Influence of scandium on luminescence YSAG:Yb$^{3+}$

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Abstract. In this work, the effects of scandium introduction on the luminescence of yttrium scandium (Sc) aluminium garnet powders doped with ytterbium (YSAG: Yb$^{3+}$) were investigated. Based on photoluminescence (PL) and photoluminescence excitation (PLE) spectra we made conclusions about the influence of scandium concentration and location on emission properties of ytterbium ions in YSAG. On the one hand, an analysis of the data showed that the increase of Sc concentration leads to broadening spectral lines regardless of a location of scandium ions in the crystal structure. On the other hand, the photoluminescence intensity of ytterbium ions in YSAG is more sensitive to scandium in the octahedral site than to scandium in the dodecahedral site.

1. Introduction

Solid-state optical media doped with Yb$^{3+}$ ions are attracting great attention due to the prospects for the creation on their basis of active media of tunable femtosecond lasers and quantum generators operating on the principle of mode-locking. [1, 2, 3]. Optical media based on yttrium-aluminum garnet (YAG) and its solid solutions are of particular interest. A promising representative of these solid solutions are materials based on laser ceramics of yttrium-scandium-aluminum garnet (YSAG), the concentration of scandium in which can reach 30 at. % [4]. Sc$^{3+}$ ions in YSAG can substitute for Y$^{3+}$ and Al$^{3+}$, forming a dodecahedral and octahedral environment with the surrounding oxygen ions, respectively. Due to the difference in ionic radii of scandium and cations, in the place of which it is incorporated, the introduction of scandium affects the structural features of YSAG and the parameters of the crystal field. This should lead to changes in the luminescence of the YSAG doped with rare-earth activators. The aim of this work was to study the effect of scandium on the luminescent properties of YSAG: Yb$^{3+}$.

2. Materials and methods

The samples under study were powder materials used to create laser ceramics based on YSAG: Yb$^{3+}$ containing 10 at.% ytterbium and various concentrations of scandium (Table 1). The samples were synthesized in the research laboratory of ceramic and technology of chemistry of NCFU according to the method described in the work [5].

To measure the luminescent properties, we used a spectrometric complex based on a monochromator MDR-41 (JSC Lomo). The photoluminescence spectra were measured upon excitation of the samples by radiation with a wavelength of 918 nm, which corresponds to the
transition from the ground state of the Yb$^{3+}$ ion to the third excited one. Photoexcitation spectra were measured by recording luminescence at a wavelength of 1029 nm.

**Table 1.** Composition of the studied samples YSAG:Yb$^{3+}$.

| №  | Composition                     | $\text{Sc}_Y$, at.% | $\text{Sc}_Al$, at.% | Total Sc content, at.% | Sample |
|----|--------------------------------|---------------------|----------------------|------------------------|--------|
| 1  | (Y$_{2.55}$Yb$_{0.25}$Sc$_{0.20}$)[Sc$_{0.20}$Al$_{1.80}$][Al$_3$]O$_{12}$ | 6.67                | 10                   | 8                      | $D_1$  |
| 2  | (Y$_{2.15}$Yb$_{0.25}$Sc$_{0.60}$)[Sc$_{0.40}$Al$_{1.60}$][Al$_3$]O$_{12}$ | 20                  | 20                   | 20                     | $D_2$  |
| 3  | (Y$_{2.25}$Yb$_{0.25}$Sc$_{0.50}$)[Sc$_{0.50}$Al$_{1.50}$][Al$_3$]O$_{12}$ | 16.67               | 25                   | 20                     | $D_3$  |
| 4  | (Y$_{2.35}$Yb$_{0.25}$Sc$_{0.40}$)[Sc$_{0.60}$Al$_{1.40}$][Al$_3$]O$_{12}$ | 13.33               | 30                   | 20                     | $D_4$  |
| 5  | (Y$_{2.55}$Yb$_{0.25}$Sc$_{0.20}$)[Sc$_{0.80}$Al$_{1.20}$][Al$_3$]O$_{12}$ | 6.67                | 40                   | 20                     | $D_5$  |
| 6  | (Y$_{2.70}$Yb$_{0.30}$)[Al$_{1.70}$][Al$_3$]O$_{12}$ | 0                   | 0                    | 0                      | $D_6$  |
| 7  | (Y$_{2.69}$Yb$_{0.29}$Sc$_{0.08}$)[Sc$_{0.15}$Al$_{1.85}$][Al$_3$]O$_{12}$ | 2.61                | 6.5                  | 4.15                   | $D_7$  |
| 8  | (Y$_{2.52}$Yb$_{0.25}$Sc$_{0.32}$)[Sc$_{0.15}$Al$_{1.85}$][Al$_3$]O$_{12}$ | 7.67                | 7.5                  | 7.6                    | $D_8$  |
| 9  | (Y$_{2.56}$Yb$_{0.29}$Sc$_{0.15}$)[Sc$_{0.25}$Al$_{1.75}$][Al$_3$]O$_{12}$ | 5                   | 12.5                 | 8                      | $D_9$  |
| 10 | (Y$_{1.80}$Yb$_{0.30}$Sc$_{0.90}$)[Sc$_{0.60}$Al$_{1.40}$][Al$_3$]O$_{12}$ | 30                  | 30                   | 30                     | $D_{10}$|

3. Results

The measured photoluminescence excitation and luminescence spectra are shown in figures 1(a) and (b), respectively.

![Figure 1](image_url). Normalized photoluminescence excitation (a) and luminescence (b) spectra of YSAG: Yb$^{3+}$ powders with different scandium content.

As can be seen from figure 1 (a), the three most intense bands with maxima at 918, 941, and 969 nm are distinguished on photoexcitation. These bands correspond to electronic transitions in the Yb$^{3+}$ ion from the ground $^2\text{F}_{7/2}$ multiplet to three excited Stark sublevel of the $^2\text{F}_{5/2}$ multiplet [6].

Figure 1 (b) shows that the luminescence spectra exhibit 5 characteristic bands with maxima at 969, 986, 1006, 1029, and 1048 nm. The peak with a maximum of 969 nm corresponds to transitions from the upper sublevel of the $^2\text{F}_{5/2}$ multiplet to the second and third sublevels of the $^2\text{F}_{7/2}$ multiplet, as well as a transition from the lower sublevel of the $^2\text{F}_{5/2}$ multiplet to the main sublevel of the $^2\text{F}_{7/2}$ multiplet. In the band with a maximum of 986 nm, a transition occurs from the upper sublevel of the $^2\text{F}_{5/2}$ multiplet to the fourth sublevel of the $^2\text{F}_{7/2}$ multiplet. The peak with a maximum at 1006 nm corresponds to a transition from the second sublevel of the $^2\text{F}_{5/2}$ multiplet to the second and third sublevels of the $^2\text{F}_{7/2}$ multiplet. In the region of the main peak with a maximum of 1029 nm, three transitions are realized: one transition is from the second sublevel of the $^2\text{F}_{5/2}$ multiplet to the fourth...
sublevel of the $^2F_{7/2}$ multiplet, two transitions are from the lower sublevel of the $^2F_{7/2}$ multiplet to the second and third sublevels of the $^2F_{7/2}$ multiplet. The peak with a maximum at 1048 nm is associated with the transition from the lower sublevel of the $^2F_{5/2}$ multiplet to the upper sublevel of the $^2F_{7/2}$ multiplet. It should be noted that the absence of maxima for some transitions is caused by the broadening of the elementary bands and their strong spectral overlap.

An analysis of the obtained spectral distributions showed that an increase in the total concentration of scandium in YSAG leads to broadening of the bands in both the photoexcitation and luminescence spectra. As an example, figure 2(a) shows the dependence of the full width at half maximum (FWHM) for the luminescence band with a maximum at 1029 nm on the scandium concentration. It can be seen from this figure that the FWHM of the luminescence peak is 9.4 nm for pure YAG: Yb$^{3+}$ (sample D6), but the introduction of 30 at. % scandium led to the increase of the width to 11.8 nm (sample D10). In [7], when studying the luminescence of YSAG: Yb$^{3+}$ with a scandium content of 25 at. %, the half-width of the peak with a maximum at a level of 12.5 nm was obtained, which was explained by structural changes in garnet associated with disordering of the crystal lattice upon the introduction of high concentrations of Sc. Apparently, a similar situation is observed in our case.

![Figure 2](image_url)

**Figure 2.** The dependence of the FWHM on the total Sc content in the sample (a) and the dependence of photoluminescence on the scandium concentration at the dodecahedral site YSAG: Yb$^{3+}$ (b).

It should be noted that an increase in the proportion of scandium in the dodecahedral site relative to the octahedral one at a fixed total concentration (samples from D3 to D5) leads to a slight increase in the intensity of the YSAG:Yb$^{3+}$ luminescence band with a maximum of 1029 nm (figure 2(b)). At the same time, an increase in the Sc fraction in the octahedral position from 7.5 at. % (sample D8) to 40 at. % (sample D5) at a constant Sc concentration in the dodecahedral position causes a significant decrease in the photoluminescence. This dependence is in good agreement with the previously reported results [7, 8, 9]. For example, according to Feng et al. [9], an increase in the scandium content in the aluminum site to 75 at. % led to a decrease in the photoluminescence intensity by about 1.5 times, compared with a pure YAG: Yb$^{3+}$ sample. We assume that, the reason for this is also the structural changes in the garnet lattice after the introduction of scandium. Despite the fact that the 4f-transitions in the Yb$^{3+}$ ion are magnetic dipole and practically insensitive to the strength and symmetry of the crystal field, it was previously shown in work [10] that various materials, depending on the local symmetry of the Yb$^{3+}$ site, are characterized by different values of the branching ratio for the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition. In other words, structural changes in the material can affect the relaxation processes in Yb$^{3+}$. Thus, taking into account the type of $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition, the effect of scandium on photoluminescence is mainly associated with a change in the efficiency of ytterbium quenching processes.
Considering a number of works [4, 11] devoted to the study of the YSAG: Yb$^{3+}$ structure, it should be noted that an increase in the scandium concentration from 6 to 20 at. % in the dodecahedral site leads to a decrease in the YSAG lattice parameter from 12 to 11.72 Å. At the same time, the change in the scandium concentration in the octahedral position does not have such a significant effect on the structural parameters, but it can lead to a disordered crystal lattice and formation of intrinsic defects. Such changes in the structure, apparently, can affect the processes of radiative and nonradiative relaxation in YSAG: Yb$^{3+}$.

Therefore, we can conclude that structural changes leading to the contribution redistribution of possible relaxation pathways of Yb$^{3+}$ ion, as well as changes affecting mechanisms of the luminescence quenching in YSAG: Yb$^{3+}$ cause the change in the YSAG: Yb$^{3+}$ luminescence intensity with an increase in the scandium concentration.

4. Conclusion

In this work, we studied the effect of the scandium concentration in YSAG: Yb$^{3+}$ solid solutions on the photoluminescence of ytterbium ions. It is shown that an increase in the total concentration of scandium in YSAG leads to broadening of the bands in the photoexcitation and luminescence spectra, which can be attributed to the structural disordering of the garnet crystal lattice. It was found that scandium ions in dodecahedral (site of Y$^{3+}$) and octahedral (site of Al$^{3+}$) sites of the garnet have a different effect on the photoluminescence intensity of YSAG: Yb$^{3+}$. So, an increase in the concentration of scandium in the octahedral site leads to a decrease in the photoluminescence intensity, while an introduction of scandium into the dodecahedral site causes an increase in the photoluminescence of Yb$^{3+}$. The effect of scandium on the luminescence intensity is apparently associated with the redistribution of possible relaxation paths of the excited Yb$^{3+}$ ion and changes in the mechanisms of quenching of radiative transitions.

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