ON THE POSSIBILITY OF INVESTIGATION OF THE "STARK" STRUCTURE OF Tr³⁺ ION SPECTRA IN DISORDERED FLUORIDE CRYSTAL SYSTEMS

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A comprehensive investigation of BaF_2–LaF_3–Nd^{3+} crystals show that it should be possible to analyze the Stark structure of TR^{3+} ion spectra in mixed fluoride systems (solid solutions). These systems belong to a class of crystals with disordered structures, characterized by a diversity of activator centers. The analysis includes a study of absorption, luminescence, and stimulated-emission spectra of BaF_2–LaF_3–Nd^{3+} crystals in a broad temperature range and broad range of LaF_3 and activator concentrations. The results permit one to introduce the concept of activator ion pseudocenter and to propose a "Stark" scheme of the energy levels of the Nd^{3+} ions. The observed stimulated transitions A–10,534 Å, B–10,580 Å, ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and C–13,300 Å ($^4F_{3/2} \rightarrow {}^4I_{13/2}$) are identified. The most important spectroscopic and generation parameters required for a theoretical analysis of laser operation are analyzed and assessed.

THE recently accumulated results of investigations of optical properties, and particularly lasing properties, of multicomponent fluoride crystals (solid solutions with disordered structure) activated with rare-earth element ions (TR^{3+}) allow us to conclude that the synthesis of such compounds is one of the reliable ways of obtaining crystalline laser media with satisfactory characteristics. A large number of mixed fluoride crystals with TR^{3+} have been synthesized by now, and approximately 30 lasers have been developed on their basis (see the reviews[1]). Some of them cause the lasers to have unique properties. Thus, lasers on the basis of CaF_2–YF_3–Nd^{3+} and α-$NaCaYF_6$–Nd^{3+} crystals are capable of generating at up to $\sim 1000°K$[2,3], and those based on CaF_2–YF_3–Nd^{3+} and CaF_2–SrF_2–BaF_2–YF_3–LaF_3–Nd^{3+}[3] retain their basic output parameters (efficiency η') in a wide range of temperatures. The idea of producing disordered crystals was successfully employed also for other crystals, for example $LaNa(MoO_4)_2$–Nd^{3+}[4,5]. A distinguishing feature of this class of media is that the TR^{3+} ions are contained in the composition of many activator centers (AC) that differ in structure. This causes the absorption spectra of these substances to consist of broad intense bands, greatly increasing the utilization of the radiation energy of the excitation sources compared with the simple crystals on the basis of which they have been obtained[6]. On the other hand, the migration of the energy over the excited states of the AC helps obtain satisfactory working laser parameters.

If we compare the degree to which optical properties of single-component and mixed laser crystals with TR^{3+} have been investigated, the studies of the stimulated emission (SE) of the former was already based in the majority of cases on the availability of extensive spectroscopic material. For the multicomponent systems, on the other hand, the situation is reversed, namely, results of lasing experiments have been accumulated but there is practically no information on the spectroscopic properties of these systems. Obviously, such a situation

hinders the search for new crystals of this promising laser media. In our opinion, this lag is due to the fact that the researchers were "stopped" by the broadbands in the optical spectra, which at first glance indeed seemed to be difficult to study. Our preliminary investigation of various mixed fluoride systems with TR^{3+} ions has shown that their spectroscopic properties can in many cases be analyzed all the same.

The present investigation was stimulated by the general interest in crystals with disordered structures and TR^{3+} ions, particularly, their spectral, lasing, and structure properties. We report the results of a comprehensive investigation of spectroscopic and lasing characteristics of mixed fluoride BaF_2–LiF_3 crystals activated with Nd^{3+} ions. We investigated the absorption, luminescence, and SE spectra (transitions $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$) in a broad temperature interval. The obtained results enable us to introduce the concept of the pseudocenter of TR^{3+} ions in such media. A "Stark" scheme of energy levels of the Nd^{3+} ions has been constructed, and the observed stimulated transitions have been identified: A–10,534 Å, B–10,580 Å (77°K), and C–13,300 Å (77°K). We have analyzed and estimated the most important spectroscopic and lasing parameters needed for a theoretical analysis of the laser operation.

INVESTIGATED CRYSTALS

In the first lasers[7] based on the multicomponent compound BaF_2–LiF_3–Nd^{3+} we used samples with 70 wt.% of BaF_2 and 30 wt.% LaF_3, the Nd^{3+} ion concentration ranging from 0.5 to ~ 1 wt.%. Subsequent x-ray phase investigations of the BaF_2–LaF_3 system[8,9] have shown that the region of stable solid solutions of the structure O_h^5–$Fm3m$ extends to ~ 55 mol.% LaF_3. In our experiments we used BaF_2–LaF_3 crystals of fluorite structure with different compositions, synthesized by the Stockbarger method. The activator concentration ranged from 0.2 to 6 wt.% and that of LaF_3 from

5 to 40%. Lasing was investigated with BaF$_2$—LaF$_3$ (~30 wt.%) crystals containing from 0.5 to 4.5 wt.% Nd^{3+} ions and in the form of cylindrical rodes of 13 to 80 mm length and 5—6 mm diameter, with plane-parallel end faces (~15"). We have also used the single-component crystals LaF$_3$—Nd^{3+} and BaF$_2$—Nd^{3+} (type I), certain properties of which have been investigated in[10,11], and type LGS-1 commercial glass.

EXPERIMENTAL APPARATUS AND RESEARCH METHODS

The overall absorption spectra of EaF$_2$—LaF$_2$—Nd^{3+} at 300°K were investigated with the EPS-2U spectrophotometer. A detailed investigation of the structure of their bands, on the other hand, was performed with diffraction spectrometers with larger resolution (~0.2 cm^{-1}), and also with a modified UR-20 IR spectrometer (working range from 1 μ; resolution 5—10 cm^{-1}). In the study of the spectrum corresponding to the transition $^4I_{9/2} \rightarrow {}^4I_{11/2}$ (~2000 cm^{-1}), we used a metallic Dewar with windows of NaCl. In this case, when the Dewar was filled with liquified nitrogen, the approximate sample temperature was 90°K. In all other low-temperature spectroscopic experiments we used cryostats made of foamed plastic and light pipes made of quartz or ruby. An analysis of the absorption and luminescence at 77 and 300°K in individual groups was carried out with DFS-12 instruments. Infrared luminescence (the transition $^4F_{3/2} \rightarrow {}^4I_J$) was also investigated with the aid of the monochromatic instrument IKS-21 with a PbS photoresistance, whose spectral sensitivity was calibrated against radiation from the SI-10-300 standard source and a synchronous-phase detector.

The high-temperature spectroscopic and laser investigations, and also the measurement of the lifetime τ of the excited state $^4F_{3/2}$, were carried out with the aid of the experimental technique described in[3,12]. We must stop to discuss here the method of measuring τ in crystals with disordered structure and having a variety of AC, particularly in our medium BaF$_2$—LaF$_3$—Nd^{3+}. It is known that the optical spectra of such systems constitute broad bands, the strong inhomogeneous broadening of which is connected with superposition of individual narrow lines belonging to different centers. Then, assuming that the entire radiation is connected with a single transition ($^4F_{3/2} \rightarrow {}^4I_{11/2}$), the time behavior of the damping of the luminescence of all the centers is registered in the experiment in the form of a "complicated-exponential" oscillogram, and can be expressed by

$$I_l(t) = \sum_k I_0^k \exp(-t/\tau_k),$$

where I_0^k is the initial maximum intensity of the luminescence of the k-th center (at an exciting-pulse duration $\tau_{exc} \ll \tau_k$). However, since the existing excitation-energy migration has in such media a probability $\overline{W}_m = 1/\tau_m$, the bands behave like homogeneously-broadened ones. For the case when τ_m is much smaller than τ of the shortest-lived center of the entire ensemble, the luminescence band has a "homogeneous" character. In this case the character of I(t) is determined mainly by a single exponential. On the other hand, in our case τ_m is apparently of the same order of magnitude as τ, which leads in final analysis to a "complica-

ted exponential." Taking this circumstance into account, we have always analyzed a definite section of the time oscillogram of the luminescence damping obtained in the measurement of τ (the central part at the normalized amplitude). Obviously, the value of τ measured by us is the lifetime "averaged" both with respect to τ_k and with respect to τ_m.

To estimate the cross section σ_e of the induced transition in the group $^4F_{3/2} \rightarrow {}^4I_{11/2}$, we used the Fachtbauer-Ladenburg formula[13].

In experiments on stimulated emission, we used a laser consisting of cylindrical chambers with elliptic cross sections, with optical efficiency 0.3—0.5 and with xenon lamps of the type IFP-400 or IFP-800. The investigations were carried out both in the "free" pulsed-generation regime (low and high temperatures up to 950°K) and in the giant-pulse regime (the Q-switch was a rotating 90° prism[14]), and also under conditions of quasicontinuous excitation with pumping by radiation from pyrotechnic light sources[15]. In all cases, the resonator was made up of external confocally-mounted spherical mirrors (R ≈ 576 mm) with multilayer dielectric coatings (the transmission at the generation wavelength λ_g was ~1%).

In low-temperature lasing experiments (77°K), the working crystal was placed in a tubular glass cryostat. In this case, the connection between the active element and the optical resonator was with the aid of special light pipes. The SE spectra (transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$) were photographed (I-1070 film) with a DFS-8 diffraction spectrograph with linear dispersion ~5.9 Å/mm (working bandwidth up to 11,000 Å). In these experiments the reference spectrum was the radiation from a lamp with a hollow cathode (Fe), which was registered in the third order of the grating.

In the study of the induced transition B (13,300 ± 5 Å, ~7520 cm^{-1}) ($^4F_{3/2} \rightarrow {}^4I_{13/2}$ (~3944 cm^{-1})), which in our experiments was observed only at 77°K, we used a ZMR-3 mirror monochromator and an InAs photodiode (time constant ~10^{-6} sec). In these experiments, additional absorption was introduced in the resonator (crystal with TR, having an absorption ~5 cm^{-1} at the wavelengths 1.06 μ) so as to prevent generation at the principal transitions A and B ($^4F_{3/2} \rightarrow {}^4I_{11/2}$). The dielectric mirrors used in this case had a transmission ~70% at $\lambda = 1.06$ μ. The threshold excitation energy E_{thr} and the generation energy E_g were registered by the usual methods, and the loss (α) at the emission wavelength was measured with the aid of semi-transparent mirrors having calibrated transmission. The other spectroscopic and generation parameters were investigated by well known methods.

EXPERIMENTAL RESULTS

Absorption experiments. Information was obtained concerning the position of the levels of almost all the terms of the Nd^{3+} ions in BaF$_2$—LaF$_3$ crystals in the transparency band, which, as shown by our measurements (spectrophotometers EPS-2U and UR-20), extends from 0.22 to 10.5 μ (sample thickness ~5 mm). We confine ourselves here to the spectra which we shall need for further analysis. In particular, we are interested in the lowest terms, which are connected directly with SE.
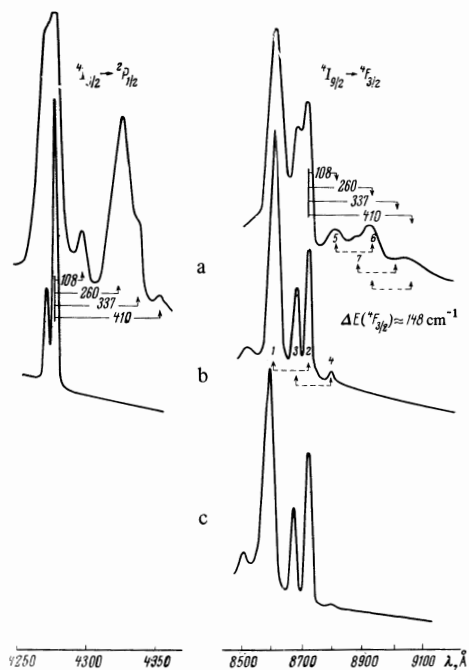
FIG. 1. Absorption spectra of the crystal BaF_2-LaF_3 ($\sim$ 30 wt. %) – Nd^{3+} ($\sim$ 4.5 wt. %) at 300°K (a) and 77°K (b) and of BaF_2-LaF_3 (20 wt. %) – Nd^{3+} ($\sim$ 0.2 wt. %) at 77°K (c). The dashed brackets indicate the splitting of the term $^4F_{3/2}$, and the arrows designate the positions of the levels of the term $^4I_{3/2}$ (in cm^{-1}).
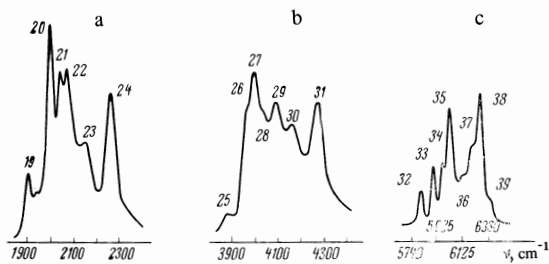

FIG. 2. Absorption spectra of the BaF_2-LaF_2-Nd^{3+} crystal: a) 90°K, transition $^4I_{9/2} \to {}^4I_{11/2}$; b) 77°K, transition $^4I_{9/2} \to {}^4I_{13/2}$; c) 77°K, transition $^4I_{9/2} \to {}^4I_{15/2}$.

Figure 1 shows the absorption spectra obtained at 77 and 300°K with the DFS-12 instrument, corresponding to the transitions $^4I_{9/2} \to {}^2P_{1/2}$ and $^4I_{9/2} \to {}^4F_{3/2}$. A study of the concentration series (relative to LaF_3 with 10 wt. % and higher) of the BaF_2– LaF_3 crystals has shown that the character of these (and other) spectra remains essentially constant at a given temperature, only the peak absorption coefficients k of the individual lines change, but their proportionality is retained. Figure 2 shows spectra obtained at $\sim$ 90°K with the IR spectrophotometer UR-20, corresponding to the transitions $^4I_{9/2} \to {}^4I_{15/2}$ ($\sim$ 6100 cm^{-1}), $^4I_{9/2} \to {}^4I_{13/2}$ ($\sim$ 4080 cm^{-1}), and $^4I_{9/2} \to {}^4I_{11/2}$ ($\sim$ 2100 cm^{-1}).

To determine the dependence of the relative quantum luminescence yield $\eta(c)$ on the activator concentration, we analyzed the integral absorption $\overline{K} = \int k(\nu)d\nu$ of the principal bands ($^4G_{11/2}$, $^2G_{7/2}$, $^4F_{7/2}$, $^4S_{3/2}$, and $^4F_{3/2}$) on the content of the Nd^{3+} ions (at a constant composition

of BaF_2 and 30 wt.% of LaF_3). It is also nearly directly proportional to the variation of c (from 1 to 4.5 wt.%).

Luminescence experiments. An analysis of the overall spectrum (connected with the transitions $^4F_{3/2} \to {}^4I_j$ has made it possible to estimate the coefficients of photon density distribution among the four luminescence groups: 21, 69, 9 and $\sim 1\%$ respectively for $^4F_{3/2} \to {}^4I_{9/2, 11/2, 13/2, 15/2}$. A detailed structure of the luminescence spectra, corresponding to the transitions $^4F_{3/2} \to {}^4I_{9/2, 11/2}$, is shown in Fig. 3.

Figures 4 and 5 show the dependences of the lifetime τ of the excited state $^4F_{3/2}$ of the Nd^{3+} ions in BaF_2—LaF_3 on the concentration c of the activator and on T. We see that an appreciable shortening of τ takes place when the Nd^{3+} contents exceeds 1 wt.%. An analysis of $\tau(T)$ for crystals with differing impurity concentrations has revealed, a different character of the behavior of this de-
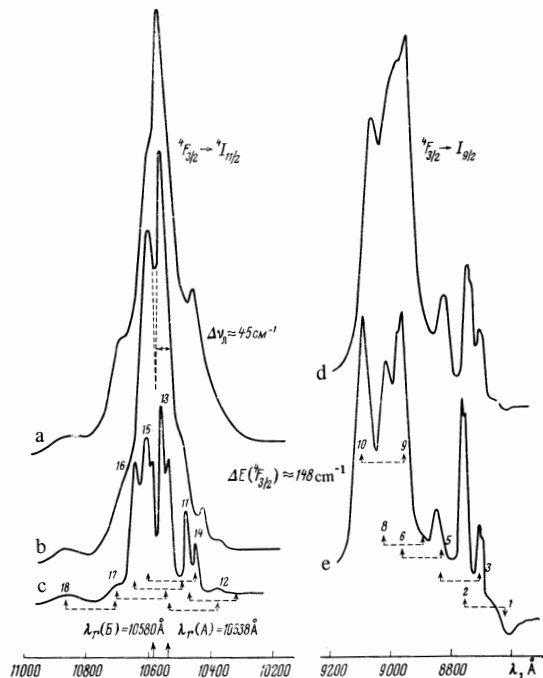

FIG. 3. Luminescence spectra of the following crystals: a) BaF_2-LaF_3 ($\sim$ 30 wt. %) – Nd^{3+} ($\sim$ 1 wt. %) at 300°K; b) the same at 77°K; c) BaF_2-LaF_3 ($\sim$ 5 wt. %) – Nd^{3+} ($\sim$ 1 wt. %) at 77°K; d) BaF_2-LaF_3 ($\sim$ 30 wt. %) – Nd^{3+} ($\sim$ 1 wt. %) at 77°K; e) BaF_2-LaF_3 ($\sim$ 5 wt. %) – Nd^{3+} ($\sim$ 1 wt. %) at 77°K.
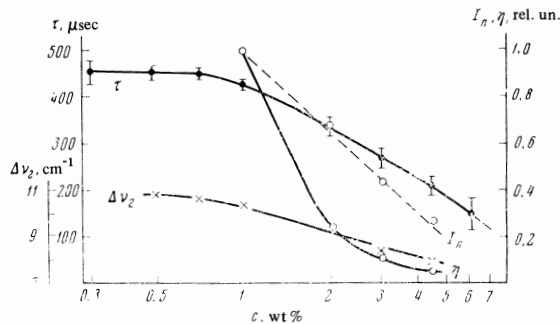
FIG. 4. Concentration dependences of τ, η, and $\Delta\nu_g$ (transition A) and of the luminescence intensity I_l at 300°K of the crystal BaF_2-LaF_3 – Nd^{3+}.
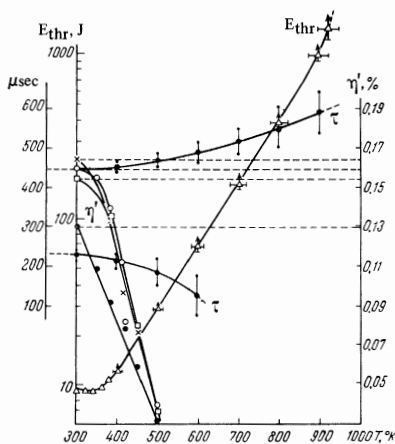
FIG. 5. Temperature dependence of E_{thr}, η, and of the lifetime τ of the excited state $^4F_{3/2}$ of BaF_2-LaF_3 — Nd^{3+} crystals. The measurements of η were made at the following exciting-pulse durations: ● — 300 μsec, × — 400 μsec, ○ — 500 μsec, □ — 900 μsec.

FIG. 6. Scheme showing the splitting of the terms $^4F_{3/2}$ and $^4I_{9/2-15/2}$ of Nd^{3+} ions in BaF_2-LaF_3 at 77°K. The level positions are indicated in cm⁻¹, and the transitions between them are indicated in A. The thick arrows denote stimulated transitions

pendence. Thus, for BaF_2LaF_3 samples with large Nd^{3+} content (more than 2 wt.%) the $\tau(T)$ curves behave in "normal" fashion, i.e., the usual temperature quenching is observed. On the other hand, for crystals with low Nd^{3+} concentration (less than 1 wt.%), an increase of τ was observed. In these experiments, to eliminate the influence of the reabsorption, thin layers of crystals were excited by radiation from an ISSh-100 lamp. It must be noted here that the observed anomaly is present also in many other mixed fluoride systems[16]. Figure 4 shows also plots of $\eta(c)$ and of the integral intensity $I_l(c)$ of the luminescence (transition $^4F_{3/2} \to {}^4I_{11/2}$).

A detailed study of the optical spectra has made it possible to construct the level scheme of the Nd^{3+} ions in BaF_2-LaF_3. Part of this scheme is shown in Fig. 6. We have confined ourselves to the structure of the terms of $^4F_{3/2}$ and ^4I_J. This, on the one hand, is due to the fact that the positions of the levels has been found with great reliability (in absorption and in luminescence), and on the other hand, as already noted above, induced transitions between the levels of the $^4F_{3/2}$ and ^4F_J terms are possible. We see that the total splitting of the $^4I_{9/2-13/2}$ terms is equal to 410, 360 and 380 cm⁻¹. For these, the accuracy with which the level positions are determined is ±15 cm⁻¹. The transitions designated by the dashed lines correspond to insufficiently distinct lines in the investigated spectra. For convenience in comparing the transitions on the shown scheme with the corresponding lines of the spectra (Fig. 1—3), tie-in numbers have been provided.

The cross section of the induced transitions was estimated from the formula

$$\sigma_e = \frac{\lambda_g^2}{8\pi^2 n^2} \frac{W_{sp}}{\Delta\nu_l},$$

where n is the refractive index, $\Delta\nu_l$ is the width of the luminescence line corresponding to the induced transition, $W_{sp} = 1/\tau_{rad}$ is the probability of the spontaneous transition. Unfortunately, it is difficult to determine σ_e for the transition A (10, 534 Å) of the crystal BaF_2-LaF_3-Nd^{3+} with a high degree of accuracy. First, the determination of $\Delta\nu_l(A)$, as seen from Fig. 3, is
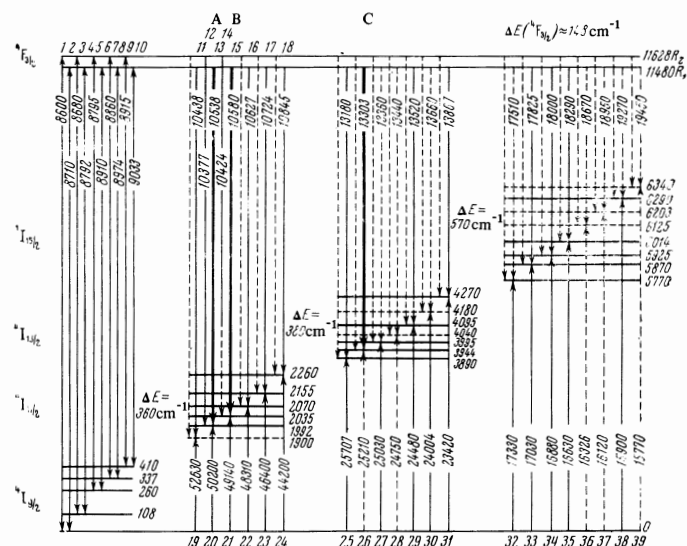
impossible without a very laborious resolution of the overall contour of the luminescence band of the transition $^4F_{3/2} \to {}^4I_{11/2}$ into individual components. However, by analyzing the concentration and temperature spectra of this luminescence group we managed to arrive at the conclusion that at 300°K it can be assumed that $\Delta\nu_l(A) = 75 \pm 20$ cm⁻¹. The next difficulty lies in the determination of the radiative lifetime τ_{rad}. Experimentally, τ is the total lifetime of the excited state $^4F_{3/2}$ (with allowance for transitions to all the levels of the ^4I_J terms). The constancy of $\tau(T)$ at room temperature (see Fig. 5) allows us to conclude that the probabilities of nonradiative transitions to the levels of these terms are small. Then, taking into consideration the magnitude of the splitting of the $^4F_{3/2}$ term and the fact that the transition A begins with the lower level R_1, and also assuming that the character of the broadening, as a result of $\tau_m \ll \tau$, of the entire luminescence band ($^4F_{3/2} \to {}^4I_{11/2}$) is homogeneous, we can put $\tau_{rad} = \tau D_l/D_l(A)$. Here D_l is the density of photon emission at all the levels of the multiplet ^4I_J, and $D_l(A)$ pertains only to the line A. As already mentioned, the transition $^4F_{3/2} \to {}^4I_{11/2}$ accounts for approximately 69% of all the emitted photons, while the line A accounts for only 27 ± 10%. Taking into account the scatter of all the quantities that enter in the expression for σ_e, we estimate the cross section of the induced transition A at (2.3 ± 2) × 10⁻²⁰ cm². At 300°K, the value of τ_{rad} (c ≈ 1 at.%) of the transition (~ 11,480 cm⁻¹) $^4F_{3/2} \to {}^4I_{11/2}$ (~1992 cm⁻¹) can be assumed to be equal to 1.57 ± 0.3 msec.

For comparison, an analogous estimate of σ_e was made also for the laser transition $^4F_{3/2} \to {}^4I_{11/2}$ of the neodymium glass LGS-1 (τ = 350 μsec at 300°K). In this case $\sigma_e = (1 \pm 2) \times 10^{-20}$ cm². We could estimate σ_e of the transition C only at 77°K, since it is very difficult to estimate $\Delta\nu_l$ at 300°K even with a great degree of approximation. With τ_{rad} (77°K, c ≈ 1 wt.%) of the transition (11, 480 cm⁻¹) $^4F_{3/2} \to {}^4I_{13/2}$ (~ 3944 cm⁻¹)

equal to 53 ± 10 msec, we get $\sigma_e(C) \sim 1 \times 10^{-21}$ cm^2 with a large scatter.

Investigation of the SE parameters. Figure 5 shows the temperature dependences of E_{thr} and η'. The curves were obtained with BaF_2-LaF_3 crystals containing 0.5 wt.% of Nd^{3+} ions (length ~ 45 and diameter ~ 6 mm). The optic quality of these samples was low, and knots were seen in the entire volume. We see that the limiting working temperature was $\sim 920°$K. The investigation of $\eta'(T)$ was carried out at different durations of the exciting light pulse τ_{exc}. In the study of this characteristic, we attempted not to go too far outside the manufacturers recommendations for the operation of the IFP-800 lamp. We see that starting with $\tau_{ext} \approx 400$ μsec the efficiency of the laser changes little. Under identical conditions, but with crystals (of similar quality) ~ 80 mm long, the absolute value of η' was approximately 1.5–2 times larger. The losses in these crystals were estimated from the formula $\alpha = [2l(\gamma - 1)]^{-1}\ln R_2^{-1}$, where R_2 is the reflection coefficient of the output mirror, l is the length of the crystal, and γ' is the ratio of E_{thr} at a certain R_2 to its value at $R_2 = 1$. Thus, for the samples with which the data of Fig. 5 were obtained, $\alpha = (5 \pm 2) \times 10^{-2}$ cm^{-1}. We had at our disposal a crystal BaF_2-LaF_3 (~ 30 wt.%)$-Nd^{3+}$ (~ 1 wt.%) 13 mm long and 5.3 mm in diameter, with satisfactory optical quality, whose α was smaller by one order of magnitude. At $300°$K, a laser based on this crystal started to generate at $E_{thr} \sim 2.7$ J.

The high-temperature SE spectra of the laser based on the crystal BaF_2-LaF_3 (~ 30 wt.%)$-Nd^{3+}$ (~ 0.5 wt.%) are shown in Fig. 7. At $300°$K, generation takes place at the line A with $\lambda_g = 10,534 \pm 2$ Å (9493 cm^{-1}). With increasing temperature, λ_g shifts towards longer wavelengths with $\Delta\lambda/\Delta T \approx 5.2 \times 10^{-2}$ Å/deg. At $77°$K, generation (transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$) of a laser based on the crystal BaF_2-LaF_3 (~ 30 wt.%)$-Nd^{3+}$ (~ 1 wt.%), as seen from Fig. 7, is possible at two lines with $\lambda_g(A) = 10,538 \pm 2$ Å (~ 9490 cm^{-1}) and $\lambda_g(B) = 10,580 \pm 5$ Å (~ 9450 cm^{-1}), with E_{thr} equal to 15 and 50 J, respectively. The high values of E_{thr} are determined in this case by the additional losses occurring in the long (110 mm) light pipes. At $77°$K, with E_{thr} exceeded by a factor of three, we have $\Delta\nu_g = 17 \pm 2$ for line A and $\Delta\nu_g = 30 \pm 3$ cm^{-1} for line B. The line broadening at $77°$K
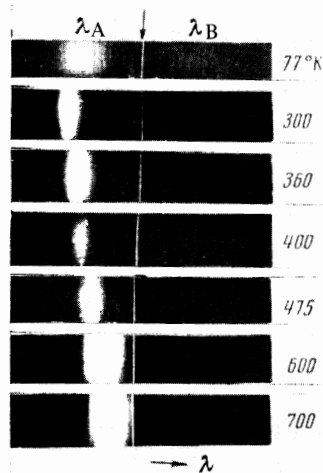

FIG. 7. Spectra of induced radiation of the crystals BaF_2-$LaF_3 - Nd^{3+}$ (~ 1 wt. %). The reference line width $\lambda = 10,561.5$ Å is indicated by the arrow.

can apparently be attributed to the factors considered in[17], or to the presence of two light pipes acting as interferometers in the resonator. Unfortunately, we were unable to investigate the parameters of the induced transition $C(13,300 \pm 10$ Å) in such detail. The difficulty lay in the photoelectric determination of λ_g and in the high $E_{thr} \approx 500$ J (the crystal had $E_{thr} = 2.7$ J at $300°$K at $\lambda_g = 10,534$ Å). Identification of the observed induced transitions has shown that they connect the lower R_1 level (11,480 cm^{-1}) of the term $^4F_{3/2}$ with the 2035 and 1992 cm^{-1} components of the term $^4I_{11/2}$ and 3944 cm^{-1} of the term $^4I_{13/2}$. The induced transitions are marked by thick arrows in the level scheme (Fig. 6).

In all the generation experiments, the excitation took place in the $BaF_2-LiF_3-Nd^{3+}$ crystals absorption bands located in the range from 0.5 to 0.9 μ. This was attained by using a ZhS-17 glass filter. Our investigations have shown that the effect of "aging" of $BaF_2-LaF_3-Nd^{3+}$ crystals ($Nd^{3+} \rightarrow Nd^{2+}$) does not become as strongly manifest as, for example, for $CaF_2-YF_3-Nd^{3+}$ crystals[18].

Experiments performed at $300°$K under Q-switching conditions have shown that in this case the output radiation energy decreases sharply compared with the "free" pulse generation, and this comes into play noticeably already at Q-switching times $\sim 10^{-5}$ sec. In the continuous regime, when pumped with radiation from a pyrotechnic source (Zr fuel, $KClO_4$ oxidizer), generation is already possible when a charge ~ 100 mg is ignited.

DISCUSSION OF RESULTS

The results of a preliminary investigation of a number of multicomponent fluoride crystals with TR^{3+} ions allow us to conclude that the structure appearing in the broad bands of the optical spectra of these crystals, connected with transitions between individual terms, may be a peculiar Stark structure of these crystals. Indeed, the aggregate of our spectroscopic and lasing investigations of the $BaF_2-LaF_3-Nd^{3+}$ system yielded sufficiently convincing evidence favoring the foregoing assumption.

1. On the basis of the results of the study of the spectral properties, we constructed the energy-level scheme of the Nd^{3+} ions and identified the observed induced transitions. The only levels assumed to be reliably established in the scheme were those whose positions were determined by several possible methods. Thus, to establish the energy of the levels of the lowest ^4I_J terms, both absorption and luminescence experiments were performed and data on the spectroscopy of the SE were used as a control. In most cases the structure of the bands was well analyzed, and the determined transitions were connected with the levels of the scheme. As a rule, no "extra" lines were observed in the spectra. The fact that the observed lines are a "Stark structure" may be confirmed further by the results of the concentration investigations of the peak and integral absorption coefficients of both the individual lines and of the bands. As indicated above, these coefficients increase linearly with increasing activator concentration (in the investigated series of crystals).

2. From a comparison of the $BaF_2-LaF_3-Nd^{3+}$ sys-

tem with the simple BaF$_2$—Nd^{3+} crystals it follows that the number of centers in the latter increases sharply with increasing Nd concentration (in the interval up to 2 wt.%). This becomes clearly manifest in the spectra: new lines appear and their intensities become redistributed[11]. On the other hand, in BaF$_2$—LiF$_3$ crystals at a constant ratio of the components BaF$_2$ and LaF$_3$ (for example, 70 and 30 wt.%) and in the Nd^{3+} ion concentration range from 0.2 to 6 wt.%, the structure of the band does not change noticeably on going from 77 to 300°K. This circumstance makes it possible to state that no new AC are produced in BaF$_2$—LaF$_3$—Nd^{3+} in an amount that can be registered under conditions of our experiments. In this respect, these crystals are similar in their properties, for example, to the disordered system LaNa(MoO$_4$)$_2$—Nd^{3+}[4,5], the spectra of which revealed analogous concentration features. All this favors the assumption that the decisive factor in the production of impurity centers and their variety in BaF$_2$—LaF$_3$: Nd^{3+} crystals, as well as in other similar mixed crystal systems, are the crystal chemical properties, i.e., the degree of disorder of the crystal structure, connected with the formation of a variety of nonequivalent positions. Thus, the spectra of BaF$_2$—LaF$_3$ (~ 5 wt.%)—Nd^{3+} (~ 1 wt.%) reveal, besides the intense lines, also distinct satellites (Fig. 3c—transition $^4F_{3/2} \rightarrow \, ^4I_{11/2}$ and Fig. 3e—transition $^4F_{3/2} \rightarrow \, ^4I_{9/2}$), which merge with the principal peaks with increasing LaF$_3$ concentration. These facts indicate that at a small LaF$_3$ content the degree of disorder has not yet reached "saturation." The situation is different at large LaF$_3$ concentrations. In this case the BaF$_2$—LaF$_3$—Nd^{3+} crystals have spectra whose forms do not depend on the activator content (from 0.2 to 4.2 wt.%). This is demonstrated in Figs. 1a and c.

3. How many types of AC are produced in BaF$_2$—LaF$_3$: Nd^{3+} crystals and what is their structure? Our results, of course, cannot provide exhaustive answers to these questions. By investigating the forms of the "Stark" lines and their positions in the entire group corresponding to the transition between the levels of two terms, it is possible to conclude that the character of the inhomogeneous broadening of these pseudo-lines is due to a superposition of individual Stark components of centers that are very close in structure, i.e., we can propose a situation, for example, wherein Nd^{3+} replaces in BaF$_2$—LaF$_3$ Ba^{2+} or La^{3+} ions that have several little-differing nonequivalent positions characterized by close crystal fields. Of course, to verify this assumption it is necessary to carry out x-ray structure investigations of BaF$_2$—LaF$_3$—Nd^{3+}.

That such a situation is probable is indicated by the data of[19], in which an x-ray structure analysis of the multicomponent fluoride system CaF$_2$—CaF$_3$, which is closely "related" to BaF$_2$—LiF$_3$, has shown that the Ca^{2+} and Ce^{3+} can form in the perfluoride structure several polyhedra that are close in shape, i.e., they can have several isostructural nonequivalent positions, and their "set" is no longer as large[1)][6]. This experimen-

tal fact gives grounds for assuming that the obtained spectroscopic results contain information on the BaF$_2$—LaF$_3$ crystal field surrounding the Nd^{3+} ions, being a field averaged over all close types of spectra. In this connection it is advantageous to introduce for such multicomponent crystals with TR^{3+} with disordered structure the concept of a pseudocenter, characterizing an ensemble of close (isostructural) AC with quasi-degenerate energy levels. Such concepts apparently guided the authors of papers on spectroscopic investigations of TR^{3+}-activated glasses[20], mixed LaNa(MoO$_4$)$_2$ crystals,[4] and inorganic liquids[21] having properties common with the mixed fluoride systems.

4. One practically important property of BaF$_2$—LaF$_3$—Nd^{3+} is the ability to generate at high temperatures (up to ~ 920°K). Our data also show that BaF$_2$—LaF$_3$—Nd^{3+} can be suitable also for cw lasers. As to the induced transition C (~ 13,300 Å), in practice it is very difficult to observe it, owing to the small σ_e compared with the main transition A (~ 10,534 Å). In the present investigation, the observed induced transitions helped verify additionally the correctness of the energy-level scheme of the ions Nd^{3+} in BaF$_2$—LaF$_3$, as in our other similar investigations[22]. Unfortunately, the information obtained with their aid is not understandable in all cases. For example, when T increases from 300°K, λ_g(A) increases, with $\Delta\lambda/\Delta T \approx 5.2 \times 10^{-2}$ Å/deg, indicating a change in the parameter of the unit cell of BaF$_2$—LaF$_3$—Nd^{3+}, and at the same time this line is shifted at 77°K in the same direction (see Fig. 7).

5. Temperature spectroscopic and generation investigations of the BaF$_2$—LaF$_3$—Nd^{3+} system have shown that the probabilities of nonradiative transitions from the levels of the terms $^4F_{3/2}$ and ^4I_J (most distinctly from $^4I_{11/2}$) are small. This is verified by measurements of τ(T), E_{thr}(T), η'(T), and $\eta'(\tau_{ext})$. Unfortunately, the characteristic Debye temperature T_D for BaF$_2$—LaF$_3$—Nd^{3+} is unknown, as is the spectral composition of the phonons. But if it is assumed that T_D of the system BaF$_2$—LaF$_3$ is close to T_D of the simple crystals BaF$_2$ (~ 282°K[23]) and LaF$_3$ (~ 360°K[24]), then the acoustic phonon with the shortest wavelength will have ν = 200—250 cm^{-1}. According to[25], it can be assumed that in our system there can be excited optical phonons of high energy. In spite of the rather approximate considerations regarding the phonon states of the BaF$_2$—LaF$_3$ crystal, it is seen from the level scheme (Fig. 6) that the minimum energy gap between the components of the terms $^4F_{3/2}$ and $^4I_{15/2}$ is almost ten times larger than that of the shortest-wavelength phonon. It is clear that the probability of the decay of the levels of the term $^4F_{3/2}$ with participation of phonon processes is small. It is also seen that the probability of relaxation from the levels of the term $^4I_{11/2}$ is small. In this case the gap is somewhat smaller (~ 1500 cm^{-1}), but is still large for the occurrence of direct single-phonon processes. Low-temperature generation experiments show that the lifetime of the final term (for laser processes) $^4I_{11/2}$ is of the same order of magnitude as τ_g, i.e., 10^{-4}—10^{-6} sec.

Interest attaches to the τ(T) dependence of the term $^4F_{3/2}$, particularly its anomalous character for crystals with small Nd^{3+} content (Fig. 5). The nature of this

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1) It is shown in [19] that the most probable coordination Ca^{2+} and Ca^{3+} polyhedra in the mixed fluoride system CaF$_2$-CaF$_3$ are dekahedra, in which the F^{1-} ions which do not enter in the ordinary sites of the CaF$_2$ cells (octahedra) do not lie exactly in the interstices but have their own coordinates.

phenomenon, which was first discussed in[16], is still unclear. We propose at present the existence of several possible causes of this effect. First, at high temperatures there can occur a raising of the symmetry of the main AC that enter in the pseudocenter of the Nd^{3+} ions and determine its properties. If it is assumed that the coefficients with which the Nd^{3+} enter in them are the largest of all the AC of the ensemble, then at low activator concentrations a certain temperature raising of the symmetry[2) should decrease the probability of the spontaneous transitions, and this causes lengthening of τ. Nor can we exclude a mechanism whereby W_m increases with increasing T, and the excitation becomes redistributed among centers with larger τ. The increase of W_m of $BaF_2 - LaF_3 - Nd^{3+}$ with increasing T may be indicated by the value of $\Delta\nu_g$ of the induced transition A at 77 and 300°K, (see Fig. 7). Acceleration of migration in this system accompanies also an increase of the activator concentration (Fig. 4). The concentration luminescence quenching that takes place in the crystals $BaF_2 - LaF_3 - Nd^{3+}$ can be connected with the nonresonant mechanism of excitation transfer between neighboring ions with emission of phonons; this transfer can follow the scheme $^4F_{3/2} \rightarrow {}^4I_{15/2}$ for one ion in the excited state $^4I_{9/2} \rightarrow {}^4I_{15/2}$ for another in the ground state.

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