DOUBLE FREQUENCY GENERATION IN NEODYMIUM-ACTIVATED LaF₃ CRYSTALS

A. M. PROKHOROV, V. A. SYCHUGOV, and G. P. SHIPOLO

P. N. Lebedev Physics Institute, USSR Academy of Sciences
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Theoretical analysis of double frequency generation in some Nd³⁺ doped crystals (LaF₃, mixed crystals, and CaWO₄) shows that, besides a definite ratio of laser transition probabilities, the principal condition of double frequency generation is a relatively low probability of the ⁴¹₁₁/₂ → ⁴¹₂₀(W₂₁) transition. The results of the analysis are confirmed by the study of the time characteristics of the output emission from a CaF₂ – YF₃ : Nd³⁺ laser at two frequencies. They are also confirmed by the study of thermal dependence of the generation threshold of the LaF₃ : Nd³⁺ laser and of the saturation effect used as a basis of computing the value of W₁₁ ≈ 10⁻⁵–10⁻⁶ sec⁻¹.

LaF₃ : Nd³⁺ crystals were first studied in¹⁻². It was established that it is possible to generate the lines λ₁ = 10,400 Å and λ₂ = 10,630 Å with different thresholds. These lines correspond to transitions from the lower level of the ⁴¹₂₃/₂ term to two different levels of the ⁴¹₁₁/₂ term (see diagram in Fig. 1 a). Line 1 has a lower threshold than line 2 in the temperature range near 77°K¹¹ or near 300°K¹³. An analogous phenomenon is observed in the case of mixed crystals (CaF₂ – YF₃ and a-NaCaYF₃) doped with Nd³⁺ (λ₁ ≈ 10,540 Å, λ₂ ≈ 10,630 Å, T ~ 300°K) and operating on the same principle (Fig. 1 a), and in the case of CaWO₄ : Nd³⁺ crystals that generate the lines λ₁ ≈ 10,580 Å and λ₂ ≈ 10,650 Å with different thresholds. The last two transitions correspond to transitions from both levels of the ⁴¹₂₃/₂ to the same level of term ⁴¹₁₁/₂ (Fig. 1 b). The generation threshold of line 1 here is lower than that of line 2 at T = 295°K¹⁴ and below down to ~ 203°K¹⁵.

The observed phenomenon can be attributed to the fact that in the course of generation of line 1 the population of term ⁴¹₂₃/₂ increases with rising pump energy in accordance with the rising population of term ⁴¹₁₁/₂ because of the relatively low decay rate. Since the lower level of transition 2 in scheme 1 a is higher (or the upper level in scheme 1 b is lower) than the corresponding level of transition 1 (Δν₂₁ = 206 cm⁻¹ for LaF₃, Δν₂₁ = 80 cm⁻¹ for mixed crystals, and Δν₂₁ = 63 cm⁻¹ for CaWO₄) line 2 is also generated at some value of the pump energy. This also means that we should expect a delay in the onset of generation of line 2 relative to that of line 1.

Consequently the generation of two frequencies in LaF₃, in mixed crystals, and in CaWO₄, doped with Nd³⁺, is completely explained by the low probability of the transition ⁴¹₁₁/₂ → ⁴¹₂₀ as compared to the probability of relaxation between the levels within the terms ⁴¹₁₁/₂ and ⁴¹₂₃/₂.

ANALYSIS OF DOUBLE FREQUENCY GENERATION SCHEMES IN THE STATIONARY CASE

The analysis of the above phenomenon can be based on kinetic equations derived for a five-level scheme (Fig. 1 a). These equations have the following form:

\[ \begin{align*}
\frac{dN_1}{dt} &= -N_1W_{21} - (N_1 - N_0)B_{43}, \\
\frac{dN_2}{dt} &= (N_2 - N_0)B_{42}a_{42} + N_1W_{21} - N_2W_{32} + N_4W_{34}, \\
\frac{dN_3}{dt} &= N_3W_{34} - (N_1 - N_0)B_{43}a_{43} - (N_1 - N_0)B_{42}a_{42}, \\
\frac{dN_4}{dt} &= -N_4W_{34} + (N_1 - N_0)B_{43}a_{43}, \\
N_0 &= N_1 + N_2 + N_3 + N_4 + N_5, \\
du_{42} &= -a_{42}u_{42} + B_{42}a_{42}hv_{42}(N_4 - N_3), \\
du_{43} &= -a_{43}u_{43} + B_{43}a_{43}hv_{43}(N_4 - N_3).
\end{align*} \]

Here Nᵢ are the energy level populations, Wᵢⱼ are probabilities of nonradiative transitions, Bᵢⱼ are Einstein coefficients for stimulated transitions, uᵢ and uᵢⱼ are radiation densities, and aᵢ and aᵢⱼ are total losses in the optical resonator at the transitions frequencies νᵢ and νᵢⱼ. Spontaneous emission and some nonradiative transitions were neglected in (1). In deriving these equations and in the subsequent analysis it is assumed that W₃₄ ≫ B₅₆, and W₃₄ ≫ W₂₃.

We first consider the case of generation at the frequency ν₄₂ (ν₄₂ > ν₄₃). Here the stationary value of emission energy density u₄₂ as a function of pumping is

\[ u_{42} = \frac{W_{34} + W_{32}}{B_{32}a_{42}} \left( \frac{B_{56}a_{43}}{B_{32}a_{42}} - 1 \right), \]

where the value

\[ u_{42} = \frac{W_{34}}{B_{32}} \left( \frac{B_{56}a_{43}}{a_{42}} - 1 \right) \]

is proportional to the limiting value of emission energy density in the resonator. Figure 2 shows a plot of u₄₂ as a function of B₅₆.

The possibility of generation at the frequency ν₄₃ is determined by the nature of the variation of population difference between levels 4 and 5 depending on pumping. This difference is determined by the following formula:

\[ \text{population difference} = \frac{B_{56}a_{43}}{a_{42}} - 1 \]
Analysis of (3) shows that $\Delta N_{43}$ increases with pumping (Fig. 2) so that under certain conditions the generation threshold can be reached at the frequency $\nu_43$. The corresponding value of $B_{43}\nu_{43}$ is

$$B_{43}\nu_{43} = \frac{(B_51 - B_{43})W_{43}}{(N_0\nu_3, a_3^{-1}B_32(2W_{43} - W_{23}) - (B_{43} - B_{41}) (2W_{23} + W_{32})}.$$  

(4)

Here $\xi = \alpha_{34}\nu_{43}/\alpha_{43}\nu_{43}$ (practically $\xi > 1$). If $\xi B_{42} - B_{43} > 0$, the quantity $B_{03}\nu_{43}$ is also larger than zero. This condition corresponds to our assumption that generation at the frequency $\nu_43$ occurs first. Consequently the above analysis shows that the decay rate of the lower laser level plays a significant role and can explain the experimentally observed phenomenon.

It is appropriate to investigate the case where generation at the frequency $\nu_43$ occurs first. The emission density function in the resonator then has a form similar to (2):

$$u_{21} = u_{21}' \left[ \frac{2W_{21} + 2W_{23} + W_{32}}{W_{23}} + \frac{W_{21}}{B_{43} a_{13}} \right],$$  

where

$$u_{21}' = \frac{W_{21}}{B_{43} (N_0\nu_3, a_3^{-1} - 1)},$$

and the population difference between levels 4 and 2 is determined by

$$\Delta N_{42} = N_0 B_{43}\nu_{43} [(2W_{21} + 2W_{23} + W_{32}) W_{21} - B_{43} a_{13}] + W_{21}^2 W_{23} - B_{43} a_{13}.$$

An analysis of this equation shows that $\Delta N_{42}$ decreases with pumping (Fig. 2). Thus if long-wave generation occurred first, no short-wave generation can take place in the stationary case.

We now consider the case when generation occurs simultaneously at two frequencies $\nu_{43}$ and $\nu_{42}$. A stationary solution of (1) leads to the relation

$$(W_{23} - W_{21}) a_{13} + \xi u_{43}(W_{21} - W_{23} - W_{31}) = W_{21}^2 W_{23} / [B_32 - B_{43} / B_32 a_{13}].$$  

(6)

The consequences of this relation are, first, that generation of two frequencies is possible in the stationary case if $\xi B_42 - B_{43} > 0$, i.e., generation at the frequency $\nu_{43}$ occurs first, and second, that an increase in emission density at one frequency causes a decrease of emission density at the other. The range of pump energies where double frequency generation is possible is determined by the expression

$$\Delta (B_{43}\nu_{43}) = \frac{u_{21}' W_{21}^2 W_{23} (B_{43} - B_{41})}{N_0 B_{43} a_{13} (W_{23} - W_{21})};$$  

(7)

the starting point of this range being determined by (4).

If all three above cases are summed up, the emission density in the resonator as a function of pumping $B_{43}\nu_{43}$ is schematically represented by the graph in Fig. 3.

Similar results can be obtained when a system of kinetic equations is solved for an energy level scheme in which the upper laser level has two components (Fig. 1 b)\(^1\). The solution is obtained under the same conditions as in the case of Fig. 1 a, except that $W_{43} < W_{43}$ instead of $W_{21} < W_{32}$. In this case the coupling between $u_{43}$ and $u_{42}$ has the form

$$u_{43}(W_{43} - W_{41}) + \xi u_{42}(W_{32} - W_{31} - W_{31}) = W_{43}^2 W_{41} / B_{43} B_{42}$$  

(8)

where $\xi = \alpha_{34}\nu_{43}/\alpha_{43}\nu_{43}$. The generation of two frequencies is possible here if $\xi B_{21} - B_{43} > 0$. The range of pump energies in which simultaneous generation of the frequencies $\nu_{43}$ and $\nu_{42}$ is possible is approximately equal to

$$\Delta (B_{43}\nu_{43}) = \frac{\xi a_{43} [B_{43} W_{43} - B_{41} W_{41}] W_{43}^2}{N_0 B_{43} a_{43} (W_{43} - W_{43})};$$  

(9)

The starting point of this range corresponds to the generation threshold at the frequency $\nu_{42}$

$$B_{43}\nu_{43} = \frac{W_{21} a_{13} [B_{43} W_{43} - B_{41} W_{41}] [W_{43} + 2W_{43}]}{(2W_{21} + 2W_{23} + W_{32}) W_{23} - B_{43} a_{13} W_{43} - 2W_{43}}$$  

(10)

In both energy level schemes the ratio of pumping range values allowing for the generation of both transitions to the pump energy corresponding to emission at the longer wavelength has the form

$$\Delta (B_{43}\nu_{43}) = \frac{W_{43}}{W_{21} [1 - \exp(-\Delta\nu_4/kT)]}$$  

(11a)

for the scheme in Fig. 1 a, and

$$\Delta (B_{43}\nu_{43}) = \frac{W_{43}}{W_{43} [1 - \exp(-\Delta\nu_4/kT)]}$$  

(11b)

for the scheme in Fig. 1 b.

If $W_{21} < W_{43}$ and $W_{23} < W_{43}$, then $\Delta (B_{43}\nu_{43}) / B_{43}\nu_{43} \sim 1$.

**EXPERIMENTAL RESULTS**

In our experiments we used LaF$_3$:Nd$^{3+}$ crystals grown by the Stockbarger method and having a neodymium concentration of 1–2% by weight. These crystals generated lines 1 ($\lambda_1 \approx 10,400$ Å) and 2 ($\lambda_2 \approx 10,633$ Å) only at $T = 77$°K and line 3 ($\lambda_3 \approx 10,633$ Å) only at $T = 300$°K. We studied the output energy as a function of temperature and generation threshold as a function of temperature in the pulse mode. In the first case a twin lamp elliptical reflector with separate power supply to the lamps was used to increase the pumping energy. To avoid saturation in the lamps, their load did not exceed 60% of the rated value. The measurements were performed at

\(^1\) The CaWO$_4$:Nd$^{3+}$ laser operating according to the scheme in Fig. 1 b generates two frequencies in the stationary case \(\nu_{43} \sim \nu_{43}\).
room temperature. In the second case we used a single-lamp elliptical reflector and the crystal was cooled with liquid nitrogen or its vapors. In both cases the short-wave portion of the spectrum of the IFP-800 lamps was absorbed by the ZbS-17 filter to avoid the "aging" effect in crystals.

According to Fig. 4, an increase in pumping energy is accompanied by the effect of saturation of the output energy for various values of

$$a = c \frac{\ln R_1}{2L}$$

where $R_1$ and $R_2$ are the mirror reflection coefficients. Using (5) and the measured relationships (Fig. 4) we can approximately evaluate the probability $W_{21}$ assuming that $W_{21} \ll W_{32}$. This gives a value of $W_{21} \sim 10^{-6} \text{sec}^{-1}$.

To make this probability more precise we attempted to achieve monochromatic excitation of LaF$_3$:Nd$^{3+}$ crystals with the ruby laser light. The laser emission was focused with a long-focus lens on the end face of the crystal (diameter 5 mm). The generation threshold of this material as well as of CaF$_2$:Dy$^{3+}$ and CaWO$_4$:Nd$^{3+}$ was due to the weak absorption at the wavelength $\lambda = 6943 \text{Å} (k = 0.124 \text{cm}^{-1})$. The low strength of the LaF$_3$:Nd$^{3+}$ crystals prohibits the use of high pumping energies (at 40–50 J of monochromatic pumping the crystals break down). Nevertheless the ruby laser can be used as a pump source for the LaF$_3$:Nd$^{3+}$ crystals to achieve monochromatic excitation of LaF$_3$:Nd$^{3+}$.

The temperature dependence of the generation threshold of lines 1 and 2 (Fig. 5) was investigated for three samples without seeds and therefore had an arbitrary orientation of the optical axis (C) with respect to the axis of the active element (F) (i.e., with respect to the direction of radiation). In Fig. 5 curves 1 and 1', 2 and 2', and 3 and 3' correspond to crystals with angles between C and F of 90°, 30°, and 5°.

The study of polarization of the generation lines showed that the short-wave line has a preponderant $\pi$-polarization (the electric vector $\vec{e}$ is parallel to the CF plane) and the long-wave line has a $\sigma$-polarization ($\vec{e}$ is perpendicular to the CF plane).

Time characteristics of generation pulses were studied on CaF$_2$:YF$_3$:Nd$^{3+}$ crystals (92% CaF$_2$, 6% YF$_3$, 2% NdF$_3$) that generated two frequencies at room temperature. The generation thresholds of lines 1 and 2 were 38 and 40 J respectively. The generation lines in the spectrum were picked up by two FEU-28 photomultipliers placed at the output of the DFS-8 using special prisms. The oscilloscopic traces of pulses taken at various pumping energies (some are given in Fig. 6) show a delay in the start of generation of line 2 with respect to line 1 (Fig. 6a). As pumping energy is increased the generation threshold is reached in the initial stage of the pumping pulse where the slope is steep and thus the delay almost vanishes there (Fig. 6b and 6c). When the excess over threshold is considerable generation of line 1 is observed only in the beginning and at the end of the pumping pulse (Fig. 6c).

DISCUSSION OF RESULTS

It follows from (6) that the energy density of the short-wave radiation in the resonator may not exceed a certain definite value:

$$u_{42} \leq (\frac{B_4 - B_3}{r_{42}}) W_{12} W_{12}/B_{12} B_{12}(W_{12} - W_{32}).$$

Setting $B_{42} \approx 2B_{43} = 2 \times 10^{-10} \text{cm}^3/\text{j} \cdot \text{sec} (\xi_{42} \approx 2 \times 10^{-10} \text{cm}^3)$, $W_{12} \approx 10^{-4} \times 10^{-6} \text{sec}^{-1}$, and the reflection coefficient of the output mirror to equal 90%, we find that the limiting power of output emission at the higher frequency is $\sim 10^{-6} \times 10^{-8} \text{W}$. In the pulse mode such powers can be reached at low pump energies (less than 100 J) as shown by the oscilloscopic traces in Fig. 6 for example.

The study of time characteristics of double frequency generation pulses confirms our assumptions stated at the beginning of this paper, and the results of analyzing the scheme of Fig. 1a presented in Fig. 3. In the first place, there is the delay of the start of long-wave generation relative to the short-wave generation that is most clearly observed at low pump excess over threshold (Fig. 6a), since the generation thresholds were similar for both frequencies. In the second place, as is apparent from comparing Fig. 6b and Fig. 6c, the energy of the short-wave component quickly reaches its limiting value with increasing pump energy, while the main portion of the total generation energy is emitted by the long-wave component, i.e., a "red shift" effect is observed.
The results of the study of the "red shift" performed by Kaminski\(^\text{11,12}\) also confirm our assumptions and conclusions. This is particularly evident in the case of yttrium-fluorite crystals (see Fig. 3 in\(^\text{13}\)) at first the entire generation energy falls on line B (\(\lambda_B \approx 10,540 \\text{Å}\)) and then, after the generation threshold of line C (\(\lambda_C \approx 10,632 \\text{Å}\)) is exceeded, energy is redistributed between lines B and C so that when \(E_{\text{pump}} > 10E_{\text{th(B)}}\) the main portion of the energy falls on the C component. It was also noted in\(^\text{13}\) that an analogous "red shift" effect is observed in KGSS and LGs glasses. It appears that the results of our analysis of double frequency generation schemes can be generalized to the case of continuous distribution of Stark components, as in glasses and liquids. This can provide the basis for a complete explanation of the shift towards the red of the intensity maximum in the generation spectrum. However even the above analysis provides a complete qualitative picture of this phenomenon.

LaF\(_3\) crystals have a Debye temperature (\(T_D\)) of \(\sim 400^\circ\text{K}\)\(^\text{14}\) and thus the nonradiative transition from the lower level of term \(^3_{11/2}\) to the upper level of term \(^3_{5/2}\) (\(\Delta \nu \approx 1700 \text{ cm}^{-1}\)) requires the participation of 6–7 phonons; this apparently is the reason for the relatively low value of \(W_{31} \approx 10^{-4} \times 10^5 \text{ sec}^{-1}\) and for the associated effect of emission energy saturation with increasing pump energy. This conclusion seems to be valid also for mixed crystals with \(T_D \approx 400^\circ\text{K}\), i.e., in their case we should also observe the saturation effect in plotting the output energy as a function of pumping energy as long as the "red shift" effect is present.

It was noted in\(^\text{11,12}\) that a minimum was observed in the curve of thermal dependence of the threshold in LaF\(_3\):Nd\(^{3+}\) and some other crystals. The same source attempted to relate the temperature of the minimum generation threshold \(T_m\) with \(T_D\). While in\(^\text{11}\) \(T_m\) was found to lie in the range 400–450\(^\circ\text{K}\) for LaF\(_3\):Nd\(^{3+}\), our measurements yield \(T_m\) values in the range 77–160\(^\circ\text{K}\) (Fig. 5). This difference in \(T_m\) we ascribe to the difference in the angles between C and F of the investigated crystals. It seems that in\(^\text{14}\) the crystal had \(< \text{CF} \approx 30^\circ\). Therefore the location of the threshold minimum has no direct relation to \(T_D\). This concerns not only the LaF\(_3\):Nd\(^{3+}\) crystals. We note that in the case of YAG:Nd\(^{3+}\) this minimum is observed at \(T_m \approx 230^\circ\text{K}\), while \(T_D \approx 700^\circ\text{K}\)\(^\text{18}\).

The analysis of data given in\(^\text{6,12}\) shows that the minimum in the thermal dependence of the threshold is observed whenever generation occurs at two or more frequencies and always for the long-wave component. In cases when there is only one line we observe a smooth rise of the threshold with the temperature. This permits us to use our results for a qualitative explanation of some features of the thermal dependence of the generation threshold. In the first place as noted earlier, if generation occurs first at the frequency \(\nu_a\), the generation threshold cannot be reached at \(\nu_a\) in the stationary case. Thus a rapid rise of this threshold with temperature in the pulse mode at \(T > T_0\) is to be expected (\(T_0\) is the temperature at which the generation thresholds at the frequencies \(\nu_a\) and \(\nu_a\) are equal).

The rise of the generation threshold at the frequency \(\nu_a\) for \(T < T_0\) can be understood with the aid of the formula determining the generation threshold at the frequency \(\nu_a\) as a function of emission density at the frequency \(\nu_a\):

\[
(B_{31a}W_{31a})_{\nu_a} = W_{31a}W_{31a}W_{31a}\left\{\frac{B_{31a}N_{\nu_a}}{O_{\nu_a}} - B_{31a}(W_{31} - W_{31a}) + W_{31a}W_{31a}\right\}.
\]

(12)

Insofar as the generation threshold at the frequency \(\nu_a\) decreases when \(T < T_0\), \(u_{\nu_a}\) increases faster with increasing pump energy and the generation threshold at the frequency \(\nu_{a1}\) increases according to (12). However the increase of \(u_{\nu_a}\) is limited by its nonlinear variation with increasing pump energy (see (2)). Therefore the generation threshold at the frequency \(\nu_{a1}\) can nevertheless be reached at a certain value of pump energy. Consequently the increase in generation threshold at the long-wave transition at \(T < T_0\) is bound with the decrease of the threshold at the short-wave transition. Obviously the minimum of generation threshold will be observed at some temperature \(T_m\) close to \(T_0\).

\(^2\)In the case of Pr\(^{3+}\) in LaCl\(_3\) theoretical computation yields the value of \(W(3P_1 \rightarrow 3P_0) \approx 3 \times 10^5 \text{ sec}^{-1} (\Delta \nu \approx 1200 \text{ cm}^{-1})\)\(^\text{15}\).
The analysis of double frequency generation schemes and of the results of experimental research leads to the following conclusions.

1. Double frequency generation according to schemes of Figs. 1 a and 1 b is possible under two main conditions:
   a. \( W_{21} \ll W_{22} \), \( \xi B_{42} > B_{41} \), scheme of Fig. 1a;
   b. \( W_{21} \ll W_{43} \), \( \xi B_{42} W_{44} > B_{33} W_{43} \), scheme of Fig. 1b.

2. The range of temperatures within which we can observe double frequency generation is determined first of all by the last inequalities above under conditions (a) and (b); therefore in the case of anisotropic crystals (LaF$_3$ : Nd$^{3+}$, CaWO$_4$ : Nd$^{3+}$) \( T_0 \) depends on the mutual orientation of C and F.

3. The minimum of the generation threshold in the temperature dependent function exists only in the region of double frequency generation.

4. In the case of LaF$_3$ : Nd$^{3+}$ we observe the effect of generation energy saturation with increasing pumping enabling us to evaluate the quantity \( W_{21} \sim 10^4 - 10^5 \) sec$^{-1}$. This value of \( W_{21} \) we ascribe to the low Debye temperature (~400°K).

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