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SPECTROSCOPIC INVESTIGATION OF STIMULATED EMISSION FROM LASERS BASED ON $CeF_3:Nd^{3+}$ *CRYSTALS*

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We investigate the absorption, luminescence, excitation, and generation spectra as well as the lifetimes of the $^4F_{3/2}$ metastable state of CeF_3 crystals activated with Nd^{3+} ions at 4.2, 77, and 300°K. Diagrams of crystalline splitting of the $^4F_{3/2}$ and $^4I_{11/2}$ terms directly involved in the stimulated transitions are presented.

INTRODUCTION

AMONG the large number of fluoride crystals[1] used as active media in lasers, the cerium fluoride crystals are known the least. We know only of one brief note by O'Connor and Hargreaves,[2] containing data on stimulated emission from a $CeF_3:Nd^{3+}$ laser at 90°K. The note also reports that energy transfer from the crystal (CeF_3) matrix to the activator ions (Nd^{3+}) was observed in the generation mode.

In contrast to the divalent-metal fluorides of the CaF_2 type, the optical spectra of CeF_3 crystals activated with ions of rare-earth elements (TR^{3+}), just as LaF_3, should be mainly determined by one type of optical center, owing to their crystallochemical properties manifested at sufficient impurity concentrations. This renders the above crystal an interesting object of various spectroscopic studies. The present paper contains the results of experimental studies of absorption, luminescence, excitation and stimulated emission spectra as well as the lifetimes of the excited state (τ) of CeF_3 crystals activated with Nd^{3+} ions at 4.2, 77, and 300°K.

CRYSTAL SPECIMENS

CeF_3 crystallizes into a hexagonal lattice with a space group D_{6h}^3–C6/mcm and has the structure of tysonite (LaF_3).[3] According to more recent data of Mansmann,[4] the group of LaF_3 type crystals is D_{3d}^4–p3ci.

The CeF_3 crystals used in the experiments were synthesized from melt by the dropping-crucible method (see [1] for example). The Nd was introduced into the initial material as NdF_3 and its concentration varied from 0.3 to 6% by weight. The specimens had the form of cylindrical rods with plane parallel end faces (10") and were ~25 mm long and ~5 mm in diameter. The orientation of their optical axis c varied; in some crystals it coincided with the direction of the geometric axis F and in others it lay in the plane normal to F.

EXPERIMENTAL APPARATUS AND METHOD OF INVESTIGATION

The absorption and luminescence spectra of $CeF_3:Nd^{3+}$ crystals were investigated at 4.2, 77, and 300°K, using the DFS-12, PGS-2, and SP-700 instruments according to the methods described in [5,6]. The excitation spectrum was studied with a SPM-2 quartz monochromator and a DRSh-1000 super-high pressure mercury lamp. The lifetimes of the $^4F_{3/2}$ metastable state of Nd^{3+} ions were determined from sequential oscilloscopic traces of luminescence quenching.[7]

The stimulated emission characteristics were studied with the aid of two laser flash pump reflectors. Generation at 300°K was studied with a flash reflector having a light efficiency of ~0.5 and described in detail in [8]. The low temperature experiments were performed with another system[9] having a lower light efficiency of 0.15. The energy transfer from the CeF_3 crystal matrix to the Nd^{3+} ions in the generation mode was investigated with tubular filters made of BS-10 and ZhS-17 glass and of quartz.

The spectral composition of the stimulated emission was studied photographically with a DFS-8 diffraction spectrograph having a dispersion of ~5.9 Å/mm (grating replica with 600 lines/mm) and the I-1070 infrared film. As reference we used the third-order emission spectrum of a lamp with a hollow iron cathode.

The threshold values E_t of the electrical energy. were determined by detecting generation with a FÉU-28 photomultiplier connected to an S1-16 oscilloscope. To record E_t of the individual emission lines, the photomultiplier was placed in the output focal plane of the DFS-8. Polarization studies were performed with a Nicol prism.

SPECTROSCOPIC AND GENERATION PROPERTIES OF THE CRYSTALS

Figure 1 shows the absorption spectrum of the $CeF_3:Nd^{3+}$ (4% by weight) crystal obtained at 300°K with a SP-700 spectrophotometer. We see that the most intense bands are situated between 14,000 and 22,000 cm^{-1}. The CeF_3 *crystal also appears to have* strong ultraviolet (uv) absorption with an edge at ~33,000 cm^{-1}. This is due to the broad intense absorption band of Ce^{3+} ions connected with the allowed transitions between the 4f and 5d configurations ($^2F_{5/2} \rightarrow {}^2D$).

A detailed investigation of the structure of $^4F_{3/2}$, $^4I_{11/2}$, and $^4I_{9/2}$ terms was performed with the DFS-12 spectrometer and the PGS-2 spectrograph. An analysis of the absorption spectra corresponding to the transi-

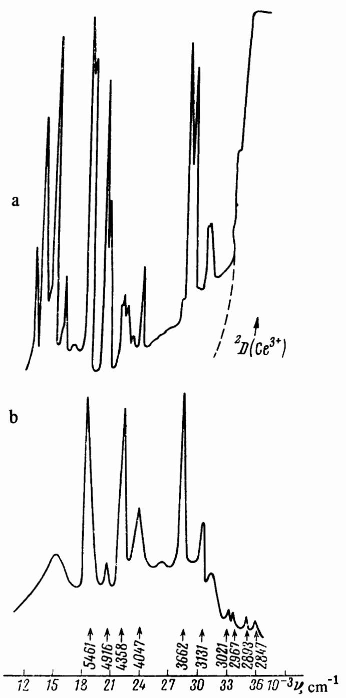


FIG. 1

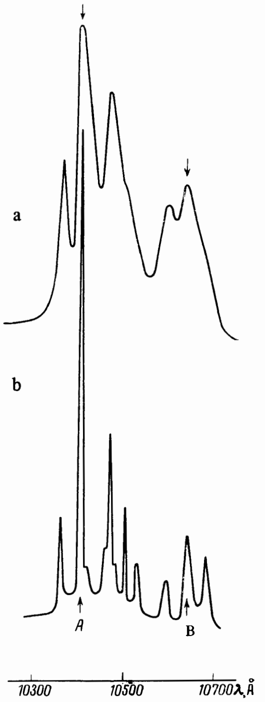


FIG. 2

FIG. 1. Spectra at 300°K: a—absorption of CeF_3 : Nd^{3+} (4% by weight); b—excitation (the arrows denote the position of mercury lines of the DRSh-1000 lamp).

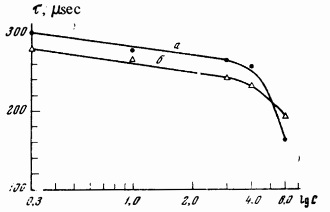
FIG. 2. Luminescence spectra of the CeF_3: Nd^{3+}(4% by weight) crystal; transition $^4F_{3/2} \to {}^4I_{11/2}$: a—at 300°K; b—at 77°K.

tion $^4I_{9/2} \to {}^2P_{1/2}$ allowed us to determine the position of the first excited levels of the ground-state term. According to our measurements, they are situated 45 and 144 cm^{-1} above the zero level, at 77°K. The luminescence spectra (transition $^4F_{3/2} \to {}^4I_{9/2}$, temperature 77°K) yielded the position of the remaining two levels of the $^4I_{9/2}$ term (303 and 510 cm^{-1}). The results of investigation of the absorption and luminescence transitions due to the $^4F_{3/2}$ term showed that its level splitting is 45 ± 1.5 cm^{-1} at 77°K and 44 ± 3 cm^{-1} at 300°K.

As we know, the most intense luminescence of Nd^{3+} ions in crystals couples the terms $^4F_{3/2}$ and $^4I_{11/2}$. Figure 2 shows the luminescence spectra of the CeF_3 : Nd^{3+} (4% by weight) crystal obtained at 77 and 300°K with the DFS-12 spectrometer. The width of the luminescence lines for which generation was recorded equals $\Delta\nu = 9 \pm 2$ cm^{-1} and $\Delta\nu(B) = 20 \pm 5$ cm^{-1} at 77°K, and $\Delta\nu(A) = 24 \pm 5$ cm^{-1} and $\Delta\nu(B) = 33 \pm 5$ cm^{-1} at 300°K in crystals with 4% by weight of Nd^{3+} ions. We note here that the luminescence spectra as shown are not corrected for the spectral sensitivity of the photomultipliers and the reflection coefficients of the DFS-12 gratings.

As indicated above, O'Connor and Hargreaves[2] detected an interaction between the CeF_3 crystal lattice and the Nd^{3+} activator ions so that the energy stored in the Ce^{3+} ions belonging to the crystal matrix is transferred to the Nd^{3+} generating centers when excited by ultraviolet light. According to these authors the pumping of the CeF_3 : Nd^{3+} crystals with the full spectrum of the laser pump lamp of the 3EGG-FX-51 type reduced E_t by 7% in comparison to the case in which the ultraviolet radiation of the pump lamp was filtered out of the pump spectrum. Consequently we performed an experiment to study Nd^{3+} ion excitation spectrum in the CeF_3 crystal that was designed to verify the presence of such an energy transfer and its efficiency if it does take place. Figure 1b shows the results of this experiment. The emission from the excitation source (DRSh-1000) passed through the SPM-2 monochromator and illuminated the investigated specimen whose luminescence was detected by the FÉU-28 photomultiplier. The emission spectrum of the DRSh-1000 pump source has a constant continuum serving as a background for intense lines.[10] Consequently we obtained an excitation spectrum that was "modulated" by the emission spectrum of the DRSh-1000 lamp. In Fig. 1b the arrows indicate the position of the Hg lines. We see a weak luminescence of the Nd^{3+} ions excited by the ultraviolet emission of the mercury lamp (lines 2847, 2893, 2967, and 3021 Å) that falls on the short-wave absorption edge of the CeF_3 crystal. According to these results the CeF_3 : Nd^{3+} system appears to undergo an energy transfer from CeF_3 to the Nd^{3+} ions although such a transfer is very inefficient.1)

FIG. 3. Lifetimes of the excited state at $^4F_{3/2}$ of Nd^{3+} ions in CeF_3 crystals as functions of concentration: a—at 300°K; b—at 77°K.



The results of measuring the lifetimes τ of the $^4F_{3/2}$ metastable state at 77 and 300°K are shown in Fig. 3. We see that τ variation is insignificant below activator concentration of 4% by weight and that $\tau_{300} > \tau_{77}$. However with concentrations above 4% by weight the lifetime is sharply reduced both at 77 and 300°K. At the same time the concentration-dependent function of τ_{300} has a steeper slope.

The spectral composition of stimulated emission from CeF_3 : Nd^{3+} lasers and the values of E_t for the individual generation lines substantially depend on the mutual orientation of the optical (c) and geometric (F) axes of the crystal. A transition from room temperature to 77°K is accompanied by some changes in the generation spectra, in particular by a shift of the emission lines and redistribution of their intensities and E_t. The stimulated emission spectra at 77 and 300°K are given in Fig. 4 and the spectral position of these lines and their E_t are tabulated.

When E_t is exceeded five times the crystal whose c axis is parallel to F has generation line widths $\Delta\nu_g(A) \approx 2.5$ cm^{-1} and $\Delta\nu_g(B) \approx 9$ cm^{-1} at 300°K, and $\Delta\nu_g(A) = 0.8 \pm 0.2$ cm^{-1} and $\Delta\nu_g(B) = 1.5 \pm 0.2$ cm^{-1} at 77°K.

To verify the existence of energy transfer during stimulated emission the CeF_3 : Nd^{3+} crystals were inserted into tubular filters inside the pump system of

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1) The existence of a direct optical excitation of luminescence in very faint absorption bands of Nd^{3+} ions is hardly possible within a wavelength range where the CeF_3 is totally opaque (33,000 – 36,000 cm^{-1}).

Weight in % Nd^{3+}	Orientation	Spectral composition* Å (cm^{-1})	E_t^{**} . J	Polarization***
		300° K		
4	c ~ ⊥ F	A10410 (9606) Б10638 (9400)	25 8.5	E ~ ⊥ c E ~ ⊥ c
5	c ~ ∥ F	A10410 (9606) Б10638 (9400)	8.5 7.5	NP NP
		77° K		
4	c ~ ⊥ F	A10404 (9612) Б10639 (9399)	3.5 6.0	E ~ ⊥ c E ~ ∥ c
5	c ~ ∥ F	A10404 (9612) —	~2.5 —	NP NP

*The designations of the generation lines is the same as in the LaF_3: Nd^{3+} crystals [11].

**The E_t values are corrected for the efficiency of pump reflectors at 77 and 300°K.

***NP - laser beam is not polarized.

the laser. Several specimens with Nd^{3+} ion content ranging from 1 to 5% by weight were investigated. Comparative measurements of E_t with various filters failed to reveal a drop in the excitation threshold. The accuracy of our measurements was ~ 2%. $LaF_3:Nd^{3+}$ crystals were used as controls under the same conditions. We observed that the ratio E_t(ZhS-17)/E_t(quartz) for CeF_3 was equal to the corresponding ratio for LaF_3. This shows that the effect of energy transfer from the crystal (CeF_3) matrix to the Nd^{3+} ions is not observed in the generation mode.

All the above values of E_t correspond to the case of an optical resonator consisting of two external spherical mirrors with multilayer dielectric coatings having an ~ 2% transmission at ~ 1.06 μ.

CONCLUSION

The obtained experimental results of the study of absorption, luminescence, and stimulated emission spectra were used to draw a Stark level diagram for the $^4F_{3/2}$ and $^4I_{11/2}$ terms of Nd^{3+} ions in a CeF_3 crystal at 77 and 300°K shown in Fig. 5. We see that at 77 and 300°K stimulated transitions (bold arrows in the diagram) connect the lower level of the $^4F_{3/2}$ term with various components of the $^4I_{11/2}$ term.

The performed polarization study showed that the spectral composition of generation and the E_t values are closely related to the mutual orientation of the c and F axes. Unfortunately the optical axis of the crystals used was not clearly defined which hampered the performance of more elaborate experiments. Crystals of $CeF_3:Nd^{3+}$ with rigorously oriented axes c ∥ F and c ⊥ F will be synthesized for use in more detailed studies of the polarization relationships.

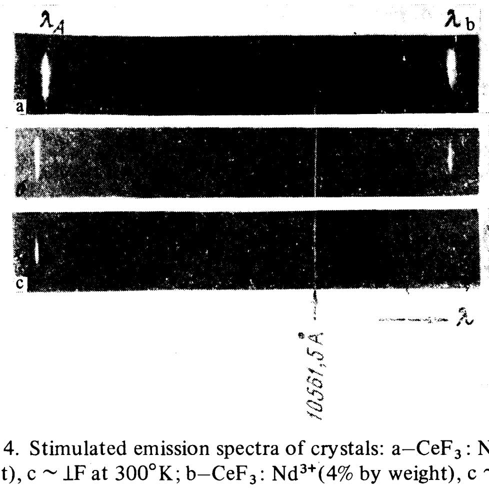

FIG. 4. Stimulated emission spectra of crystals: a–CeF_3 : Nd^{3+} (4% by weight), c ~ ⊥F at 300°K; b–CeF_3: Nd^{3+}(4% by weight), c ~ ⊥F at 77°K; c–CeF_3: Nd^{3+}(5% by weight), c ~ ∥F at 77°K.

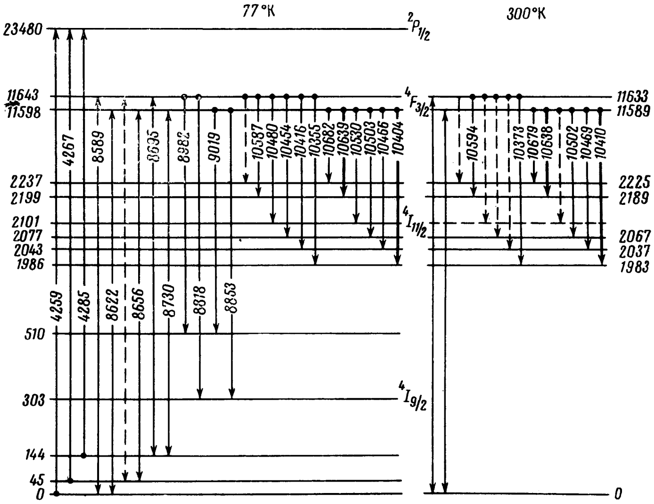

FIG. 5. Crystalline splitting diagrams of terms $^4F_{3/2}$, $^4I_{11/2}$, and partially $^2P_{1/2}$ and $^4I_{9/2}$ of Nd^{3+} ions in the CeF_3 crystal. Indicated level position is in cm^{-1} and level transitions in Å. Bold arrows denote stimulated transitions.

The study of the functions τ(C) and τ(T) revealed an anomalous temperature-dependent behavior of the lifetime of the $^4F_{3/2}$ term. As Fig. 3 shows, $\tau_{77} < \tau_{300}$. Considering the similarity of physical properties of the CeF_3 and LaF_3 crystals and the almost identical pattern of their crystalline splitting diagrams of the terms (see Fig. 6 of [8] and Fig. 5 of this paper) we can assume that energy loss channels occur in the $CeF_3:Nd^{3+}$ crystals at 300°K with activator concentrations of ~4% by weight due to cross-relaxation processes among the levels of the $^4I_{15/2}$ term just as in the case of the $LaF_3:Nd^{3+}$ crystal.[12]

The above series of investigations showed that the $CeF_3:Nd^{3+}$ crystals just as the $LaF_3:Nd^{3+}$ crystals[8] offer a very convenient matrix for activation with TR^{3+} ions. This is fully confirmed by the above generation parameters: the poor optical quality of the crystals permitted us nevertheless to reach fairly low excitation thresholds.

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[1] A. A. Kaminskiĭ and V. V. Osiko, Izv. AN SSSR, seriya Neorg. materialy (Inorganic Materials Series) **1**, 2049 (1965); **3**, 417 (1967).

[2] J. R. O'Connor and W. A. Hargreaves, Appl. Phys. Lett. **4**, 208 (1964).

[3] Structural Inorganic Chemistry, A. K. Wells, ed., Oxford, 1962.

[4] M. Mansmann, Z. anorg. allgem. Chemie **331**, 98 (1964).

[5] Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, Zh. Eksp. Teor. Fiz. **49**, 420 (1965) [Sov. Phys.-JETP **22**, 295 (1966)].

[6] Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, Zh. Eksp. Teor. Fiz. **49**, 724 (1965) [Sov. Phys.-JETP **22**, 501 (1966)].

[7] Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, Zh. Eksp. Teor. Fiz. **49**, 1022 (1965) [Sov. Phys.-JETP **22**, 710 (1966)].

[8] M. V. Dmitruk and A. A. Kaminskiĭ, Zh. Eksp. Teor. Fiz. **53**, 874 (1967) [Sov. Phys.-JETP **26**, 531 (1968)].

[9] A. A. Kaminskiĭ and N. I. Sukhov, PTÉ No. 4, 273 (1967).

[10] A. A. Shishlovskiĭ, Prikladnaya fizicheskaya optika (Applied Physical Optics), Fizmatgiz, 1961.

[11] A. A. Kaminskiĭ, ZhETF Pis. Red. **6**, 615 (1967) [JETP Lett. **6**, 115 (1967)].

[12] C. K. Asawa and M. Robinson, Phys. Rev. **141**, 251 (1966).

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