Damage to the Surface of Lithium Niobate by Light

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The dependence of the threshold of breakdown of a lithium niobate surface by laser irradiation is studied at temperatures between 20 and 950 °C. A nonmonotonic growth of the threshold with temperature, by 10–12 times, is observed. A discontinuous increase of the breakdown threshold at the Curie temperatures is observed in $BaTlO_3$ and $LiTaO_3$ crystals. A breakdown mechanism is proposed, based on light absorption by shallow traps in the surface layer. The effect of the ferroelectric properties of lithium niobate on the breakdown process is discussed.

THE process of breakdown of the surface of lithium-niobate crystals under the influence of laser radiation has many characteristic features[1] that distinguish it from other transparent dielectrics. The surface breakdown threshold of this material, fillowing a single irradiation by a laser pulse, is 400–500 MW/cm^2. When this power is decreased by a factor of 3.5, the surface breakdown occurs after 20–30 laser pulses (flashes) are applied to it; we shall henceforth call this effect "accumulation." The breakdown threshold determined by the accumulation is 120 ± 30 MW/cm^2, which is much lower than the surface breakdown thresholds of glass and ruby, in which the breakdown occurs without accumulation. The surface breakdown threshold of lithium niobate depends little on the quality of the surface finish.

The purpose of the present study was to continue the research initiated in [1] on surface breakdown of lithium niobate under the influence of Q-switched laser radiation at a wavelength $\lambda = 1.06\,\mu$. We investigated the temperature dependence of the breakdown thresholds in the temperature interval 20–950°C. A nonmonotonic increase of the threshold was observed when the temperature was increased by 10–12 times over room temperature. We investigated also the temperature dependence of the surface endurance of $LiTaO_3$ and $BaTiO_3$ crystals. We discuss a surface breakdown mechanism for lithium niobate, based on the increase of the absorption of the laser radiation as a result of population of shallow traps connected with the reduced niobium Nb^{4+}. We discuss the effect of free carriers of the surface layer of ferroelectric crystals on the process of their surface breakdown under the influence of laser radiation.

Investigations of the surface endurance were carried out using a single-mode neodymium-glass laser with energy ~0.1 J and pulse duration 20 nsec. The radiation was focused on the surface of carefully polished samples by a spherical lens with f = 15 cm.

In the investigations of the temperature dependences, the samples were placed in a through channel of an oven. The surface breakdown was monitored visually through the side window of the oven and revealed by the appearance of a spark and by the considerable increase of the scattering of the radiation of a probing HeNe laser by the damaged surface. The sample temperature was determined with a chromel-alumel thermocouple. No special measures were taken to stabilize the temperature, which was kept constant within ± 30°.

The temperature dependence of the surface breakdown threshold of lithium niobate under the influence of laser radiation is shown in Fig. 1.

In the temperature interval 20–170°C, the breakdown threshold remains unchanged at 120 MW/cm^2. When the temperature is increased from 170 to 330°C, a smooth increase of the breakdown threshold by a factor 4.5 takes place, and is accompanied by a lifting of the accumulation effect. At a temperature above 330°C, the breakdown occurs without accumulation. With further heating, the endurance of the surface at T = 470°C and at T = 900°C increases by another 2 and 1.5 times, respectively. Thus, the lithium niobate surface breakdown threshold increases a total of 10–12 times under the influence of laser radiation when heated from 20 to 950°C.

The surface breakdown thresholds of $LiTaO_3$ and $BaTiO_3$ do not change when heated, up to temperatures corresponding to the Curie points of these materials (600–610° for $LiTaO_3$ and 120° for $BaTiO_3$). On going through the Curie temperature, a jumplike increase of the endurance takes place, by 2.5–3 times for $LiTaO_3$ and 1.5–2 times for $BaTiO_3$. The increase of the surface endurance of these materials is also accompanied by a loss of the accumulation effect. It should be noted that the surface endurances of glass and ruby measured by us remain practically unchanged in the temperature interval 20–700°C. This agrees with the results of [2].

Thus, the temperature dependence of the surface endurance of lithium niobate differ significantly from that of other transparent dielectrics.

It was proposed in [1] that the anomalously low surface endurance of lithium niobate is connected with the presence in it of a thin surface layer with a reduced oxygen content. Let us examine concretely how such a surface can break down under the influence of laser radiation.

We assume that the surface layer contains traps of two types with different ionization potentials, which are due to the oxygen vacancies and to the reduced Nb^{4+} (Fig. 2).

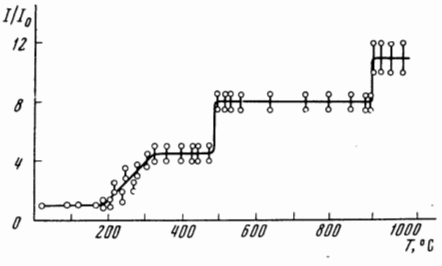

FIG. 1. Temperature dependence of the threshold of surface breakdown of lithium niobate.

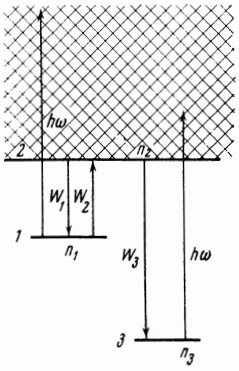

FIG. 2. Energy levels of the traps in the surface layer of lithium niobate.

Since the absorption of the laser radiation transfers the electrons from the shallow traps to higher levels in the conduction band, we shall assume that the cross section for the absorption of the laser radiation for shallow traps is much larger than for deep ones. Under thermal-equilibrium conditions, the electrons fill the traps in accordance with a Boltzmann distribution, i.e., they are mainly concentrated in the deep traps. Under the influence of the laser radiation, the electrons are knocked out from the deep traps and the shallow ones become partially filled, causing the laser-radiation absorption coefficient to increase from pulse to pulse and causing breakdown of the surface as a result of strong heating. With increasing sample temperature, during the time between the pulses, the shallow traps become depleted, because of thermoionization, and accumulation ceases starting with a certain temperature.

If the assumption of the existence of traps is valid, then the shallow traps can become depleted not only because of thermal ionization, but also under the influence of light. To verify this assumption, an additional experiment was performed. A lithium-niobate surface was illuminated by a focused light beam from a 500-W incandescent lamp. The spectral composition of the illumination was varied with the aid of filters. The laser radiation was focused on the surface of the investigated samples by a long-focus lens in such a way that its intensity at the input and output surfaces, relative to the laser beam, coincided. The intensity of the laser radiation was chosen such that both surfaces broke down after 5–7 flashes.

The beam from the incandescent lamp was directed at an angle to the laser beam and illuminated only the sample input surface exposed to the laser. The time between pulses was ~60 sec.

It turned out that illumination with incoherent light with wavelength $\lambda > 0.5\,\mu$ does not damage the input surface at a given intensity after repeated irradiation (> 30 flashes), whereas the output surface which is not exposed to the light, break down as before after 5–7 flashes. This method makes it possible to increase the endurance of the illuminated surface by 1.5–2 times.

We note that no increase in the endurance is observed when the surface is illuminated by the complete spectrum of the incandescent lamp. This is apparently connected with the equalization of the ionization probabilities of the shallow and deep traps, which follows the increasing light frequency, so that there is no preferred ionization of the shallow traps.

The proposed model enables us to make some estimates. In particular, we can estimate the lifetime of the electrons at the shallow traps (level 1 of Fig. 2). Under the influence of the laser radiation, the electrons from the deep traps are transferred to the conduction band and then some return to level 3, while others populate level 1.

Assume that N electrons were transferred to level 1 by one laser pulse. After the pulse, as a result of thermoionization, the electrons are returned to the conduction band, with a probability W_2, and then, by recombination with probability W_3, they go over to level 3. They are then again captured by the free traps 1, with probability W_1.

The kinetics of this process can be described by the system of equations[1)]

$$\begin{aligned} dn_1/dt &= W_1 n_2 - W_2 n_1, \\ dn_2/dt &= W_2 n_1 - W_3 n_2 - W_1 n_2, \\ dn_3/dt &= W_3 n_2, \quad n_1 + n_2 + n_3 = N, \end{aligned} \tag{1}$$

where $W_2 = W_{20} \exp(-\Delta/kT)$, Δ is the ionization potential of the shallow trap, k is Boltzmann's constant, and T is the temperature.

Solving the system (1) with respect to n_1, we obtain the time dependence of n_1:

$$n_1 = N \exp(-t/\tau), \tag{2}$$

Where $\tau \approx 1/W_2$ is the lifetime of level 1.

Let us examine the accumulation effect. Neglecting saturation, we can obtain an expression for the number of electrons at a shallow trap after the passage of the m-th pulse, in the form

$$n_1^{(m)} = N \frac{1 - e_m}{1 - e_1}, \tag{3}$$

where $e_m = \exp(-m\delta t/\tau)$ and δt is the time between pulses.

Recognizing that $N = \gamma Q$ (Q is the laser-radiation energy density per pulse and γ is a proportionality coefficient), and that the absorption coefficient $\alpha^{(m)}$ of the surface layer after the passage of m pulses is equal to $\alpha^{(m)} = \sigma n_1^{(m)}$, where σ is the cross section of the transition, we obtain

$$\alpha^{(m)} = A \frac{Q[1 - e_m]}{1 - e_1}, \quad A = \gamma\sigma. \tag{4}$$

The factor $[1 - e_m]$ in (4) describes the increase of the absorption coefficient at a given energy density with decreasing number of flashes.

The maximum absorption coefficient can be obtained under the condition $e_m \ll 1$, and amounts to

$$\alpha_{max} = AQ/(1 - e_1). \tag{5}$$

Assuming that breakdown is produced by an energy Q^* absorbed in the surface layer, we can write down the following expression for the breakdown threshold Q_{thr} determined by the accumulation, $Q^* = Q_{thr}\alpha_{max}$, or with allowance for (5)

$$Q^* = AQ_{thr}^2/(1 - e_1). \tag{6}$$

[1)]We describe the depletion of shallow traps by first-order kinetics. However, similar results can be also obtained by describing the process by second-order kinetics[3].

For $Q > Q_{thr}$, breakdown occurs at $\alpha < \alpha_{max}$ under the condition

$$AQ^2 \frac{1-e_m}{1-e_1} = Q^*. \quad (7)$$

From (6) and (7) we obtain the dependence of the breakdown threshold on the number of flashes m:

$$Q^{(m)} / Q_{thr} = 1 / (1-e_m)^{1/2}. \quad (8)$$

Varying the parameter τ at a given δt, we can obtain a satisfactory agreement between the curve described by (8) and the experimental one given in [1] (Fig. 3) for $\tau = 150$ sec.

When δt exceeds τ by 3–5 times, we get $Q^{(m)} \approx Q_{thr}$ already at m = 1, corresponding to breakdown without accumulation.

Let us turn to the temperature dependence of the breakdown threshold (Fig. 1). This dependence is obtained at $\delta t = 15$ sec. From the temperature dependence it follows that at $T > 330$°C we have $\tau < 15$ sec. Obviously, by increasing the intervals between pulses, we can attain satisfaction of the condition $\delta t > \tau$ at lower temperatures.

Indeed, when the intervals between pulses are increased from 15 to 60 sec, a noticeable attenuation of the accumulation effect is observed at a sample temperature T = 120°C; whereas at $\delta t = 15$ sec the surface breakdown occurs after 4–5 flashes, at $\delta t = 60$ sec the surface, at the same energy density, does not break down after multiple irradiation (>50 flashes), and its breakdown threshold increases by a factor 1.5–2.

Of course, the estimates given above are quite crude, but they agree satisfactorily with experiment.

Thus, the proposed model describes the accumulation of breakdown after several dozen flashes, and the temperature dependence of the breakdown threshold at temperatures 20–450°C. This model, however, does not explain the jumplike change in the endurance at the temperatures 470 ± 30°C and 900 ± 30°C, nor the increased endurance of $LiTaO_3$ and $BaTiO_3$ at temperatures corresponding to the Curie points of these materials. It is therefore advisable to consider one more feature of lithium niobate, namely, that it is ferroelectric at room temperature.

It is known[4,5] that in the surface layer of a ferroelectric there exist free carriers with density $\rho_S = P_S$, where P_S is the spontaneous polarization. In the case of lithium niobate, the spontaneous polarization amounts to $\sim 50\ \mu C/cm^2$, and consequently $\rho_S = 50\ \mu C/cm^2$. The thickness of the surface layer of a ferroelectric amounts to 10^{-4}–10^{-5} cm,[5] and consequently the free-carrier concentration is 10^{18}–10^{19} cm^{-3}, corresponding to an average absorption coefficient 10^1–10^2 cm^{-1}. Such a high absorption coefficient at power densities ~550 MW/cm^2 (the breakdown threshold at 330°C) can heat the surface to a temperature ~1500°C, which suffices to break down the material.

The spontaneous polarization in $LiNbO_3$ crystals decreases with increasing temperature. The temperature dependence of the spontaneous polarization for lithium niobate is known only for T below 400°C.[6] However, as reported in [7,8], phase transitions accompanied by a jumplike change in the unit-cell parameters occur in lithium niobate at temperatures 580 and 900°C. It can be assumed that near these temperatures there is a noticeable decrease of the spontaneous polarization, and consequently also of the concentration of the compensating carriers of the surface layer, which should in turn lead to a decrease in the absorption coefficient and to a corresponding increase of the breakdown threshold.

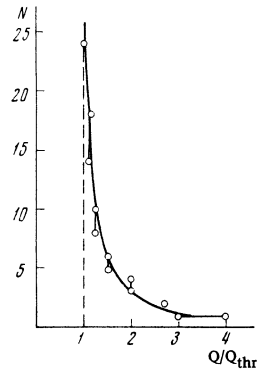

FIG. 3. Experimental and calculated dependences of the breakdown threshold on the number of flashes. O–experimental points, solid line–calculated curve, N–number of laser flashes.

The jumplike increase of the threshold at the Curie temperatures in $BaTiO_3$ and $LiTaO_3$ crystals is also a confirmation of the fact that the free carriers of the surface layer play a noticeable role in the surface breakdown of ferroelectric crystals under the influence of laser radiation.

Thus, the process of surface breakdown of lithium niobate at low (< 330°C) temperatures is determined by the absorption of light by the shallow traps, whereas at temperatures > 330°C the decisive role is apparently played by absorption of light by the free carriers of the surface layer.

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