ENERGY TRANSFER FROM Yb TO Er IN THE INORGANIC LIQUID $SOCl_2$–$GaCl_3$

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In some crystals and glasses activated simultaneously with ytterbium and erbium ions, radiationless energy transfer with sensitization of erbium ions is observed [1]. The possibility of such sensitization is due to the presence for the Yb^{3+} ion of the $^2F_{5/2}$ radiative level which coincides with the $^4I_{11/2}$ absorption level of the Er^{3+} ion.

The mechanism of radiationless energy transfer in liquid solvents between RE ions has been examined in a number of works [1-3]. The ion donor can nonradiatively transfer its energy to the ion-acceptor in the following way: by an inductive-resonance mechanism, assuming overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor; by an exchange-resonance mechanism, occurring on overlap of the electron clouds of the donor and acceptor, or by a nonresonance mechanism, occurring under the condition that the emission frequency of the donor be higher than that of the acceptor.

It should be noted that sensitization is effective only when reverse energy transfer from the radiative level of the acceptor to a lower-lying absorptive level of the donor does not occur. Specifically in view of the nonmaintenance of this condition the attempt at sensitization of the Nd^{3+} ion by RE ions in the liquid solvent $POCl_3$–$SnCl_4$ turned out to be ineffective [4].

The choice of solvent greatly affects energy transfer between RE ions in liquid systems. Radiationless energy transfer between RE ions in solutions is facilitated by the location of the anions in the inner sphere of the complex. The ionization process, which is facilitated by a high donor number of the solvent, on the contrary, increases the probability of a transition of the anion from the inner sphere of the complex to the outer [5, 6]. A study of an aprotic inorganic solvent based on $SOCl_2$, having a low value of the donor number DN_{SbCl_5} is of interest. We did not find any information on sensitization of the Er^{3+} ion by RE ions in such a solvent in the literature.

This work is devoted to an investigation of the process of energy transfer from ytterbium to erbium in the binary aprotic inorganic solvent $SOCl_2$–$GaCl_3$.

With this goal the $YbCl_3$–$ErCl_3$–$SOCl_2$–$GaCl_3$ system was investigated. The Yb^{3+} ion has a single absorptive level, due to which in this system reverse energy transfer from Er^{3+} is of low probability, and therefore introduction of the donor in large concentrations is possible.

We used ytterbium and erbium chlorides, obtained by solution of the oxides in HCl. The chlorides obtained were purified by recrystallization and were dried over P_2O_5 in a vacuum drying chamber, gradually increasing the temperature to 200°C for 48 hr.

Gallium chloride was obtained by chlorination of metallic gallium by gaseous dry HCl.

Solutions of ytterbium and erbium chlorides in $SOCl_2$–$GaCl_3$ were prepared in solvothermal conditions at 50°C.

Absorption spectra were taken on an SF-20 spectrophotometer.

Luminescence spectra in the 900-1600 nm region were recorded on a SDL-1 spectrometer. Luminescence was excited by the radiation of a DRSh-250-3 mercury-quartz lamp with different light filters. A PbS photoresistance was used as a luminescence receiver.

The luminescence decay times were determined using a pulsed taumeter with exponential scanning.

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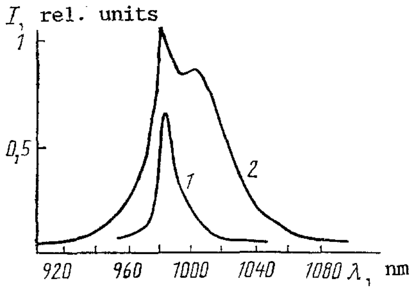

Fig. 1

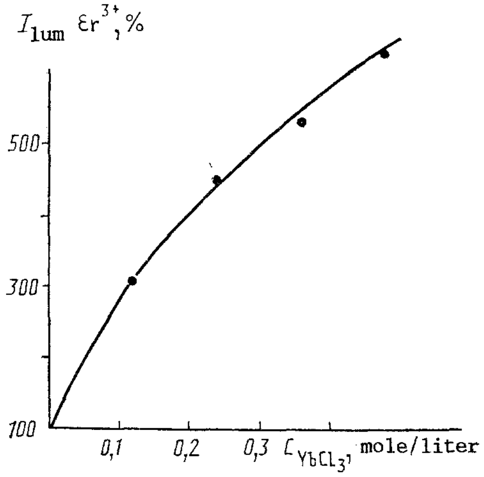

Fig. 2

Fig. 1. Absorption spectrum of Er^{3+} ion (1) and luminescence spectrum of Yb^{3+} ion (2) in $SOCl_2$–$GaCl_3$ at 300 K.

Fig. 2. Er^{3+} luminescence intensity ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition) versus concentration of the donor Yb^{3+} in the $YbCl_3$-$ErCl_4$–$SOCl_2$–$GaCl_3$ system.

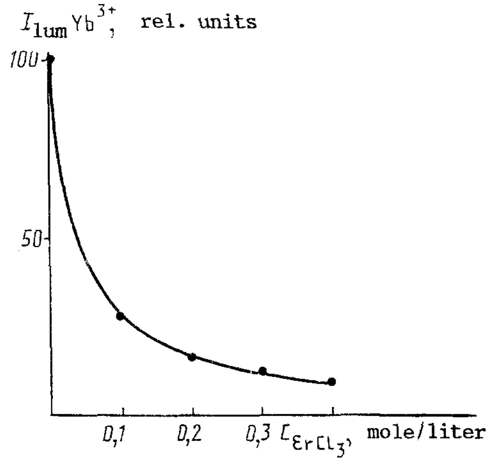

Fig. 3

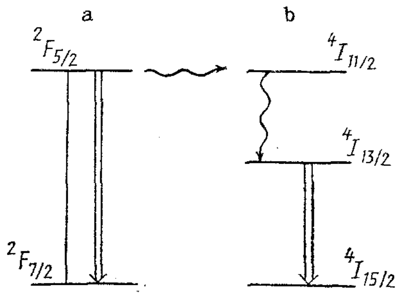

Fig. 4

Fig. 3. Yb^{3+} luminescence intensity versus concentration of the acceptor Er^{3+} in the $YbCl_3$–$ErCl_3$–$SOCl_2$–$GaCl_3$ system.

Fig. 4. Scheme of radiationless energy transfer between Yb^{3+} (a) and Er^{3+} (b) ions in $SOCl_2$–$GaCl_3$.

The spectral-luminescent properties of Yb^{3+} and Er^{3+} ions in $SOCl_2$–$GaCl_3$ were studied for two series of solutions, in the first of which the ytterbium chloride concentration remained constant (0.1 mole/liter), while the erbium chloride concentration varied from 0.1 to 0.4 mole/liter. In the second series the erbium chloride concentration remained constant at 0.02 M, while the ytterbium concentration increased from 0.12 to 0.48 M.

In Fig. 1 absorption spectra of Er^{3+} and luminescence spectra of Yb^{3+} in $SOCl_2$–$GaCl_3$ are given at 20°C in the 900-1100 nm region. As seen from Fig. 1, the luminescence spectrum of Yb^{3+} in this region ($^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) completely overlaps the absorption spectrum of Er^{3+} ($^4I_{15/2} \rightarrow {}^4I_{11/2}$). This can be made possible by the presence of energy transfer according to an inductive-resonance mechanism.

On an increase in the ytterbium chloride concentration in solutions with a constant erbium chloride content a substantial increase in the intensity of erbium luminescence occurs in the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ electronic transition (λ_{max} = 1540 nm) (Fig. 2). The given effect cannot be explained by ordinary resorption.

In a series of solutions in which the ytterbium chloride concentration remained constant, with an increase in the $ErCl_3$ concentration, a sharp decrease in both the Yb^{3+} luminescence intensity (Fig. 3) and in the values of $\tau_{Yb^{3+}}$ was observed, which indicates the predominant dynamic character of energy transfer from Yb^{3+} to Er^{3+}. In this case the luminescence decay law of the donor at all $ErCl_3$ concentrations turned out to be nonexponential.

The authors of [7] examined the decay law and quantum yield of luminescence in the general case of a power dependence of the probability of energy transfer on the distance between the donor and acceptor and obtained the formula (neglecting diffusion)

$$I(t) = \exp\left\{-\frac{\tau}{\tau_0} - \frac{C_A}{C_0}\Gamma\left(1-\frac{3}{s}\right)\left(\frac{\tau}{\tau_0}\right)^{3/s}\right\}, \tag{1}$$

where Γ is a gamma function; C_0 is the critical concentration of energy transfer connected with the critical distance of energy transfer (R_0) by the following expression:

$$C_0 = 3(4\pi R_0^3)^{-1}, \tag{2}$$

s acquires the values 6, 8, and 10 for dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions respectively.

Calculations using Eq. (1), performed on a computer, showed that the best agreement of the experimental and calculated values of I(t) is observed for s = 6, and in this case C_0 is equal to 0.13 mole/liter and R_0 = 1.58 nm (for solutions with C_{ErCl_3} = 0.2 mole/liter).

Consequently, in the RE ion pair studied, dipole-dipole interactions dominate, and thus the conclusions of the authors of several works on display in nonradiative energy transfer between RE ions of other types of interactions, dipole–quadrupole, etc. were not confirmed [8].

Thus, in the $YbCl_3$–$ErCl_3$–$SOCl_2$–$GaCl_3$ system radiationless energy transfer from the Yb^{3+} ion to Er^{3+} by an inductive-resonance mechanism was accomplished, leading to sensitization of erbium luminescence. In this case the dipole–dipole type of interaction between these ions is predominant. This process is shown schematically in Fig. 4.

LITERATURE CITED

1. Laser Phosphate Glasses [in Russian], Moscow (1980).
2. M. N. Tolstoi, Spectroscopy of Crystals [in Russian], Moscow (1970), pp. 124-135.
3. V. V. Ovsyankin and P. P. Feofilov, Spectroscopy of Crystals [in Russian], Moscow (1970), pp. 135-143.
4. B. M. Antipenko, I. M. Batyaev, V. L. Ermolaev, et al., Opt. Spektrosk., 29, No. 2, 335 (1970).
5. B. M. Antipenko and V. L. Ermolaev, Opt. Spektrosk., 30, No. 1, 75 (1971).
6. B. M. Antipenko, I. M. Batyaev, and T. A. Privalova, Zh. Neorg. Khim., 20, No. 1, 12 (1975).
7. V. L. Ermolaev, E. N. Bodunov, E. B. Sveshnikova, and T. A. Shakhverdov, Radiationless Transfer of Electronic-Excitation Energy [in Russian], Leningrad (1977).
8. L. G. Van Uitert, J. Lumin., 4, No. 1, 1 (1971).