HIGH-TEMPERATURE EFFECTS OBSERVED IN STIMULATED EMISSION FROM CaF_2 and LaF_3 CRYSTALS ACTIVATED WITH Nd^{3+}

A. A. Kaminskii
Crystallography Institute, USSR Academy of Sciences
Submitted 15 May 1967, resubmitted 20 June 1967
ZhETF Pis'ma 6, No. 5, 615-619 (1 September 1967)

High-temperature spectroscopic investigations of stimulated emission of $CaF_3:Nd^{3+}$(type 1) and $LaF_3:Nd^{3+}$ lasers revealed several new effects, namely a resonant temperature sensitization effect and an associated rise in the generation line intensity, and the effect of temperature degeneracy of the induced transitions. The purpose of the experiments was to obtain information on the processes occurring in the excited state at high temperatures, and also to determine the high-temperature limit of laser operation.

The spectroscopic and lasing characteristics of $CaF_2:Nd^{3+}$ and $LaF_3:Nd^{3+}$ at low temperatures and at 300°K have been investigated in sufficient detail. The main results of these investigations are contained in [1 - 7].

Our experiments were performed with a laser incorporating a high-temperature illuminator of elliptic cross section with IFP-800 lamp and external spherical mirrors with multilayer dielectric coatings, having an approximate transmission of 0.7% at 1.06 μ. The stimulated-emission spectra were recorded on I-1070 photographic film with the aid of a diffraction spectrograph(DFS-8, ~ 5.9 Å/mm). The reference spectrum was radiation from a lamp with hollow iron cathode in third order. The generation thresholds were measured in the usual manner. In the investigation of $E_{thr}(T)$ for individual lines, the photomultiplier was placed in the exit focal plane of the DFS-8 instrument.

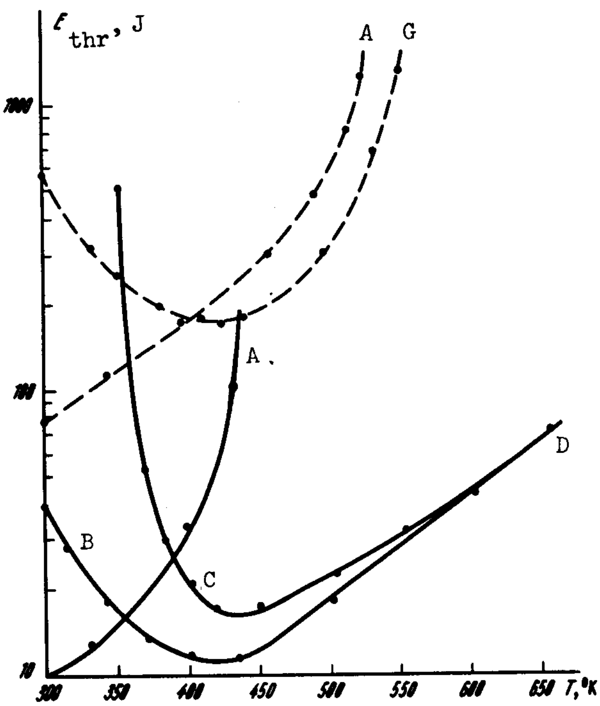

Fig. 1. Threshold vs. temperature for $CaF_2:Nd^{3+}$ and $LaF_3:Nd^{3+}$ crystals.

Figure 1 shows the obtained plots of $E_{thr}(T)$ for $CaF_2:Nd^{3+}$ and $LaF_3:Nd^{3+}$. The previously obtained spectrum [1] of a $CaF_2:Nd^{3+}$ laser at 300°K showed only one generation line (A) with wavelength 10461 Å (9559 cm^{-1}). As seen from the figure, its threshold increases monotonically with temperature, and the line cannot be excited in practice at ~550°K. At 300°K the generation spectrum has, besides line A, a simultaneous line G with λ = 10630 Å (9407 cm^{-1}), hitherto unobserved because of the high excitation threshold. Its

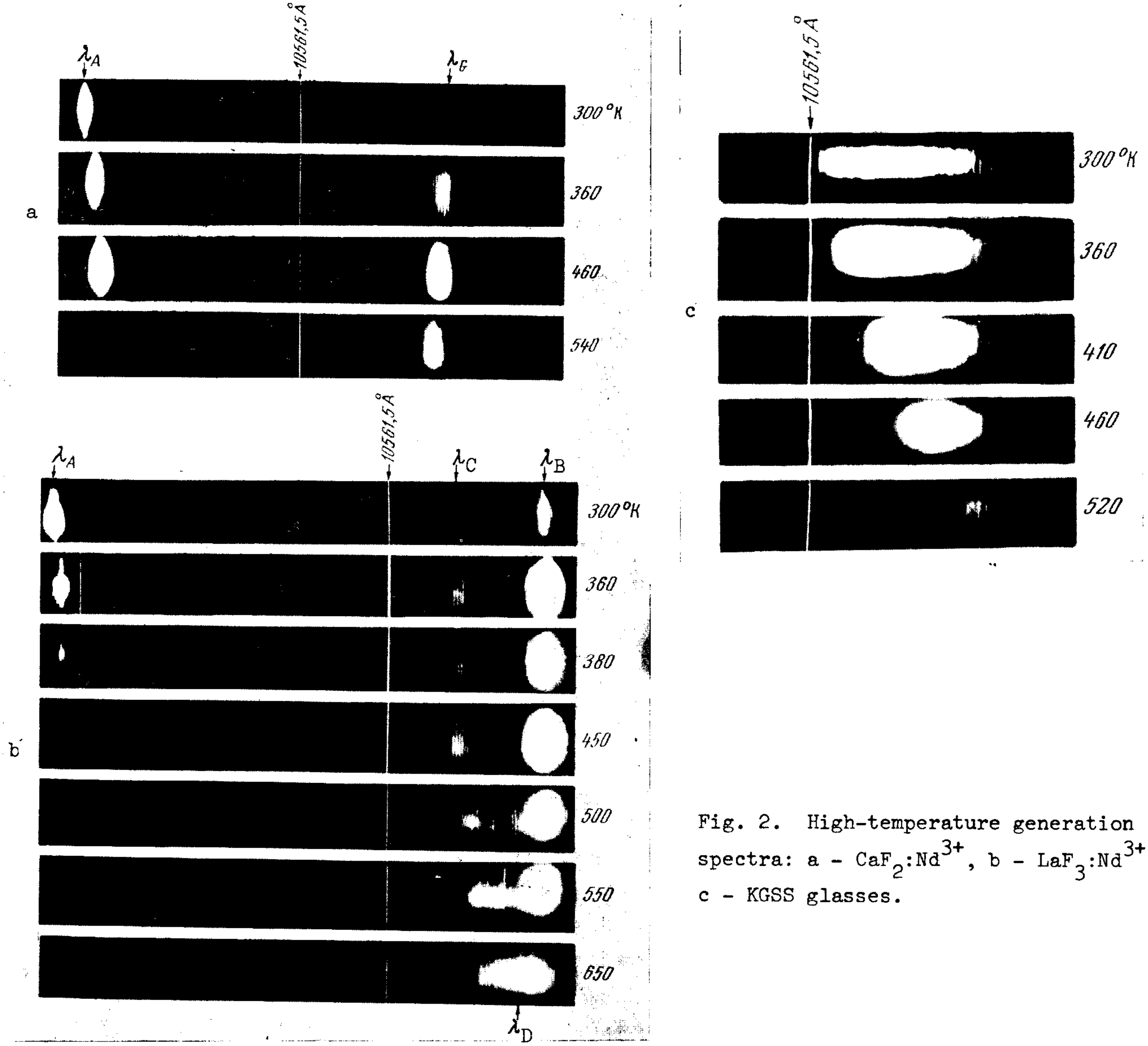

Fig. 2. High-temperature generation spectra: a – $CaF_2:Nd^{3+}$, b – $LaF_3:Nd^{3+}$, c – KGSS glasses.

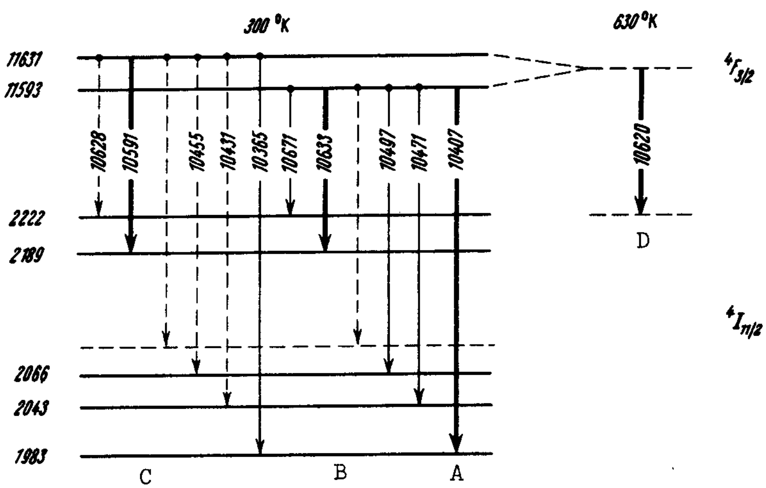

Fig. 3. Crystalline splitting of $^4F_{3/2}$ and $^4I_{11/2}$ terms of $LaF_3:Nd^{3+}$ crystal.

$E_{thr}(T)$ plot is characterized by an unusual behavior. At T ≈ 440°K it has a minimal excitation energy, less than one-third the threshold for 300°K. The high-temperature spectra of the stimulated emission of $CaF_2:Nd^{3+}$ crystals (0.5 wt.%) are shown in Fig. 2a.

An $LaF_3:Nd^{3+}$ laser also emits at 300°K on two wavelengths, line A with λ = 10407 Å (9609 cm^{-1}) and line B with λ = 10633 Å (9405 cm^{-1}) [7]. The $E_{thr}(T)$ plots for these lines are drawn solid in Fig. 1. We see that line A is present in the spectrum only up to T ≈ 440°K and generation above this temperature is impossible on this line. The behavior of $E_{thr}(T)$ of line B is very similar to that of the long-wave component of the $CaF_2:Nd^{3+}$ generation spectrum apart from the slight difference that the $LaF_3:Nd^{3+}$ laser continues to emit at higher temperatures. The second "unique" feature of this system is that at T ≈ 360°K a new generation line appears in the spectrum, with λ = 10594 Å (9439 cm^{-1}). This line cannot be excited at 300°K. The "uniqueness" of this situation lies in the fact that this is the first known case when lasing is possible only at high temperatures.

The spectral position of the generation line B and the $E_{thr}(T)$ dependence approach asymptotically the analogous parameters of line A. The high-temperature generation spectra of the $LaF_3:Nd^{3+}$ laser (1 wt.%) are shown in Fig. 2b. The processes described above can be understood by turning to the Stark scheme of the crystal splitting of the terms $^4F_{3/2}$ and $^4I_{11/2}$, which are directly connected with the induced transitions (Fig. 2). We see that lines B and C are due to transitions from the levels of the $^4F_{3/2}$ term (the splitting ΔE at 300°K is ∿ 38 cm^{-1}) to the same Stark component of the $^4I_{11/2}$ term, which is 2189 cm^{-1} away from the ground level at 300°K. At 300°K, the induced transition B begins at the lower level (11593 cm^{-1}). At higher temperatures the splitting of the metastable term $^4F_{3/2}$ becomes smaller, and the populations of its levels become equalized. It must be noted that ΔE of the $^4F_{3/2}$ term is equal to 43 cm^{-1} at 77°K and 44 cm^{-1} at 20°K [8]. Complete degeneracy of the levels of the $^4F_{3/2}$ term, as can be seen from the generation spectrum and from the behavior of $E_{thr}(T)$, sets in at T ≈ 630°K, and all that remains in the emission spectrum is obe broad line D with λ = 10620 Å. It is apparently legitimate to call this process temperature degeneracy of the induced transitions.

The final results of our investigations and a more detailed analysis of the nature of the observed effects will be published in a separate paper. Nonetheless, the experimental data presented above already lead to certain conclusions regarding the phenomena occurring at high temperatures.

The buildup of the line C (LaF_3)and the lowering of E_{thr} for lines G and B (CaF_2 and LaF_3) at T ≈ 450°K can be connected with the increase of the probabilities of nonradiative transitions from the Stark components at which the induced transitions terminate. Such a behavior of the systems investigated by us should be connected with the occurrence of thermal vibrations of the crystals. This should lead in final analysis to a sharp increase in the useful population difference of the working levels. This assumption is well confirmed by the experimental fact that for lines B and C (LaF_3), which are connected with the same final level 2189 cm^{-1} (Fig. 3), the $E_{thr}(T)$ curve has the same form. Favoring this circumstance is also the closeness of the Debye temperatures of our crystals and of the extrema of the observed $E_{thr}(T)$ plots. Mention should be make of the theoretical paper of Kiel [9], who showed that the transition probabilities in rare-earth ions should depend strongly on the thermal vibrations of the crystal, and particularly on ω_D.

In conclusion we must also note that the high-temperature spectroscopic investigation of the stimulated emission was carried out on more than 15 lasers using crystals and glasses ($Y_3Al_5O_{12}:Nd^{3+}$, $FaF_2:YF_3:Nd^{3+}$, $BaF_2:LaF_3:Nd^{3+}$, $CaWO_4:Nd^{3+}$, α-$NaCaYF_6:Nd^{3+}$, KGSS-7 and others). Besides the effects described above, the experiments confirmed the existence of autoresonant sensitization in mixed fluoride systems and glasses, and its connection with the thermal vibrations of the crystals. Figure 2c shows the high-temperature spectra of generation of KGSS-7 neodymium glass. The narrowing of the generation line at high temperatures shows that the probability of cross-relaxation of energy between different optical centers increases. Our investigations have also shown that the lasers operating at the highest temperatures are those based on fluoride crystals, and a laser based on α-gagarinite emits up to 1000°K. All this indicates that the method of high-temperature spectroscopy is very interesting and highly promising.

The author is grateful to Kh. S. Bagdasarov, M. V. Dmitruk, V. V. Osiko, and B. P. Sobolev for supplying the crystals for the experiments.

[1] A. A. Kaminskii, L. S. Kornienko, and A. M. Prokhorov, Zh. Eksp. Teor. Fiz. 48, 476 (1965) [Sov. Phys.-JETP 21, 318 (1965)].
[2] Yu. K. Voron'ko, A. A. Kaminskii, and V. V. Osiko, ibid. 49, 420 (1965) [22, 295 (1966)].
[3] H. H. Caspers, H. E. Rast, and R. A. Buchanan, J. Chem. Phys. 42, 3214 (1965).
[4] C. K. Asawa and M. Robinson, Phys. Rev. 141, 251 (1966).
[5] M. B. Schulz and C. D. Jeffries, Phys. Rev. 149, 270 (1966).
[6] E. Wong, O. Statsudd, and D. Johnston, Phys. Rev. 131, 990 (1963).
[7] M. V. Dmitruk and A. A. Kaminskii, Zh. Eksp. Teor. Fiz. 53, 874 (1967) [Sov. Phys.-JETP 26 (1968].
[8] L. F. Johnson, J. Appl. Phys. 34, 897 (1963).
[9] A. Kiel, Electron. Quant. 3 Conf. Internat. Paris, Paris-NY, 765 (1964).