst mode and 80 ns for Q-switched mode.

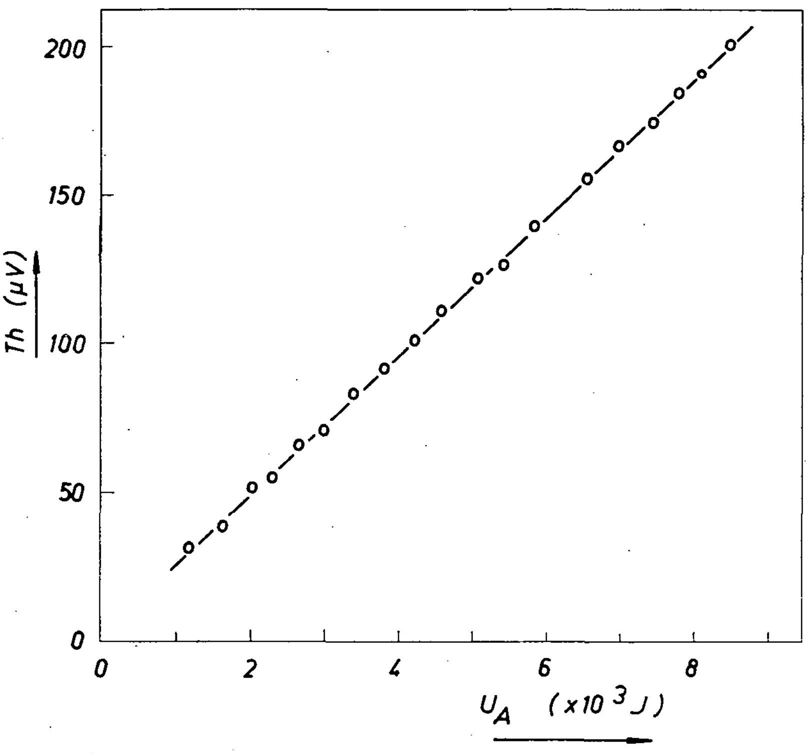

Fig. 2. Calibration curve of the thermoelement, obtained with a calibrated calorimeter for measuring the energy. The abscissa shows the flash energy, the ordinate the electric signal of the thermoelement.

Experimental results

Transmission measurements

In the transmission measurements the beam incident perpendicularly on the crystal plate was controlled, besides the grey filters, by changing the pumping energy.

Because the transmitted energy as a function of pumping energy showed high divergences, the mean of several measurements was used for calculations. In order to permit the use of the arrangement described in the broadest energy range possible, measurements were made also with laser beam focussed on the V_2O_5 surface in the case of both modes.

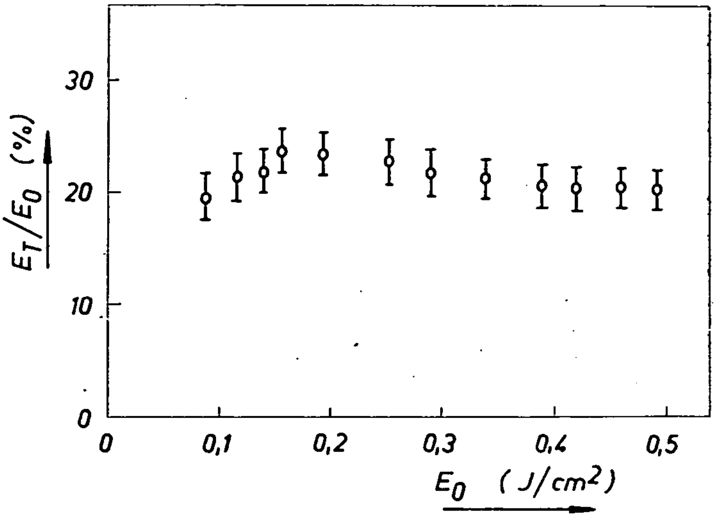

Fig. 3. Percentual transmission *vs.* incident energy density of unfocussed burst mode laser light.

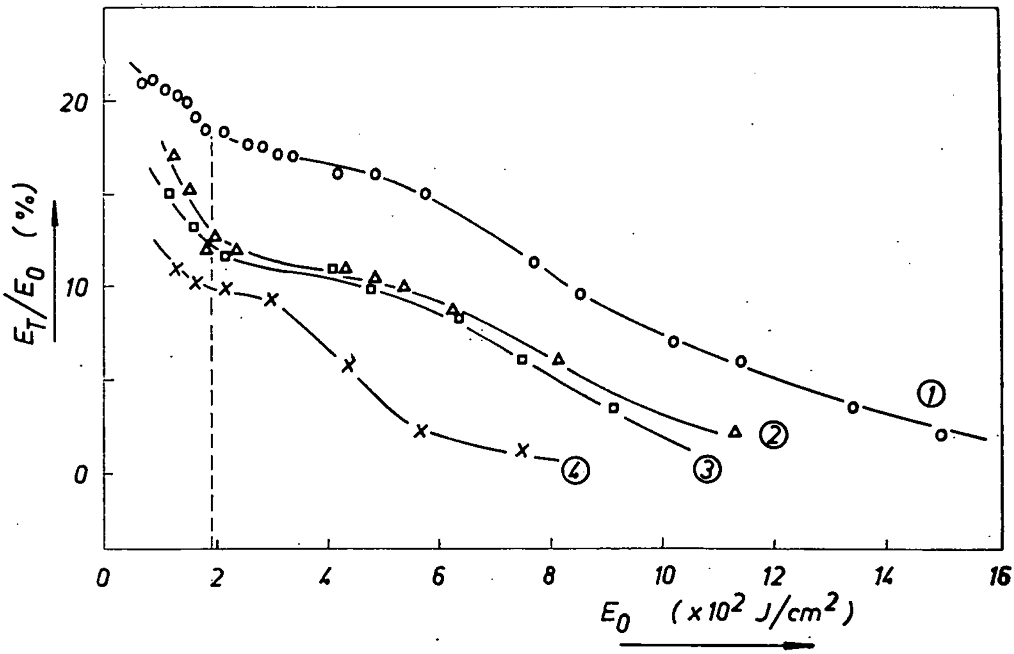

Fig. 4. Transmission of burst mode laser light focussed on the surface.

In Fig. 3 the percentual transmission of unfocussed burst mode laser light can be seen as a function of energy density.

Each point of measurement, showing also the maximum deviations, was calculated from the mean of several measurements. It can be seen that the transmission of the crystal plate studied, instead of being constant in the range of energy density investigated, is dependent on intensity. The transmission increases with higher energy densities in the energy interval 0.11—0.17 J/cm^2, then, after reaching a maximum, becomes constant or slowly decreases.

Fig. 4 shows the transmission of burst mode laser light focussed on the surface.

Curves (1) to (4) correspond to transmission curves of crystal plates with thicknesses increasing in the order of numeration. Curve (1) belongs to the same crystal plate as used for measuring the transmission values of Fig. 3. In the range of energy density studied, several break points can be observed in each transmission curve. The first of these pertains to the damage indicated by the plasma flash. This break point occurs in the case of all four samples at the intensity $1.9 \cdot 10^2$ J/cm^2 (marked by a broken vertical line in the figure). At energy densities higher then the damage threshold further decrease of the transmission can be observed.

Q-switched unfocussed laser light was used for determining the transmission curves of the three samples of different thickness shown in Figs. 5 and 6.

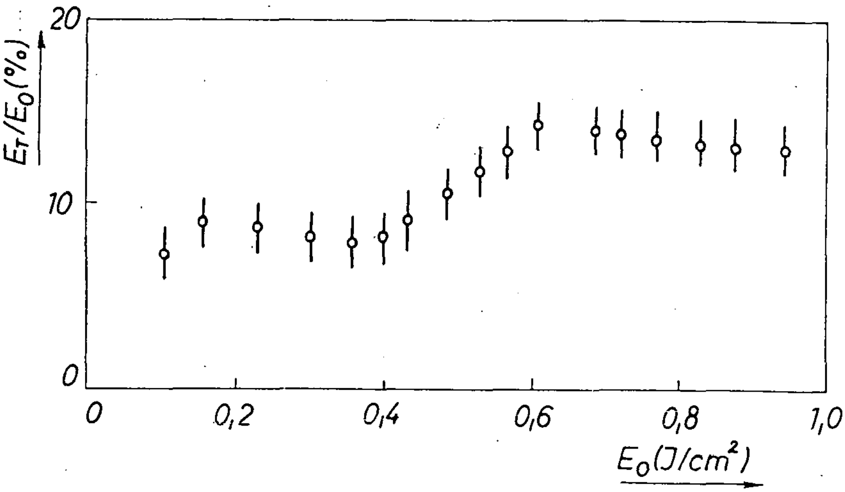

Fig. 5. Transmission of Q-switched unfocussed laser light.

It can be seen that the shape of the transmission curves is similar to that of the transmission curve obtained with unfocussed burst mode laser light, shown in Fig. 3; the transmission first increases with energy density, then after a maximum 0.6 J/cm^2 begins to decrease slowly. The rate of increase is the highest in the energy density interval 0.4—0.6 J/cm^2.

Fig. 7 shows the transmission curves measured with Q-switched focussed laser light for five samples of different thicknesses.

The energy threshold of damaging is observed at 25 J/cm^2 for all five samples.

It should be remarked that for samples the thickness of wich prevented transmission measurements, the damage threshold indicated by the plasma flash was the same as that given above, namely ~190 J/cm^2 for burst mode and ~25 J/cm^2 for Q-switched laser light.

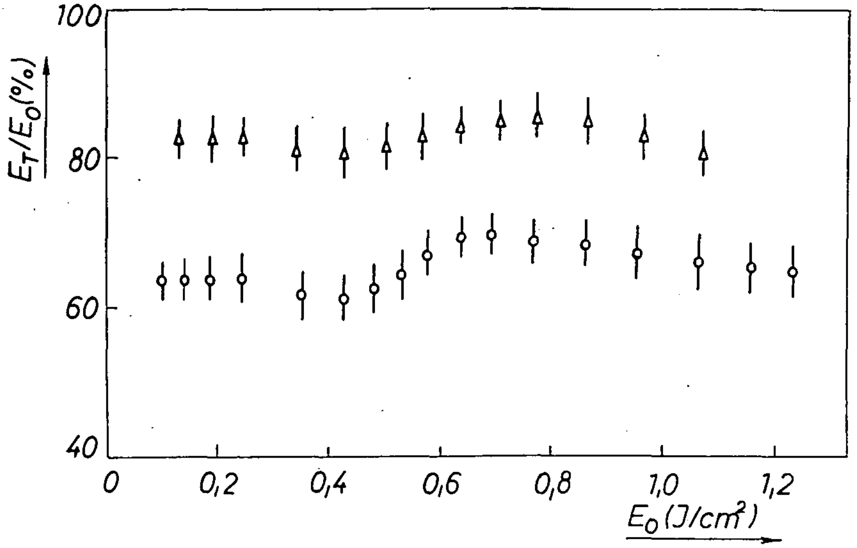

Fig. 6. Transmission of Q-switched unfocussed laser light.

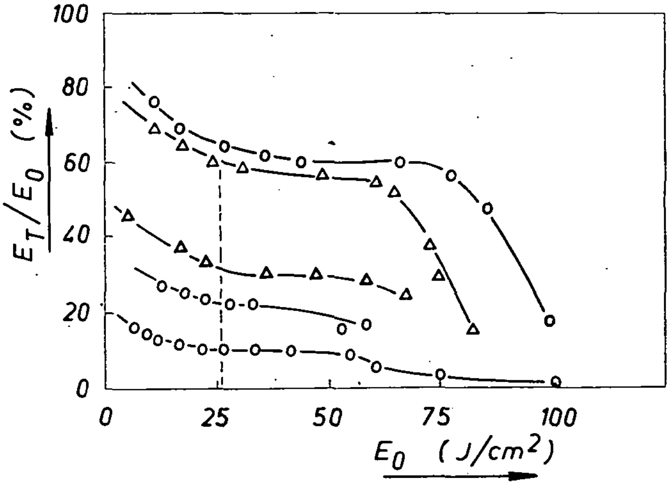

Fig. 7. Transmission of Q-switched focussed laser light.

Morphology of damages

The surface of the samples irradiated by burst mode and *Q*-switched laser pulses was studied with reflected light, using a microscope.

In some cases damages indicated by a circular dark spot could be observed already below the damage threshold value. Such alterations were observed on the samples and surface domains wich were less satisfactory from the optical point of view. Up to the threshold value of damaging energy or at energy densities only slightly exceeding this value the shape of the observed spot was always cicular.

At energy densities significantly higher then the damaging threshold the spot lost its circular form on the impact of the laser pulse of ms duration; it became elongated in the direction of the crystallographis *c* axis and a well observable crater formed on the surface. The diameter of the crater decreased towards the interior

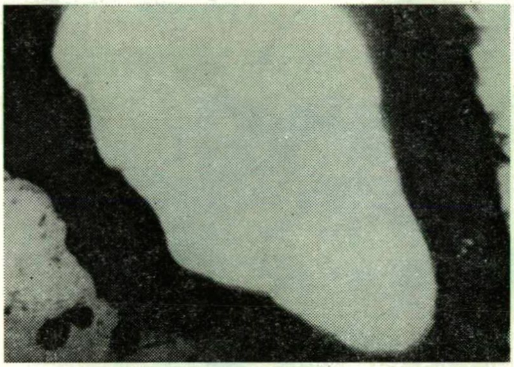

Fig. 8. Microphotograph of a crystal plate perforated by burst mode laser light at 800 J/cm² energy density.

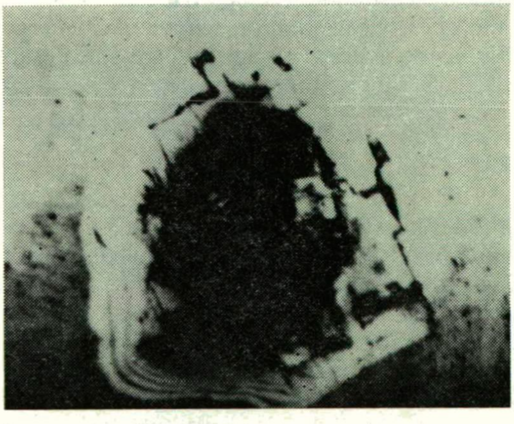

Fig. 9. Microphotograph of a crystal plate, damaged by 29 J/cm² energy density.

of the crystal. At energy densities wich caused perforation of the crystal plate, craters of decreasing diameter towards the interior of the plate were observed on both surfaces.

Fig. 8 is a microphotograph of the crystal plate perforated at 800 J/cm^2 energy density. The traces of the material ejected to the brim of the crater can be well observed as a dark ring.

The spots obtained with Q-switched laser pulses were always circular; elongations could never be observed.

In Fig. 9 a damage caused by a Q-switched pulse of 29 J/cm^2 energy density can be seen; this value exceeds only slighly the damaging threshold.

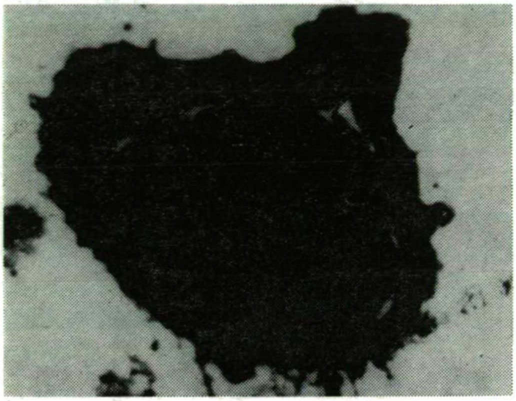

Fig. 10. Microphotograph of a crystal surface with higher energy density (5mJ0 /c^2).

The damages of the crystal are well indicated by the fractures in its lamellar structure and the appearence of interference fringes.

Fig. 10 shows the effect of irradiation with higher energy density (50 J/cm^2). Similarly as in Fig. 8, the material ejected and solidified on the brim of the crater can be well seen as a dark ring in this figure, too.

Discussion of the results

Interpretation of the transmission curves

The increases found in the transmission curves unequivocally point to non-linear effects occurring on the interaction of laser light with the material investigated. The increase in transmission observed in the energy density range 0.11—0.17 J/cm^2 in burst mode, similarly to that found between 0.4—0.6 J/cm^2 in the Q-switched mode can be explained by fading of the material, caused by the balance between the ground state and excited states of the atoms. The higher degree of fading observed in the case of Q-switched laser impulses can be explained by the circumstance that the spontaneous emission during the short pulse of $\tau=80$ ns is negligible, while in the burst mode the spontaneous emission cannot be neglected owing to the long duration of the pulse ($\tau = 0.8$ ms), and thus the atoms returning to the ground state may repeatedly take part in the absorption. Similar results were obtained by BELIKOVA *et al.* [20, see also 21] who investigated the absorption of a ruby crystal.

The decrease in transmission observed at higher energy densities points to the increase of the absorption coefficient of the material with increasing intensity. This may be due chiefly to free electrons raised by one-electron absorption from impurities of low energy level into the conduction band. These electrons, scattered on phonons or defects, may cause further absorption and hereby increase the absorption coefficient compared to that of linear absorption. As the temperature of the material strongly increases during the interaction with laser light [15], the thermoionization caused by the high temperature contributes to the increased number of free carriers. It could be demonstrated that in V_2O_5 at 1000 °K the density of carriers may reach $7 \cdot 10^{16}$ cm^{-3}.

Interpretation of transmission curves obtained by Q-switched laser light

The absorption due to the non-linear effects discussed above leads to damages on the surface of the samples. The plasma produced in the moment of the damaging exerts a shielding effect on the incident radiation, causing further decrease in the transmission. With increasing incident energy density, the size of the damaged domain increases and the plasma formed leads to further increase in absorption. In the damaged domain the probability of light scattering also increases, the material melts and evaporates, and the light is intensely absorbed by the ion cloud formed from the molten and evaporated material; this explains the strong decrease in transmission at high energy densities.

Further remarks on the possible mechanism of damages

The difference in order of magnitude of the damage thresholds of burst mode and *Q*-switched mode laser pulses points to differences in character of the mechanism in the two cases.

Analysis of the experimental results shows that the damages caused by burst mode pulses occur in the following way. Part of the laser light is intensely absorbed on inclusions, purities and defects of microstructure. In these points the material melts and the light absorption becomes even more intensive in the liquid phase. In addition, the probability of light scattering on acoustic phonons also increases [22]. The role of strongly absorbing metallic inclusions present in the V_2O_5 is especially important [21, 23]. The strong energy absorption leads to explosion and the shock wave following the explosion causes damages in the material. The determining character of structure defects in the production of damages is shown by the elongation of the damaged domains in the direction of the crystallographic *c* axis. The duration of the pulse emitted by a *Q*-switched laser is very short, 10^{-7} s, therefore the phenomena connected with heat propagation cannot play a role. This is supported by the consistently circular shape of the damaged domain in the case of *Q*-switched laser pulses, in contrast to the elliptic form of the damaged domains of burst mode laser pulses. It seems very probable that the surface defects, dislocations, impurities have an important role also in this case. As known from the literature [24], the density of centres absorbing at 1μ in V_2O_5 reaches $1.5 \cdot 10^{18}$ cm^{-3}, and the density of surface dislocations 10^7 cm^{-2} (25). The defects in the surface layer form a quasi-continuous spectrum wich corresponds to the trap levels almost continuouly filling the upper part of the band gap. Impurity atoms and defects may be easily ionized by intense light, producing free electrons in the surface layer. The free carriers in the field of the intensive light wave are able to further light absorption through interaction with phonons and defects. Direct band-to-band one-photon absorption may contribute to the absorption, though its probability is low owing to $h\nu < \Delta E$ ($h\nu$ is the photon energy and ΔE is the band gap width 2.4 eV). The non-radiative recombination of the electron-hole pairs formed enhances the heating of the material.

According to GRINDBERG [7] the absorptionof non equilibrium carriers generated by the laser light becomes significant in the case of high electric fields. This absorption is ultimately responsible for the sublinearity of the transmission curves. Thus the free electrons formed by one- and multiphoton interactions transfer the excess energy to the lattice, wich evaporates due to the heating and produces a dense ionized gas layer above the surface [26]. As a result of avalanche ionization a plasma flash occurs, followed by a shock wave wich may reach the velocity of 10—15 km/s. [20]. Then the more important breaks and fractures are formed due to the shock waves. The fact that the diameter of the damaged domains, 0.2—0.5 mm, is always greater then their depth, 20—90 μ, can be explained by the cicumstance that, on the one hand, the light pulse is strongly shielded by the plasma formed at hre surface and, on the other hand, the density of defects descreases with increasing depth.

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РАЗРУШЕНИЕ МОНОКРИСТАЛЛОВ V_2O_5 ЛАЗЕРНЫМ ЛУЧЕМ

Л. Нанаи, И. Хевеши и И. Кечкемети

В настоящей статье представлены результаты исследований оптической прочности монокристаллов V_2O_5. Определена оптическая прочность поверхности, ориентированной в направлении (010), при засветках лучем лазера, работавщего в миллисекундном и гигантском режимах излучения. Предложен механизм разрушения V_2O_5.