Cooperative Luminescence in $YbPO_4$

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$YbPO_4$ was found to show weak green (497 nm) luminescence when excited by infrared (1 μm) light. It is concluded, on the basis of measurements of excitation intensity dependence and decay time, that this luminescence is due to the emission of a photon by a pair of excited Yb^{3+} ions in cooperation.

The interaction between rare-earth ions in solids is known to induce such cooperative phenomena as cooperative optical absorption,[1] Raman luminescence,[2] and cooperative energy transfer.[3,4] We report in this Letter the first observation of "cooperative luminescence," i.e., the emission of a photon by a pair of excited ions in cooperation. The observation has been made by using $YbPO_4$.

We have found that $YbPO_4$ crystalline powder shows very weak visible green luminescence when excited by near infrared light of about 1 μm. The spectrum at room temperature is shown in Fig. 1. The spectrum at low temperature is nearly the same. The Yb^{3+} ion has only one excited state, $^2F_{5/2}$, located at about 10^4 cm^{-1} above the ground state $^2F_{7/2}$, so that it cannot fluoresce in the visible region. The luminescence spectrum of the Yb^{3+} ion in $YbPO_4$ due to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition is centered at 998 nm.

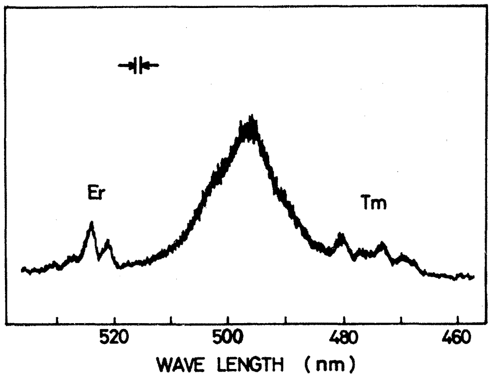

FIG. 1. Emission spectrum in the green region of $YbPO_4$ excited by infrared light of about 1 μm at room temperature. The rather broad emission peaked at 497 nm is due to cooperative luminescence of the Yb^{3+} ion, while the other sharp lines are infrared-stimulated luminescence of Er^{3+} and Tm^{3+} ions involved as impurities.

It is noted that the photon energy of the green luminescence peak is nearly exactly twice the energy of the normal (single-ion) luminescence. This implies that the green luminescence is caused by the simultaneous radiative relaxation of a pair of excited Yb^{3+} ions accompanied by the emission of a photon in the following manner:

$$\mathrm{Yb}^*(^2F_{5/2}) + \mathrm{Yb}^*(^2F_{5/2}) \rightarrow \mathrm{Yb}(^2F_{7/2}) + \mathrm{Yb}(^2F_{7/2}) + h\nu.$$

We wish to call this luminescence "cooperative luminescence" by analogy with the term "cooperative absorption."

The single-ion luminescence involves a number of transitions between the Stark levels of the excited and ground states. Since the cooperative luminescence is composed of various combinations of these transitions, it is quite reasonable that the spectrum of the cooperative luminescence shown in Fig. 1 is unusually broad in comparison with the usual emission spectra of various rare-earth ions in crystals. The rather sharp lines in Fig. 1 are due to the luminescences of Tm^{3+} and Er^{3+} ions involved as impurities with concentrations less than 50 ppm. The luminescence of these ions is excited by infrared light through two- or three-step energy transfer from Yb^{3+} ions.[5]

If the observed green luminescence is due to the process mentioned above, its intensity should show a quadratic dependence on the intensity of infrared-excitation light. Figure 2 shows this dependence. The slope of the curve is 1.87, which is nearly equal to the expected value of 2. The maximum effective intensity of infrared-excitation light in the figure was 10^{19} photons/cm^2 sec. In this case the ratio of the intensity of the 497-nm emission to that of the 998-nm emission was measured to be 10^{-6}-10^{-8}.

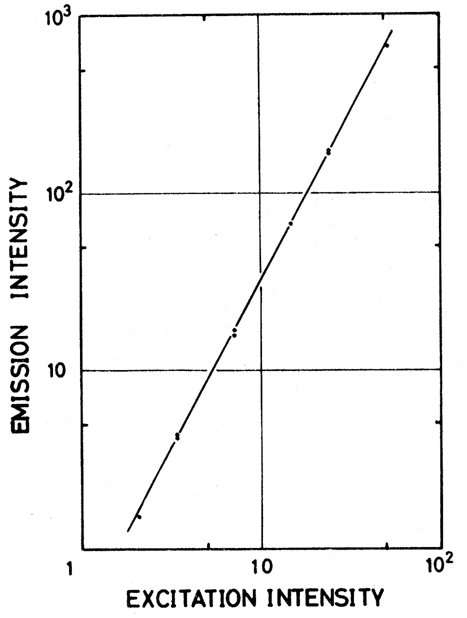

FIG. 2. Dependence of the intensity of the 497-nm emission in $YbPO_4$ on the intensity of infrared-excitation light at room temperature.

Figure 3 shows the decay curves of the intensities of the 497- and 998-nm luminescences measured by using 30-μsec pulse infrared light as the excitation source. The single-ion luminescence shows a simple exponential decay with a time constant of 0.64 msec. On the other hand, the cooperative one decays with a time constant of 0.36 ± 0.05 msec, which is nearly the half of that for the single-ion luminescence, although there is some deviation from an exponential curve in the tail. The decay of the intensity of single-ion luminescence is expressed by $I_s(t) \propto n_s(t) = n_{s0}\exp(-t/\tau_s)$, where n_s is the number of excited ions. Similarly for cooperative luminescence, $I_c(t) \propto n_c(t) = n_{c0}\exp(-t/\tau_c)$, where n_c is the number of pairs of excited ions. Since $n_c(t)$ is regarded as being proportional to $n_s(t)^2$, one obtains that $\tau_c = \tau_s/2$. The results shown in Fig. 3 indicate that this relation actually holds.

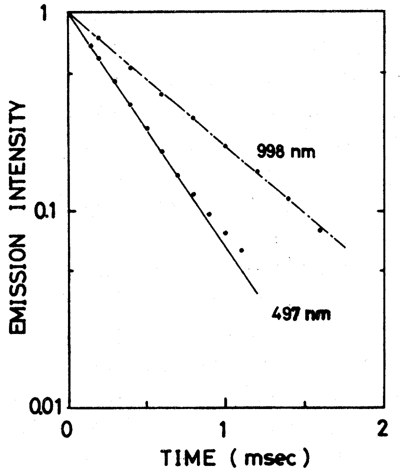

FIG. 3. Decay curves for single-ion luminescence at 998 nm and cooperative luminescence at 497 nm in $YbPO_4$ at room temperature under excitation by infrared-pulse light of 30 μsec duration.

In order to examine the possibilities that the 497-nm luminescence might be due to some kinds of rare-earth ions involved as impurities, the spectra and decay rates of infrared-excited luminescence were measured for $YbPO_4$ samples doped with 1 mole% Ho, Er, or Tm. Since these ions are known to emit visible luminescence under infrared excitation due to energy transfer from the Yb^{3+} ion,[5] they were chosen as the ions to be tested. It was found that the emission spectra of these ions are definitely different from that of the 497-nm luminescence in Fig. 1 with respect to both the energy position and the shape, and that the intensity of the 497-nm luminescence is reduced in the presence of these ions, probably because of energy transfer from the Yb^{3+} ion to these ions. The decay curves of the luminescences of Ho^{3+}, Er^{3+}, and Tm^{3+} ions under infrared excitation were quite different from that of the 497-nm emission in the respects that the decay rates were several times faster than that of the 497-nm emission, and that the rise of emission intensity was observed after the decay of 30-μsec excitation-pulse light, the intensity reaching its maximum at times of 40 to 100 μsec after the pulse light. This kind of rise of emission intensity was not observed in the case of the 497-nm emission. Furthermore, in the whole visible region no emission lines due to impurities, except those attributed to Tm^{3+} and Er^{3+}, were found. These facts clearly exclude the possibility that the 497-nm emission might be due to an impurity.

Cooperative luminescence is understood just as the reverse process of cooperative optical absorption.[1] Dexter[6] interpreted the mechanism of cooperative absorption by taking electric-multipolar interaction between rare-earth ions into account. Dorman[7] observed that in $PrCl_3$ the ratio of the oscillator strength for the cooperative absorption of Pr^{3+} $({}^3P_0 + {}^3F_2)$ to that for the single-ion absorption $({}^3P_0)$ is 1.3×10^{-5}. The theoretical calculation by Shinagawa[8] gave a value one order of magnitude smaller for this ratio. One may assume that in a pair of excited ions the ratio of the intensity of cooperative luminescence to that of single-ion luminescence is the same as the ratio of the oscillator strengths for cooperative and single-ion absorptions. At the maximum excitation intensity used in our experiment, 10^{19} photons/cm^2 sec, the ratio of the number of excited Yb^{3+} ions existing in the stationary state is estimated to be 10^{-5}, if one takes a value of 10^{-21} cm^2 for the absorption cross section of Yb^{3+} ion and 0.6 msec for the lifetime. Then, the ratio of the number of pairs of excited ions to that of single excited ions is 10^{-5}, and one expects that the ratio of the intensity of cooperative luminescence to that of single-ion luminescence is $10^{-5}\times10^{-5}=10^{-10}$. The experimentally observed ratio 10^{-6}-10^{-8} appears larger than this value beyond experimental error.

It is well known that in highly activated rare-earth phosphors, excitation energy migrates resonantly from one ion to another. The probability of this process was experimentally obtained by Gandrud and Moos[9] to be 7×10^9 sec^{-1} for $PrCl_3$ ($^3F_3$, $^3F_6$) and $NdCl_3$ ($^4I_{15/2}$, $^4I_{13/2}$). A theoretical calculation by Miyakawa and Dexter[10] gave a value of 1.3×10^{12} sec^{-1}. We have to take this effect into consideration in our discussion.

Let γ and β be the probabilities of the creation and annihilation, respectively, of an excited ion pair in cooperation caused by excitation energy migration. Then the intensity of single-ion luminescence under steady excitation is given as $I_s = W_s x N$, while that of cooperative luminescence is $I_c = W_c(\gamma/\beta)x^2N$, where W_s and W_c denote the radiative transition probabilities, N is the number of ions per unit volume, and x is the ratio of excited ions. The transient change of the intensity of cooperative luminescence after the decay of pulse excitation light is given, with the assumption that $\beta^{-1} < \tau_s$, as

$$I_c(t) = W_c\{1-(1-\beta/\gamma)\exp(-\beta t)\} \times (\gamma/\beta)x_0^2 N \exp(-2t/\tau_s).$$

This indicates that $I_c(t)$ curve shows the rise with the time constant of β^{-1} and its decay is governed by the time constant of $\tau_s/2$, consistently with the discussion made already.

At the maximum excitation intensity in our experiment, I_c/I_s was 10^{-6}-10^{-8} and x is 10^{-5}. Since one can assume that $W_c/W_s \sim 10^{-5}$, one expects that $\gamma/\beta = 10^2$-10^4. This leads to $\beta = 10^6$-10^8 sec^{-1} with the assumption of $\gamma \sim 10^{10}$ sec^{-1}. In our measurement of decay curves using pulse excitation, the time resolution was less than 10^{-5} sec. Therefore, it is not unreasonable that the rise in the $I_c(t)$ curve was not observed. However, it seems that one cannot neglect the effect of the migration of excitation energy in the interpretation of cooperative luminescence.

In summary, we can conclude that the weak 497-nm luminescence in $YbPO_4$ with the photon energy nearly equal to twice the energy of the normal 998-nm luminescence of the Yb^{3+} ion is due to the emission of a photon from a pair of excited Yb^{3+} ions in cooperation. Strong experimental evidence is provided by the facts that the intensity of the 497-nm luminescence shows a quadratic dependence on excitation intensity, and that the decay-time constant of the 497-nm luminescence is nearly half of that of the 998-nm luminescence.

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