Light induced three-dimensional polar structure in ruby crystals

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It is established from luminescence spectra that intense laser irradiation of a concentrated ruby crystal produces three-dimensional regions (domains) with a strong internal electric field whose projection along the C_3 axis of the crystal is oriented opposite to the external field. The external electric field also strongly affects the formation of this three-dimensional polar structure (TDPS).

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It was recently observed[1] that intense laser irradiation of concentrated ruby at $T = 10$ K induces a doublet splitting of the lines in the ruby spectrum. This splitting is apparently analogous to the well-known "pseudo-Stark" splitting of lines in a uniform external electric field $\mathbf{E}\|C_3$,[2] resulting from the opposite displacement of the levels of Cr^{3+} ions, which occupy in the centrosymmetric (D_{3d}) Al_2O_3 lattice two noncentrosymmetric (C_3 group) positions A and B that differ in their inversion. It was concluded in Ref. 1 that a strong (up to 10^6 V/cm) uniform internal electric field is induced in a ruby by laser irradiation.

Our investigations were performed primarily at $T = 77$ K in thin (~ 0.1 mm) single-crystalline plates consisting of Al_2O_3 : 0.5% Cr, cut out along the basal surface ($\perp C_3$). Transparent electrodes were deposited on both sides of the plates, to which an external field $\mathbf{E}\|C_3$ could be applied. The intensity of the effective electric field (more precisely, its $z\|C_3$ component) in the crystal was determined from the magnitude of the pseudo-Stark splitting of the R_1 line $\bar{E} \rightarrow {}^4A_2$ in the luminescence spectrum: $\Delta\nu(\text{cm}^{-1}) = 0.78 \times 10^{-5} |E_z|$ (V/cm).[3]

An Ar laser beam (2 W, 514.5, 501.7, 496.5, 488.0, 476.5, and 457.9-nm lines) was directed normally to the surface of the crystal. The laser operator in two regimes: 1) with high power density in the beam $I \sim 1$ kW/cm^2, which induces an internal field[1] in the illuminated region of the specimen and 2) with low density $\lesssim 1$ W/cm^2, in which case the Ar beam serves only to excite luminescence but does not alter the state of the excited region. The R_1 luminescence spectra were reordered at $T = 77$ K under conditions 2.

When the specimen is irradiated with laser radiation $I \approx 1$ kW/cm^2 and there is no external field ($E_z = 0$), in accordance with Ref. 1, the R_1 line in the spectrum (Fig. 1a) soon after the beginning of excitation is split into a symmetrical doublet (Fig. 1b). In addition, the rate of growth of the quantity $\Delta\nu$ up to its stationary value $\Delta\nu_{\max} = 2.9$ cm^{-1} increases with I. At $I = 1$ kW/cm^2, $\Delta\nu_{\max}$ was reached in 10 min. After the optical pumping is turned off, the state of the irradiated region of the specimen, characterized by the splitting of the R_1 line $\Delta\nu_{\max}$ in the spectrum,[1)] remains

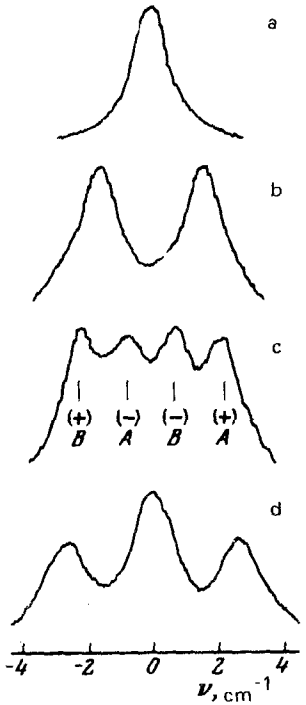

FIG. 1. R_1 luminescence line of ruby, a—Before laser irradiation; b,c,d—after irradiation. b) $E = 0$; c) $E = 185$ kV/cm; d) $E = 370$ kV/cm.

indefinitely both at 77 K and when the specimen is heated to 20 °C (the state was observed to last for up to two years). The quantity $\Delta\nu_{max}$ corresponds to the presence of an internal effective electric field with $|\mathscr{E}_z^{max}| = 370$ kV/cm in the specimen.

Next, an external electric field E_z was applied to the specimen with a laser-induced internal electric field (doublet splitting of the R_1 line in the spectrum). It was found that each of the components of the "starting" doublet is split symmetrically and linearly with respect to $|E_z|$ in the external field (Fig. 1c) and the magnitude of the splitting is equal to the pseudo-Stark splitting.[3] As a result, R_1 represents a quartet, whose extreme components diverge with increasing $|E_z|$, while the inner components converge (until they coalesce, Fig. 1d).

This demonstrates directly that the irradiated crystal contains three-dimensional regions ("domains"), in which the projection of the internal field $\mathscr{E}_z^{max}$—with identical absolute magnitude—has the opposite sign ($\pm|\mathscr{E}_z^{max}|$). The external field E_z in the "+" and "−" domains is parallel or antiparallel to the z projection of the internal field. Therefore, the z projection of the total effective field in these two polar regions is different and the R_1 emission gives in the spectrum two pseudo-Stark doublets with different $\Delta\nu$, each of which corresponds to A and B positions of Cr^{3+} ions in the domains (see identification in Fig. 1c).[2)] The approximately identical intensity of all components in the quartet (Fig. 1c) indicates both that the volumes of the + and −

regions are identical and that the average concentrations of Cr^{3+} ions in the A and B positions in them are nearly equal.

In subsequent experiments, we studied the light-induced formation of the three-dimensional polar structure (TDPS) under conditions when the specimen during irradiation is located in a constant *external* electric field E_z. From an analysis of the pattern of the R_1 splitting it was established that intense ($I \sim 1$ kW/cm^2) irradiation of the specimen with $E_z \lesssim 370$ kV/cm$^2 = \mathscr{E}_z^{\max}$ leads to formation of polar regions with an internal field in the specimen. The polar structure formed remains after irradiation ceases (with the external field removed at the same time) and consists of two types of domains. In the + domains, which occupy a large part of the irradiated volume of the specimen, the z projection of the internal field is oriented along the external field E_z, in which irradiation occurred and is equal to $\mathscr{E}_z^+ = |\mathscr{E}_z^{\max}| - |E_z|$. In the − domains, which occupy a smaller volume, the z projection of the internal field is oriented opposite to E_z and is equal to $|\mathscr{E}_z^-| = |\mathscr{E}_z^{\max}| + |E_z|$. In this case, the difference in the volumes of the two polar regions increase with $|E_z|$. The R_1 line in the spectrum of such specimens (Fig. 2) represents a symmetrical quartet with unequal (reflecting the unequal + and − volumes) intensity of external and internal components. The stationary structure described also arises as a result of laser irradiation, in an external field $|E_z| < 370$ kV/cm, of specimens already containing TDPS (obtained beforehand, for example, with $E_z = 0$).

Laser irradiation of specimens in high external fields, $E_z > 370$ kV/cm, does not lead to the formation of any TDPS in them. If, on the other hand, TDPS was created in the specimen beforehand (for example, by irradiation with $E_z = 0$), then irradiation of the specimen in a field $E_z > 370$ kV/cm completely destroys it.

It was also established that the formation of TDPS with laser irradiation occurs only when the irradiated crystal is cooled. Above temperatures $T = 130$–140 K, TDPS are not formed with irradiation, while laser irradiation of specimens with TDPS created beforehand (at $T = 77$ K) completely destroys the TDPS.

From the results presented above, it follows that under intense ($I \approx 1$ kW/cm^2) laser irradiation of concentrated ruby crystal, the crystal reaches with time, irrespective of its original state, a steady state, which is determined by the conditions under which the irradiation occurs: intensity of the external field E_z as well as temperature.

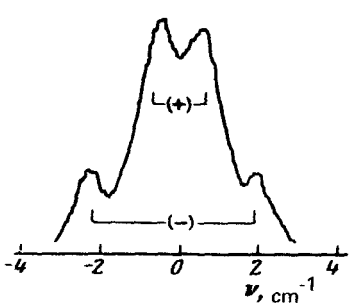

FIG. 2. R_1 line in the spectrum of the crystal in zero external field after irradiation of the crystal in an external field $E = 185$ kV/cm.

For $T < 130$–140 K (with $E_z = 0$ or for $0 \leqslant |E_z| < |\mathscr{E}_z^{\max}| = 370$ kV/cm ($T = 77$ K, the steady state is a state with TDPS and in addition, in the latter case, for all E_z the "stationary" internal field in the domains is established at a level such that the z projection of the effective total (internal plus external) field is equal to $\pm |\mathscr{E}_z^{\max}| = \pm 370$ kV/cm. The state formed with the TDPS is metastable and remains for a long time after the optical pumping is turned off both at low temperatures and when the crystal is heated (at least up to 300 K). For $T > 130$–140 K ($E_z = 0$) and $E_z > 370$ kV/cm ($T = 77$ K), the uniform state of the crystal without TDPS is stationary.

The reasons for the appearance of TDPS in laser-irradiated ruby crystals require further study. Directional charge transport via two-step (via ^2E) optical excitation of interacting Cr^{3+} ions plays an important role.[1] The nonuniformity of the distribution over the "polar" positions A and B (its magnitude is very low, see Fig. 1c) was investigated in Ref. 1 as an orienting factor, giving rise to the appearance of electric polarity in the crystal with an inversion center. In addition ot these effects, it is also interesting to study the important role of collective effects due to polar ordering (see, for example, Ref. 5), resulting from the interaction of electric dipoles created with light-induced directional charge transport in the ruby lattice.

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[1)]The lines $R_2(\overline{2A} \rightarrow {}^4A_2)$, absorption lines $B_1, B_2({}^4A_2 \rightarrow {}^2T_1)$, and the N_2 lines also exhibit doublet splitting (in an external field, all of them exhibit pseudo-Stark splitting[2–4]).

[2)]In the case of triplet splitting (Fig. 1d), the internal and external fields in the "minus" domains cancel out each other and the R_1 line is not split.

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