

Sensitization of luminescence of trivalent rare-earth ions (TR^{3+}) by Eu^{2+} ions in NaBr crystals

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An effective energy transfer from Eu^{2+} to the trivalent rare-earth ions Pr, Nd, Tb, Ho, Dy, and Er is observed in $\text{NaBr}:\text{Eu}^{2+}:\text{TR}^{3+}$ ions. The intensity of the TR^{3+} ion luminescence is increased in this case by two or three orders of magnitude.

We have previously reported effective sensitization of the luminescence of Ho^{3+} by Eu^{2+} ions in NaBr.^[1–3] The transfer of energy from Eu^{2+} to Eu^{3+} and Sm^{3+} was noted in CaSO_4 ,^[4] in NaF,^[5] and in oxysulfides,^[6] as well as to Ho^{3+} in CaF_2 .^[7] In all these cases, however, unlike in $\text{NaBr}:\text{Eu}^{2+}:\text{TR}^{3+}$, there is a negligible increase in the luminescence brightness.

It is assumed that the lower levels of the excited state of the Eu^{2+} ions are the result of stimulated interaction of the configurations $4f^7$ and $4f^6 5d^1$. Owing to the interaction of the Eu^{2+} ion with local and crystal-lattice vibrations,^[8] the absorption and luminescence spectra constitute broad bands with appreciable Stokes losses (on the order of 5000 cm^{-1}).

The luminescence band (maximum 444 nm, half-width 16000 cm^{-1} , nonelementary band) of Eu^{2+} overlaps the absorption spectra of most trivalent rare-earth elements. Inasmuch as in most cases this overlap takes place for the TR^{3+} lines connected with transitions to metastable levels, one can expect, owing to the large Stokes losses in the luminescence of Eu^{2+} , a resonant energy transfer^[9] from Eu^{2+} to TR^{3+} .

To verify this hypothesis, we have grown $\text{NaBr}:\text{Eu}^{2+}(1 \times 10^{-2} \text{ mol. \%}) + \text{TR}^{3+}(5 \times 10^{-3} \text{ mol. \%})$ single crystals ($\text{TR}^{3+} = \text{Pr, Nd, Tb, Dy, Ho, Er}$) by the procedure described in^[2], and investigated the luminescence and excitation spectra of these crystals.

It turns out that the excitation spectra of all the mentioned TR^{3+} contain bands with maxima at 335, 350, and

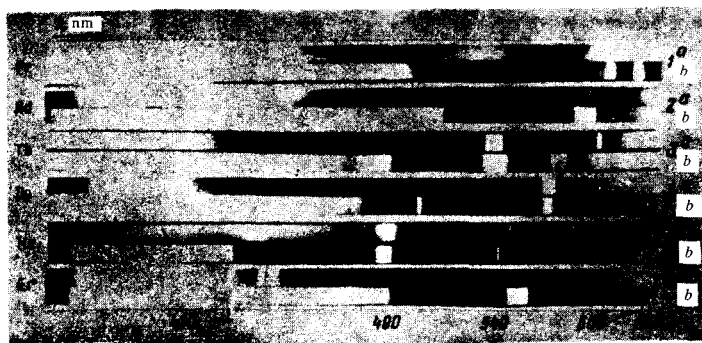
375 nm, corresponding exactly to the absorption of the Eu^{2+} ion in NaBr.^[10]

The emission kinetics of Eu^{2+} is altered and reveals a component that depends on the TR^{3+} concentration (τ ranges from 2.3×10^{-7} to 3.9×10^{-7} sec). At equal excitation, the luminescence brightness of the TR^{3+} in these crystals increases by 100–1000 times in comparison with the luminescence brightness of $\text{NaBr}:\text{TR}^{3+}$.

The figure shows the luminescence spectra of $\text{NaBr}:\text{TR}^{3+}$ (spectra "a") and $\text{NaBr}:\text{TR}^{3+}:\text{Eu}^{2+}$ (spectra "b"). We see that the spectra "b" differ from the spectra "a" (with the exception of the spectra of Tb^{3+} , which are represented in both cases by the transitions $^5D_4 - ^7F_7$). This indicates a change in the TR^{3+} excitation conditions. It is seen particularly clearly in the case of Nd^{3+} , where not only the $^4F_{3/2}$ but even the $^4G_{7/2}$ levels are radiative.

It follows from the foregoing that in all the cases described above there is transfer of energy from Eu^{2+} to TR^{3+} . Since the integral absorption coefficient in the $f-d$ absorption band of Eu^{2+} is several orders larger than that of the $\text{TR}^{3+} f-f$ absorption band, the luminescence intensity of the latter increases appreciably even at small integral overlaps of the absorption and luminescence bands of the acceptor and donor, respectively.

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Luminescence spectra of single crystals of $\text{NaBr}:\text{TR}^{3+}$ (a) and $\text{NaBr}:\text{TR}^{3+}:\text{Eu}^{2+}$ (b) obtained by ultraviolet excitation in the region 330–390 nm (77°K).

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