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Modulation of the Yb^{3+} to Er^{3+} energy transfer in $LiNbO_3$ crystals by applying magnetic field

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Abstract

Energy transfer from Yb^{3+} to Er^{3+} in $LiNbO_3$ in dependence with an external applied magnetic field is studied. As a result, the probability of the energy transfer, and therefore the up-converted luminescence of Er^{3+} is either enhanced or inhibited, depending on the intensity of the magnetic field. This effect is explained in terms of the matching between the energy level of the two species, related to the effective Landé factor of each ion.

Keywords: Insulators; Optical properties; Magnetic measurements; Luminescence

1. Introduction

Since the first observation by Auzel in 1966 [1], Yb^{3+} to Er^{3+} energy transfer process is the subject of an overwhelming number of studies. This process allows for pumping Er^{3+} in the spectral region of 980 nm, where InGaAs strained diodes emit efficiently, but where the absorption from Er^{3+} ($^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition) is weak. To enhance the emission of Er^{3+}, co-doping with Yb^{3+} is a standard resource, because this ion absorbs strongly in the 1 μm region, and since it only has two levels ($^2F_{7/2}$, fundamental and $^2F_{5/2}$, excited), it absorbs only in this region, not affecting the emission of Er^{3+}. Yb^{3+} to Er^{3+} energy transfer is particularly interesting due to two useful emissions of the latter ion. The first one is the 1.5 μm emission ($^4I_{13/2} \rightarrow {}^4I_{11/2}$), lying in the spectral range of maximum transmission of silica fibers used in communications. In this sense, Er^{3+} and Er^{3+}, Yb^{3+} doped fiber amplifiers have been extensively studied. The other interesting transition is the green emission by up-conversion ($^4S_{3/2} \rightarrow {}^4I_{15/2}$), which can be lased [2] to produce visible coherent radiation.

Towards the fabrication of devices, it may be interesting to develop a modulation system that enhances or inhibits the Yb^{3+} to Er^{3+} transfer and thus the Er^{3+} emission. In this work we show that this is possible by applying a magnetic field, because of the induced match or mismatch between the energy levels of Yb^{3+} and Er^{3+} ions. This will be done by comparing the relative intensity of the green up-conversion of erbium versus the cooperative luminescence [3] of Yb^{3+} in dependence with an external magnetic field. Cooperative luminescence is a special energy transfer process that occurs only in Yb^{3+} doped materials, and is due to a simultaneous de-excitation of two Yb^{3+} ions via a virtual level, resulting in the emission of a single photon of double energy than that of the single-ion transition. The transition probability of this process is typically 10^{-6} of the single-ion transition probability [4]. It will be shown that the ratio between cooperative luminescence and up-conversion, and thus the energy transfer probability, is strongly affected by an external magnetic field. This effect is interpreted in terms of the different Landé g factors involved. This is, to our knowledge, the first time to measure Yb^{3+} to Er^{3+} energy transfer in the presence of a magnetic field. The employment of this technique may give a lot of information about the Landé factors of excited states, multisites [5] and magnetic interaction between ions.

We chose $LiNbO_3$ as a crystal host for the Er^{3+} to Yb^{3+} transfer because of its excellent electro-optic, acousto-optic and non-linear properties. Er^{3+}:$LiNbO_3$ [6] and

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Yb^{3+}:$LiNbO_3$ [7,8] have been studied as singly doped materials, and recently also Er^{3+} to Yb^{3+} transfer has been studied in $LiNbO_3$ [9,10]. The mechanism of the up-conversion luminescence when Yb^{3+} transfers its energy to Er^{3+} is stepwise and non-radiative. Moreover, some of the authors have recently demonstrated highly efficient green laser action by self-frequency doubling in single domain and periodically poled MgO:$LiNbO_3$ [11–13].

2. Experimental

Yb^{3+}(4.2%):$LiNbO_3$ samples were grown in our laboratory by the Czochralski method. It is known that normally starting Yb_2O_3 powders usually contain Er_2O_3 impurities, so we chose a 99.9% pure Yb_2O_3 powder to allow for some Er^{3+} traces in the crystal. Since we were trying to demonstrate that energy transfer is being affected by the magnetic field, we needed very low concentrations of Er^{3+} in the sample to avoid cross relaxation between Er^{3+} pairs. The samples were mounted in a cryostat provided of a superconducting magnet, able to generate fields up to 14 T. The excitation source was a Ti:sapphire tuned at 918 nm (an absorption peak of Yb^{3+}). The spectra were recorded with a CCD camera.

3. Results and discussion

Fig. 1 shows the visible luminescence of the sample under Ti:sapphire excitation at 918 nm. The band around 550 nm is the green Er^{3+} up-conversion from Er^{3+} ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition), and the band from 490 to 540 nm is the cooperative luminescence from Yb^{3+} pairs. Further details on cooperative luminescence in Yb^{3+}:$LiNbO_3$ can be seen elsewhere [14,15]

Regarding Er^{3+} up-conversion, former studies [9,10] have shown that even in relatively strongly doped $LiNbO_3$ crystals (0.5% mol.) this is a stepwise process, in which two Yb^{3+} ions transfer consecutively their energy to the Er^{3+} ion. Our Er^{3+} concentration is much lower, so the cross relaxation processes between Er^{3+} pairs must be rejected, and a stepwise process is even more likely to take place. This is an important point, because if the up-conversion process involved a cross relaxation, no transfer process would be needed.

Fig. 2 shows the cooperative emission from Yb^{3+} and the up-conversion from Er^{3+} for several values of the applied magnetic field (0, 1, 2 and 4 T). It can be seen that the ratio between the integrated emissions of the up-conversion and the cooperative luminescence is not constant with the magnetic field. Thus, this ratio was monitored versus the magnetic field. We chose cooperative luminescence as the process to which normalize the up-conversion emission because both of them are two-photon processes, and they are going to have a quadratic dependence on the lowering of the absorption bands due to the splitting of the levels. Fig. 3 shows the ratio between the integrated emissions of the Er^{3+} up-conversion and the Yb^{3+} cooperative luminescence versus the magnetic field. As seen, this ratio increases from 0 to 0.5 T in about 43% and then it decreases monotonically down to a 57% at 4 T. For the up-conversion luminescence to take place, two consecutive transfer processes must be achieved, one to the $^4I_{11/2}$ and another one to the $^4F_{7/2}$. The process is sketched in Fig. 4. In general, the probability of the energy transfer depends on the overlap integral between the emission spectrum of the donor and the absorption spectrum from the acceptor. In our case, since we have two steps, the up-converted emission by energy transfer depends both on the overlap between the emission energy of Yb^{3+} (ΔE(Yb)) and absorption of Er^{3+} ($\Delta E(Er_1)$), and between ΔE(Yb) and the excited state absorption from $^4I_{11/2}$ and

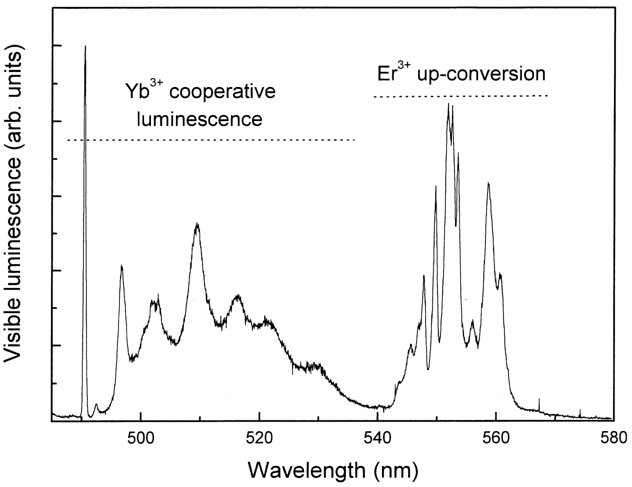

Fig. 1. Cooperative luminescence from Yb^{3+} and green up-conversion from Er^{3+}.

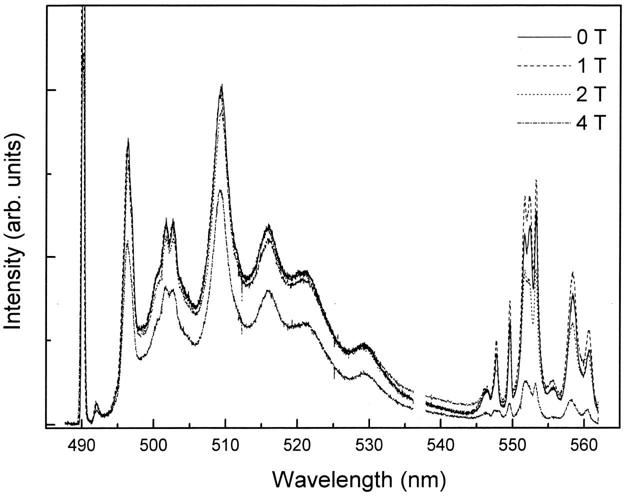

Fig. 2. Cooperative luminescence and up-conversion for several magnetic fields.

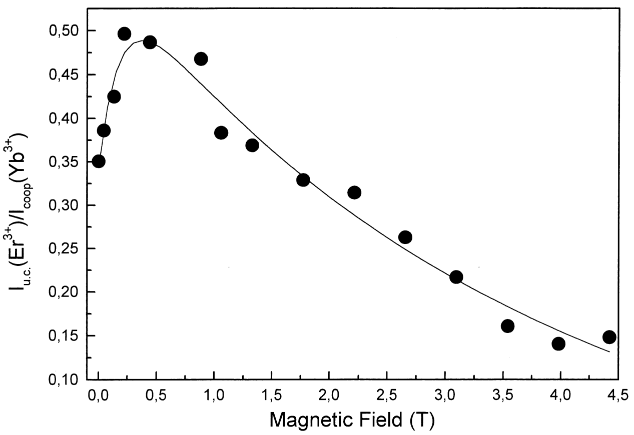

Fig. 3. Ratio between the integrated intensities of cooperative luminescence and up-conversion versus the magnetic field.

$^4F_{7/2}\Delta E(\mathrm{Er}_2)$. Thus, there are two possible effects of the magnetic field on the energy transfer process: (a) on the resonance between $\Delta E(\mathrm{Yb})$ and $\Delta E(\mathrm{Er}_1)$; and (b) on the resonance $\Delta E(\mathrm{Yb})$ and $\Delta E(\mathrm{Er}_2)$. In any of these cases, the transfer is process being affected. The reason for this effect lies in the strong difference between the g factors of the two species, Er^{3+} and Yb^{3+}. Er^{3+} and Yb^{3+} have an odd number of 4f electrons, so the J quantum number is half integer. The point symmetry of Li^+ site, where rare earth impurities enter the LiNbO_3 crystal is C_3, and splits the $^{2S+1}L_J$ spin–orbit terms into $J+1/2$ Stark levels, with double degeneracy. When applying an external magnetic field, these Kramers doublets of Er^{3+} and Yb^{3+} split in two levels with single degeneracy. This energy splitting is given by:

$$\Delta E = g_{\mathrm{eff}}\ \mu H$$

where g_{eff} is the effective Landé factor ($g_\parallel$ or $g_\perp$), μ is Bohr's magneton and H is the modulus of the magnetic field. The energy levels involved in our case are $^2F_{7/2}$ (ground) and $^2F_{5/2}$ (excited) from Yb^{3+}, and $^4I_{15/2}$ (ground), $^1I_{11/2}$ (intermediate) and $^4F_{7/2}$ (upper) from Er^{3+}. The g factor involved is $g_\parallel$ (g_{zz}), because the c-axis of the sample was parallel to the magnetic field. The g factor of Er^{3+} is 15.5 [16], while the one of Yb^{3+} is 4.86 [6]. Therefore, the levels of the two ions split with increasing magnetic field in a different way because of their different g values. There exists a certain value of the magnetic field at which the overlap between the levels of Yb^{3+} and Er^{3+} is maximum, as so is the intensity if the up-converted luminescence.

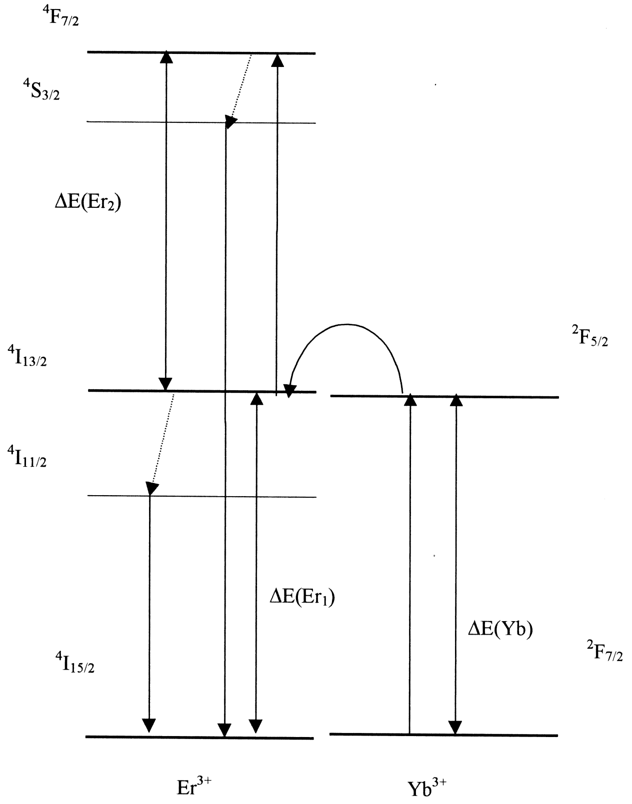

Fig. 4. Scheme of the up-conversion by energy transfer process.

4. Conclusions

We have demonstrated that the Yb^{3+} to Er^{3+} transfer can be both enhanced or inhibited by the application of an external magnetic field, and that this effect is due to the big difference between the g factors of the $^4I_{15/2}$ level of Er^{3+} and the other levels involved. Further work is currently being done to quantify this effect. We believe this is the first time that such a process is reported, and optimized results (more intense enhancement or inhibition of the transfer with lower applied field) can be obtained by appropriately choosing the acceptor species and the host material.

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