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Spectroscopic properties of Fe^{3+} in GGG and the effect of co-doping with rare-earth ions

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Abstract

The spectroscopic properties of Fe^{3+} in tetrahedral d-sites of GGG and the effect of co-doping with Tm^{3+} are investigated. It is thus shown that a very efficient energy transfer from Fe^{3+} (d) to Tm^{3+} takes place due to a good superposition of Fe emission and $\text{Tm } ^3\text{H}_6 \rightarrow ^3\text{H}_4$ absorption spectra and due to a favorable packing of the d-sites around the dodecahedral site occupied by Tm. It was also found that the Fe-sensitized luminescence of Tm has different spectral and temporal characteristics from the normal emission of this ion in GGG.

Trivalent thulium in garnets, either as activator (A) or sensitizer (S) for Ho^{3+} offers interesting prospects for two-micron laser emission. Unfortunately the absorption bands of Tm are weak and thus the pump efficiency is low. A common way to improve the pump efficiency is the sensitization with transition ion metals which show strong and broad absorption matching better with the existing pump sources. A very important condition for sensitization is a fast S-A energy transfer and this implies a good match of S emission and A absorption spectra, short S-A distances and a good packing of A ions around the sensitizer.

The garnet crystals offer two sites for the transition ions, the octahedral a-site (of local C_{3i} symmetry) and the tetrahedral d-site (S_4), the preference for substitution being determined by the mismatch of ionic radii of the dopant and host cation and on the electronic structure of the former. The d-sites show a better packing around the dodecahedral c-site (D_2 symmetry) occupied by the rare-earth ions and the minimal d-c distance is shorter than the octahedral a-c distance. Cr^{3+} , the usual sensitizer for Tm^{3+} , occupies only the octahedral sites in garnets, i.e. not the most favorable sites for sensitization. This work investigates the possibilities of Tm sensitization by Fe^{3+} which could occupy both the a- and d-sites in these lattices. We used in this investigation GGG crystals grown by Czochralski technique and doped by Fe^{3+} (0.5 at %) or $\text{Fe}^{3+}/0.5$ at % Tm^{3+} (5 at %).

The lowest spectral term of the ground electronic configuration $3d^5$ of Fe^{3+} is a spin sextet (^6S) while the excited states are spin quartets or doublets. This leads to the forbiddenness of transitions between the ground and excited states. However the spin-orbit mixing of the sextet and quartet spin states lessons to a given extent this interdiction for sextet \rightarrow quartet transitions. The corresponding terms are split by the cubic component of the crystal field according to the rules $^6\text{S} \rightarrow ^6\text{A}_1$, $^4\text{P} \rightarrow ^4\text{T}_1$, $^4\text{D} \rightarrow ^4\text{E} + ^4\text{T}_2$, $^4\text{F} \rightarrow ^4\text{A}_2 + ^4\text{T}_1 + ^4\text{T}_2$, $^4\text{G} \rightarrow ^4\text{A}_1 + ^4\text{E} + ^4\text{T}_1 + ^4\text{T}_2$ and the Tanabe-Sugano diagrams which show the position of the crystal field levels as function of the crystal field strength are similar for octahedral and tetrahedral coordination. The crystal field states are further split by the spin-orbit interaction. $^6\text{A}_1 \rightarrow \Gamma_7 + \Gamma_8$; $^4\text{A}_2 \rightarrow \Gamma_8$; $^4\text{E} \rightarrow \Gamma_6 + \Gamma_7 + \Gamma_8$; $^4\text{T}_2 \rightarrow \Gamma_6 + \Gamma_7 + 2\text{T}_8$ and the lower symmetry component of the crystal field could split further the Γ_8 quartets into doublets.

The tetrahedral site lacks inversion and thus electric dipole transitions between states of the ground $3d^5$ electronic configuration are allowed owing to the mixing from σ add-parity states. However, in the octahedral sites, which have inversion, these transitions are forbidden, unless lower-symmetry perturbations are present. Thus in case of the isolated Fe^{3+} centers in diluted garnets we could expect that the optical spectra will be dominated by the tetrahedral centers. Indeed, weak and broad absorption bands covering all the visible spectrum have been observed, in our samples except for a strong and sharp line at 421.26 nm (accompanied by a structural phonon sideband), which was attributed to the ${}^6A_1 \rightarrow {}^4T_2(4D_2)$ transition of Fe^{3+} (d) center. We also remark the beginning of a broad band at about 535 nm (attributed to ${}^6A_1 \rightarrow {}^4T_2(4G)$ transition) and several non-resolved lines in the region 470-490nm, connected with ${}^6A_1 \rightarrow {}^4E$, ${}^4A_1(4G)$ transitions. A very intense absorption band is seen in the region of 250nm and, as in other Fe^{3+} systems [1,2] and this could be attributed to charge transfer transitions inside the octahedral and tetrahedral centers. As remarked for other systems, this band could lend intensity to the intra $3d^5$ transitions close to it.

A strong emission was observed by pumping in any of the lines observed in absorption and it consists of three relatively sharp lines at 753.3nm, 754.8nm and 756.8nm, companied by a broad phonon sideband with several shoulders (figure 1). The origin of this triplet is not clear but its presence at very low temperatures shows that it could not be connected with a structure of the emitting state. At the same time this could not be due to the crystal field splitting of the ground state, which usually is of the order of 10^{-2} cm^{-1} . The static excitation spectrum for this emission (figure 2) evidences clearly the transitions seen also in absorption. The wavelength of the sharp lines of emission correspond to a ${}^4T_1(4G) \rightarrow {}^6S_1$ transition for a ratio (D_2/B) in the Tanabe-Sugano diagram around 1, i.e. a value characteristic for tetrahedral Fe^{3+} in octahedral sites ($D_2/B \sim 2$). With increasing temperature the sharp emission Fe^{3+} lines broaden while the phonon sideband broadens and gains strength so as at 300K it dominates completely the emission and extends over all the range from 760 to 850nm. The luminescence decay is exponential with a lifetime of about 4.5ms at 300K.

The emission band of Fe^{3+} (d) shows a very good superposition with $Tm \text{ } {}^3H_6 \rightarrow {}^3H_4$ absorption, especially at the room temperature ; this suggests the use of Fe^{3+} in tetrahedral positions as sensitizer for Tm. Co-doping GGG with Fe^{3+} (0.5 at %) and Tm^{3+} (5 %) has a very strong effect upon Fe^{3+} and Tm^{3+} absorption and emission. Thus a well resolved satellite (T) of the sharp absorption M line ${}^6A_1 \rightarrow {}^4T_2(4D)$ of Fe^{3+} was observed at 419.56 nm ; similar satellites could be expected in other Fe^{3+} transitions but they cannot be resolved because the large linewidth. Excitation in the transition ${}^6A_1 \rightarrow {}^4T_2(4D)$ of Fe at 421.26 nm leads to an emission similar to that observed in Fe- only doped samples, but the lines are broadened and dips at the wavelengths corresponding to $Tm \text{ } {}^3H_6 \rightarrow {}^3H_4$ absorption have been observed in the broad emission sideband. Besides the radiative Fe \rightarrow Tm transfer testified by these dips, a strong non-radiative transfer, manifested by a marked modification of Fe^{3+} luminescence decay takes place, the effect being stronger at higher temperatures. The observed decay could be fitted with a Forster $8t^{1/2}$ law, corresponding to an electric dipole interaction between donor and acceptor only at long time (longer than about 500 μ s) after the beginning of decay, which is much faster than predicted by this law. By contrary, no Fe^{3+} emission was observed by exciting in the T satellite at 419.56nm.

Excitation in Fe absorption lines leads also to $Tm^{3+} \text{ } {}^3H_4 \rightarrow {}^3H_6$ emission (no emission was observed from higher energy levels of Tm) but this is dominated by the presence of three new centers (observed also in absorption), whose transition $W_1 \rightarrow Z_1$ is shifted from the normal line N (794.98nm) to 795.33nm (center F_1), 795.29 nm (center

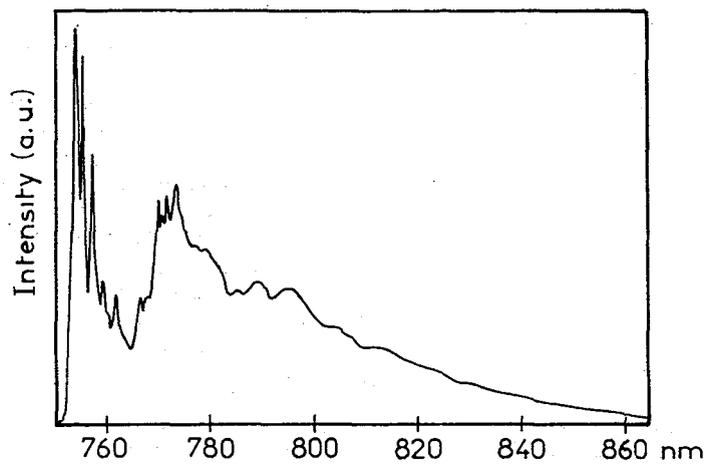


Fig. 1 : Emission spectrum of tetrahedral Fe^{3+} center in GGG, 12 K

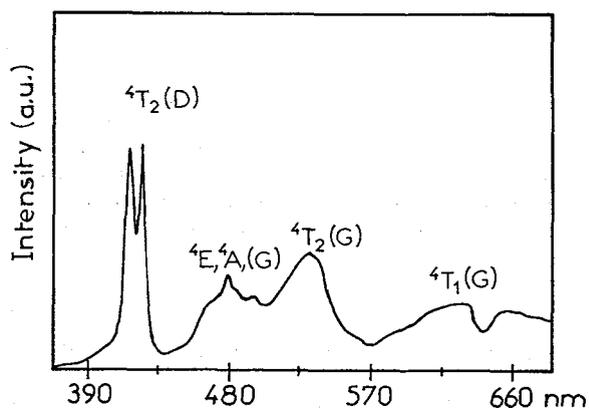


Fig. 2 : Static excitation spectrum for Fe^{3+} emission in GGG, 300 K

F₂) and 795.05nm (center F₃). An important feature of these emission spectra is the apparition of transition W₁->Z₂, absent in emission of N centers (this transition is forbidden in the D₂ symmetry of the unperturbed c-site) : this is strong for the centers F₁ and F₂ which show the largest shift from N emission but it is absent in emission of F₃ which is the closest to N. The emission F₁ could be excited when pumping in the satellite T, while that of centers F₂ and F₃ is excited in various ratios by pumping at different wavelengths inside the absorption M (peaking at 421.26nm). The three new Tm centers emit simultaneously when pumping with a frequency-doubled YAG:Nd laser (532nm) in the broad Fe³⁺ absorption band ⁶A₁->⁴T₂ (4G) which due to its linewidth does not show selectivity. Regardless the wavelength of pump in Fe lines, Tm shows also emission at the wavelength corresponding to the unperturbed (or less perturbed) centers N. However, while the emission of centers F₁, F₂ and F₃ does not show rise time when pumping in Fe, the emission of N shows a risetime which reflects the behavior of the beginning of Fe³⁺ decay in the co-doped samples.

Thus the observed absorption and emission behavior of Fe and Tm in GGG : Fe, Tm suggests that the satellites T, F₁, F₂ and F₃ correspond to static crystal field perturbations inside of several near Fe³⁺ (d) - Tm³⁺ pairs. The intensity of satellite T could be correlated with the statistical probability of having one of the two n.n. c-sites around the d-site occupied by a Tm ion. This suggests that the satellite T in Fe absorption and satellite T1 in Tm emission (which is excited by pumping in T) reflect the effect of the same structural formation, most likely a n.n. Fe(d)-Tm pair, while the other two (F₂ and F₃) satellites correspond to the next two kinds of pairs. The temporal behavior of luminescence indicates that the Fe-Tm energy transfer inside these formations is very fast and it thus leads to a complete quenching of Fe emission. Thus the Fe³⁺ emission in co-doped samples corresponds to Fe³⁺ ions having more distant Tm neighbors, a fact which is also confirmed by the similarity of the beginning of Fe³⁺ luminescence decay and the rise portion of Tm³⁺ N emission.

The observed behavior exemplifies the efficiency of sensitization of rare-earth luminescence in garnets with transition ions in tetrahedral sites. However, the modification of the spectral and temporal characteristics of rare-earth sensitized emission should be taken into account when using this sensitization for practical purposes.

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