High-resolution luminescence spectroscopy study of down-conversion routes in NaGdF₄:Nd³⁺ and NaGdF₄:Tm³⁺ using synchrotron radiation

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Down-conversion in lanthanide doped luminescent materials is a promising route to significantly enhance the energy efficiency of silicon solar cells, plasma display panels, or mercury-free lighting tubes because it results in the emission of two photons for each absorbed higher energy photon. The Gd³⁺/Eu³⁺ ion couple shows down-conversion of vacuum-ultraviolet light into visible light with an efficiency close to 100%. The low absorption strength of the ⁶G⁷/₂ levels of Gd³⁺ (the starting point of the down-conversion process), however, prevents efficient excitation of the down-conversion process and therefore application. We have performed a high resolution luminescence spectroscopy study, using synchrotron radiation, in order to investigate the possibility to use the strong 4f→5d absorption transitions of Nd³⁺ and Tm³⁺ to sensitize the high energy ⁶G⁷/₂ level of Gd³⁺ in the phosphors NaGdF₄:2%Nd³⁺ and NaGdF₄:2%Tm³⁺. Tm³⁺ appears to be an efficient sensitizer of the ⁶G⁷/₂ state of Gd³⁺. It was also found that sensitization is followed by two successive energy transfer processes exciting two Tm³⁺ ions in the ³H₄ state which results in the emission of two infrared photons for one absorbed vacuum-ultraviolet photon. Nd³⁺ is not a good sensitizer of the ⁶G⁷/₂ state in NaGdF₄. Instead Nd³⁺ efficiently transfers its energy by cross relaxation to the lower energy ⁵D₂ states of Gd³⁺ but leaving the Nd³⁺ ion excited in the ⁴F₃/₂ state. Successive energy transfer from Gd³⁺ back to Nd³⁺ excites a second Nd³⁺ ion in the ⁴F₃/₂ state. Also, in this case, two infrared photons can be emitted for one absorbed vacuum-ultraviolet photon.

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I. INTRODUCTION

There is a real need for luminescent materials that emit two visible or infrared (IR) photons for each absorbed vacuum-ultraviolet (VUV) or ultraviolet (UV) photon. Such quantum cutting (or quantum splitting) phosphors can be applied in plasma display panels (PDPs), Hg-free lighting tubes, or solar cells to raise energy efficiency.¹⁻⁴

In PDPs and Hg-free lighting, phosphors are applied, which need to convert high energy VUV light from a noble gas discharge (between 7 and 9 eV) into visible red, green, and blue lights (1.7–3 eV).⁵ Although the quantum efficiency of currently applied conventional phosphors is close to the possible maximum (100%),⁶ the energy efficiency is rather low due to the large difference between the excitation and emission energies. Application of quantum cutting phosphors can, in principle, raise the energy efficiency by a factor of 2.¹

Silicon solar cells hamper with a very similar problem. Although the UV and visible part of the solar spectrum is efficiently absorbed by silicon, the excitation energy in excess of the silicon band gap that is about 1.2 eV is lost by thermalization. It has been calculated that in the ideal case, a quantum cutting luminescent material converting UV and visible light into IR light can enhance the energy efficiency of a solar cell from 29% to 37%.⁴

The phenomena of quantum cutting can be achieved by an energy relaxation mechanisms generally referred to as down-conversion. Wegh et al.¹ discovered a promising phosphor LiGdF₄:Eu³⁺, in which down-conversion is achieved by a two step energy transfer process between two different lanthanide ions Gd³⁺ and Eu³⁺ (see Fig. 1). After a Gd³⁺ ion has been excited into the high energy ⁶G⁷/₂ state, cross relaxation occurs between Gd³⁺ and Eu³⁺ (dashed arrows) resulting in an excited Eu³⁺ ion ready to emit a red photon. Cross relaxation is followed by a second energy transfer step from Gd³⁺ (curved arrow) that excites a second Eu³⁺ ion that will emit one photon and is followed by multiphonon relaxation (dotted arrow) to the ground state. The emission process of each Eu³⁺ ion results in two photons which have a lower energy than the absorbed VUV photon. The energy efficiency of a silicon solar cell can be increased by using quantum cutting phosphors in PDPs and Hg-free lighting tubes because it results in the emission of two photons for each absorbed higher energy photon. The Gd³⁺/Eu³⁺ ion couple shows down-conversion of vacuum-ultraviolet light into visible light with an efficiency close to 100%. The low absorption strength of the ⁶G⁷/₂ levels of Gd³⁺ (the starting point of the down-conversion process), however, prevents efficient excitation of the down-conversion process and therefore application. We have performed a high resolution luminescence spectroscopy study, using synchrotron radiation, in order to investigate the possibility to use the strong 4f→5d absorption transitions of Nd³⁺ and Tm³⁺ to sensitize the high energy ⁶G⁷/₂ level of Gd³⁺ in the phosphors NaGdF₄:2%Nd³⁺ and NaGdF₄:2%Tm³⁺. Tm³⁺ appears to be an efficient sensitizer of the ⁶G⁷/₂ state of Gd³⁺. It was also found that sensitization is followed by two successive energy transfer processes exciting two Tm³⁺ ions in the ³H₄ state which results in the emission of two infrared photons for one absorbed vacuum-ultraviolet photon. Nd³⁺ is not a good sensitizer of the ⁶G⁷/₂ state in NaGdF₄. Instead Nd³⁺ efficiently transfers its energy by cross relaxation to the lower energy ⁵D₂ states of Gd³⁺ but leaving the Nd³⁺ ion excited in the ⁴F₃/₂ state. Successive energy transfer from Gd³⁺ back to Nd³⁺ excites a second Nd³⁺ ion in the ⁴F₃/₂ state. Also, in this case, two infrared photons can be emitted for one absorbed vacuum-ultraviolet photon.

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FIG. 1. Schematic energy level diagram of Gd³⁺ and Eu³⁺ in LiGdF₄. The observed quantum splitting process by down-conversion involving cross relaxation (dashed arrows), energy transfer (curved arrow), and multiphonon relaxation (dotted arrow) leads to the emission of two red photons by Eu³⁺ (solid arrows) for each Gd³⁺ ion that is excited in its ⁶G⁷/₂ state. Note that for clarity, not all energy levels are shown.
second red photon. The quantum efficiency of LiGdF$_4$:Eu$^{3+}$ was reported to be close to 190%.$^1$

A drawback of this phosphor is the low absorption efficiency into the high energy $G_{7/2}$ state of Gd$^{3+}$. The absorption transition is spin and parity forbidden and, therefore, weak. These problems were emphasized by Feldmann et al.$^5$ who showed that the external quantum efficiency, a more practical quantity that also takes into account the absorption efficiency of LiGdF$_4$:Eu$^{3+}$, was only 32%. Clearly, the sensitization of high energy $G_{7/2}$ state of Gd$^{3+}$ is of crucial importance.

Several reports can be found in literature on the sensitization of Gd$^{3+}$ by other ions with high absorption cross section and efficient energy transfers to the $G_{7/2}$ state of Gd$^{3+}$. Babin et al.$^8$ considered the role of Pb$^{2+}$ as a sensitizer for the $G_{7/2}$ state of Gd$^{3+}$. Peijzel et al.$^9$ successfully used Tm$^{3+}$ as a sensitizer in LiGdF$_4$:Eu$^{3+}$, Tm$^{3+}$ but discovered at the same time that the cross-relaxation step from Gd$^{3+}$ to Eu$^{3+}$, described above Fig. 1, was quenched by more efficient cross relaxation from Gd$^{3+}$ to Tm$^{3+}$. A similar competing cross relaxation from Gd$^{3+}$ to Nd$^{3+}$ was found by Jia et al. in LiGdF$_4$:Nd$^{3+}$.$^{10}$

In this work, the ions Nd$^{3+}$ and Tm$^{3+}$ in hexagonal NaGdF$_4$ are investigated as potential sensitizers for the high energy Gd$^{3+}$ $G_{7/2}$ state. In NaGdF$_4$, both ions have 5$d$ states at higher energies than the Gd$^{3+}$ $G_{7/2}$ state which makes energy transfer energetically possible. They also have no 4$f$ levels close in energy below the 5$d$ states, which makes a nonradiative relaxation from the 5$d$ states to the 4$f$ states of Tm$^{3+}$ or Nd$^{3+}$ improbable. In addition, these ions are expected to have 5$d$$\rightarrow$4$f$ emission bands that spectrally overlap with the Gd$^{3+}$ $G_{7/2}$ states, which makes a resonant energy transfer from Nd$^{3+}$ or Tm$^{3+}$ to Gd$^{3+}$ possible.

The host material NaGdF$_4$ is a member of the hexagonal NaLnF$_4$ family (Ln=Y, La-Lu). Its structure was first determined for NaNdF$_4$, and its Na$^{+}$/Ln$^{3+}$ disorder was recently refined for NaLaF$_4$ and NaGdF$_4$. Due to its cation disorder, the two slightly different Ln$^{3+}$ sites and the short Ln-Ln distances of two times 3.61 Å and six times 3.92 Å for the example of NaGdF$_4$, it is the most efficient up-conversion sensitizer in NaGdF$_4$:Nd$^{3+}$. The product is dried, and the addition of HF and drying are repeated. The solid, which consists of a mixture of M$^{3+}$ and NaF according to x-ray diffraction, is ground up in a mortar, transferred into a glassy carbon boat, and heated to 550 °C in a HF/Ar gas stream for 20 h. The sample is heated in a tubular furnace in a gas tight nickel apparatus (alloy 600) which is inert to HF gas. In this step, the reaction toward hexagonal NaMF$_4$ plus excess NaF takes place. Traces of O are removed by the HF gas stream. The powder is ground up again and heated to 590 °C in an Ar gas stream for another 20 h. This step improves the crystallinity and optical properties of the material. Finally, the product is washed with water to dissolve the excess NaF and then dried at 100 °C. All samples were checked by x-ray powder diffraction. They show the hexagonal NaLaF$_4$ phase together with a small residue of about 0.5% NaF.

B. Spectroscopic measurements

Luminescence excitation spectra were recorded at the Deutsche Elektronen-Synchrotron (DESY) in Hamburg (Germany) using the SUPERLUMI station of HASYLAB. The spectral region of excitation was 50–335 nm with a fixed resolution of 0.3 nm. A R6358P Hamamatsu photomultiplier tube (PMT) connected to a triple grating Czerny-Turner monochromator SpectraPro-308i from Acton Research, Inc., was used to measure excitation spectra of UV to visible luminescence. All excitation spectra were corrected for the wavelength dependent excitation intensity. Details of this excitation facility were described elsewhere.

Luminescence emission spectra were recorded with a liquid nitrogen cooled charge coupled device (CCD) detector of Princeton Instruments, Inc., connected to the monochromator described above. The sensitive spectral range was between 200 and 1100 nm with a resolution close to 1 nm. All emission spectra were corrected for the wavelength dependent detection efficiency. Time resolved emission spectra were recorded with a fast PMT connected to the same monochromator by setting a desired time window (gate) after pulsed synchrotron excitation. All presented data were recorded at 10 K.

II. EXPERIMENTAL PROCEDURES

A. Materials synthesis

Powder samples of phase-pure hexagonal NaLaF$_4$:2% Nd$^{3+}$ and NaGdF$_4$:2% M$^{3+}$ (M=Nd or Tm) were prepared from rare-earth oxides Re$_2$O$_3$ (Re=La, Nd, Gd, and Tm) of 5N or 6N purity (Metal Rare Earth Ltd.), Na$_2$CO$_3$ (Alfa, 5N), and aqueous 65% HNO$_3$ (Merck, p.a.) and 40% HF acids (Merck, supra pure). Batches were typically calculated for 5 g of product. The stoichiometric mixture of the respective rare-earth oxides was dissolved in a small amount of HNO$_3$ in a Teflon beaker, evaporated to dryness, dissolved in water, and the fluorides MF$_3$ precipitated with HF. The liquid is evaporated and HF is added again. For the work with HF acid or gas, appropriate safety precautions have to be taken. The respective amount of Na$_2$CO$_3$ to obtain a 2:1 ratio of Na to M is dissolved in water in a separate beaker and slowly added to the mixture. Care has to be taken to avoid spilling due to the CO$_2$ evolution.

The product is dried, and the addition of HF and drying are repeated. The solid, which consists of a mixture of MF$_3$ and NaF according to x-ray diffraction, is ground up in a mortar, transferred into a glassy carbon boat, and heated to 550 °C in a HF/Ar gas stream for 20 h. The sample is heated in a tubular furnace in a gas tight nickel apparatus (alloy 600) which is inert to HF gas. In this step, the reaction toward hexagonal NaMF$_4$ plus excess NaF takes place. Traces of O are removed by the HF gas stream. The powder is ground up again and heated to 590 °C in an Ar gas stream for another 20 h. This step improves the crystallinity and optical properties of the material. Finally, the product is washed with water to dissolve the excess NaF and then dried at 100 °C. All samples were checked by x-ray powder diffraction. They show the hexagonal NaLaF$_4$ phase together with a small residue of about 0.5% NaF.
excitation spectrum (curve a) monitoring the Nd$^{3+}$ emission at 178 nm. The excitation spectrum shows bands between 130 and 160 nm corresponding to the $4f^2 5d^1 \rightarrow 4f^3$ configuration of Nd$^{3+}$. The emission spectrum consists of both $4f^2 5d^1 \rightarrow 4f^3$ $[I_{2J}, F_{2J}, G_{2J}]$ emissions at 178, 225, and 255 nm respectively, and $4f^3 \rightarrow 4f^3$ emission around 875 nm corresponding to the Nd$^{3+}$ $4F_{3/2} \rightarrow 4I_{9/2}$ transition. The ratio between $5d \rightarrow 4f$ and $4f \rightarrow 4f$ emissions upon Nd$^{3+}$ 5d excitation is controlled to a large extent by the energy gap between the Stokes shifted lowest energy 5d state and the first lower energy 4f$^3$ state. Only when this gap is small enough [typically <7500 cm$^{-1}$ (Ref. 15)], nonradiative feeding of the $2G_{9/2}$ level of Nd$^{3+}$ (around 48,000 cm$^{-1}$) is possible. Under these conditions, a large number of $4f^3 \rightarrow 4f^3$ emission lines in the UV and visible spectral range are observed. Since only very weak $4f^3 \rightarrow 4f^3$ emission lines are observed in NaLaF$_4$:Nd$^{3+}$, it must be concluded that 5d $\rightarrow 4f$ emission is the dominant relaxation route after Nd$^{3+}$ 4f $\rightarrow$ 5d excitation. The observed $4F_{3/2} \rightarrow 4I_{9/2}$ emission around 875 nm is the result of radiative feeding of the $4G_{9/2}$ (255 nm) and the $4F_{7/2}$ (225 nm) states, as indicated in Fig. 3(a).

B. Down-conversion in NaGdF$_4$:2% Nd$^{3+}$

The emission spectrum of NaGdF$_4$:Nd$^{3+}$ under Nd$^{3+}$ $4f^3 5d^1$ excitation at 156 nm is plotted in Fig. 4(a).

When this emission spectrum is compared with the emission spectrum of NaLaF$_4$:Nd$^{3+}$, also excited at 156 nm (Fig. 2), it can be observed that the Nd$^{3+}$ 5d $\rightarrow$ 4f emission is completely quenched in NaGdF$_4$:Nd$^{3+}$. Instead, Gd$^{3+}$ emission from the $6P_{3/2}$ and the $6I_{15/2}$ levels to the $8S_{7/2}$ ground state is observed at 279 and 313 nm, respectively, as well as emission from the $4D_{3/2}$ and $4F_{3/2}$ levels of Nd$^{3+}$ [see Fig. 4(a)]. Clearly, energy is transferred completely from the 5d states of Nd$^{3+}$ to the 4f levels of Gd$^{3+}$. Figure 4(b) represents the emission spectrum of NaGdF$_4$:Nd$^{3+}$ under direct Gd$^{3+}$ excitation into a $6G_{7/2}$ level at 202 nm. At this excitation wavelength, emission from the $6G_{7/2}$ Gd$^{3+}$ level is observed, as indicated by the black dots. Since these emissions were not observed under Nd$^{3+}$ 5d excitation, it must be concluded that energy transfer from Nd$^{3+}$ to Gd$^{3+}$ proceeds to any of the lower energy $6D_{J}, 6I_{J}$, and $6P_{J}$ states of Gd$^{3+}$ and not the $6G_{J}$ states.

This energy transfer route is confirmed by the excitation spectra plotted in Fig. 5 monitoring the Gd$^{3+}$ $8S_{7/2} \rightarrow 6P_{3/2}$ emission at 592 nm [spectrum (a)] and the Gd$^{3+}$ $6P_{3/2} \rightarrow 8S_{7/2}$ emission at 313 nm [spectrum (b)]. Spectrum (a) directly proves that $6G_{7/2}$ emission at 592 nm can only be excited into the $6G_{J}$ levels themselves but not into the Nd$^{3+}$ 5d states. Spectrum (b) confirms that the Gd$^{3+}$ $6P_{3/2} \rightarrow 8S_{7/2}$ emission at 311 nm is sensitized by the Nd$^{3+}$ 5d states.
FIG. 5. Excitation spectra of NaGdF₄:2%Nd³⁺ recorded at 10 K monitoring (a) the Gd³⁺ ⁴G₇/₂ → ⁵P₃/₂ transition at 592 nm, (b) the Gd³⁺ ⁶P₃/₂ → ⁸S₇/₂ transition at 313 nm, and (c) the Nd³⁺ ⁴D₃/₂ → ⁴I₉/₂ transition at 383 nm.

The selective energy transfer from the 5d states of Nd³⁺ to the lower energy states of Gd³⁺ can be explained by a favorable spectral overlap between the lower energy ⁴D₂, ⁴I₉, and ⁶P₃/₂ states of Gd³⁺ and the ⁴f⁵d → ⁴f³ emission bands of Nd³⁺. Figures 6(a) and 6(b), representing the Nd³⁺ 5d → ⁴f emission and the Gd³⁺ ⁴f → ⁴f excitation spectrum, respectively, indeed confirm a good spectral overlap around 255 nm between Nd³⁺ ⁴f⁵d → ⁴f³[⁴G₂] emission and Gd³⁺ ⁸S₇/₂ → ⁶D₁ absorption. Figure 3(b1) shows the identified cross-relaxation process in NaGdF₄:Nd³⁺ that explains the selective energy transfer from Nd³⁺ to Gd³⁺.

Jia et al. recently studied sensitization of Gd³⁺ by Nd³⁺ in LiGdF₄:Nd³⁺ and assumed a cross-relaxation process from the 5d states of Nd³⁺ to the higher energy ⁶G_J levels of Gd³⁺. They, however, at the same time, noted that cross-relaxation to the lower lying ⁶D₂, ⁶I₉, and ⁶P₃/₂ states of Gd³⁺ could not be excluded on the bases of their experimental data. Our data clearly show that in NaGdF₄:Nd³⁺, the lower energy Gd³⁺ levels are sensitized by the 5d states of Nd³⁺. 

Our conclusion is based on the excitation spectrum monitoring Gd³⁺ ⁶G₇/₂ emission that shows no Nd³⁺ 5d excited states [see Fig. 5(a)] and the favorable spectral overlap between the ⁵d → ⁴f Nd³⁺ emission and the Gd³⁺ ⁸S₇/₂ → ⁶D₁ absorption (Fig. 6). Because no emission from the ⁶G₇/₂ level of Gd³⁺ was observed in LiGdF₄:Nd³⁺, a simple proof as was given in this work cannot be given. The emission of Nd³⁺ in LiGdF₄ is, however, expected to be the same as in LiYF₄:Nd³⁺ (Ref. 10) which, in turn, is the same as in NaGdF₄:Nd³⁺ (see Ref. 16 and Fig. 6 of this work). Spectral overlap between Nd³⁺ emission and Gd³⁺ absorption in LiGdF₄:Nd³⁺ will therefore be the same as in NaGdF₄ which suggests that sensitization of the high energy ⁶G_J levels does not take place in LiGdF₄:Nd³⁺.

The emission from the ⁴D₂ state of Nd³⁺ [see Fig. 4(a), which is observed under Nd³⁺ ⁵d excitation, is the result of a partial energy transfer from the ⁵P₃/₂ level of Gd³⁺ to Nd³⁺, as indicated by the vertical arrow in Fig. 3(b2)]. This transfer is demonstrated by the observation of Nd³⁺ ⁵D₃/₂ emissions under direct Gd³⁺ ⁸S₇/₂ → ⁵D₂ excitation at 273 nm [see Fig. 4(c)]. In addition, excitation spectrum (c) plotted in Fig. 5, monitoring the Nd³⁺ ⁴D₃/₂ → ⁴I₉/₂ emission at 383 nm, clearly reveals the Gd³⁺ ⁸S₇/₂ → ⁶P₃/₂, ⁶I₉, and ⁶G_J transitions, which confirms the Gd³⁺ → Nd³⁺ back transfer.

The above described down-conversion process involving a two step energy transfer process from Nd³⁺ to Gd³⁺ [step 1, Fig. 3(b1)] and back from Gd³⁺ to Nd³⁺ [step 2, Fig. 3(b2)] can result in the emission of two IR photons by Nd³⁺ (⁴F₃/₂ → ⁴I₉/₂) for each absorbed VUV photon (between 130 and 160 nm). The first cross-relaxation step [Fig. 3(b1)] populates the Nd³⁺ ⁴F₃/₂ state and the Gd³⁺ ⁶D₂/₁ state. Subsequently, the back-transfer step discussed above [Fig. 3(b2)] populates the Nd³⁺ ⁵D₃/₂ levels. Finally, the Nd³⁺ ⁴F₃/₂ state is populated the second time by Nd³⁺ ⁴P₃/₂ → ⁴F₉ emission [Fig. 3(b3)]. Further experimental evidence for this down-conversion process can be found by comparing the emission spectra plotted in Figs. 4(a) and 4(c) that are both normalized at 383 nm, i.e., the Nd³⁺ ⁵D₃/₂ → ⁴I₉/₂ emission line. The enhanced IR emission (around 875 nm) under Nd³⁺ ⁵d excitation [Fig. 4(a)] compared to direct Gd³⁺ ⁶I₉ excitation [Fig. 4(c)] is the expected consequence of the down-conversion process described above. Note that, although with poor quantum efficiency, there is a change for emission of three photons for an absorbed VUV photon, i.e., two times ⁴F₃/₂ → ⁴I₉/₂ and one times ⁴D₂ → ⁴F₉.

Finally, it is interesting to note that the emission spectrum obtained under direct Gd³⁺ ⁶G_J excitation at 202 nm, shown in Fig. 4(b), also shows enhanced IR emission compared to ⁶I₉ excitation at 273 nm [Fig. 4(c)]. This can be explained by down-conversion involving a two step energy transfer process from the ⁶G₇/₂ level of Gd³⁺ to the ⁴F₅/₂ level of Nd³⁺ that was described earlier by Jia et al. for LiGdF₄:Nd³⁺. The first step is cross relaxation involving the Gd³⁺ [⁶G₇/₂ → ⁵P₃/₂] and the Nd³⁺ [⁴I₉/₂ → ⁴F₉] transitions, as indicated by the vertical arrows in Fig. 3(c), resulting in excitation of the Nd³⁺ ⁴P₃/₂ state and excitation of the Gd³⁺ ⁴P₃/₂ state.
second step is the previously described back transfer process resulting in excitation of a second Nd$^{3+}$ ion into the $^4F_{3/2}$ state [see Figs. 3(b2) and 3(b3)].

From an application point of view, it must be noted that this excitation spectrum therefore proves energy transfer from the 5$d$ states of Tm$^{3+}$ to the 4$f$ states of Gd$^{3+}$. This strongly suggests that energy is transferred from the 5$d$ states of Tm$^{3+}$ to the 4$f$ states of Gd$^{3+}$. The emission spectrum of NaGdF$_4$:Tm$^{3+}$ recorded under 313 nm excitation at 252 nm. The two spectra were normalized at the $^3P_0 \rightarrow ^3H_4$ transition.

D. Down-conversion in NaGdF$_4$:2 % Tm$^{3+}$

Figure 8(a) shows the excitation spectrum of NaGdF$_4$:Tm$^{3+}$ monitoring Gd$^{3+}$ emission at 313 nm. Besides the expected Gd$^{3+}$ 4$f^2$ lines, the spectrum contains the same broad band features that were observed in the excitation spectra of NaLaF$_4$:2 % Tm$^{3+}$ monitoring Tm$^{3+}$ 5$d$→4$f$ emission and are therefore assigned to the 5$d$ states of Tm$^{3+}$. This excitation spectrum therefore proves energy transfer from the 5$d$ states of Tm$^{3+}$ to the 4$f$ states of Gd$^{3+}$. The emission spectrum of NaGdF$_4$:Tm$^{3+}$ recorded under Tm$^{3+}$ 5$d$ excitation at 143 nm is plotted in Fig. 9(a). It is dominated by Gd$^{3+}$ $^5P_{3/2} \rightarrow ^5S_{7/2}$ emission at 313 nm which confirms efficient energy transfer from Tm$^{3+}$ to Gd$^{3+}$.

In Fig. 6, the Tm$^{3+}$ 5$d$→4$f$ emission spectrum is compared with the Gd$^{3+}$ excitation spectrum. It shows that the 5$d$→4$f$ emission only has spectral overlap with the $^6G_J$ states of Gd$^{3+}$. Contrary to the situation for NaGdF$_4$:Nd$^{3+}$, there is no 5$d$→4$f$ emission overlapping with the lower energy $^6D_J$, $^6I_J$, and $^6P_J$ states of Gd$^{3+}$. This strongly suggests that energy is transferred from the 5$d$ states of Tm$^{3+}$ to the $^6G_J$ state of Gd$^{3+}$, as indicated by the curved arrows in the time resolved emission spectra plotted in the inset of Fig. 7. The fast component of the emission (solid curve) was recorded between 3 and 10 ns after pulsed synchrotron excitation. The slow component (dashed curve) was recorded between 60 and 180 ns. The emission spectrum is composed of two emission bands at 161.6 and 176.8 nm with a short decay time, which correspond to the spin-allowed 5$d$→4$f$ transition starting from the high spin 5$d$ state of Tm$^{3+}$ (Ref. 16) to the $^3F_4$ and $^3H_4$ states. Another emission band at 167.5 nm with a longer decay time corresponds to the spin-forbidden 5$d$→4$f$ transition starting from the low spin 5$d$ state of Tm$^{3+}$ (Ref. 17) to the $^7H_4$ state. These transitions are indicated in Fig. 10(a). The excitation spectrum monitoring both the spin allowed and spin forbidden 5$d$→4$f$ transitions around 177 nm, shown in Fig. 7 [trace (b)], consists of 4$f$→5$d$ excitation bands of Tm$^{3+}$ between 120 and 150 nm.
The most likely cross-relaxation route is observed, there must be an efficient cross relaxation indicated by the dashed arrows in Fig. 10. Since there is no direct transfer route from the 5\(^2\)\(E\) state of Tm\(^{3+}\) to the 3\(^4\)\(H_4\) state of Gd\(^{3+}\), the high intensity of the Gd\(^{3+}\) 3\(^2\)\(H_4\) state because it is located at a too low energy. This explains the lack of 3\(^2\)\(H_4\) emission. In this case, three photons are needed for energy transfer from Gd\(^{3+}\) to the 3\(^2\)\(P_0\) state of Tm\(^{3+}\). Since only weak 3\(^2\)\(H_4\) emission is observed, it must be concluded that cross relaxation mainly involves the 3\(^2\)\(H_4\) state that has emission around 1250 nm which is outside the sensitive area of our CCD detector.

**IV. CONCLUSIONS**

VUV to IR luminescence excitation and emission measurements have revealed in detail how energy relaxes back to the ground state via complex energy transfer and emission scenarios after VUV excitation into the 5d states of Nd\(^{3+}\) and Tm\(^{3+}\) in NaGdF\(_4\). In both systems, quantum splitting is observed that can result in the emission of two IR photons for each absorbed VUV photon.

Nd\(^{3+}\) 4\(f^2\)5\(d^1\) → 4\(f^6\) emission in NaLaF\(_4\):2\%Nd\(^{3+}\) is quenched in NaGdF\(_4\) by an identified cross-relaxation process involving the transitions 4\(f^2\)5\(d\)\(--\rightarrow\)4\(f^6\) (\(G_f\)) on Nd\(^{3+}\) and 8\(S_{7/2}\) → 6\(D_{j}\) on Gd\(^{3+}\). This results in Nd\(^{3+}\) emission from the 4\(F_{3/2}\) state in the IR after nonradiative relaxation from the 4\(G_f\) state. A second photon from the 4\(F_{3/2}\) state of Nd\(^{3+}\) can be emitted after Gd\(^{3+}\) (6\(P_{3/2}\)) → Nd\(^{3+}\) (2\(^2\)\(H_4\)) energy transfer followed by Nd\(^{3+}\) 2\(^2\)\(H_4\) → 4\(D_{3/2}\) nonradiative relaxation and Nd\(^{3+}\) 4\(F_{3/2}\) → 4\(F_{3/2}\) emission. Direct excitation of the Gd\(^{3+}\) 6\(G_{7/2}\) state in NaGdF\(_4\):2\%Nd\(^{3+}\) results in quantum splitting through down-conversion as described recently by Jia et al.\(^{10}\) in LiGdF\(_4\):Nd\(^{3+}\).

Tm\(^{3+}\) 4\(f^1\)5\(d^1\) → 4\(f^{12}\) emission in NaLaF\(_4\):Tm\(^{3+}\) is quenched in NaGdF\(_4\) by cross relaxation involving the spin-allowed and spin-forbidden 4\(f^1\)5\(d\) → 4\(f^{12}\) (3\(^2\)\(H_4\), 3\(^2\)\(F_4\)) transitions on Tm\(^{3+}\) and the 8\(S_{7/2}\) → 6\(G_{j}\) transitions on Gd\(^{3+}\). This cross-relaxation step results in weak IR Tm\(^{3+}\) emission from the 3\(^2\)\(H_4\) and 3\(^2\)\(H_5\) states and strong Gd\(^{3+}\) 3\(^2\)\(P_3/2\) emission. After cross relaxation, a small fraction of energy is transferred from the 3\(^2\)\(P_0\) and 3\(^2\)\(F_4\) states of Gd\(^{3+}\) to the 3\(^2\)\(P_0\) state of Tm\(^{3+}\) which is followed by Tm\(^{3+}\) 3\(^2\)\(P_0\) → 3\(^2\)\(H_4\) emission and successive 3\(^2\)\(H_4\) → 3\(^2\)\(H_6\) emission. In this case, three photons are emitted for one absorbed VUV photon.
4 T. Trupke, M. A. Green, and P. Wurfel, J. Appl. Phys. 92, 1668 (2002).