STIMULATED EMISSION FROM LaF_3-Nd^{3+} *CRYSTAL LASERS*

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Absorption, luminescence, and generation spectra of LaF_3 crystals activated with Nd^{3+} ions are studied at 300 and 77°K. Schemes of crystalline splitting of the $^4F_{3/2}$ and $^4I_{11/2}$ terms which are directly connected with the stimulated transitions are presented.

INTRODUCTION

THE current list of crystals used in optically pumped lasers contains about 40 names.[1,2] Noteworthy in this series are materials based on fluorides of elements of groups II and III of the periodic system. These substances are suitable for activation with di- and trivalent rare-earth elements (TR^{2+} and TR^{3+}) and can also be used as a base for the preparation of mixed fluoride crystals. Their use in quantum electronics gave rise to new methods of controlled change and improvement of generation characteristics of crystal lasers. Because of this it is important to carry out comprehensive spectroscopic and lasing-action studies of the individual compounds and their solid solutions.

This paper presents the results of experimental studies of absorption, luminescence, and stimulated-emission spectra of LaF_3 crystals activated with Nd^{3+} ions. Earlier reports[3-5] dealt with the EPR spectrum of this crystal doped with TR^{3+}, and with luminescence quenching and some spectral characteristics due to the Nd^{3+} ions. Our preliminary studies of the generation spectrum disclosed a serious disagreement with the data cited in the quasi-review paper by Johnson.[6][1)] Therefore we set an additional aim of improving the accuracy of his data.

THE INVESTIGATED CRYSTALS

Lanthanum fluoride crystallizes in a hexagonal lattice with space group $D_{6h}^3 - C6/mcm$. The crystal structure of this material was determined by Zalkin and Templeton.[7] In the LaF_3 crystal structure the fluorine atoms form wavy layers on both sides of a middle layer consisting of La^{3+} and F^{1-} ions appearing as six-segment rings. Figure 1a shows the LaF_3 crystal structure.[8] We see that the La^{3+} ion is surrounded by 11 F^{1-} ions. Six of these form a trigonal prism at distances 2.77 Å from the La^{3+} ion, and the remaining five lie at the vertices of a trigonal bipyramid. In the latter case the distances between the La^{3+} and F^{1-} ions are somewhat shorter (Fig. 1b). Such an envelope represents a polyhedron with 11 vertices. The distribution of the polyhedra in the LaF_3 crystal is shown in Fig. 1c.

In contrast with fluoride crystals of the fluorite types, lanthanum fluoride has a number of remarkable properties. One of these is that the well developed isomorphism of the rare-earth fluorides and the LaF_3 predetermines a uniform insinuation of the TR^{3+} ions among the centers of the same structure. Thus, as expected, when the activator density is high enough the optical spectra are basically determined by a single type of optical center. This condition usually exerts a favorable effect on the generation characteristics.

The LaF_3 crystals used in our experiments were synthesized from the melt by the Czochralski method.[9,10] Neodymium was introduced into the initial material as a fluoride and its concentration amounted to 1% by weight. Experimental specimens were prepared from the grown single crystals. In the experiments designed to study stimulated emission we used cylindrical rods of the LaF_3-Nd^{3+} crystal ~ 30 mm long and ~6 mm in diameter. The end faces of the crystal were plane parallel within ~30″.

EXPERIMENTAL APPARATUS AND METHOD

Absorption and luminescence spectra of LaF_3-Nd^{3+} crystals were investigated at 300 and 77°K using the

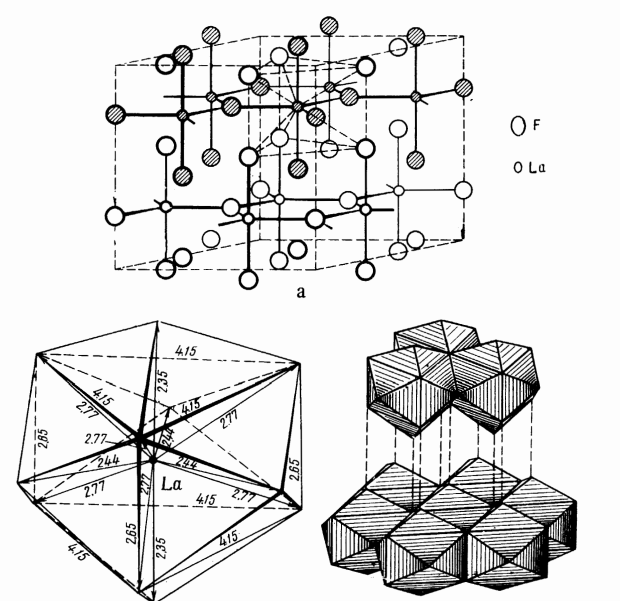

FIG. 1. Structure of the LaF_3 crystal. (a) – stratified pattern of crystalline structure; (b) – eleven-vertex envelope of the La^{3+} ion; (c) – packing of polyhedra in the LaF_3 crystal.

1)We are not aware of any special study of the generation characteristics of LaF_3-Nd^{3+} crystals.

DFS-12 and EPS̆-2U instruments and a methodology described earlier.[11-13]

Two lasers were used to study the stimulated emission characteristics. Generation at 300°K was studied with a cylindrical reflector of elliptic cross section and illumination efficiency of ~0.5[14] (2a = 31 mm, 2b = 28 mm, and 2c = 13.5 mm); the reflector contained a type IFP-400 xenon flash lamp. The optical resonator consisted of external spherical mirrors (R ≈ 500 mm) with multilayer dielectric coatings in a confocal configuration. We used several output mirrors whose transmittivity ranged from 0.7 to 35% at λ = 1.06 μ. Low-temperature experiments were carried out with the laser described in detail in [15]. Its illumination efficiency was lower than the above and amounts to ~0.15.

The spectral composition of generation was studied photographically with a DFS-8 diffraction spectrograph with a dispersion of ~5.9 Å/mm (grating with 600 lines/mm), using an I-1070 film. As a standard we used the third-order emission spectrum of a lamp with a hollow iron cathode. To determine the threshold electric energy required by the pump lamp, we used an FÉU-28 photomultiplier as generation detector connected to an S1-16 pulse oscilloscope. The threshold excitation energies for individual emission lines were recorded by photoelectron multipliers placed in the output plane of the DFS-8.

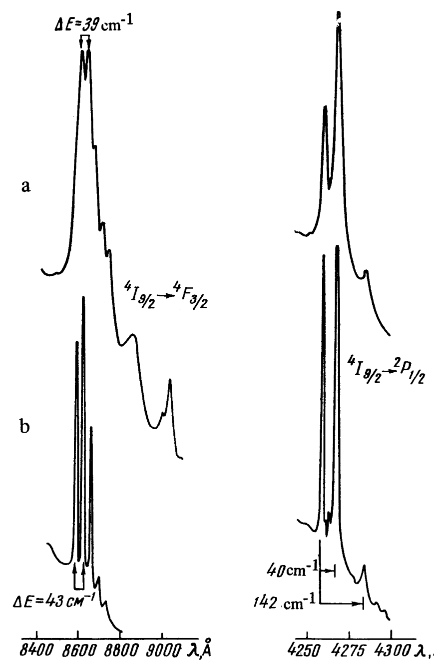

FIG. 3. Absorption spectrum of LaF_3-Nd^{3+} crystal corresponding to transitions $^4I_{9/2}\to{}^4F_{3/2}$ and $^4I_{9/2}\to{}^2P_{1/2}$: (a) – at 300°K, and (b) – at 77°K.

OPTICAL AND GENERATION PROPERTIES OF LaF_3–Nd^{3+} CRYSTALS

The absorption spectra of the investigated LaF_3–Nd^{3+} crystals were studied to obtain data for the construction of the energy level splitting scheme of the Nd^{3+} ion and also to reveal the main excitation bands of this crystal as an active laser element. Figure 2 shows the absorption spectrum of an LaF_3 crystal containing about 1% by weight of Nd^{3+} ions. The spectrum was obtained with the EPS-2U spectrophotometer at 300°K. Certain intense bands are marked by their peak absorption coefficients K. We see that the main absorption bands lie in the region from 12,000 to 20,000 cm^{-1}.

A detailed examination of the structure of the $^4F_{3/2}$ and $^4I_{11/2}$ terms that take a direct part in the stimulated emission was carried out with the high resolution DFS-12 spectrometer. Figure 3 shows the absorption spectra corresponding to the $^4I_{9/2}$–$^4F_{3/2}$ transition obtained at 77 and 300°K. According to our measurements, the level splitting of the $^4F_{3/2}$ term is 43 ± 2 cm^{-1} at 77°K and 39 ± 2 cm^{-1} at room temperature. Figure 3 also shows the absorption spectrum corresponding to the $^4I_{9/2}$–$^2P_{1/2}$ transition. The most intense peaks are due to transitions from the ground level and from the first-excited level ~40 cm^{-1} away from the ground level. The investigated spectra also show components corresponding to transitions from other excited levels of the $^4I_{9/2}$ term that are 142, 299, and 503 cm^{-1} away from the ground level. It is also apparent from Fig. 3 that the spectrum contains weak lines that do not fit the level splitting scheme of the $^2P_{1/2}$ and $^4I_{9/2}$ terms. These lines seem to be due to the formation of paired or more complex associates occurring at high activator concentrations. This is also borne out by the data obtained by Voron'ko and Osiko,[16] who investigated the $^4I_{9/2}$–$^2P_{1/2}$ transition at 4.2°K.

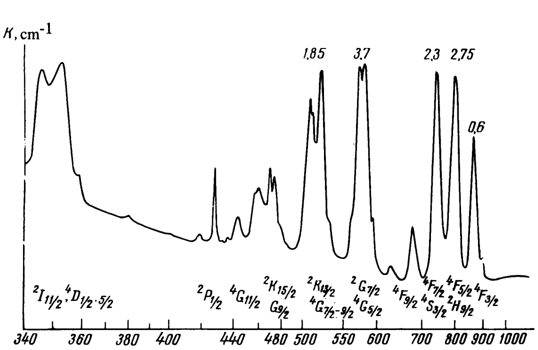

FIG. 2. Absorption spectrum of LaF_3-Nd^{3+} (1%) crystal at 300°K.

Luminescence Spectra

As we know, the Nd^{3+} is luminescent in the infrared range of wavelengths from 0.8 to 2.5 μ, corresponding to transitions from the $^4F_{3/2}$ level to four components of the main multiplet ^4I. The most intense luminescence connects the terms $^4F_{3/2}$ and $^4I_{11/2}$. Figure 4 shows the luminescence spectra of an LaF_3–Nd^{3+} crystal (1%) obtained at 77 and 300°K for transitions from the levels of the $^4F_{3/2}$ term to the components of the $^4I_{11/2}$ and $^4I_{9/2}$ terms. The observed splitting of the $^4F_{3/2}$ term and the first-excited levels of the main $^4I_{9/2}$ term is clearly seen in the luminescence spectra. The arrows in Fig. 4 designate the lines at which generation was observed.

The widths of the luminescence lines at which stimulated emission was obtained are $\Delta\nu_A \approx 9$ cm^{-1}

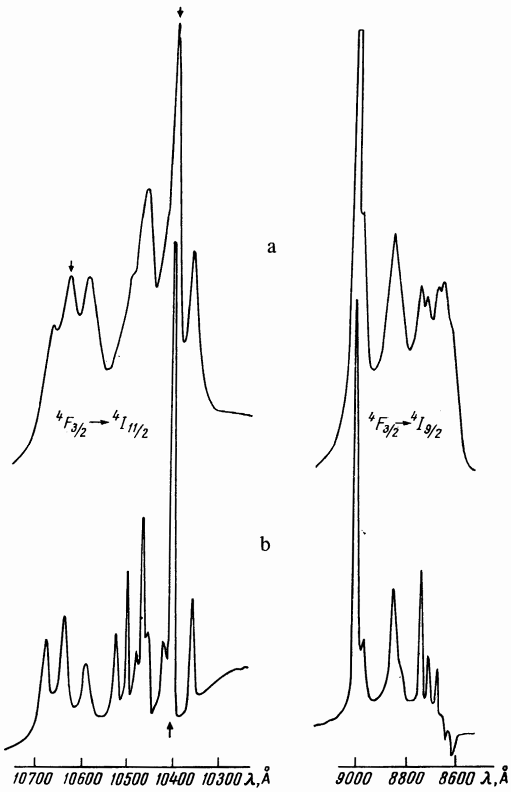

FIG. 4. Luminescence spectra of LaF_3-Nd^{3+} crystal, transitions $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$: (a) – at 300°K, and (b) – at 77°K.

(10407 Å) and $\Delta\nu_B \approx 25$ cm^{-1} (10633 Å) at 300°K, and $\Delta\nu_A \approx 3.5$ cm^{-1} (10403 Å) at 77°K.

Stimulated Emission

At room temperature a laser with LaF_3–Nd^{3+} (1%) crystal generates two lines: (A) at 10,407 ± 0.5 Å (9609 cm^{-1}), and (B) at 10,633 ± 0.5 Å (9405 cm^{-1}). The emission line widths are ~2.3 cm^{-1} for the A line and ~6 cm^{-1} for the long-wave B line. Figure 5 shows the stimulated emission spectrum of the LaF_3–Nd^{3+} crystal at 300°K. The laser begins generating the A line when the electrical energy supplied to the pump lamp reaches ~17 J; the threshold corresponding to the B line is ~42 J. According to Johnson,[6] LaF_3–Nd^{3+} lasers emit only at 10,633 Å at 300°K, and 10,399 and 10,631 Å at 77°K. However, our investigation of low-temperature generation showed that the spectrum consists only of a single line at λ = 10,403 Å (9613 cm^{-1}). At 77°K the width of this line is ~1 cm^{-1} and the threshold in a pumping system of 0.15 efficiency is ~8 J.

All the above values of threshold energy pertain to an optical resonator consisting of two identical mirrors with 0.7% transmittivity.

The losses in the investigated crystal at the emission frequency were determined by a method described earlier[17, 18] and consisting in measuring the threshold pump energy for various Q-factors of the optical resonator (the Q-factor was varied by changing the transmission of the output mirror). In this connection we carried out an experiment to measure $E_{threshold}$ as a function of τ of the output mirror. The results allowed us to determine the damping coefficient which had the value of ~0.03 cm^{-1}.

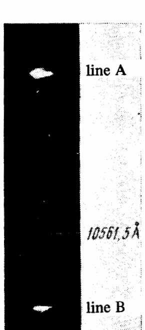

FIG. 5. Generation spectrum of LaF_3-Nd^{3+} crystal at 300°K. The position of the reference third-order iron lines is shown.

CONCLUSION

The experimental results obtained from the study of absorption, luminescence, and generation spectra were used to establish the sequence of Stark level scheme of the $^4F_{3/2}$ and $^4I_{11/2}$ terms, between which stimulated transitions take place at 77 and 300°K. These sequences are shown in Fig. 6. We see that at 77 and 300°K stimulated transitions (denoted by heavy arrows) connect the lower level of the $^4F_{3/2}$ term with various components of the $^4I_{11/2}$ term.

Our research revealed that the LaF_3 crystal is a very convenient matrix for activation with TR^{3+} ions. This is in good agreement with the aforementioned generating characteristics, with sufficiently low excitation thresholds obtained for crystal of low optical quality. On the other hand, the optical spectra are determined mainly by a single type of optical center, provided the concentration of activators is sufficiently high.

In conclusion we should note that so far the shortest-wave laser operating at 300°K and using Nd^{3+} ions is a CaF_2–Nd^{3+} unit (type I) with an emission wavelength of 10,461 Å.[19] Now, however, this property is revealed for crystals with LaF_3–Nd^{3+}.

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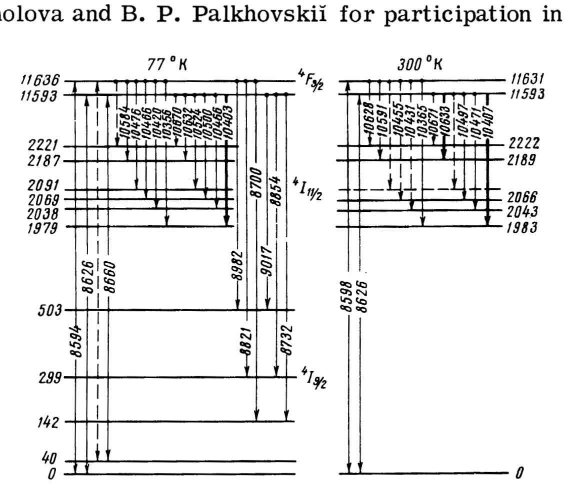

FIG. 6. Crystalline splitting of the $^4F_{3/2}$, $^4I_{11/2}$, and $^4I_{9/2}$ terms of the LaF_3-Nd^{3+} crystal. Level positions are in cm^{-1} and the transitions in Å. Stimulated transitions are denoted by heavy arrows.

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