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NaLaF₄:Pr³⁺, Yb³⁺, an efficient blue to near infra-red quantum cutter

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In order to reduce the thermalization losses in solar cells, down-conversion of blue photons into near infra-red photons is a promising solution. In the present paper, we analyse the energy transfer processes between Pr³⁺ and Yb³⁺ in NaLaF₄ and we show that an efficient quantum-cutting process occurs. Nevertheless, we also show that a back transfer from Yb³⁺ toward the ¹G₄ level of Pr³⁺ ion leading to emission beyond 1 μm reduces the potentiality of this material as a quantum cutter for Si solar cells. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4843455>]

Thermalization of electron-hole pairs created by high energy photons is responsible for the poor yield of solar cells in the blue range of the solar spectrum.¹ In order to improve this “blue” yield one can adapt the incident solar spectrum by deposition of a thin layer of a so called quantum-cutting material in front of the solar cell.^{2–4} Each incident blue photon could thus be converted into two near infra-red photons, both able to generate an electron-hole pair. A process of quantum-cutting between rare-earth ions has been proposed and recently reviewed.^{5,6} Such a mechanism was observed, for example, within the couple Pr³⁺–Yb³⁺ in SrF₂.⁷ As shown in Fig. 1, after the absorption of a blue photon by the Pr³⁺ ion by the ³P_j levels, a two-step relaxation Pr³⁺:{³P₀ → ¹G₄, ¹G₄ → ³H₄} → 2 × Yb³⁺:{²F_{7/2} → ²F_{5/2}} can occur, leading to the emission of two infra-red photons by the two excited Yb³⁺ ions.⁸

In order to be very efficient, a quantum cutter material must have the lower phonon energy as possible. Thus, fluoride materials which have quite low maximum phonon energy are good host matrix for such application. Serrano *et al.* have studied (Pr³⁺, Yb³⁺) couple and demonstrated that the first energy transfer (a) in Fig. 1 is very efficient in CaF₂ crystals.⁹ Here, we present results obtained in NaLaF₄ (NLF) co-doped with the same ion couple.

Pr³⁺–Yb³⁺ co-doped NLF was synthesized by solid state reaction, after grinding and mixing NaF(99.99% purity), LaF₃(99.9% purity) in stoichiometric proportions. All the raw materials were from Alfa Aesar company. The samples were sintered at 600 °C for 3 × 6 h (every 6 h samples were ground and mixed again) under a reducing CF₄ atmosphere in order to avoid any O₂ pollution. PrF₃(99.9% purity) and YbF₃(99.9% purity) were added in order to dope NLF with Pr³⁺ and Yb³⁺, respectively (doping rates are given in at. %). For an efficient quantum cutting process, it is necessary to have at least twice as much Yb³⁺ than Pr³⁺. On the other hand, concentrations must not be too high in order to avoid concentration quenching which could reduce the final fluorescence efficiency. Thus, samples have been doped by 0.5 at. % Pr³⁺ and 0, 1, 5 and 7 at. % Yb³⁺. The phase purity of the samples was controlled by X-ray diffraction using a Bruker D8 Advance diffractometer with Cu Kα radiation. The diffractograms were recorded from 2Θ = 10° to 70° with a 0.021° step size and a counting time of 4 s per step. The fluorescence spectra measurements were performed at room temperature with a CCD sensor associated with a monochromator TRIAX 190 from Jobin-Yvon

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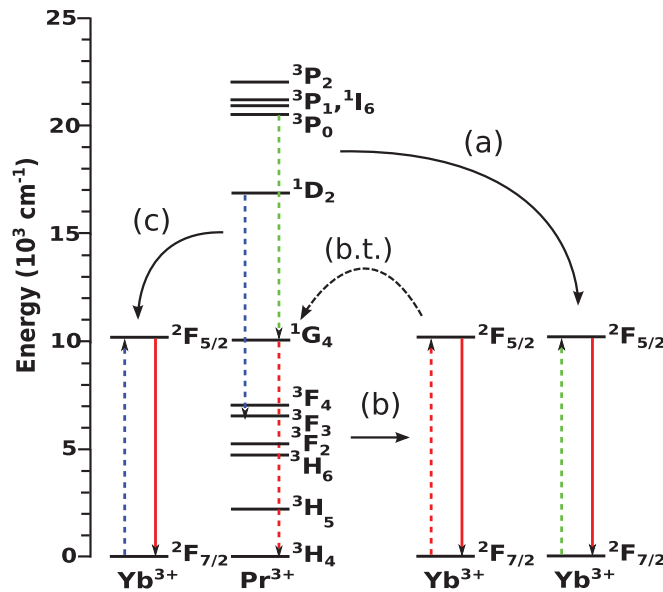


FIG. 1. Principle of quantum-cutting with Pr^{3+} and Yb^{3+} . (a)–(c) are three possible mechanisms of energy transfer from Pr^{3+} toward Yb^{3+} and (b.t.) is the back-transfer mechanism from Yb^{3+} to Pr^{3+} .

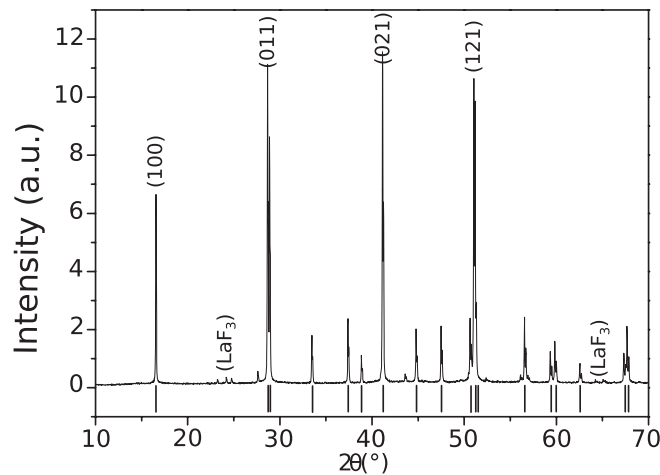


FIG. 2. XRD spectrum of NaLaF_4 . Vertical lines correspond to the related JCPDS card no. 01-075-1923. Main pics are indexed.

(3.53 nm/mm, the width of the entrance slit was set at 200 μm) using a tunable pulsed laser EKSPLA NT340 as excitation source. A 450 W Xe lamp associated with a monochromator GEMINI 180 (2.1 nm/mm, the width of slits was 1 mm) from Jobin-Yvon was used to perform excitation spectra. Fluorescence decay was recorded with a single channel analyser SR430 from Stanford company.

The diffractogram depicted in Fig. 2 exhibits a series of diffraction peaks corresponding to a pure NaLaF_4 phase (only a few very residual peaks, around 25° and 65°, corresponding to LaF_3 phase can be seen). NaLaF_4 is a high efficiency material for luminescence due to small effective phonon energy ($\sim 290 \text{ cm}^{-1}$).¹⁰ In particular, this makes the non-radiative relaxations from $^1\text{G}_4$ level very unlikely since the nearest level below ($^3\text{F}_4$) is $\sim 3000 \text{ cm}^{-1}$ apart. That also increases the fluorescence lifetime of $^1\text{G}_4$ level which is in favour of energy transfer (b) in Fig. 1.^{11–13} Figure 3 shows the emission spectrum of NLF: 0.5% Pr^{3+} , 5% Yb^{3+} excited into $^3\text{P}_2$ level at 450 nm. The observed lines mostly correspond to $^3\text{P}_0$ level emission of Pr^{3+} . This spectrum corresponds to that found in literature.¹⁴ The spin forbidden transitions from $^1\text{D}_2$ level to $^3\text{H}_j$ levels are very weak

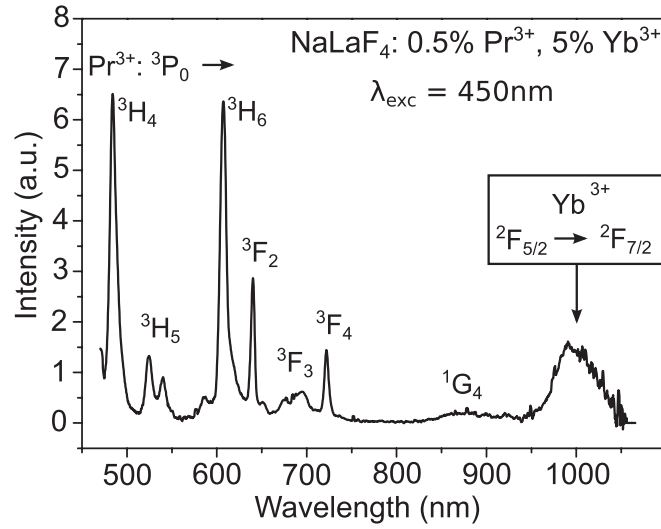


FIG. 3. Emission spectrum of NLF:0.5% Pr³⁺, 5% Yb³⁺ under excitation into ³P₂ level of Pr³⁺ at 450 nm. The emission below 900 nm comes from ³P₀ level of Pr³⁺, and the emission at 1000 nm from ²F_{5/2} level Yb³⁺ (see Fig. 1).

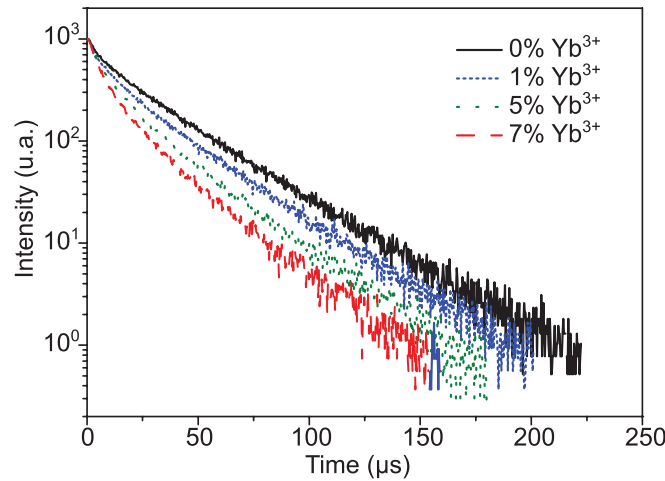


FIG. 4. Fluorescence decay of Pr³⁺ under excitation at 450 nm into ³P₂ level recorded at 610 nm corresponding to the transition ³P₀ → ³H₆.

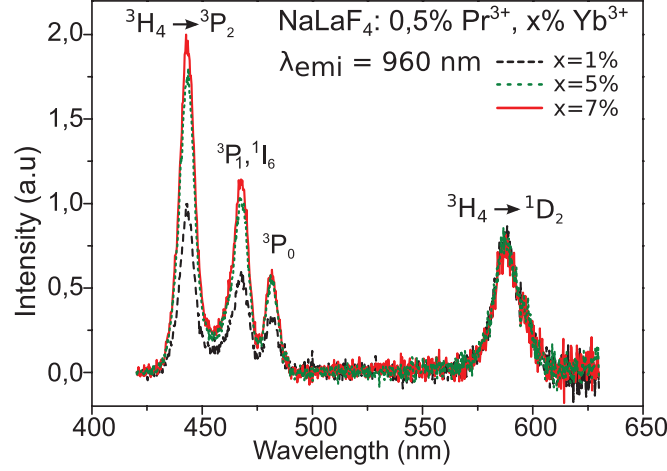
essentially because ¹D₂ level cannot be non-radiatively populated after an excitation into ³P_j. This means that the energy transfer (c) in Fig. 1 is very unlikely under excitation into ³P_j levels which is favourable to an effective quantum cutting for 1 μm emission. On the other hand, the band around 1 μm is due to the emission from ²F_{5/2} level of Yb³⁺. This shows that, energy transfer between Pr³⁺ and Yb³⁺ occurs. The question is to determine whether quantum-cutting occurs or not.

The fluorescence decay of ³P₀ level under excitation into ³P₂ level at 450 nm has been recorded in several NLF samples doped with 0.5% Pr³⁺ and x% Yb³⁺ (x = 0, 1, 5, 7) for the emission at 610 nm corresponding to the transition ³P₀ → ³H₆. As it can be seen in Fig. 4, for x = 0 the decay is exponential. As the Yb³⁺ concentration increases, the decay becomes more and more inexponential and the lifetime decreases. The values are gathered in Table I. The average lifetime listed in Table I is calculated by the following formula:

$$\tau = \frac{\int_0^{\infty} I(t) \cdot t \cdot dt}{\int_0^{\infty} I(t) \cdot dt} \quad (1)$$

TABLE I. Lifetime of 3P_0 and 1D_2 levels of Pr^{3+} and transfer efficiency $Pr^{3+} \rightarrow Yb^{3+}$ in NLF : 0.5% Pr^{3+} , x% Yb^{3+} .

Yb^{3+} (at. %)	3P_0 lifetime (μs)	Transfer efficiency 3P_0 (%)
0	29.7	0
1	26.0	13
5	21.4	28
7	18.1	39

FIG. 5. Excitation spectra of emission at 960 nm of $^2F_{5/2}$ Yb^{3+} level in several samples with a variable Yb^{3+} concentration.

and the transfer efficiency η_x in NLF : 0.5% Pr^{3+} , x% Yb^{3+} with the formula:

$$\eta_x = 1 - \frac{\tau_x}{\tau_0}, \quad (2)$$

where τ_x is the average lifetime of Pr^{3+} in the sample co-doped with 0.5% Pr^{3+} , x% Yb^{3+} , and τ_0 is the lifetime of Pr^{3+} in the sample single doped with 0.5% Pr^{3+} . The transfer probability in the case of dipole-dipole interaction is given by Dexter formula:¹⁵

$$P_{dd}(R) = \frac{3c^4 \hbar^4 \sigma_A}{4\pi n^4 \tau_S R^6} \int \frac{f_S(E) F_A(E)}{E^4} dE. \quad (3)$$

Thus, it depends on the distance between donor and acceptor ions and on the overlap integral between the donor emission and the acceptor absorption. The value of this integral does not change when the ions concentration increases, so the transfer probability is only function of distances between ions, i.e., function of ions concentrations. The intensity of excitation bands corresponding to different energy transfers depends on the transfer probabilities and, therefore, varies the same way as a function of ions concentrations whatever the transfer. Thus, if energy transfers occurring after excitation into 1D_2 or 3P_0 are both only one step energy transfers, the intensity of the corresponding excitation bands should vary the same way when the Yb^{3+} concentration increases. In order to point out the quantum cutting process and to evaluate its efficiency, we have recorded the excitation spectra of several samples by monitoring the emission of Yb^{3+} at 960 nm. At this wavelength we carefully checked that the emission comes mainly from Yb^{3+} $^2F_{5/2}$ and that the contribution from Pr^{3+} 1G_4 is negligible. They are depicted in Fig. 5.

The excitation spectrum of Yb^{3+} emission shows a first band between 580 nm and 610 nm which corresponds to excitation through 1D_2 level, and three other bands between 440 nm and 500 nm which correspond to excitation through 3P_j levels of Pr^{3+} . When the sample is excited into the 1D_2 level, there are two ways to transfer the energy toward Yb^{3+} ion: either via the transfer (c)

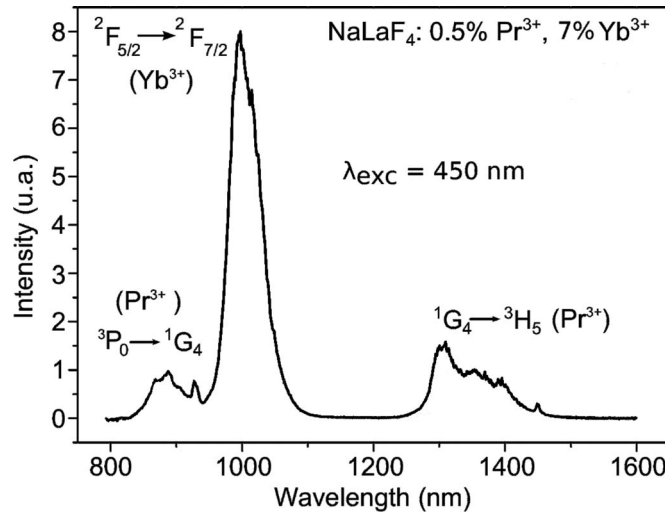


FIG. 6. Infra-red emission spectrum of NLF:0.5% Pr³⁺, 7% Yb³⁺ under excitation into ³P₂ level of Pr³⁺.

in Fig. 1, or via the transfer (b) in Fig. 1 after the transition $^1D_2 \rightarrow ^1G_4$ occurred. But in both cases, only one Yb³⁺ ion can be excited. Instead, when the initial excitation populates ³P₀ level, two Yb³⁺ ions can be excited; the first one by the cross-relaxation energy transfer (a) in Fig. 1 ($^3P_0, ^2F_{7/2} \rightarrow ^1G_4, ^2F_{5/2}$) and the second one by the energy transfer (b) in Fig. 1 ($^1G_4, ^2F_{7/2} \rightarrow ^3H_4, ^2F_{5/2}$). To have a chance to observe such a process, each Pr³⁺ ion needs to have at least two Yb³⁺ ions nearby. Indeed, the lifetime of ²F_{5/2} level of Yb³⁺ is longer ($\tau_{F_{5/2}} = 935 \mu\text{s}$) than the lifetime of ¹G₄ level of Pr³⁺ ($\tau_{G_4} = 300 \mu\text{s}$). So, to have an efficient transfer (b) in Fig. 1 which occurs necessarily after transfer (a) in Fig. 1, another Yb³⁺ ion in its ground state in the vicinity of Pr³⁺ is needed. If this occurs, the relative intensity of the bands corresponding to the ³P_j levels in the excitation spectra should increase compare to that of ¹D₂ band. By normalizing the excitation spectra on the ¹D₂ band, we can show that quantum cutting effectively occurs for high Yb³⁺ concentrations. The relative intensity in the excitation spectrum of ³P_j band grows when the concentration increases. For the 7% Yb³⁺ concentration, this intensity is twice the intensity recorded for the 1% Yb³⁺ concentration. This means that there are two times more Yb³⁺ ions excited from ³P₀ in that case. Since the first step of energy transfer from ³P₀ and from ¹D₂ should vary the same way, the fact that the intensity doubles for ³P_j levels means that the second step (energy transfer from ¹G₄ level) occurs and is as efficient as the first step. At this concentration and for higher Yb³⁺ concentrations, the quantum cutting is very efficient. The efficiency of the first step being 39% (see Table I) the total energy transfer efficiency from ³P₀ can be estimate around 78%. Serrano *et al.* show that the efficiency of the first step transfer can reach a value of 97% in KY₃F₁₀ for a Yb³⁺ concentration of 20%,¹² so we can hope that by increasing furthermore the concentration we could almost reach a 200% efficiency for quantum cutting process in NLF.

If quantum cutting was the only process existing between Pr³⁺ and Yb³⁺ ions, as it becomes more and more efficient with the increasing of Yb³⁺ concentration, the emission of ¹G₄ level should vanish because the transfer (b) in Fig. 1 becomes more and more efficient inducing a decrease of the ¹G₄ population. In Fig. 6, we show emission in the infra-red region for 7 at. % concentration of Yb³⁺. The emission from ¹G₄ is clearly seen and is partly due to a back transfer from Yb³⁺. In order to point out it, we recorded emission spectra of ¹G₄ level under excitation into Yb³⁺ at 980 nm. In single doped sample with Pr³⁺ no emission from ¹G₄ is detected, but in double doped samples with Pr³⁺ and Yb³⁺, an emission around 1.3 μm is detected which corresponds to the Pr³⁺ transition $^1G_4 \rightarrow ^3H_5$. This clearly demonstrates the back transfer from Yb³⁺ to Pr³⁺. An example for NLF:0.5% Pr³⁺, 1% Yb³⁺ is shown in Fig. 7. Unfortunately, when the Yb³⁺ concentration increases this back transfer from Yb³⁺ to Pr³⁺ reduces the emission intensity of Yb³⁺. Thus, the

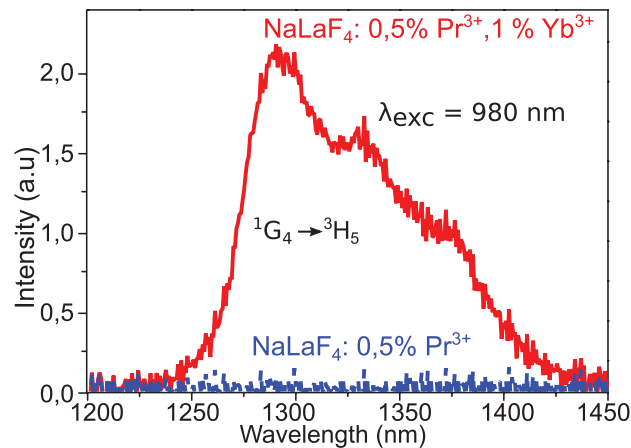


FIG. 7. Infra-red emission spectra of NLF:0.5% Pr³⁺, 1% Yb³⁺ under excitation into ²F_{5/2} level of Yb³⁺ at 980 nm.

partial quantum efficiency (for wavelength shorter than 1.1 μm which are useful for Si-based solar cells) is also reduced.

In summary, we studied energy transfers in NaLaF₄ co-doped with Pr³⁺ and Yb³⁺. We demonstrated that in Yb³⁺ high concentrated samples quantum-cutting occurs. We analysed precisely the energy transfers involved and we proposed a method to evaluate their respective contributions to Yb³⁺ emission. We also demonstrated that the back-transfer from Yb³⁺ toward the ¹G₄ level of Pr³⁺ makes that the whole resulting infra-red emission cannot be converted into electron-hole pairs in standard silicon solar cells, limit absorption of which is 1.1 μm , but could be valuable for other types of solar cell materials with smaller energy gap like InN or In_xGa_{1-x}N.

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