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To cite this version:
V. Lupei, M. Elejalde, A. Brenier, G. Boulon. Spectroscopic properties of Fe3+ in GGG and the effect of co-doping with rare-earth ions. Journal de Physique IV Colloque, 1994, 04 (C4), pp.C4-329-C4-332. <10.1051/jp4:1994478>. <jpa-00252741>
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 Tm $^{3}H_6{\rightarrow}^{3}H_4$ 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 thullium 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 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 quataets 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>quartet transitions. The corresponding terms are split by the cubic component of the crystal field according to the rules $^6S{\rightarrow}^6A_1$, $^4P{\rightarrow}^4T_1$, $^4D{\rightarrow}^4E{+}^4T_2$, $^4F{\rightarrow}^4A_2{+}^4T_1{+}^4T_2$, $^4G{\rightarrow}^4A_1{+}^4E_1$, $^4T_1{+}^4T_2$ 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,$^6A_1{\rightarrow}^7\Gamma_7{+}\Gamma_8$, $^4A_2{\rightarrow}\Gamma_8$; $^4E{\rightarrow}\Gamma_6{+}\Gamma_7{+}\Gamma_8$; $^4T_2{\rightarrow}\Gamma_6{+}\Gamma_7{+}2\Gamma_8$ and the lower symmetry component of the crystal field could split further the $\Gamma_8$ quartets into doublets.

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jp4:1994478
The tetrahedral site lacks inversion and thus electric dipole transitions between states of the ground 3d⁵ 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 Fe³⁺ 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 ⁶A₁→⁴T₂(⁴D₂) transition of Fe³⁺ (d) center. We also remark the beginning of a broad band at about 535 nm (attributed to ⁶A₁→⁴T₂ (4G) transition) and several non-resolved lines in the region 470-490nm, connected with ⁶A₁→⁴E, ⁴A₁(4G) transitions. A very intense absorption band is seen in the region of 250nm and, as in other Fe³⁺ systems [1,2] 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 3d⁵ transitions close to it.

A strong emission was observed by pumping in any of the lines observed in absorption and it consists of three relativity sharp lines at 753.3nm, 754.8nm and 756.8nm, accompanied 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 ⁴T₁(⁴G)→⁶S₁ transition for a ratio (D₂/B) in the Tanabe-Sugano diagram around 1, i.e. a value characteristic for tetrahedral Fe³⁺ in octahedral sites (D₂/B≈2). With increasing temperature the sharp emission Fe³⁺ 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 Fe³⁺ (d) shows a very good superposition with Tm ³H₆→³H₄ absorption, especially at the room temperature ; this suggests the use of Fe³⁺ in tetrahedral positions as sensitizer for Tm. Co-doping GGG with Fe³⁺ (0.5 at %) and Tm³⁺ (5 %) has a very strong effect upon Fe³⁺ and Tm³⁺ absorption and emission. Thus a well resolved satellite (T) of the sharp absorption M line ⁶A₁→⁴T₂ (4D) of Fe³⁺ was observed at 419.56 nm ; similar satellites could be expected in other Fe³⁺ transitions but they cannot be resolved because the large linewidth. Excitation in the transition ⁶A₁→⁴T₂ (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 ³H₆→³H₄ absorption have been observed in the broad emission sideband. Besides the radiative Fe→Tm transfer testified by these dips, a strong non-radiative transfer, manifested by a marked modification of Fe³⁺ luminescence decay takes place, the effect being stronger at higher temperatures. The observed decay could be fitted with a Forster 8t₁/₂ law, corresponding to an electric dipole interaction between donor and acceptor only at long time (longer than about 500μs) after the beginning of decay, which is much faster than predicted by this law. By contrary, no Fe³⁺ emission was observed by exciting in the T satellite at 419.56nm.

Excitation in Fe absorption lines leads also to Tm³⁺ ³H₄→³H₆ 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 W₁→Z₁ is shifted from the normal line N (794.98nm) to 795.33nm (center F₁), 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 \( W_1 \rightarrow Z_2 \), absent in emission of N centers (this transition is forbidden in the \( D_2 \) 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 \( \Fe^{3+} \) absorption band \( ^6A_1 \rightarrow ^4T_2 \) (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 \( \Fe^{3+} \) 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 \( \Fe^{3+} \) (d) - \( \Tm^{3+} \) 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 \( \Fe^{3+} \) emission in co-doped samples corresponds to \( \Fe^{3+} \) ions having more distant Tm neighbors, a fact which is also confirmed by the similarity of the beginning of \( \Fe^{3+} \) luminescence decay and the rise portion of \( \Tm^{3+} \) 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.

References