

## NATURE OF "AGING" OF FLUORITE AND YTTROFLUORITE CRYSTALS ACTIVATED

BY  $\text{Nd}^{3+}$  UNDER STIMULATED EMISSION CONDITIONS

S. Kh. BATYGOV and A. A. KAMINSKIĬ

Crystallography Institute, Academy of Sciences, U.S.S.R.

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We investigate photoreduction of  $\text{Nd}^{3+}$  ions to  $\text{Nd}^{2+}$  in  $\text{CaF}_2:\text{YF}_3$  crystals, induced by powerful light pulses from an exciting lamp operating under stimulated emission conditions. Photoreduction results in "aging" of the crystals. This effect, which is harmful for generation, is ascribed to the existence of "cubic" optical centers in the crystals. Several ways of removing the "aging" effect are proposed on the basis of the experimental data.

## INTRODUCTION

ONE of the main problems of the physics of lasers with optical excitation is at present the stability of their active media in the stimulated-emission mode. On the one hand, this problem touches upon physico-chemical processes (change of valence) which occur under the influence of strong light pulses from the excitation sources, and on the other hand it touches on irreversible mechanical damage of the laser active elements (crystals or glasses) under the influence of the stimulated emission of super high power.

In recent years Voron'ko, Kaminskiĭ, and Osiko with their co-workers<sup>[1-9]</sup> carried out comprehensive investigations of the generation and spectroscopic characteristics of crystals such as fluorite activated with trivalent rare-earth elements ( $\text{TR}^{3+}$ ). The results of these investigations lead to the creation of lasers based on new active media—crystals of mixed fluorites with  $\text{TR}^{3+}$ <sup>[10-19]</sup>. These materials have the structure of typical crystals, but occupy a position intermediate between crystals and glasses in their spectral properties. The excitation thresholds of lasers based on these active media are much lower than that of lasers with crystals of individual fluorides, and the efficiencies are larger by hundreds of times.

In the study of stimulate emission of both mixed and simple fluoride crystals activated with  $\text{Nd}^{3+}$  ions, one of the authors observed an "aging" effect<sup>[2,19]</sup>, which is manifest in a gradual deterioration of the generation parameters, and in some cases leads to complete cessation of generation. Subsequent investigations have shown that the "aging" is connected with the effect of the photoreduction  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  under the influence of powerful light pulses from the excitation source<sup>[20]</sup>. It must be noted that the process  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  was observed before only under the action of hard radiation, during the course of chemical reactions, or in electrolysis.

Taking into account the urgency of investigating the problem of crystal stability under stimulated emission and the prospects of using mixed fluoride crystals with  $\text{TR}^{3+}$  for lasers, our present investigation had two purposes: first, a detailed investigation of the conditions and mechanism of the photoreduction  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  in the crystals  $\text{CaF}_2$  and  $\text{CaF}_2:\text{YF}_3$  in the generation mode, leading to the "aging" effect. The second problem con-

sisted of disclosing the possibilities for synthesizing activated fluoride crystals which are not subject to this harmful effect during the course of stimulated emission, and also obtaining data on the most favorable excitation regime of these crystals.

## CRYSTALS FOR THE INVESTIGATIONS

The experiments were made on  $\text{CaF}_2$  and  $\text{CaF}_2:\text{YF}_3$  crystals activated with  $\text{Nd}^{3+}$  ions grown from the melt by the dropping-crucible method in a measured fluoriding atmosphere<sup>[21]</sup>. The concentration of the activator in the  $\text{CaF}_2$  crystals varied from 0.2 to 0.5 wt.%. Some fluorite samples, contained besides neodymium small amounts of  $\text{Ce}^{3+}$  and  $\text{O}^{2-}$  ions. The yttrifluorite crystals had a variable composition both with respect to  $\text{Nd}^{3+}$  (1–4 wt.%) and with respect to  $\text{YF}_3$  (3–7 wt.%). Out of the synthesized single crystals we cut out for our investigations samples in the form of cylindrical rods 45–75 mm long, with diameter 5.5–7.5 mm. The end faces were plane-parallel to within not more than 30", and the lateral surface was polished.

## EXPERIMENTAL APPARATUS AND INVESTIGATION METHODS

All the experiments on the study of the "aging" effects were made in the stimulate emission mode. The laser consisted of a cylindrical illuminating system of elliptic cross section, ~90 mm long, with optical efficiency ~0.5<sup>[22]</sup>. In one of the focal regions was located a xenon flash lamp (IFP-800), and in the other the working crystal, which could be surrounded with filters made of type BS-10 or ZhS-17 glass. The optical resonator was produced by spherical multilayer dielectric mirrors, which were installed confocally. At a generation wavelength  $\lambda = 1.06 \mu$ , the employed reflectors had transmission coefficients ~0.5, 3, and 15%. The crystal and lamp were cooled by an air stream.

The threshold excitation energy was measured with the aid of a photomultiplier with an oxygen-caesium photocathode and an S1-16 oscilloscope. The output energy of the laser was registered with a spherical calorimeter (diameter 150 mm), the inside surface of which was covered with a white diffusely-reflecting paint with a constant reflection coefficient in the range from 0.3 to 2  $\mu$ . The radiation detector in the calorimeter was a

thermopile feeding a multirange high-resistance micro-voltmeter (type F-116/2). The threshold sensitivity of the calorimeter was  $\sim 10^{-3}$  J.

The procedure for investigating the ‘aging’ effect connected with the photoreduction  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  consisted of the following: first, before exposing the crystals to the laser illuminating system, we registered their absorption and luminescence spectra at 77 and 300°K, using an SP-700 spectrophotometer and a DFS-12 spectrometer, by a procedure described in<sup>[6,7]</sup>, in such a way as to be able to compare them with the spectra of the crystals subjected to the optical radiation. The absorption spectra could be used to reveal the presence of  $\text{Nd}^{2+}$  ions in the investigated crystals. The investigated samples were then placed in the illuminator, where they were subjected to strong light pulses of the total emission spectrum of the IFP-800 lamp<sup>[19,20]</sup>. After irradiation, their optical spectra were again investigated.

Prior to the experiments aimed at investigating the photoreduction  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$ , we measured in all the crystals the threshold excitation energies, using mirrors having different reflection coefficients. We measured the generation energy at an output-mirror transmission  $\sim 3\%$  and at the nominal electric energy fed to the IFP-800 lamp (800 J). The crystals were then exposed to a series of flashes produced with the lamp fed at a constant electric energy  $\sim 500$  J. The temperature measurements have shown that at a pulse repetition frequency 0.03 Hz the investigated crystals were heated on the average 2° from one flash to the other. To prevent the possible thermal oxidation  $\text{Nd}^{2+} \rightarrow \text{Nd}^{3+}$ , we used series with few flashes (10–40) depending on the character of the experiment and on the concentration of the  $\text{Nd}^{3+}$  and  $\text{Y}^{3+}$  ions in the crystals. After each series of light flashes, the crystals was cooled to room temperature and the measurements of the excitations thresholds and the generation energy were repeated. The ‘aging’ curves were plotted on the basis of these data.

The reflecting surface of our illuminator was a galvanically deposited layer of silver which was subsequently polished. Experiments have shown that after 150–200 flashes of the excitation lamp, the silver was oxidized by the ozone produced in the chamber, and the reflection coefficient of the working surface began to decrease. This was particularly noticeable in the ultraviolet region of the spectrum, which plays the main role in the  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  process. We therefore had to re-polish the reflecting surface of the elliptic illuminator every 150–200 flashes during the course of the experiments.

As indicated above, preliminary investigations have shown that heating of the investigated crystals leads to thermal oxidation  $\text{Nd}^{2+} \rightarrow \text{Nd}^{3+}$ . We therefore investigated the thermoluminescence spectra, using a setup consisting of a special heater producing a heating rate of  $\sim 0.4$  deg/sec. The luminescence from the crystal was fed with the aid of a quartz light pipe of 10 mm diameter to an FEU-28 photomultiplier, in front of which standard filters KS-19 and SZS-20 were mounted. The signal from the photomultiplier was fed through a dc amplifier to a PS-01 electronic potentiometer.

It is known that in four-level lasers the threshold excitation energy depends strongly on the Q of the optical resonator, which is determined at small mirror

transmission coefficients essentially by the harmful losses in the active medium. This circumstance makes it possible to determine experimentally the damping coefficient in the working crystal by measuring the threshold energies of excitation at two different values of the reflection coefficient of the output mirror<sup>[23]</sup>. The expression relating the threshold excitation energy, the reflection coefficient of the output mirror  $R_2$  at  $R_1 = 1$ , and the loss in the active medium is

$$W_{\text{thr}} = \frac{\alpha l - \ln R_2/2}{\tau_r [(\sigma N_0 l - \alpha) + \ln R_2/2]}, \quad (1)$$

where  $\alpha$  is the attenuation coefficient in  $\text{cm}^{-1}$ ,  $\tau_r$  the radiation lifetime of the working transition,  $R_2$  the reflection coefficient of the output mirror,  $l$  the length of the crystal,  $N_0$  the concentration of the active particles in  $1 \text{ cm}^3$ , and  $\sigma$  the cross section of the working transition.

If we assume that  $\alpha \ll \sigma N_0$ , which is usually always satisfied also for the case  $R_1 = R_2 = 1$ , then expression (1) is written in the form

$$W_{\text{thr}} = \alpha / \sigma N_0 \tau_r. \quad (2)$$

Denoting by  $\gamma'$  the ratio of the threshold excitation energy at a certain value  $R_2$  to its value at  $R_2 = 1$ , we get

$$\gamma' = \frac{\sigma N_0}{\alpha} \frac{2\alpha l - \ln R_2}{2\sigma N_0 l + \ln R_2},$$

then the expression for the damping coefficient will take the form

$$\alpha = \frac{1}{2l} \ln \frac{1}{R_2} \left[ \gamma' \left( 1 + \frac{\ln R_2}{2\sigma N_0 l} \right) - 1 \right]^{-1}. \quad (3)$$

If we choose the length of the investigated crystals such as to satisfy the inequality  $2\sigma N_0 l \gg \ln R_2^{-1}$ , then formula (3) is transformed to the simple form

$$\alpha = \frac{\ln R_2^{-1}}{2l(\gamma' - 1)}. \quad (4)$$

This expression was subsequently used by us to determine the loss produced upon formation of  $\text{Nd}^{2+}$  ions in our crystals.

## EXPERIMENTAL RESULTS

**CaF<sub>2</sub>:Nd<sup>3+</sup>.** To investigate the effect of photoreduction, we chose crystals with optimal activator content for stimulated emission,  $\sim 0.5$  wt.%<sup>[2]</sup>. The absorption crystals of the CaF<sub>2</sub>:Nd<sup>3+</sup> crystals are shown in Fig. 1. They were obtained with the SP-700 instrument at 300°K. Spectrum a corresponds to a sample having a small content of oxygen and cerium. These, as is well known, are characterized by broad absorption bands, lying in the region from 35,000 to 50,000  $\text{cm}^{-1}$ .

Since thermal oxidation  $\text{Nd}^{2+} \rightarrow \text{Nd}^{3+}$  is possible in our crystals already at temperature 50–70°C, the irradiation process used in the investigation of the photoreduction effect  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  consisted of alternating series of ten flashes. Absorption of this excitation light heated the crystals to 10–20°C. The experimentally obtained results are shown in Fig. 2a. The ‘aging’ curve 1 belongs to the crystal CaF<sub>2</sub>:Nd<sup>3+</sup> with small content of Ce<sup>3+</sup> and O<sup>2-</sup> ions. It was plotted on the basis of data obtained by studying two identical samples and, as can be seen, demonstrates quite well the reproducibility of the process  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  under the same conditions. In con-

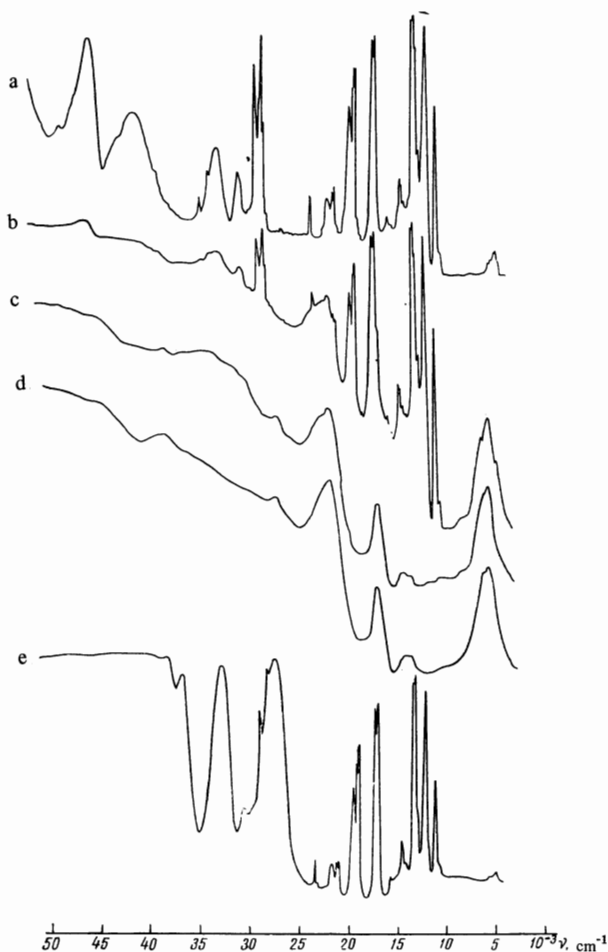


FIG. 1. Absorption spectrum: a – of  $\text{CaF}_2:\text{Nd}^{3+}$  ( $\text{Ce}^{3+}$ ,  $\text{O}^{2-}$ ) crystal prior to irradiation, b – of the same crystal after irradiation, c – difference spectrum, d – of  $\gamma$  irradiated  $\text{CaF}_2:\text{Nd}^{3+}$  crystal, e – of  $\text{CaF}_2:\text{Nd}^{3+}$  crystal with large content of  $\text{Ce}^{3+}$  ions.

nection with the fact that the photoreduction effect is connected with the intensity of the exciting radiation, we investigated one of these crystals under similar conditions, but now we fed to the IFP-800 lamp not 500 but 800 J. In Fig. 2a this “aging” curve is numbered 2. We see that the behavior of the “aging” curves depends strongly both on the additional impurities and on the intensity of the exciting light.

After the crystals were subjected to 1000 flashes of light, their color changed from light lilac, which is characteristic of media activated with  $\text{Nd}^{3+}$  ions, to light brown. The absorption spectrum of the irradiated crystal  $\text{CaF}_2:\text{Nd}^{3+}$  ( $\text{Ce}^{3+}$  and  $\text{O}^{2-}$ ) is shown in Fig. 1b. We see that besides the bands due to the  $\text{Nd}^{3+}$  ions there appeared absorption in the ultraviolet region and several broad bands in the visible and in the near infrared. To be able to separate the spectrum belonging to the  $\text{Nd}^{3+}$  ions, we obtained the difference spectrum (Fig. 1c), by placing the non-irradiated crystal in one channel of the SP-700 and the irradiated one in the other. We see that the differential spectrum is the absorption spectrum of the divalent neodymium ion<sup>[24]</sup>. Figure 1d shows for comparison the absorption spectrum of a  $\text{CaF}_2$  crystal in which the  $\text{Nd}^{3+}$  was reduced by  $\gamma$  radiation from a cobalt source ( $\text{Co}^{60}$ ).

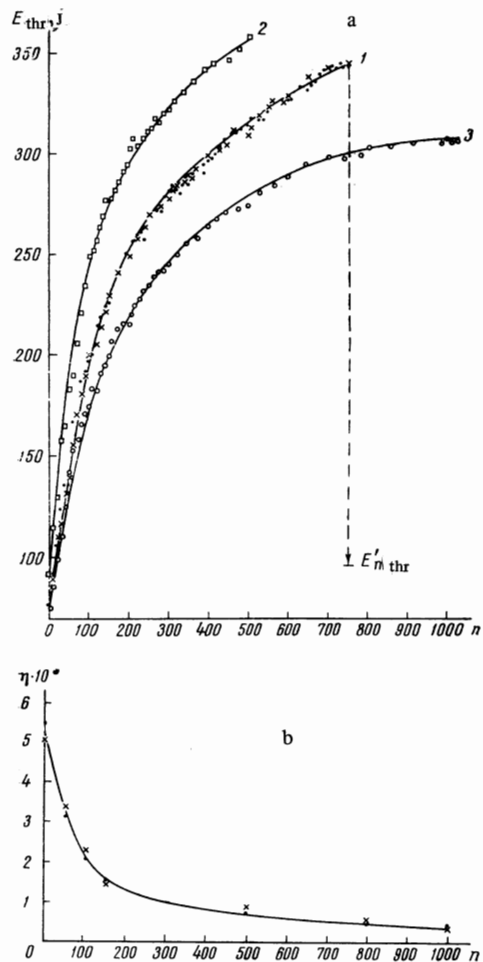


FIG. 2. Fluorite “aging” curves. a – Plots of  $E_{\text{thr}}(n)$ : 1 – for two identical samples of  $\text{CaF}_2:\text{Nd}^{3+}$  ( $\text{Ce}^{3+}$ ,  $\text{O}^{2-}$ ), energy 500 J; 2 – for the same crystal, energy 800 J; 3 – for crystal  $\text{CaF}_2:\text{Nd}^{3+}$  with large cerium content, energy 500 J. b – Plots of  $\eta(n)$  for two identical samples of  $\text{CaF}_2:\text{Nd}^{3+}$  ( $\text{Ce}^{3+}$ ,  $\text{O}^{2-}$ ),  $n$  – number of flashes.

Since the “aging” connected with the photoreduction  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  influences not only the excitation threshold but also the efficiency ( $\eta$ ), we measured simultaneously the output generation energy. For the  $\text{CaF}_2:\text{Nd}^{3+}$  ( $\text{Ce}^{3+}$  and  $\text{O}^{2-}$ ) crystals, the dependence of  $\eta$  on the number of flashes is shown in Fig. 2b. These curves were obtained at an output-mirror transmission  $\sim 0.5\%$  and at an electric energy 800 J fed to the lamp.

Using the procedure described above, we estimated the losses in both non-irradiated and in the “aged” crystals. The attenuation coefficient  $\alpha$  in the samples not subjected to light radiation was found to be  $\sim 2 \times 10^{-3} \text{ cm}^{-1}$ . It increased after 1000 flashes to  $\sim 10^{-2} \text{ cm}^{-1}$  in the case of the crystals with  $\text{Ce}^{3+}$  and  $\text{O}^{2-}$  ions added.

Figure 3a shows the spectrum of the thermoluminescence of the  $\text{CaF}_2:\text{Nd}^{3+}$  (2%) crystal exposed to  $\gamma$  radiation at a dose  $\sim 4 \times 10^7$  rad. We see that the main peak lies in the temperature region  $\sim 420\text{K}$ .

$\text{CaF}_2:\text{YF}_3:\text{Nd}^{3+}$ . The optical spectra of the yttrio-fluorite crystals were investigated in sufficient detail in<sup>[9,10,15]</sup>, and will not be discussed here. We note only that they differ significantly from the spectra of fluorite crystals. As shown in<sup>[6,25]</sup>, the  $\text{CaF}_2:\text{Nd}^{3+}$  crystals have

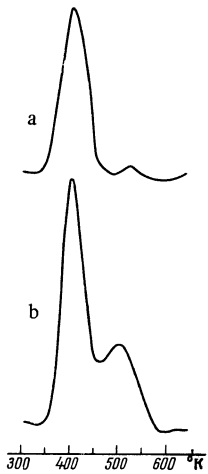


FIG. 3. Thermoluminescence spectra of the crystals CaF<sub>2</sub>:Nd<sup>3+</sup> (a) and CaF<sub>2</sub>:YF<sub>3</sub>:Nd<sup>3+</sup> (b).

Since we are interested now only in the qualitative effect, we shall simplify the problem and assume that to a clear cut Stark structure of the optical spectra up to “laser” activator concentrations, whereas CaF<sub>2</sub>:YF<sub>3</sub>:Nd<sup>3+</sup> crystals are characterized by broad absorption and emission bands, which cannot be resolved into individual components even at helium temperatures. It is shown in [9,15] that this is connected with the existence in these crystals of a large amount of optical centers of different structures. In this connection, it is difficult in principle to analyze the centers of the yttrifluorite crystals on the basis of the change in the optical spectra during the light-irradiation process, as was done for CaF<sub>2</sub>:Nd<sup>3+</sup> crystals [20]. The absorption spectra of non-irradiated and irradiated CaF<sub>2</sub>:YF<sub>3</sub>:Nd<sup>3+</sup> crystals are given in [19]. The yttrifluorite crystals also acquire a light-brown coloring when exposed to powerful flashes of light.

Figure 4a shows the “aging” curves  $E_{thr}(n)$ , where  $n$  is the number of light flashes, of six CaF<sub>2</sub>:YF<sub>3</sub>:Nd<sup>3+</sup> crystals. We see that, unlike the CaF<sub>2</sub>:Nd<sup>3+</sup> crystals, in this case the “aging” process proceeds in a somewhat different fashion. First, even after 50–60 light flashes dynamic equilibrium is established between the Nd<sup>3+</sup> → Nd<sup>2+</sup> and Nd<sup>2+</sup> → Nd<sup>3+</sup> effects, and additional radiation does not change the generation threshold noticeably. The character of the experimental  $\eta(n)$  dependence for the investigated crystals (Fig. 4b) correlates very well with the  $E_{thr}(n)$  dependence. Figure 4a shows the difference  $\Delta E_n$  between the values of  $E_{thr}$  of the investigated samples before and after irradiation. This efficiency ratio is denoted by  $\beta_n$ .

All the “aged” CaF<sub>2</sub>:YF<sub>3</sub>:Nd<sup>3+</sup> crystals were subjected to heat treatment for one hour at 500°C. Subsequent spectroscopic and generation investigations have shown that they have recovered their initial characteristics almost completely. For some of these crystals we repeated the complete “aging”—thermal oxidation cycle, and again the parameters were close to the initial ones. In one of the crystals, CaF<sub>2</sub>:7%YF<sub>3</sub>:1%Nd<sup>3+</sup>, the “aging” cycle was performed a third time, but this time with an energy ~800 J fed to the lamp. As seen from Fig. 4 (dash-dot curves), the Nd<sup>2+</sup> ion content is larger than in the case when the energy was ~500 J. All

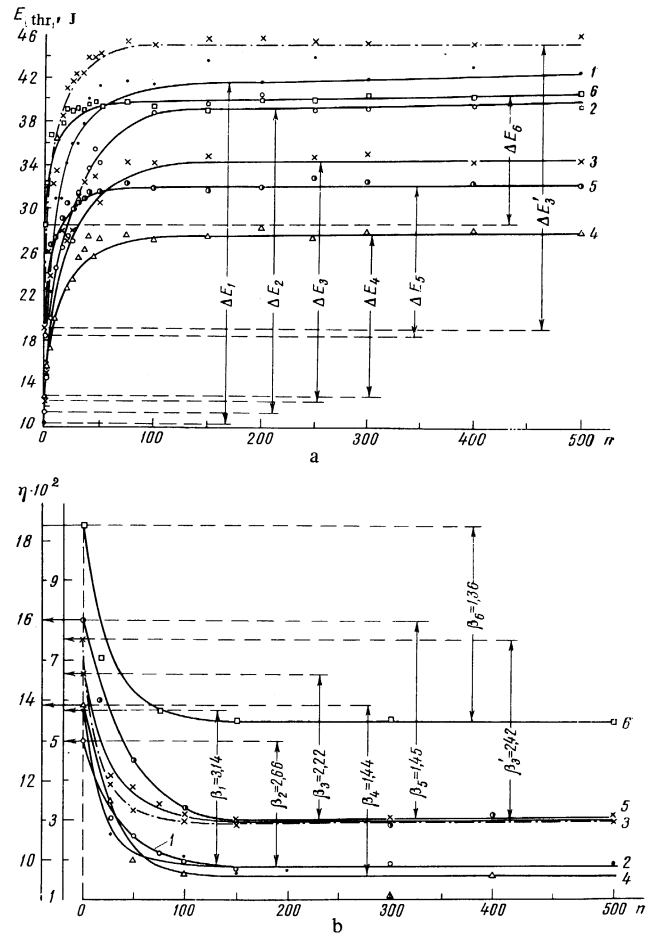


FIG. 4. Yttrifluorite “aging” curves: a —  $E_{thr}(n)$ , b —  $\eta(n)$ , 1 — CaF<sub>2</sub>:3%YF<sub>3</sub>:1%Nd<sup>3+</sup>, 2 — CaF<sub>2</sub>:5%YF<sub>3</sub>:1%Nd<sup>3+</sup>, 3 — CaF<sub>2</sub>:7%YF<sub>3</sub>:1%Nd<sup>3+</sup>; 4 — CaF<sub>2</sub>:5%YF<sub>3</sub>:3%Nd<sup>3+</sup>, 5 — CaF<sub>2</sub>:6%YF<sub>3</sub>:3%Nd<sup>3+</sup>, 6 — CaF<sub>2</sub>:7%YF<sub>3</sub>:4%Nd<sup>3+</sup>. Energy for all six cases — 500 J, the dash-dot curve corresponding to case 3 was obtained for 800 J.

the curves shown in Fig. 4 were obtained with the laser operating in such a regime, that the crystal temperature did not exceed 20–30°C. An analysis of  $E_{thr}(n)$  dependence at different temperatures of the active element was carried out with the CaF<sub>2</sub>:3%YF<sub>3</sub>:1%Nd<sup>3+</sup> crystal. These investigations were aimed at obtaining information concerning the most favorable lasing regime for a laser based on yttrifluorite with Nd<sup>3+</sup>. Figure 5 illustrates the results. We see that when the crystal temperature is low, the photoreduction Nd<sup>3+</sup> → Nd<sup>2+</sup> proceeds in the usual fashion (level B). But when the crystal is heated to ~100°C, a noticeable lowering of the excitation threshold (level C) is observed even during the generation processes. This circumstance indicates clearly that the two opposing processes Nd<sup>3+</sup> → Nd<sup>2+</sup> and Nd<sup>2+</sup> → Nd<sup>3+</sup> exist simultaneously. In the case of intermediate temperatures, the rate of formation of the Nd<sup>2+</sup> slows down somewhat.

It is also seen from this figure that a noticeable general increase of  $E_{thr}$  appears. This change is connected with the fact that, owing to the insufficiently good optical finish of the crystal, it is subject during the course of operation to slight mechanical damage. In this connection, the initial value of  $E_{thr}$  (level A) does not

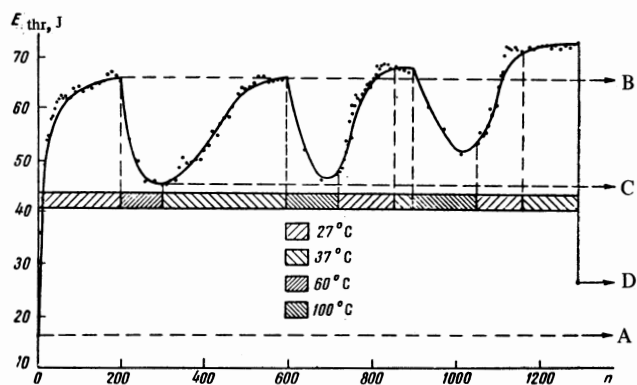


FIG. 5. "Aging" curve of  $\text{CaF}_2:\text{YF}_3:\text{Nd}^{3+}$  crystal as a function of the temperature.

correspond to the excitation threshold after the heat treatment (level D).

For the investigated six  $\text{CaF}_2:\text{YF}_3:\text{Nd}^{3+}$  crystals, we determined the losses at the generation frequency, for both the non-irradiated and irradiated samples. Figure 6 shows the dependence of  $E_{\text{thr}}$  of the irradiated (dashed lines) and non-irradiated samples at three values of  $\tau$  of the output mirror. We see that this dependence has the characteristic appearance possessed by active laser materials operating on the four-level scheme.

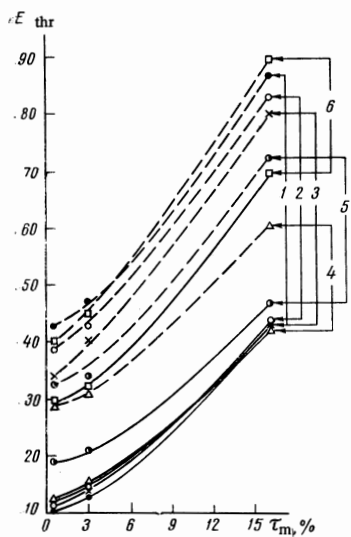


FIG. 6. Plot of  $E_{\text{thr}}(\tau)$  of yttrifluorite crystals against the transmission of the output mirror.

On the basis of these experimental data we determined with the aid of (4) the attenuation coefficients  $\alpha$ . The results of the calculations are shown in Fig. 7, where the abscissas represent the combined  $\text{Nd}^{3+}$  and  $\text{Y}^{3+}$  ion concentration. We see that the loss in yttrifluorite crystals increases somewhat with increasing neodymium content. This is due to the deterioration of the quality of the crystal; this deterioration is associated with the technology. This also shows that  $\text{CaF}_2:\text{YF}_3:\text{Nd}^{3+}$  crystals exposed to light radiation are subject to losses that decrease with increasing total  $\text{Nd}^{3+}$  and  $\text{Y}^{3+}$  concentration (dashed line). This is evidence that, other conditions being equal, fewer  $\text{Nd}^{2+}$  ions

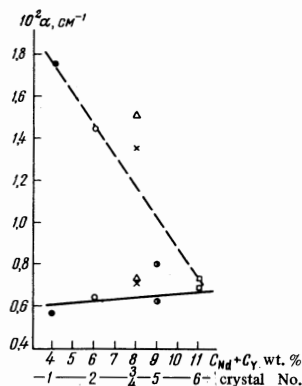


FIG. 7. Attenuation coefficients of irradiated and non-irradiated yttrifluorite crystals.

are produced in samples with large activator and yttrium contents.

## DISCUSSION OF RESULTS

Thus, which optical centers with  $\text{Nd}^{3+}$  in the investigated crystals are subject to damage with formation of centers with  $\text{Nd}^{2+}$ ? It is proposed in [8] that the  $\text{TR}^{3+}$  ions that go over into the divalent state are those contained in the so called "cubic" centers. These associates are  $\text{TR}^{3+}$  ions that replace the calcium ions in the fluorite lattice and have no local compensation of the excess charge. The appearance of a free electron near the "cubic" center can cause the electron to be captured and this leads to the formation of the  $\text{TR}^{2+}$  ions. We shall now attempt to analyze the nature of the occurrence of free electrons. Usually in the case of the photo-reduction effect  $\text{TR}^{3+} \rightarrow \text{TR}^{2+}$  under the influence of radiation, the quantum energy is much larger than the forbidden band, and the formation of the electrons during ionization occurs in accordance with the band-band scheme. In our case, the maximum quantum energy, which is determined by the transmission of the quartz tube of the IFP-800 lamp is  $\sim 6.2$  eV ( $\sim 2,000$  Å), whereas the width of the forbidden band of  $\text{CaF}_2$  is  $\sim 10.6$  eV [26]. In analyzing this situation, whereby on the one hand we have the presence of the  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  process and on the other hand the causes considered above, we have proposed in [20] the existence of two possibilities for the formation of free electrons. These are either a multistage ionization mechanism, or the production of electrons with participation of impurity levels with energy  $\sim 6.2$  eV. The latter mechanism is more probable, since our crystals contain of necessity, besides neodymium, also the impurity ions  $\text{Ce}^{3+}$ ,  $\text{Y}^{3+}$ , etc., which produce additional levels in the forbidden band.

As shown earlier [20], in  $\text{CaF}_2:\text{Nd}^{3+}$  crystals which have no noticeable amounts of harmful impurities, the process  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  does not lead to a noticeable increase of  $E_{\text{thr}}$ . On the other hand, if the crystals contain  $\text{Ce}^{3+}$  and  $\text{O}^{2-}$  ions, the "aging" curve (Fig. 2a, curve 1) offers evidence of a gradual decrease of the  $\text{Nd}^{2+}$  ion content. Contributing to this process may be the deeper levels of the hole localization of the impurities near the valence band, in analogy with the  $\text{Dy}^{3+}:\text{Ce}^{3+}$  system in  $\text{CaF}_2$  [27]. Account must also be taken of the possible existence of a tunnel mechanism for the transfer of the electron from the reducing ion to the "cubic"

$\text{Nd}^{3+}$  centers.

The ‘aging’ curves of the  $\text{CaF}_2:\text{YF}_3:\text{Nd}^{3+}$  crystals exhibit a faster variation and tend to saturate rapidly. A noticeable concentration of  $\text{Nd}^{2+}$  ions is produced even after the first few light flashes. This circumstance favors the second mechanism of free-electron formation, with participation of the impurity levels. It is seen from Fig. 4 that  $\Delta E_n$  and  $\beta_n$  decrease rapidly with increasing total concentration of the  $\text{Nd}^{3+}$  and  $\text{Y}^{3+}$  ions. Such a behavior of the  $E_{\text{thr}}(n)$  and  $\eta(n)$  curves confirms once more the correctness of the earlier conclusions<sup>[9]</sup>, namely that the concentration of the ‘cubic’ centers responsible for the formation of the  $\text{Nd}^{2+}$  ions should decrease with increasing content of the trivalent ions.

Starting from the foregoing, we can explain the nature of the ‘aging’ of the  $\text{CaF}_2$  and  $\text{CaF}_2:\text{YF}_3$  crystals in the stimulated-emission mode as follows: The appearance of  $\text{Nd}^{2+}$  ions (Fig. 1b) leads to the formation of parasitic absorption at the frequency of the  $\text{Nd}^{3+}$  ion generation. In addition, a noticeable absorption sets in at the frequencies at which the excitation bands are located. If the chemical composition of the crystals contributes to the formation of  $\text{Nd}^{2+}$  ions, then the generation may be completely stopped after prolonged irradiation.

We now consider several ways of eliminating this harmful effect, as suggested by our experimental data.

1. As shown in<sup>[2]</sup>, the use of filters which cut off the ultraviolet radiation of the excitation lamps prevent formation of the  $\text{Nd}^{2+}$ . This is the most accessible and simplest way, but the use of filters in lasers complicates the construction of the illuminator and decreases its optical efficiency.

2. A second method may be additional doping of the crystals with optically inactive impurities, which have a larger cross section for the capture of the free electrons than the  $\text{Nd}^{3+}$  ions.<sup>[20]</sup>

3. For  $\text{CaF}_2:\text{YF}_3:\text{Nd}^{3+}$  crystals, a third way is to choose the temperature regime. Let us consider this possibility in somewhat greater detail. Heating the crystals to 420°K leads to a large increase of the rate of the  $\text{Nd}^{2+} \rightarrow \text{Nd}^{3+}$  reaction, as is evidenced by the thermoluminescence curve shown in Fig. 3b. A direct experiment, designed to investigate ‘aging’ in the generation mode as a function of the crystal temperature, has shown that under stimulated emission conditions one can indeed attain with such a regime, that the equilibrium of the reversible process  $\text{Nd}^{3+} \rightleftharpoons \text{Nd}^{2+}$  shifts towards  $\text{Nd}^{3+}$ . Our results show that, from the point of view under consideration, the most convenient temperature is  $\sim 120^\circ\text{C}$ .

As regards  $\text{CaF}_2:\text{Nd}^{3+}$  crystals, although their thermoluminescence curve has also a peak at  $\sim 120^\circ\text{C}$ , heating will affect adversely the generation characteristics, for reasons connected with the increased luminescence line width of the stimulated transmission and the shortening of  $\tau_r$ .

4. To eliminate the harmful of ‘aging’ in yttrifluorite crystals, there is still one more way—regulation of the concentration of the ‘cubic’ centers with the  $\text{Nd}^{3+}$  ions, since they are the only ones that become divalent. An increase in the content of the trivalent ions leads to a relative decrease of the content of the ‘cubic’ cen-

ters, and if the concentrations of the trivalent are high enough, it leads to an absolute decrease. This is well confirmed by the plot of the attenuation coefficient  $\alpha$ , shown in Fig. 7 (dashed line). If we go over to the ‘aging’ curves we see that in yttrifluorite crystals with total trivalent-ion impurity concentration 11 wt.%, the value of  $\eta$  has decreased to 1.36, as compared with sample no. 1, where this ratio amounted to 3.14 (Fig. 4).

5. In  $\text{CaF}_2:\text{Nd}^{3+}$  crystals, the small concentration of the  $\text{Ce}^{3+}$  ion impurity contributes to the  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  transition as a result of formation of deep levels of hole localization, and is a harmful factor. However, if the content of the  $\text{Ce}^{3+}$  ions is large a decrease is possible in the reduction of the  $\text{Nd}^{3+}$  ions, owing to the filtering action of the cerium absorption bands. Figure 1e shows the absorption spectrum of a  $\text{CaF}_2:\text{Nd}^{3+}$  crystal with large  $\text{Ce}^{3+}$  ion concentration, and Fig. 2a shows its ‘aging’ curve (Fig. 3).

## CONCLUSION

The investigations of the nature of ‘aging’ of  $\text{CaF}_2$  and  $\text{CaF}_2:\text{YF}_3$  crystals activated with  $\text{Nd}^{3+}$  ions in the stimulated emission mode have shown that this process is due to the effect of photoreduction of the ions,  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$ , which occurs when powerful light flashes from the excitation lamp act on the crystals.

The observed effect of photoreduction of the ions  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  is associated with the presence in the  $\text{CaF}_2:\text{Nd}^{3+}$  and  $\text{CaF}_2:\text{YF}_3:\text{Nd}^{3+}$  of ‘cubic’ centers which have positive effective charges, that is, centers capable of capturing electrons. The concentration of the ‘cubic’ centers determines the maximum possible content of the  $\text{Nd}^{2+}$  ions; on the other hand, under concrete experimental conditions their number depends on the intensity of the exciting light, on the impurities, and on many other factors. We have analyzed the possible ways of formation of free electrons when the investigated crystals are exposed to pumping light flashes. The experimental results favor the mechanism connected with ionization of impurity levels with energy  $< 6.2$  eV.

We have shown that the effect of the photoreduction  $\text{Nd}^{3+} \rightarrow \text{Nd}^{2+}$  in fluorite is influenced by certain extraneous impurities. Thus, for example, small additions of  $\text{Ce}^{3+}$  and  $\text{O}^{2-}$  ions contribute to the valence transition of neodymium. These produce, on the one hand, additional levels of hole localization, increasing the stability of the  $\text{Nd}^{2+}$  ions. On the other hand, the resultant additional levels in the forbidden band open up one more channel for the formation of free electrons.

The foregoing analysis of the experimental data on the investigation of the photoreduction of  $\text{Nd}^{3+}$  ions in  $\text{CaF}_2$  and  $\text{CaF}_2:\text{YF}_3$  has made it possible to propose several methods for eliminating the harmful effect of ‘aging’ in the generation mode. As shown above, some ways touch upon problems involving the technology of the crystals, while others consist in choosing the correct temperature regime of the laser operation and the use of additional filters.

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