

Inhomogeneous broadening and splitting of lines in spectra of YAG:Tm

M.N. Popova, E.P. Chukalina, S.A. Klimin, M.-Ch. Chou

Abstract. The shape and fine structure of lines due to Tm^{3+} $f-f$ electronic transitions in multifunctional $\text{Y}_3\text{Al}_5\text{O}_{12}$ garnet crystals have been studied by high-resolution spectroscopy. The observed inhomogeneously broadened lines have a Lorentzian shape, suggesting that point defects make a predominant contribution to the inhomogeneous broadening. Moreover, Y_{Al} antisite defects, which are formed during high-temperature melt growth, produce spectral satellites near the main lines.

Keywords: YAG:Tm, high-resolution spectroscopy, line shape, spectral satellites.

1. Introduction

Yttrium aluminium garnet (YAG), $\text{Y}_3\text{Al}_5\text{O}_{12}$, crystals offer excellent mechanical and thermal properties, are chemically stable, can readily be doped with rare-earth (RE) ions (which substitute for yttrium to form one type of activator centre), are suitable for the fabrication of laser ceramics (owing to their cubic structure) and are among the best doping hosts for a variety of lasers [1–11]. Like YAG:Ho, YAG:Tm crystals are known primarily as an efficient gain medium for high-power infrared lasers operating in the $2\ \mu\text{m}$ range, which are used for the generation of attosecond pulses and optical harmonics, up to the X-ray range [1, 5, 6], as well as in materials processing and medical applications [9, 11]. At present, YAG:Tm crystals are actively used in modern quantum technologies. Position D_2 , where Tm^{3+} ions substitute for Y^{3+} , has such symmetry that all electronic levels of the Tm^{3+} ions are singlets and there is no magnetic hyperfine structure (HFS). Since the nuclear spin of ^{169}Tm , the only thulium isotope, is $1/2$, there is also no quadrupole HFS. An external magnetic field lifts the degeneracy of the $\pm 1/2$ nuclear sub-levels. They have a long coherence time and can be used to build a lambda-type three-level system for optical quantum memory, with a third level in the optical range. A variety of optical quantum memory schemes utilising the $^3\text{H}_6 \rightarrow ^3\text{H}_4$ transition of Tm^{3+} in YAG have been demonstrated [12–17]. This transition ($\lambda \approx 793\ \text{nm}$) is accessible to commercial diode lasers, the $^3\text{H}_4$ level has a rather long lifetime (800 μs [18]),

and the phase relaxation time is 81 μs in the absence of a magnetic field ($B = 0$) and 111 μs at $B = 100\ \text{G}$ [18].

Detailed knowledge of the low-temperature optical spectrum of YAG:Tm crystals is useful for applications in quantum technologies. This paper examines inhomogeneous broadening and splitting of lines in YAG:Tm.

2. Experimental

YAG:Tm (0.05 at %) crystals were grown by the Czochralski technique at the Center of Crystal Research, National Sun Yat-Sen University. For comparison, YAG:Nd (1 %) crystals we used as well. Since garnets have a cubic structure, in the absence of a magnetic field their optical absorption is independent of light propagation direction and polarisation. YAG:Tm samples for optical studies were unoriented and were 5.9 and 10.05 mm in thickness. The samples were placed in a Cryomech ST403 closed cycle helium cryostat.

Their spectra were measured at temperatures from 5 to 20 K and frequencies from 5000 to 22500 cm^{-1} on a Bruker IFS 125HR high-resolution Fourier transform spectrometer. Note that the use of a highly stabilised He–Ne laser as an internal wavenumber scale reference in Fourier spectroscopy ensures high accuracy in determining absolute frequencies of spectral lines (typically $\sim 1/10$ of the resolution).

3. Results and discussion

Figure 1 shows the lowest frequency absorption lines, at 12604.38 and 5554.95 cm^{-1} , due to the $^3\text{H}_6 \rightarrow ^3\text{H}_4$ and $^3\text{H}_6 \rightarrow ^3\text{F}_4$ transitions from the ground state of Tm^{3+} in YAG, and the line corresponding to the transition from the ground level to the second level of the $^3\text{H}_5$ multiplet (8345.82 cm^{-1}). The shape of all three lines is well represented by Lorentzians, with a full width at half maximum $\delta\nu = 0.54, 0.96$ and $0.1\ \text{cm}^{-1}$, respectively. That the 12604.38 cm^{-1} line ($\lambda = 793.37\ \text{nm}$), employed in optical quantum memory devices [12–17], has a Lorentzian shape was demonstrated previously by Veissier et al. [19] by scanning the absorption envelope of a YAG:Tm (0.1 at %) crystal at 2 K with narrow-band ($\sim 1\ \text{MHz}$) laser light. They reported the following parameters of the line: $\delta\nu = 17\ \text{GHz}$ or $0.57\ \text{cm}^{-1}$ and peak absorption coefficient (at a frequency $\nu_0 = 377868\ \text{GHz}$ or $126904.32\ \text{cm}^{-1}$) $\alpha_0 = 2.3\ \text{cm}^{-1}$. The measured parameters of our YAG:Tm crystal ($\delta\nu = 0.54\ \text{cm}^{-1}$ and $\alpha_0 = 0.96\ \text{cm}^{-1}$) indicate that the thulium concentration in it is a factor of ~ 2.5 lower than that in the crystal studied by Veissier et al. [19].

The width of the lines shown in Fig. 1 was found to remain unchanged down to a temperature of $\sim 20\ \text{K}$, indicating that they were inhomogeneously broadened. The Lorentzian shape

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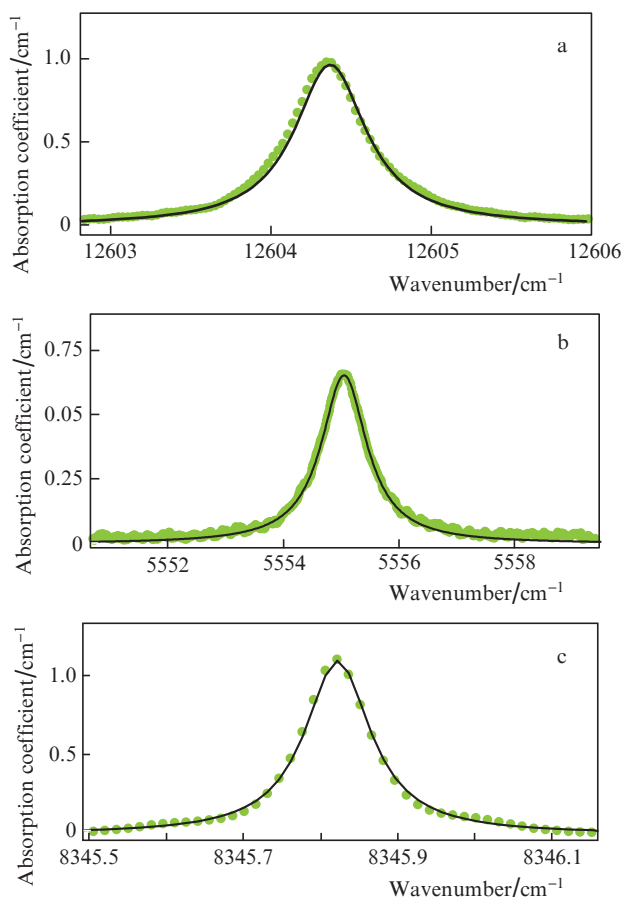


Figure 1. Shape of the lines corresponding to optical transitions of the Tm^{3+} ions in the YAG:Tm (0.05 at %) crystal (a, b) from the ground level to the lowest levels of the ${}^3\text{H}_4$ (a) and ${}^3\text{F}_4$ (b) excited state multiplets and the second level (8345.82 cm^{-1}) of the ${}^3\text{H}_5$ multiplet (c). The filled circles represent the experimental data and the curves represent the best fit Lorentzians. The spectra were measured at 5 K.

of the inhomogeneously broadened lines indicates that the broadening is predominantly due to point defects [20].

Comparing the lattice parameters of stoichiometric yttrium gallium garnet crystals (grown from fluxes at a relatively low temperature) and crystals prepared by Czochralski pulling, a high-temperature technique, Geller et al. [21] showed that, during the high-temperature growth process, a considerable fraction of the yttrium ions occupied the gallium (octahedral) site. In addition, they assumed that, in yttrium aluminium garnet crystals, a small fraction of the yttrium ions also occupied the aluminium (octahedral) site, in spite of the large difference in ionic radius between yttrium (0.9 \AA) and aluminium (0.535 \AA). Later, this assumption was validated by spectroscopic evidence [22]. Satellite lines observed in spectra of YAG:Nd crystals, whose intensity was independent of neodymium concentration, were attributed to Nd ions near Y_{Al} antisite defects. In the Fig. 2 inset, these lines are labelled P_1 and P_2 . The intensity of line M depends quadratically on the neodymium concentration. This line arises from pair centres. As shown by Agladze et al. [23], the garnet structure has three inequivalent sites for RE ions in the nearest-neighbour environment of an Y_{Al} antisite defect and three such sites for RE ions in its second-neighbour environment. These sites were assumed to correspond to the six satellite lines observed in the spectrum of a YAG:Er crystal [23].

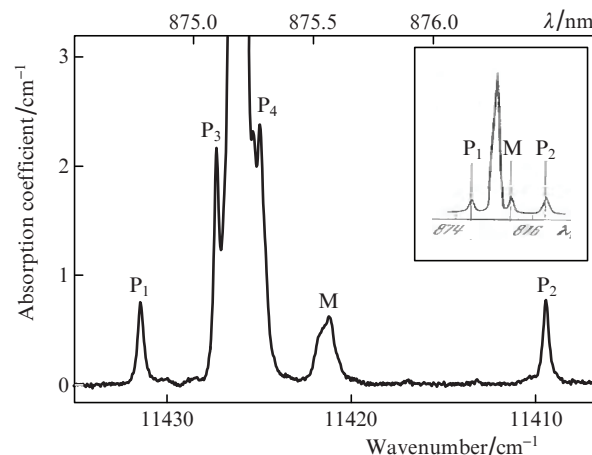


Figure 2. Main line (11426 cm^{-1}) of the $\text{Nd}^{3+} {}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$ transition in a YAG:Nd (1 at %) crystal and satellite lines of different origins; $T = 5\text{ K}$. Inset: analogous spectrum from Ref. [22].

Figure 3 shows the two lowest frequency, strong lines due to transitions from the ground state to ${}^3\text{H}_5$ multiplet levels in YAG:Tm near $1.2\text{ }\mu\text{m}$. The lines are narrower than those of other transitions ($\sim 0.1\text{ cm}^{-1}$), and there are many well-resolved satellites roughly equal in intensity. Since the thulium concentration cannot exceed 0.1 at %, the concentration of pair activator centres is negligible [22, 23] and all the satellites correspond to transitions of Tm^{3+} ions located near Y_{Al} antisite defects. The total number of satellites for the two lines is 18, which is more than might be expected with allowance for the Tm^{3+} ions located in the nearest- and second-neighbour environments of an Y_{Al} antisite defect (a total of 12). It is reasonable to assume that the satellites closest to the central lines are due to the third-neighbour environment. Like the main lines, the inhomogeneously broadened satellite lines have a Lorentzian shape due to the influence of more distant point defects. Clearly, the predominant contribution to the broadening is made by the Y_{Al} antisite defects, whose strength (propor-

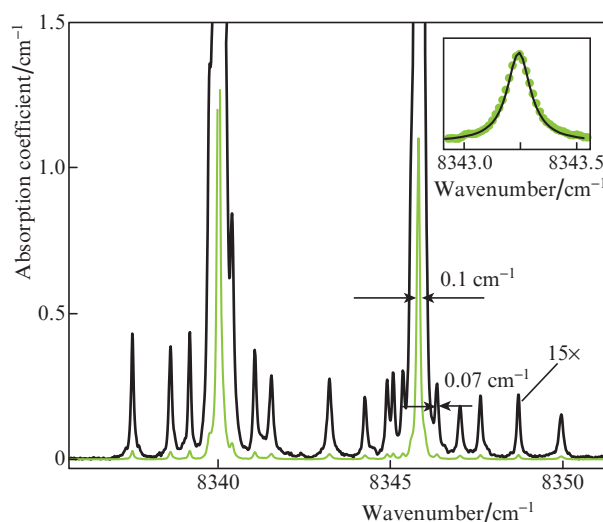


Figure 3. Main lines (8340 and 8345.8 cm^{-1}) of the $\text{Tm}^{3+} {}^3\text{H}_6 \rightarrow {}^3\text{H}_5$ intermultiplet transition in the YAG:Tm (0.05 at %) crystal and their satellites; $T = 5\text{ K}$. Inset: one of the satellites (filled circles) and the best fit Lorentzian (solid line).

tional to the difference in ionic radius between the host ion and substituent, which is $\Delta r = 0.365 \text{ \AA}$ for Y^{3+} substituting on the Al^{3+} site) far exceeds that of dopant-related defects ($\Delta r = 0.025 \text{ \AA}$ in the case of Tm^{3+} substituting for eight-coordinate Y^{3+} ions).

4. Conclusions

Yttrium aluminium garnet crystals activated with a low concentration of thulium ions, YAG:Tm, which are of interest primarily for quantum technologies, have been studied for the first time by high-resolution spectroscopy in a wide spectral range. The observed inhomogeneously broadened lines have been shown to have a Lorentzian shape, due to point defects. The predominant contribution to the broadening is made by the Y_{Al} antisite defects, which are formed in YAG crystals during high-temperature melt growth (by the Czochralski technique). Such defects distort the crystal field around nearby RE activator ions, shifting spectral lines and producing satellites of the main lines of the RE centres. In the case of YAG:Tm (0.05 at %) crystals, we were able to observe satellites due to Tm^{3+} ions located in up to the third-neighbour environment of Y_{Al} antisite defects.

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