COOPERATIVE SENSITIZATION OF LUMINESCENCE IN CRYSTALS ACTIVATED WITH RARE EARTH IONS

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Processes for which interactions between activator ions are decisive have been proposed to explain many specific regularities observed in the luminescence and stimulated emission of activated crystals. Such cooperative processes include migration of excitation energy over the activator ions, classical sensitization of luminescence, concentration quenching (especially that caused by cross relaxation [1]), cooperative absorption [2], nonlinear quenching of luminescence [3], and summation of electronic excitations [4]. We report in this note a new cooperative process which we observed in BaF_2 crystals and a few others, activated with pairs of rare-earth ions.

When BaF_2 crystals containing 10 mol.% YbF_3 and 0.5 mol.% TuF_3 were exposed to infrared from an incandescent lamp (wavelength > 0.9 μ) we observed (at room temperature) visible glow of the thulium ions. No such glow was observed under identical excitation conditions in BaF_2 crystals activated with thulium only. Spectroscopy of the observed glow has shown it to consist of two groups of lines characteristic of the Tu^{3+} ion, with maxima at 470 nm ($^1G_4$ - $^3H_6$ transition) and 670 nm ($^1G_4$ - $^3H_4$ transition) (Fig. 1a). The infrared excitation spectrum of the glow (Fig. 1c) consists of a single band with maximum at 960 nm, corresponding to the absorption band of the trivalent Yb ion ($^2F_{7/2}$ - $^2F_{5/2}$ transition, Fig. 1b). There is no Tu^{3+} absorption in this region. Photometry of the visible glow of thulium excited in the ytterbium absorption band has shown that its intensity is proportional to the square of the exciting-light intensity.

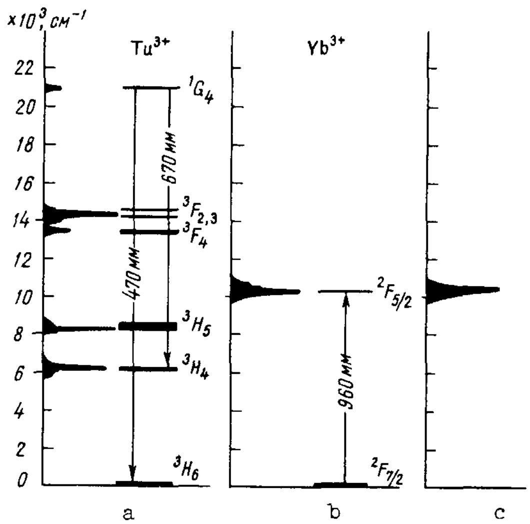

Fig. 1. a - Absorption spectrum and scheme of Tu^{3+} terms in BaF_2:Tu crystals; b - absorption spectrum of BaF_2:Yb crystals; c - infrared excitation spectrum of visible glow of Tu^{3+} in BaF_2:Tu, Yb crystals.

The appearance of visible glow of Tu when the crystals are excited in the absorption band of Yb offers evidence that an important role is played in the phenomenon by energy transfer. The main difference between the latter and classical sensitization is that the energy of the excited state of the donor (Yb, $^2F_{5/2}$) is approximately one-half the energy of the excited state of the acceptor (Tu, $^1G_4$). Energy transfer from Yb^{3+} to Tu^{3+} via the ordinary sensitized-luminescence mechanism with subsequent cumulation of the excitation energy of two Tu^{3+} ions on one of them [4] is precluded by the fact that Tu^{3+} has no levels with energy close to the $^2F_{3/2}$ level of Yb^{3+}. In exactly the same way, the phenomenon cannot be attributed to cumulation of the excitation energy on the Yb^{3+} ions and subsequent transfer of energy to the Tu^{3+} ions, since the Yb^{3+} ion does not have real excited states with energy equal to double the energy of the $^2F_{3/2}$ state. We thus are faced with an essentially new phenomenon.

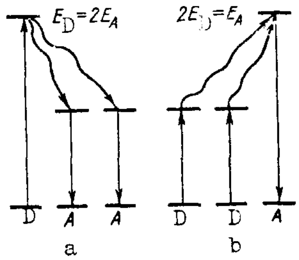

Fig. 2. a - Cooperative excitation of two acceptor ions via exchange of energy with the donor (after Dexter); b - cooperative excitation of acceptor ion via summation of the energy of two donor ions.

This phenomenon, which can be called cooperative sensitization of luminescence, is the inverse of the phenomenon considered by Dexter [5], namely simultaneous transfer of excitation energy from one donor ion to two acceptor ions (Fig. 2a) [1)]. The mechanism of cooperative sensitization is as follows: The infrared light with wavelength ≈ 960 nm excites the donors (Yb^{3+}). If direct excitation or energy migration over the excited states results in the excitation of two donor ions in the neighborhood of an acceptor ion (Tu^{3+}), then in the presence of degeneracy ($2E_D = E_A$) there is a definite probability of a resonant process wherein the donors go over to the ground state and the acceptor is excited. According to Dexter's calculations, the presence of strongly interacting donor pairs with considerably overlapping wave functions is necessary to realize such processes. In practice this requirement denotes the need for introducing into the crystals considerable donor concentrations; this agrees with our observations.

We observed similar phenomena in crystals activated with the ion pairs $Yb^{3+} + Ho^{3+}$ and $Yb^{3+} + Er^{3+}$. If these systems are excited in the region of the Yb^{3+} absorption band, visible (green) glow is observed, corresponding to the transitions from the $^5S_2$ level of Ho^{3+} or the $^4S_{3/2}$ level of Er^{3+}. Since in principle the states $^5I_6$ of Ho^{3+} or $^4I_{11/2}$ of Er^{3+} can become excited in this case via ordinary sensitization and subsequent energy cumulation, further research is necessary to ascertain whether cooperative sensitization has taken place here.

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1) The authors know of no direct experimental proof of the existence of this phenomenon.