

Tb³⁺ ion as a sensitizer for rare-earth ions in a terbium trifluoride single crystal

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The Tb³⁺ ion did not attract much attention of scientists involved in the search for new laser materials as a real laser-related ion, mostly due to the negative results of many efforts aimed at obtaining laser action from Tb³⁺-containing single crystals in the past. In fact, only once have researchers succeeded in obtaining laser action from Tb³⁺ itself [1]. There are two examples, though, of a successful application of Tb³⁺ as a donor-ion to sensitize the fluorescence of other ions, some of them (e.g., Sm³⁺) also being considered as the least prospective among the actinides in terms of obtaining laser radiation. In both cases concentration of Tb³⁺ ions in the laser crystals reached 100%. Thus, efficient sensitization of Sm³⁺ ion by Tb³⁺ ion provided low-temperature (110-130 K°) orange ⁴G_{5/2} - ⁶H_{7/2} laser action at 593.2 nm from TbF₃: Sm³⁺ (0.3 at.%) single crystal with conventional flashlamp-pumping [2]. A high concentration of donor ions played a positive role in the above case, not only due to the fact that the high concentration itself helps to overcome the problem of low cross-sections (of the order of 10⁻²¹ cm²) of absorption transitions characteristic of the Tb³⁺ ion, but also due to the significant concentration broadening of absorption lines, and besides, as supposed in [2], also due to a favorable changing of the donor-acceptor interaction parameters as the Tb³⁺ concentration increases. Efficient donor-acceptor interaction between the Tb³⁺ and Sm³⁺ ions also made possible the recent observation of room temperature orange CW ⁴G_{5/2} - ⁶H_{7/2} laser action at 605 nm from the LiTbF₄: Sm³⁺ (1 at.%) single crystal pumped by an Ar-ion 488 nm laser line [3]. The latter result, in fact, prompts one to reconsider the application potential of the Tb³⁺ ion by including the use of it as a sensitizer for rare-earth ions (probably also other than only Sm³⁺) for devising reliable CW Ar-ion laser linear frequency converters.

All of the above considerations stimulated our efforts to analyze the "sensitization power" of Tb³⁺ ion - with respect to different rare-earth ions - in TbF₃: Re³⁺ (where Re³⁺ denominates any rare-earth ion) single crystal compounds. One can study donor-acceptor interactions either by changes in decay kinetics of the metastable donor state or by changes in the stationary fluorescence intensity in the presence of acceptor ions in the host. Our analysis was based on studying the metastable ⁵D₄ level fluorescence quenching by different Re³⁺ ions (from the Pr, Nd, Sm, Eu, Dy, Ho, Er, Tm, Yb sequence), as suggested by Van Viter [4]. We have compared the quenching probabilities for the ⁵D₄ (Tb³⁺) level for different doping ions in TbF₃. The probability of excitation transfer from donor the ⁵D₄ (Tb³⁺) level to the acceptor ion under the assumption of single-exponential decay can be derived from the equation:

$$W_{\text{Tb-Re}} = 1/\tau - 1/\tau_0,$$

where τ_0 and τ are the lifetimes of the ⁵D₄ level *without* and *with* the presence of Re³⁺ impurity, respectively.

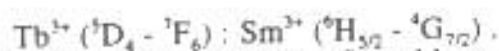
Table represents the $W_{\text{Tb-Re}}$ obtained for TbF₃: Re³⁺ crystals containing 1 at.% of impurity ions each. The fluorescence lifetime for the ⁵D₄ level in a pure TbF₃ single crystal was

found to be 780 μs at room temperature and 970 μs at 77 K. The represented data show that the highest donor-acceptor energy transfer probability was observed with those doping ions for which direct resonance interaction with the $^3\text{D}_4$ level takes place with no lattice phonons involved. Energy transfer for these ions is also temperature insensitive. Such interaction for Er^{3+} , Ho^{3+} , Pr^{3+} , and Sm^{3+} ions is accomplished through the $^4\text{F}_{3/2}$, $^4\text{F}_7$, $^3\text{P}_0$ and $^4\text{G}_{7/2}$ states, respectively.

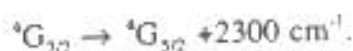
Table. Fluorescence lifetimes of $^3\text{D}_4$ (Tb^{3+}) level and probabilities of excitation transfer from $^3\text{D}_4$ (Tb^{3+}) to impurity ions in TbF_3 ; Re^{3+} crystal

Re	τ , μs		$W_{\text{Tb-Re}} \times 10^{-4}$, s^{-1}	
	300 K $^\circ$	77K $^\circ$	300 K $^\circ$	77K $^\circ$
Pr	8	---	12.4	---
Nd	6.5	---	16.5	---
Sm	3	3	33	33
Eu	42	156	2.2	0.5
Dy	160	430	0.5	0.13
Ho	9	---	11	---
Er	10	10	10	10
Tm	140	180	0.6	0.4
Yb	400	620	0.12	0.04

From the above data, it is obvious that Sm^{3+} is the best choice as an acceptor for the Tb^{3+} donor, and the excitation transfer from Tb^{3+} to Sm^{3+} occurs resonantly in accordance with the scheme:



The resonance character of energy transfer was confirmed by comparison of the $^3\text{D}_4 - ^3\text{F}_6$ fluorescence spectrum of the Tb^{3+} ion with the $^6\text{H}_{5/2} - ^4\text{G}_{7/2}$ absorption spectrum of Sm^{3+} ion in YF_3 single crystal, as represented in Figure (YF_3 single crystal is isostructural analog of TbF_3 , with quite close crystal field constants and often used for clarifying the spectroscopic situations with "self-activated" TbF_3). Note that resonant conditions are being satisfied for several energy-exchange channels simultaneously. The backward energy transfer through the same channels is not possible due to the fast nonradiative decay of the $^4\text{G}_{7/2}$ Sm^{3+} level:



Considering the possibility of "laser situation" for the impurity ions listed in Table, one should also take into consideration possible "backwards quenching" of acceptor fluorescence levels by the lower-lying donor levels. Our studies show that, in fact, only two Re^{3+} ions incorporated in TbF_3 , of the studied nine, are potentially suitable for obtaining lasing - Sm^{3+} and Eu^{3+} . The fluorescence of others is completely quenched due to the interaction with Tb^{3+} ions of the host. For the same reason, according to our data, the presence in the host crystal of minor amounts of other ions uncontrollably depletes the $^3\text{D}_4$ state, and may essentially depress the sensibilization effect.

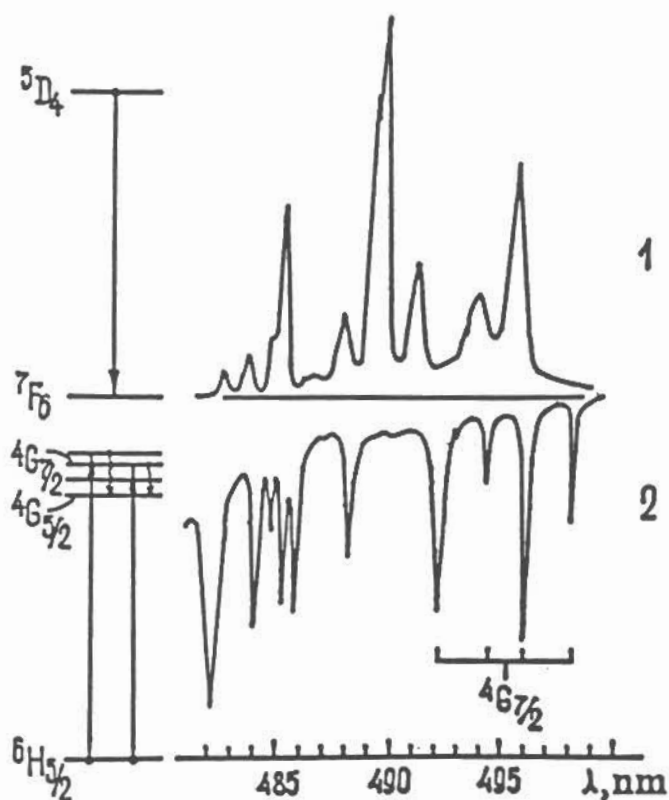


Figure. Fluorescence spectrum (${}^5D_4 - {}^7F_6$) of Tb^{3+} ion (1) and absorption spectrum (${}^6H_{5/2} - {}^4G_{5/2}, {}^4G_{7/2}$) of Sm^{3+} ion (2) in YF_3 single crystal at 77 K°.

The above analysis enables one to explain the observed efficiency of $Tb^{3+} - Sm^{3+}$ donor-acceptor pair for TbF_3 host crystal. Prediction that $Tb^{3+} - Eu^{3+}$ pair might also be a good choice for an Ar-ion laser frequency converter seems to be practical.

Laser experiments implementing Ar-ion laser for pumping of $TbF_3: Sm^{3+}$ as well as $TbF_3: Eu^{3+}$ samples are now in progress.

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References

1. H.P.Jenssen, D. Castleberry, et al. In: Digest of Techn. Papers, *CLEO* (IEEE/OSA, Washington, DC, 1973), p. 47.
2. B.N.Kazakov, M.S.Orlov, M.V.Petrov, et al. *Opt. Spectrosc. (USSR)* **47**, 1217 (1979).
3. H.P.Jenssen. In: *Advanced Solid-State Lasers*, OSA Techn. Digest (Opt.Soc. of Amer., Washigton, DC, 1995), p.73.
4. L.G.Van Vitert. - *J. Electrochemical Society* **114**, 1048 (1967).