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Multisite structure of optical spectra of activators in garnet crystals

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Abstract. The analysis of selective excitation and emission spectra of Tm^{3+} in YAG and GGG laser systems is presented. The observed multisite structure is assigned to non-stoichiometric defects. Up to six centers are separated, with complex spectra connected with lowering of the local symmetry.

INTRODUCTION

The high resolution spectra of the rare-earth ions in garnet crystals with $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ formula show a complex multisite structure. Such structures, analyzed previously especially for Nd^{3+} [1-3] and Er^{3+} [1,4] ions, were assigned to: (i) rare earth ions in normal dodecahedral c-sites; (ii) rare earth ions in c-sites perturbed by a close non-stoichiometric defect, P-satellites; (iii) pairs of rare earth ions in neighbour c-sites, M-type of satellites and (iv) rare-earth ions in octahedral a-sites, A satellites.

This paper reports several results on the Tm^{3+} spectra multisite structure in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) or $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) crystals. Tm^{3+} ($4f^{12}$) being a non-Kramers ion and having a series of forbidden transitions in normal c-sites as well as hypersensitive transitions could be a good sensor for the elucidation of the nature of multisite structure in garnets.

In the ideal garnet structure, the rare earth ion $\text{A}(\text{Y}^{3+}$ or $\text{Gd}^{3+})$ occupy c-sites with D_2 symmetry, while the octahedral a-sites with C_{3i} symmetry as well as tetrahedral d-sites with S_4 symmetry are occupied by trivalent transition metal ions, such as Al^{3+} or Ga^{3+} . The non-stoichiometric defect consists in the occupation of part of B ions in octahedral sites by rare earth ions B, this excess being specific to high temperature grown garnets.

Observed initially in the optical spectra, the non-stoichiometry of the garnets was invoked recently [5] to explain a slight deviation from cubic symmetry of the garnet crystals observed in x-ray absorption spectra.

The substitution of a cation B by a larger ion A leads to distortion of the crystalline lattice and perturbation of the crystal field around it. Thus, since each c-site is surrounded in the first coordination sphere by four A ions, one could expect different distortions depending on the replaced ion position. Distortions induced by such a defect in the second coordination sphere were also assumed to explain the Er^{3+} spectra [4]. The optical spectra of activators should reflect the statistical distribution of defects, and therefore the relative intensity of P-lines should be independent on the dopant concentration.

The Tm^{3+} replace preponderantly A ions, but its spectra present also a complex satellite structure [6,7]. The high resolution absorption, site selective excitation and emission spectra on various YAG:Tm^{3+} and GGG:Tm^{3+} samples, at low temperatures, are analyzed. Satellite structure has been observed in many Tm^{3+} transitions, ${}^3\text{H}_4 \rightarrow {}^3\text{H}_4$, ${}^3\text{F}_3$, ${}^3\text{F}_2$, ${}^1\text{G}_4$.

YAG:Tm^{3+}

In the high resolution absorption and emission spectra up to six satellites have been distinguished in the ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ Tm^{3+} transitions, three in ${}^3\text{H}_6 \rightarrow {}^1\text{G}_4$, while ${}^3\text{F}_3$ spectra are especially complex.

The six satellites in the ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ spectra could be selectively excited by pumping with a dye laser in ${}^3\text{F}_3$ multiplet. This shows that they belong to Tm^{3+} in different disturbed centers. The comparative analysis of the excitation and emission spectra for these centers with those of the main center N allows their separation into two classes: centers with spectra similar to those of main center N (shifted lines; but essentially the same as in N spectra), and centers whose spectra present additional lines, some of them corresponding to forbidden transitions in D_2 . For first category the $\text{W}_1 \rightarrow \text{Z}_1, \text{Z}_4$ transitions dominate the ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$ emission at low temperatures, while for the second category the spectra contain additional lines such as

$W_1 \rightarrow Z_2$ (corresponding to a forbidden transition in D_2) and $W_1 \rightarrow Z_3$ (an allowed transition in D_2 , but with a very low intensity) (Fig.1). One must remark that if the local axes of D_2 are chosen as in [6], $W_1(\Gamma_1) \rightarrow Z_4(\Gamma_3)$ corresponds to P_z electric-dipole transition, while $W_1(\Gamma_1) \rightarrow Z_3(\Gamma_4)$ to a P_x electric dipole allowed transition. The selective excitation spectra in 3F_3 show a similar behaviour.

GGG:Tm³⁺

The measurement of Tm³⁺ satellite structure in GGG is more difficult and practically only three satellites have been separated. The 3H_4 emission and excitation spectra for these centers are similar to those of the second type, described above for YAG:Tm; i.e. in the 3H_4 emission spectra present intense lines corresponding to $W_1 \rightarrow Z_2$, Z_3 transitions.

The absorption, selective excitation and emission spectra as well as the decay data suggest that in YAG:Tm and GGG:Tm the satellite lines could be assigned to Tm³⁺ in c-perturbed sites by non-stoichiometric defects. The observation of the additional lines, corresponding to forbidden $\Gamma_1 \rightarrow \Gamma_1$ transitions in D_2 , such as $W_1(\Gamma_1) \rightarrow Z_2(\Gamma_1)$ as well as the enhancement of other lines intensities suggest a lowering of the local symmetry and also changes of the main distortion axes. Polarization spectroscopy might give further information. We could not detect lines connected with pairs or ions in octahedral sites.

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Fig. 1. ${}^3\text{H}_4$ emission spectra for N and P. Tm^{3+} centers.

Fig. 2. ${}^3\text{F}_4$ Stark levels for various Tm^{3+} sites in YAG.