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Quantum efficiency of the down-conversion process in Bi^{3+}–Yb^{3+} and Ce^{3+}–Yb^{3+} co-doped garnets

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ABSTRACT

In order to evaluate the quantum efficiency and to establish the mechanism of down-conversion processes in $Bi^{3+}-Yb^{3+}$ and $Ce^{3+}-Yb^{3+}$ co-doped YAG ($Y_3Al_5O_{12}$) and GGG ($Gd_3Al_5O_{12}$) garnets, direct measurements of quantum yield (QY) were performed along with studies of photoluminescence (PL), photoluminescence excitation (PLE), and photoluminescence decay kinetics. The studied materials have been prepared either in the form of powders synthesized by the sol-gel method or single crystalline films grown by the liquid phase epitaxy method. Concentrations of Bi^{3+}, Ce^{3+} and Yb^{3+} ions in the studied epitaxial films were estimated using X-ray diffraction and optical absorption techniques. The obtained results testify a non-cooperative energy transfer mechanism for the Ce^{3+}–Yb^{3+} co-doped YAG with a conversion ratio (which should be 2.0 for an ideal quantum cutting mechanism) less than 1.0. At the same time, for Bi^{3+}–Yb^{3+} co-doped YAG and GGG this conversion ratio was found to be close to 2.0, suggesting quantum cutting via cooperative energy transfer from one Bi^{3+} ion to two Yb^{3+} ions.

1. Introduction

The down-conversion process (cutting one high energy photon into two low energy ones) is continuously discussed as a possible way to modify the solar spectrum and thus to enhance the efficiency of silicon solar cells (see [1–3] and references therein). The main drawback of the down-converting phosphors doped with lanthanide ions like Pr^{3+}, Gd^{3+}, Er^{3+}, or Tm^{3+} is the narrow spectral range and the low cross section of the *f-f* absorption. From this point of view, "energy donor" ions with efficient broad-band absorption in the UV to blue range look much more attractive. Recently, several systems doped with Bi^{3+}–Yb^{3+} [4–20], Ce^{3+}–Yb^{3+} [8,21–35], Eu^{2+}–Yb^{3+} [8,36–38], and Yb^{2+}–Yb^{3+} [8,39] have been reported in literature as broad-band down-convertors possibly applicable for terrestrial solar spectrum modification. In all these systems the Yb^{3+} ion was chosen as the energy "acceptor". Due to its simple energy structure with only one excited manifold and the characteristic emission around 1 μm, i.e., just above the band gap of silicon, it is considered as the best possible acceptor of the excitation energy in such double doped, ionic-like down-convertors. However, even if the donor ion has efficient broad-band absorption and there is energy transfer from this donor to Yb^{3+} ions, the mechanism and efficiency of this energy transfer remains unknown. In other words, the question remains whether the energy transfer is cooperative, resulting in quantum cutting, or non-cooperative (one-to-one photon energy transfer), which is similar to down-shifting. This should depend not only on the specific combination of dopant ions but also on the host material. It is well-known that *s-sp* transitions of Bi^{3+} ions as well as *f-d* transitions of lanthanides, such as Ce^{3+}, Eu^{2+}, or Yb^{2+}, depend strongly on the host lattice (see e.g. [40,41]).

One of possible ways to identify unambiguously the photon cutting mechanism is the photon correlation technique that was recently applied successfully for $NaLaF_4$:Pr^{3+} [42]. Another approach is a direct measurement of the quantum yield (QY) of luminescence of such down-converting materials (see e.g. [43,44]). The latter method allows also to measure the overall efficiency of the emission process, which is crucial for eventual application of the examined material for solar spectrum modification.

In spite of numerous papers devoted to the down-conversion process

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Table 1
Melts compositions used for the films growth.

Melt no.	Molar coefficients				
	R_1	K_1	K_2	R_3	R_4
G0	5.0	–	–	16.0	19.5
G1	5.0	–	–	16.0	17.4
G2	5.0	18.1	–	16.0	17.4
Y0	5.0	–	–	–	1.5
Y1	5.7	9.5	–	16.0	6.0
Y2	5.7	9.5	1.9	16.0	6.4
Y3	5.7	9.5	0.96	16.0	6.8

in various phosphors co-doped with Bi^{3+}–Yb^{3+} [4–20], up to now there is no evidence for the occurrence of quantum cutting in these materials, in the sense that two photons emitted by Yb^{3+} are produced at the expense of one photon absorbed by Bi^{3+}. Moreover, the overall quantum efficiency of luminescence in such Bi^{3+}–Yb^{3+} co-doped phosphors is, in general, unknown, except for our very recent results obtained for Bi^{3+}–Yb^{3+} co-doped $Y_4Al_2O_9$ (YAM) [43] and Gd_2O_3 [44]. In particular, our previous studies revealed that both in YAM:Bi,Yb and Gd_2O_3:Bi,Yb the conversion ratio (which should be 2.0 for an ideal quantum cutting mechanism) is not more than 1.0. It is of interest to check the situation in other Bi^{3+}–Yb^{3+} co-doped phosphors, in particular in garnets, where the Bi^{3+} absorption ($^1S_0 \rightarrow {}^3P_1$ transition) occurs at somewhat higher energies (see e.g. [15]). Moreover, to the best of our knowledge, the quantum efficiency of Bi^{3+} luminescence in garnet hosts was not yet reported.

A similar situation is found in phosphors co-doped with Ce^{3+}–Yb^{3+}. There are several reports on the down-conversion process in various crystalline and glass hosts co-doped with Ce^{3+}–Yb^{3+} [21–34], however, there is no solid evidence for the quantum cutting mechanism occurring in any of these phosphors. In particular, one of such phosphors drawing the attention of researchers is the Ce^{3+}–Yb^{3+} co-doped $Y_3Al_5O_{12}$ (YAG) [22–24,34,35]. Ce^{3+}-doped YAG is a well-known yellow phosphor with high quantum efficiency of Ce^{3+} emission (see e.g. [40,45]), therefore, the down-conversion process in this material seemed to be very attractive. However, direct measurements of the quantum yield of Ce^{3+}–Yb^{3+} co-doped YAG ceramics [23] as well as a comparison of the measured and simulated decay curves of Ce^{3+} emission at different concentrations of Yb^{3+} ions [46] did not confirm the quantum cutting mechanism in YAG:Ce,Yb. This points to the need of further studies of these and other materials possibly applicable for solar spectrum modification via down-conversion mechanism, especially in view of the recent attempts to fabricate Bi^{3+}- or Ce^{3+}-doped down-converting films on silicon substrates [47–49].

The present work aims at better understanding of the down-conversion mechanism in the Bi^{3+}–Yb^{3+} and Ce^{3+}–Yb^{3+} co-doped garnets of YAG ($Y_3Al_5O_{12}$) and GGG ($Gd_3Ga_5O_{12}$) prepared either in the form of powder or high-quality single crystalline films. The work presents, in particular, the results of direct quantum yield (QY) measurements of these garnets combined with measurements of photoluminescence (PL), photoluminescence excitation (PLE), and photoluminescence decay kinetics.

2. Samples and experimental procedures

2.1. Growth of epitaxial films

Two series of GGG-based and three series of YAG-based epitaxial films were grown. First ones are GGG:Bi and GGG:Bi,Yb, and second ones are YAG:Bi, YAG:Bi,Yb and YAG:Bi,Ce,Yb. Single crystalline films of GGG:Bi and GGG:Bi,Yb were grown on (111)-oriented pure GGG substrates, whereas the films of YAG:Bi, YAG:Bi,Yb and YAG:Bi,Ce,Yb were grown on (111)-oriented pure YAG substrates. The growth was performed by standard isothermal liquid phase epitaxy (LPE) from flux based on Bi_2O_3-B_2O_3 in air atmosphere, described in detail in Ref. [50]. The content of the dissolved oxides (Gd_2O_3 or Y_2O_3, Ga_2O_3 or Al_2O_3, Yb_2O_3 and CeO_2) and flux oxides (Bi_2O_3 and B_2O_3) was calculated using modified Blank-Nielson molar coefficients as below to obtain garnet primary phase crystallization.

$$
\begin{aligned}
R_1 &= \frac{Me_2O_3}{Re_2O_3 + Yb_2O_3}, \\
R_3 &= \frac{Bi_2O_3}{B_2O_3}, \\
R_4 &= \frac{Re_2O_3 + Yb_2O_3 + CeO_2 + Me_2O_3}{Re_2O_3 + Yb_2O_3 + CeO_2 + Me_2O_3 + B_2O_3 + Bi_2O_3} \cdot 100\%, \\
K_1 &= \frac{Re_2O_3}{Yb_2O_3}, \\
K_2 &= \frac{Y_2O_3}{CeO_2},
\end{aligned}
\tag{1}
$$

where Me_2O_3 denotes Ga_2O_3 or Al_2O_3, Re_2O_3 denotes Gd_2O_3 or Y_2O_3.

The purity of all oxides was not worse than 5 N. The films with thickness from 7 to 50 μm were grown at growth rate changed from 0.29 to 3.4 μm/min. The used melt compositions are presented in Table 1, while the parameters of the grown films are shown in Table 2. The lattice parameters a_f of films given in Table 2 were determined for the strain-free films in accordance with the equation [51]:

Table 2
Parameters of the grown films.

Film ID	Nominal composition	Melt no.	One-side thickness (μm)	Growth rate (μm/min)	Growth temperature (°C)	Crystal lattice parameter (Å)
GGG substrate	GGG	–	–	–	–	12.3790(1)
GG-1	GGG:Bi	G0	11.6	1.26	980	
GG-2		G1	33.9	3.39	1000	12.3854(1)
GGYb-1	GGG:Bi,Yb	G2	43.6	2.18	1020	
GGYb-2			33.4	0.95	1030	
GGYb-3			10.3	0.29	1035	
YAG substrate	YAG	–	–	–	–	12.0088(5)
Yb-00(1)	YAG:Bi	Y0	7.0	1.40	1050	
Yb-00(2)			42.0	1.06	1067	
YYb-1	YAG:Bi,Yb	Y1	34.7	2.29	981	12.0034(5)
YYb-2			34.0	1.35	1011	
YYb-3			50.7	1.01	1010	11.9995(5)
2YYb-1	YAG:Bi,Ce,Yb	Y2	20.2	0.81	1011	12.0000(5)
3YYb-1		Y3	23.2	0.66	1011	12.0004(5)