On the origin of the satellite structure of luminescent spectra of Cr^{3+} in YAG

LETTER TO THE EDITOR

On the origin of the satellite structure of luminescent spectra of Cr^{3+} in YAG

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Abstract. The origin of the main satellites observed in the luminescence R_1 and R_2 spectra of Cr^{3+} in melt-grown YAG is discussed and it is shown that the regular intensity ratio 1:3:3 of these satellites is consistent with a model accounting for the perturbing effect of a Y^{3+} ion in an anomalous octahedral a-site.

The luminescence spectrum of Cr^{3+} in YAG was widely investigated both for the basic interest in the electronic structure of this ion in crystals and for the practical use of Cr^{3+} as a sensitizer for the excitation of laser active rare-earth ions in this important crystal. Early investigations of the sharp R_1 and R_2 luminescence lines of Cr^{3+} in substitutional octahedral positions of flux-grown YAG have revealed the presence of several very weak satellites [1]. Further investigation of these satellites in melt-grown crystals revealed important features such as the existence of several categories of satellite and enabled determination of their line positions, excitation spectra and lifetime [2, 3]. Several possible sources of these satellites were considered, such as the isotopic composition of Cr^{3+} or unintentional departures from stoichiometry. The aim of this paper is a further investigation of these satellites in an attempt at structural assignment.

The luminescence measurements were performed at 7 K or 77 K by using the second harmonic of the YAG: Nd laser for excitation. The 532 nm radiation band is absorbed non-selectively in the broad $^4T_2$ absorption band and thus excites all (or most) of the structural centres that originate from the normal octahedral site of chromium. Various Czochralski-grown YAG crystals doped with only Cr^{3+} or with Cr^{3+} and Tm^{3+} were used in this investigation, the concentration of Cr being a few tenths of one percent.

A very important feature of the luminescence spectra at 7 K is the systematic presence of a regular structure of satellites around the emission line: three of these, with intensity ratios of 3:3:1 are clearly resolved, as shown in figure 1. These satellites are denoted by S_1, S_3 and S_4 as in previous studies [2, 3]. Other unresolved satellites are evident as shoulders of the R_1 line. At 77 K, where the emission R_2 becomes

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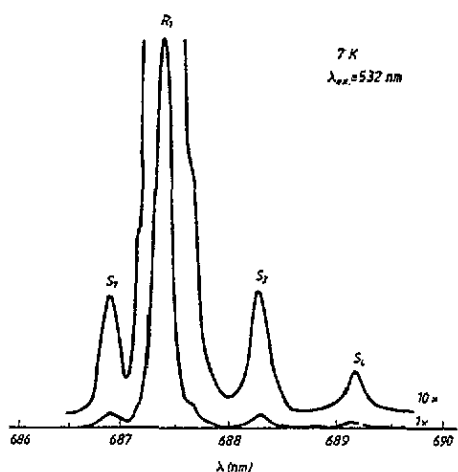
Figure 1. Luminescence R_1 of Cr^{3+} in YAG: Cr (0.2 at.%), Tm (3 at.%) at 7 K under 532 nm excitation.
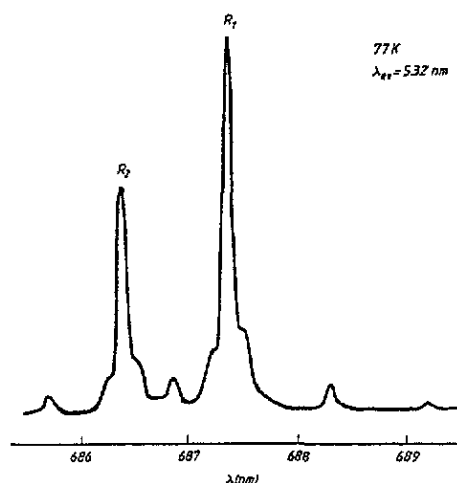
Figure 2. Luminescence lines R_1 and R_2 of Cr in YAG: Cr (0.2 at.%), Tm (3 at.%) at 77 K under 532 nm excitation.

also important, it shows a similar satellite structure, as seen in figure 2. Since the spectrum shown in figure 2 was taken at a better resolution, the shoulders on lines R_1 and R_2 are more evident.

The relative intensity of the satellite S_4, the weakest of these three, to the total intensity of lines in the spectrum is about 1.5%. The presence of these satellites in the flux-grown crystals [1], but with a much lower intensity, shows clearly that their origin must be in the differences between the high- and low-temperature grown crystals and it is not a property of the Cr^{3+} ion. A well known difference between the high-temperature (melt-grown) and low-temperature (flux-grown) rare-earth garnet crystals lies in the fact that in the former, some of the octahedral sites, normally occupied by Al^{3+} or Ga^{3+}, could be also occupied by the rare-earth ions (Y^{3+} in the case of YAG) that in the ideal garnet structure are placed normally in the dodecahedral c-sites. The degree of departure from stoichiometry depends on the difference between the ionic radii of the rare-earth and of Al^{3+} (or Ga^{3+}) and on the temperature, crystallographic direction and speed of growth: in the case of melt-grown YAG crystals the Y^{3+} ions occupy about 1.5–2% of the octahedral a-sites. Owing to the large difference between the octahedral radii of Y^{3+} and Al^{3+} this substitution produces large local distortions of the crystalline lattice that could perturb the ideal symmetry of the neighbouring cationic sites at quite large distances [4, 5].

Trivalent chromium enters the YAG lattice only in the octahedral a-sites preserving the local trigonal symmetry with inversion (C_{3i}) of the site. The closest coordination spheres of a-sites around each such a-site are: a first sphere containing eight sites (in the corners of a cube) at $0.4330a$ (a being the cubic unit cell parameter of the garnet), a second sphere of six sites (in the corners of a regular octahedron) at $0.5a$, a third sphere of 12 a-sites at $0.7071a$ and so on. The oxygen octahedra surrounding the sites do not share edges or corners with other such octahedra. However a Cr^{3+} ion at an octahedral a-site will feel the perturbing effect of the accidental Y^{3+} ions in a-sites, the perturbing effect depending on the distance between these centres and on the direction of perturbation with respect to the trigonal C_3 axis [6]. Because of

this, the eight a-sites in the first coordinating sphere surrounding the central a-site could be separated into two groups: a group containing the two sites placed on the diagonal of the cube that is coincident with the C_3 axis of the central a-site, and a group of the other six sites that are all identical with respect to this axis; it would be expected that Y^{3+} ions substituting a-sites of these two groups, although placed at the same distance from the central site, will perturb the crystal field at this site in a different manner, thus inducing two satellites in the optical spectra. The a-sites in the second coordination sphere, which has a radius only a little larger than the first one, are all identical with respect to the local C_3 axis so the Y^{3+} (a) ions on this sphere are expected to produce only a satellite in the Cr^{3+} spectrum.

In so far as the a-sites from the third sphere are concerned, although they are not all equivalent from the point of view of orientation, their much larger distance from the central site could make the differences unresolvable.

The relative intensities of the satellites in the Cr^{3+} spectrum could be calculated assuming that the Y^{3+} (a) distribution is random and equiprobable for each a-site. In this case the probability of having n Y^{3+} (a) ions in a coordination sphere containing m sites around the central a-site is

$$P_{mn} = [m!/n!(m-n)!]C^n(1-C)^{m-n} \tag{1}$$

where C is the relative concentration of Y^{3+} (a) sites with respect to the total number of a-sites. Thus in the case of low concentrations C, the probability of having a Y^{3+} (a) ion in a sphere of m sites is approximately

$$P_{m1} \simeq mC. \tag{2}$$

Assuming that the perturbation produced by the surrounding Y^{3+} (a) sites at the central Cr^{3+} sites does not change the oscillator strength of the transition of the Cr^{3+} ion, but contributes to a shift of the lines, leading to satellites, the relative intensities of these satellites produced by a Y^{3+} (a) in one of these coordination spheres will be:

(i) For the first group (two sites on axis C_3 as described above) of the first coordination sphere, $P_{2,1} \simeq C$.

(ii) For the remaining six sites of the first sphere, $P_{6,1} \simeq 6C$.

(iii) For the six sites of the second sphere, $P_{6,1} \simeq 6C$.

(iv) For the twelve sites of the third sphere $P_{12,1} \simeq 12C$.

According to this treatment, the statistical perturbing effect of Y^{3+} (a) ions in the first two coordinating spheres of a-sites around the Cr^{3+} sites leads to the appearance of three satellites of relative intensities 1:3:3. This corresponds exactly to the intensity ratios of the satellites S_4, S_3 and S_1 observed experimentally; thus these satellites could be connected in a consistent way with the perturbations produced by Y^{3+} (a) ions. A further argument in favour of this identification is that the satellite S_4, of lowest intensity, is the most shifted from the R-line, in accordance with the position of the perturbation sources on the local symmetry axis of the Cr^{3+} sites. The relative intensity of this satellite with respect to the R-line (whose probability corresponds in equation (1) to $n = 0$ and is equal to unity) is $2C$. The measured intensity ratio is somewhat lower than one would expect by taking for Y^{3+} (a) the concentration $C = 0.015$–0.020 as measured for melt-grown pure YAG crystals. However it is known that

the doping of garnet crystals with very low amounts of ions with a strong preference for the a-sites strongly reduces the process of departing from stoichiometry described above [4]; this effect is thus consistent with the present observation.

It would, however, be difficult to state now which of the satellites S_1 and S_3 corresponds to perturbation in the first or in the second sphere, although the much smaller shift of S_1 could be an indication of a second sphere perturbation. A rough estimate suggests that the shoulder observed on the long-wavelength side of the R-line could be caused by the perturbation due to Y^{3+} (a) ions in the third sphere while the shoulder on the short-wavelength side could be connected with the presence of other doping ions (the sample giving the spectra presented in figures 1 and 2 contains also 3. at.% Tm^{3+}).

In conclusion a structural model taking into account the perturbing effect of defective Y^{3+} (a) sites on the central Cr^{3+} a-site could explain important features of the satellite lines observed in the R-line luminescence of Cr^{3+} in YAG. Thus this is the first work to show the effect of departures from stoichiometry in garnet crystals on the optical properties of transition ions in octahedral sites.

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