Study on energy up-conversion in Yb, Ho:YAG crystal

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Optic parameters, such as the probabilities of radiative and non-radiative transition and the cross-relaxation probability between Yb^{3+} and Ho^{3+} ions in Yb,Ho:YAG crystal, are calculated on the basis of Judd-Ofelt and Dexter theories. The energy up-conversion process is analyzed by solving the transition rate-equations. The results show that (1) the intensity of the green fluorescence relates to the square of the concentration of the active ions; (2) the intensity increases with the concentration of sensitive ions as well, but the increasing rate goes rather too slow; (3) the efficiency of the energy up-conversion relates with the speed of the energy up-conversion and the quantum efficiency of the transiting from upper level to lower level.

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The visible laser is widely used in display, optic recording, medical diagnoses and underwater detection etc.[1]. Using the energy up-conversion of rare-earth ions is an effective approach to obtain visible laser. Analyses on the efficiency and the rule of energy up-conversion provide an important ground for choosing visible laser crystal.

The energy levels of Yb^{3+} and Ho^{3+} ions are shown in Fig. 1[2]. The energy difference ΔE_1(Ho) between the metastable states ($^5I_6$) and the ground state ($^5I_8$) is close to the energy difference ΔE_2(Yb) between the ground state ($^2F_{7/2}$) and the excited state ($^2F_{5/2}$) of Yb^{3+} ions. So Yb^{3+} ions accelerate the energy up-conversion of Ho^{3+} ions[3].

According to Fig. 1 the transition rate equations are written as follows

$$\frac{dN_7}{dt} = -Q_7N_7 + P_{c2}N_3,$$

$$\frac{dN_6}{dt} = Q_{76}N_7 - Q_6N_6,$$

$$\frac{dN_5}{dt} = Q_{75}N_7 + Q_{65}N_6 - Q_5N_5 + P_{c0}N_3,$$

$$\frac{dN_4}{dt} = Q_{74}N_7 + Q_{64}N_6 + +Q_{54}N_5 - Q_4N_4,$$

$$\frac{dN_3}{dt} = Q_{73}N_7 + Q_{63}N_6 + Q_{53}N_5 + Q_{43}N_4$$

$$-(Q_3 + P_{c2} + P_{c0})N_3 + (W + P_{c1})N_1,$$

$$\frac{dN_2}{dt} = Q_{72}N_7 + Q_{62}N_6 + Q_{52}N_5 + Q_{42}N_4$$

$$+Q_{32}N_3 - (Q_2 + P_{c0})N_2,$$

$$N = N_7 + N_6 + N_5 + N_4 + N_3 + N_2 + N_1, \quad (1)$$

where N_i is the population of the ith level of Ho^{3+} ion; $Q_{i,j}$ is the transition probabilities from level i to j, $Q_{i,j} = A_{i,j} + \omega_{i,i-1}$, where $A_{i,j}$ and $\omega_{i,i-1}$ are the radiant and non-radiant transition probabilities from level

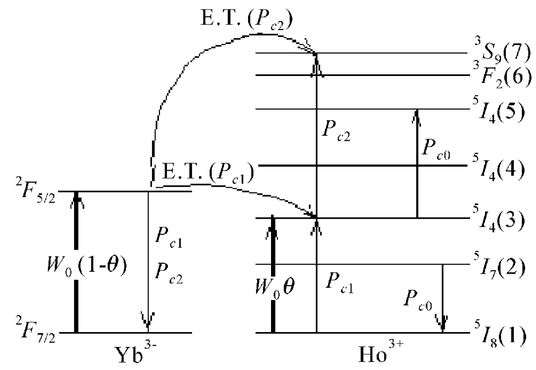

Fig. 1. Scheme of the level of Yb^{3+} and Ho^{3+} ions.

i to j respectively and $Q_i = \sum_j Q_{i,j}$. Above spectrum parameters have been calculated in Ref. [7]. θW_0 and $(1-\theta)W_0$ represent pump rates for Ho^{3+} and Yb^{3+}, respectively. $\theta = \frac{\alpha_H}{\alpha_H + \alpha_Y}$ is the relative absorption cross-section of Ho^{3+}, α_H and α_Y are the absorption cross-sections of Ho^{3+} and Yb^{3+} ions, respectively. P_{c0} represents the probability of the cross-relaxation between Ho^{3+} ions, P_{ci} is the ith cross-relaxation probability between Ho^{3+} and Yb^{3+} ions for $i = 1$ and 2. For YAG crystal P_{ci} can be calculated on the basis of the Dexter theory with

$$P_{ci} = 1.21 \times 10^{-17} \cdot f_A \cdot S/(R^6 \Delta E_D^4 \tau_D), \quad (2)$$

where $R^6 = R_0^6/(xy)$, x and y are atomic fractions of Ho^{3+} and Yb^{3+} replaced Y^{3+} respectively, $R_0 = 3.68 \times 10^{-8}$ cm is the smallest distance between Y^{3+} ions in YAG crystal. The τ_D, f_A and ΔE_D represent the fluorescence lifetime, the vibrator intensity of the acceptor and the energy difference of donor. If the probability of the cross-relaxation between Ho^{3+} self is considered, then $R^6 = R_0^6/x^2$, $S = \int_{-\infty}^{\infty} g_A(\tilde{\nu})h_s(\tilde{\nu})d\tilde{\nu}$ is the overlap integral between the normalized linear type functions $h_s(\tilde{\nu})$ of the emission band of the donor and $g_A(\tilde{\nu})$ of the absorption band of the acceptor. $\tilde{\nu}$ is the wavenumber. When both the emission and the absorption band are all the Gaussian distribution and superpose each other, the overlap integral can approximately be determined as $S \approx \frac{4}{\pi^2 \Delta\tilde{\nu}}$. When the energy exchange demands phonon to assist, Miyakawa theory[5] is required with $S = S_0 \exp(-\beta\delta E)$ for the modification, where δE is the energy difference between the two transition pair. ($\delta E = 0, 1.425, 0.3\times10^3\ \mathrm{cm}^{-1}$ for three cross-relaxations, respectively). $\beta = \alpha - \frac{\ln 2}{\hbar\omega'}$ if the multiplicity of the upper level of is equal to that of lower level. The cut-off energy of the phonon is $\hbar\omega' = 700\ \mathrm{cm}^{-1}$ in YAG crystal; as a token of the no-radiation transition the constant $\alpha = 3.2 \times 10^{-3}$ cm for YAG crystal which relates only to the host. From Refs. [2,6] and author's paper[7] the parameters are $\tau_D = 9.0, 1.1, 1.1$ ms, $f_A = 1.03, 1.42, 1.94 \times 10^{-6}$, $\Delta E_D = 0.5, 1.0, 1.0 \times 10^4\ \mathrm{cm}^{-1}$, $S_0 = 2, 5, 5 \times 10^{-4}$ cm, respectively. From Eq. (2) the three probabilities of the cross-relaxations are $P_{c0} = 2.2 \times 10^5 x^2$, $P_{c1} = 1.3 \times 10^4 xy$, $P_{c2} = 2.6 \times 10^5 xy$ (s^{-1}), respectively.

Inserting the parameters, such as Q_i, $Q_{i,j}$, P, P_{ci}, to the transition rate-equations (1), and solving rate equations in steady state, we can obtain the population N_i which versus the concentrations x and y of both active and sensitive ions and the pumping rate W. The intensity of visible fluorescence relates to the interval of the energy levels, the relative population ($N_{i1} = N_i - N_1$) and the transition probability Q_{i1}. Therefore, $(N_i - N_1)Q_{i1}/N_0$ can stand for the fluorescence intensity in discussion. The rule of the energy up-conversion is shown as Figs. 2

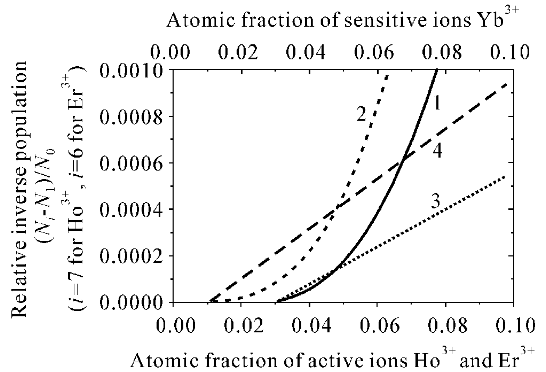

Fig. 2. The relative inverse population versus the concentration of the active and sensitive ions if pump-rate $W = 10^5$ s^{-1}. Curve 1: 5% Yb, Ho:YAG; 2: 5% Yb, Er:YAG; 3: Yb, 5% Ho:YAG and 4: Yb, 5% Er:YAG.

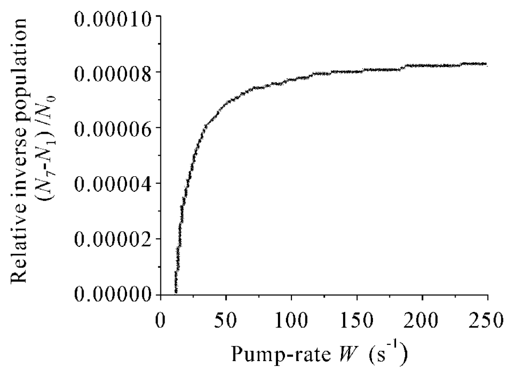

Fig. 3. The relative inverse population versus the pump-rate W for 3 at.-% Ho, 5 at.-% Yb:YAG.

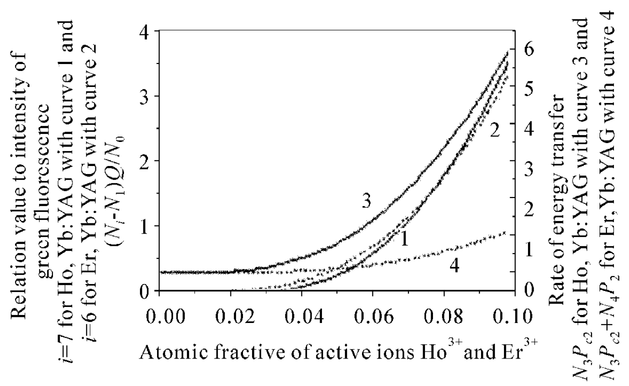

Fig. 4. The intensity of green fluorescence and the rate of energy transfer versus the atomic fraction of active ions for pump-rate $W = 10^5\ \mathrm{s}^{-1}$ in Ho, 5% Yb:YAG and Er, 5% Yb:YAG.

and 3. The intensity of best strong green fluorescence corresponding to the transition ${}^5S_2 \rightarrow {}^5I_8$, as a example, is proportional to the square of the Ho^{3+} concentration and increases with the Yb^{3+} concentration as well, but the rate of the increasing with the concentration rather too low. The fluorescence intensity strengthens with pumping rate W, but soon to be saturated. Above results are quite similar to the energy up-conversion in Yb, Er:YAG crystal[8] and other solid[9].

The energy up-conversion efficiency η is defined as the ratio of fluorescent energy E_s and excited energy E_{in}, namely $\eta \propto \frac{E_s}{E_{\mathrm{in}}}$, $E_s \propto (E_i - E_1)(N_i - N_1)Q_{i1}/N_0$, $E_{\mathrm{in}} \propto W$. It can be also got that the efficiency of energy up-conversion of $Yb^{3+} \rightarrow Ho^{3+}$ is similar to that of $Yb^{3+} \rightarrow Er^{3+}$ in YAG crystal. Because $(E_i - E_1)$ of the three crystals compared is close, $(N_i - N_1)Q_{i1}/N_0$ is used to stand for the fluorescence intensity to discuss the relation between the fluorescence intensity and x (or y) in Fig. 4.

The energy up-conversion rate, ξ, denotes the population $P_{c2}N_3$ of up-conversion in unit time. The rate of energy up-conversion of $Yb^{3+} \rightarrow Ho^{3+}$ is bigger than that of $Yb^{3+} \rightarrow Er^{3+}$ as Fig. 4 if the concentration of active ions Ho^{3+} is the same as that of Er^{3+}. It is noticed that most ions that up-converted to the high energy level will transit to metastable level via the radiation and non-radiation process, and only a small part will transit to the ground state and radiate green fluorescence. For this reason the fluorescence intensity of the up-conversion relates not only to energy up-conversion rate ξ, but also to the quantum efficiency of the radiate transition (namely ratio between the radiative and total transition probability). From the Q_j and Q_{ij} data of both Ho^{3+} and Er^{3+}, we can also estimate that the quantum efficiencies (Q_{i1}/Q_i) of the green fluorescence for Ho^{3+} and Er^{3+} are about 9.2% and 11.8%, respectively. Therefore, the intensity of the green fluorescence in Yb,Ho:YAG crystal is approximately the same as that in Yb,Er:YAG.

The efficiency η and rate ξ of the energy up-conversion of Ho^{3+} are obtained by calculating the optic parameters, such as the probabilities of radiative transition and the cross-relaxation, and by solving the transition rate-equations. These are important foundations for choosing visible laser crystal and determining the ion concentration. It has been demonstrated that Yb, Ho:YAG is as good laser crystal in energy up-conversion as Yb, Er:YAG.

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References

1. X. X. Zhang, M. Bass, and B. H. T. Chai, Proc. SPIE **1863,** 123 (1993).
2. A. A. Kamiskii, *Laser Crystals* (Springer-Verlag, Berlin, Heidelbeg, New York, 1981).
3. T. Rothacher, W. Luthy, and H. P. Weber, Opt. Commun. **155,** 68 (1998).
4. D. L. Dexter, J. Chem. Phys. **21,** 836 (1953).
5. T. Miyakawa and D. L. Dexter, Phys. Rev. B **1,** 70 (1970).
6. R. A. Hewes and J. F. Sarver, Phys. Rev. **182,** 427 (1969).
7. L. L. Huang, Y. X. Ji, X. Z. Chen, H. W. Gao, and Z. W. Gao, Opt. Instruments (in Chinese) **19,** 45 (1997).
8. L. L. Huang and Z. Hong, Acta Optica Sinica (in Chinese) **20,** 1277 (2000).
9. X. L. Zou and H. Toratani, J. Non-Crystal Solids **181,** 87 (1995).