

Visible quantum cutting through downconversion in $\text{KLiGdF}_5 : \text{Eu}^{3+}$ crystals

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Visible quantum cutting through downconversion in $\text{KLiGdF}_5\text{:Eu}^{3+}$ crystals

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Visible quantum cutting through downconversion is observed for the $\text{Gd}^{3+}\text{--Eu}^{3+}$ couple in $\text{KLiGdF}_5\text{:Eu}^{3+}$ (KLGF:Eu³⁺). In this Gd^{3+} -based fluoride, visible quantum cutting, the emission of two photons of visible light per absorbed photon, occurs upon vacuum ultraviolet excitation of Gd^{3+} at the 6G_J level via two-step energy transfer from Gd^{3+} to Eu^{3+} by cross relaxation and sequential transfer of the remaining excitation energy. The dependence of the efficiency of cross relaxation required for visible quantum cutting on the Eu^{3+} doping concentration is discussed in terms of the probability of energy transfer and the behavior of decay of the 5D_0 emission of Eu^{3+} , and it is found that the KLGF crystal doped with 2 at. % Eu^{3+} exhibits the maximum cross-relaxation efficiency of 0.4. From the number of nearest neighbors around Gd^{3+} ions and the 5D_0 emission intensity, energy transfer from excited Gd^{3+} ions is determined to extend to the fourth-nearest Eu^{3+} neighbors in the quantum cutting process. © 2005 American Institute of Physics. [DOI: 10.1063/1.2135893]

I. INTRODUCTION

Crystals doped with rare-earth ions are promising photonic sources for applications such as lasers and scintillators.¹ Recently, vacuum ultraviolet (VUV) spectroscopy of rare-earth ions has become an important field of luminescent materials research due to the emerging need for VUV-excited phosphors in applications such as plasma displays and mercury-free fluorescent tubes. In these devices, the discharge of a noble gas such as Xe is used to generate vuv radiation (147 nm), which is then converted to blue, green, or red light by a phosphor.² However, existing VUV-excited phosphors do not have sufficient conversion efficiency to achieve conversion of VUV radiation to visible light due to high energy losses associated with nonradiative relaxation processes. This is an inherent limitation of the conversion of one vuv photon to one visible photon via a phosphor. However, the high energy of vuv photons also theoretically allows a quantum efficiency of up to 200% for visible emission if two visible photons can be emitted for every VUV photon absorbed. This phenomenon is called quantum cutting or two-photon luminescence, and phosphors realizing this process are called quantum cutters.

The phenomenon of quantum cutting in the deep blue region (~ 405 nm) was observed in the early 1970s for Pr^{3+} -doped YF_3 and $\alpha\text{-NaYF}_4$.^{3,4} Research is now at the stage where the high-energy levels of rare-earth ions in the VUV region have been clarified, and the possibility of quantum cutting by two-photon emission from these levels by a single rare-earth ion have been studied.⁵ However, efficient visible quantum cutting by two-photon emission for a single rare-earth ion has yet to be realized. Recently, in an attempt to identify efficient visible quantum cutters, Wegh *et al.*^{6,7} proposed a concept based on the principle of downconversion for different combinations of two or three rare-earth ions. By this approach, quantum cutting occurs upon vuv

excitation through energy transfer (downconversion) between different rare-earth ions. Visible quantum cutting based on downconversion has been reported for $\text{LiGdF}_4\text{:Eu}^{3+}$,⁶ $\text{LiGdF}_4\text{:Er}^{3+}$, Tb^{3+} ,⁷ and $\text{CsGd}_2\text{F}_7\text{:Er}^{3+}$, Dy^{3+} .⁸

For the $\text{Gd}^{3+}\text{--Eu}^{3+}$ couple, visible quantum cutting with a quantum efficiency of higher than 100% is theoretically possible for VUV excitation in Gd^{3+} -based fluoride crystals with an optimal Eu^{3+} concentration. Our group recently reported visible quantum cutting based on downconversion for $\text{KGd}_3\text{F}_{10}\text{:Eu}^{3+}$ and $\text{KGd}_2\text{F}_7\text{:Eu}^{3+}$.⁹ In the present study, KLiGdF_5 crystal doped with Eu^{3+} (KLGF:Eu³⁺) is characterized as a potential high-efficiency VUV-excited phosphor. Visible quantum cutting occurs in this system through two-step energy transfer from Gd^{3+} to Eu^{3+} by cross relaxation and sequential transfer of the remaining excitation energy under vuv excitation. Using KLGF:Eu³⁺ crystals doped with various concentrations of Eu^{3+} , the dependence of the efficiency of cross relaxation between Gd^{3+} and Eu^{3+} on the Eu^{3+} doping concentration is discussed in terms of the probability of energy transfer between rare-earth ions and the decay and rise times in decay profiles of the Eu^{3+} emission. The characteristics of energy transfer from excited Gd^{3+} ions to neighboring Eu^{3+} ions are also investigated.

II. EXPERIMENT

KLGF crystal has a monoclinic structure with space group $P2_1/c$,¹⁰ as shown in Fig. 1. The polycrystalline samples of KLGF:Eu³⁺ doped with Eu^{3+} (0.5, 1, 2, 5, and 10 at. %) were synthesized by sintering in an inert atmosphere (Ar gas) at 570 °C for 20 h using charges of fluorides with stoichiometric composition, which assume substitution of the Eu^{3+} -ion dopant for Gd^{3+} . The phases of powders obtained after grinding were identified by x-ray powder-diffraction analysis. The excitation spectra and luminescence spectra of VUV/UV excitation were measured at room temperature using a Kokenkogyo FS-200 fluorescence spectro-

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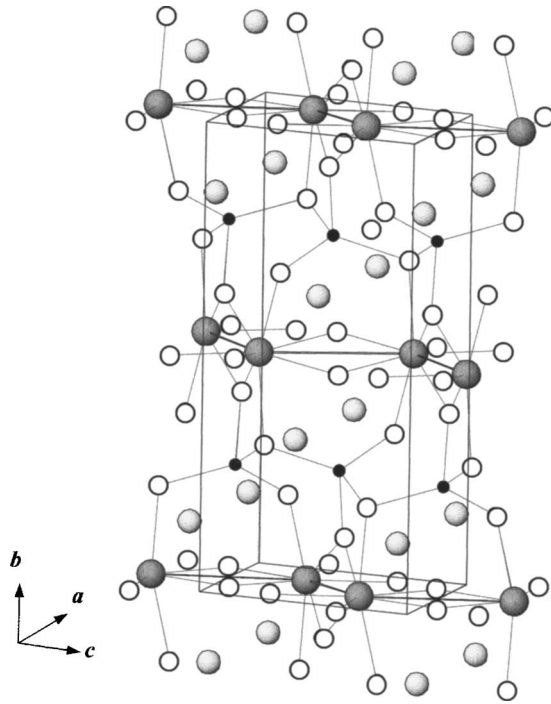


FIG. 1. Unit cell of the KLiGdF₅ crystal structure. Gd³⁺, K⁺, Li⁺, and F⁻ ions are denoted by large shaded, small shaded, solid, and open circles, respectively.

photometer. The decay curves of the Eu³⁺ luminescence were measured using a TIT time-resolved photoluminescence spectrometer.

III. RESULTS AND DISCUSSION

An energy-level diagram illustrating visible quantum cutting through two-step energy transfer in Gd³⁺-based crystals doped with Eu³⁺ is shown in Fig. 2.⁶ In this system, quantum cutting occurs upon excitation at the ⁶G_J levels of a Gd³⁺ ion. The excitation energy in the first step migrates to a neighboring Gd³⁺ ion from a Eu³⁺ ion, then part of the excitation energy is transferred to a Eu³⁺ ion by cross relaxation,

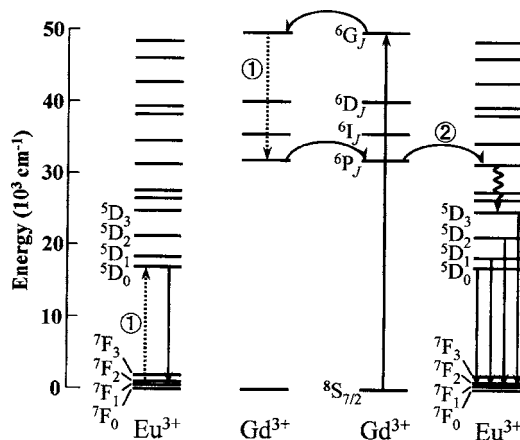


FIG. 2. Energy-level scheme showing the concept of visible quantum cutting through two-step energy transfer (downconversion) for the Gd³⁺-Eu³⁺ couple. In the first step, part of the excitation energy is transferred to a Eu³⁺ ion by cross relaxation. In the second step, the remaining energy is transferred from the ⁶P_J level of Gd³⁺ to a high-energy level of another Eu³⁺.

exciting Eu³⁺ to the ⁵D₀ level and bringing a Gd³⁺ ion to the ⁶P_J level. Subsequently, Eu³⁺ emits a visible photon due to the ⁵D₀→⁷F_J transition. In the second step, the Gd³⁺ ion in the ⁶P_J state transfers the remaining excitation energy to the high-energy state of another Eu³⁺ ion through migration via the Gd³⁺ sublattice. After fast nonradiative relaxation from this high excited state to the ⁵D_J levels, a second visible photon is emitted due to the ⁵D_{0,1,2,3}→⁷F_J transition with a normal branching ratio. Consequently, a substantial increase in the relative intensity of the ⁵D₀ emission from the ⁶G_J levels is expected if quantum cutting through two-step energy transfer occurs. The occurrence of quantum cutting can therefore be evaluated by comparing the emission spectrum for excitation at the ⁶G_J levels of Gd³⁺ (202 nm) with that at the ⁶I_J levels of Gd³⁺ (273 nm). In this study, a two-step energy transfer process yielding a visible quantum efficiency of greater than 100% is predicted for KLGF:Eu³⁺ at an optimal Eu³⁺ concentration.

The emission spectra for KLGF doped with 0.5–10 at. % Eu³⁺ were observed upon excitation at the ⁶G_J level (202 nm) and ⁶I_J level (273 nm) of Gd³⁺. Figures 3(a)–3(d) show the emission spectra for KLGF doped with 2, 0.5, 5, and 10 at. % Eu³⁺ as typical examples. The strongest emission lines in the emission spectra for all samples correspond to those for the transitions from the ⁵D₀ level, although emissions from the ⁵D₁ levels are also observed. Very weak emission lines were also observed for the ⁵D₂ and ⁵D₃ levels (data not shown). The ⁵D₀/⁵D_{1,2,3} emission intensity ratio for KLGF doped with 2 at. % Eu³⁺ [Fig. 3(a)] is 5.0 under vuv excitation at the ⁶G_J level, while that for excitation at the ⁶I_J level is 3.3. Thus, the relative intensity of the ⁵D₀ emission lines for KLGF doped with 2 at. % Eu³⁺ under excitation at the ⁶G_J level is approximately 1.5 times greater than that for excitation at the ⁶I_J level. This observed increase in relative intensity suggests that quantum cutting occurs in KLGF doped with 2 at. % Eu³⁺ upon excitation at the ⁶G_J level of Gd³⁺ (VUV) through two-step energy transfer involving cross relaxation and sequential transfer of the remaining excitation energy. The occurrence of visible quantum cutting via downconversion was observed for four KLGF:Eu³⁺ samples (0.5, 1, 2, and 5 at. % Eu³⁺) upon VUV excitation, but not for the 10 at. % Eu³⁺ sample. The maximum relative intensity was obtained for KLGF:Eu³⁺ with 2 at. % Eu³⁺.

The excitation spectra for the ⁵D₀→⁷F₁ (594 nm) and ⁵D₁→⁷F₁ (538 nm) emissions of KLGF doped with 2 at. % Eu³⁺ are shown in Fig. 4. The intensity of the ⁸S_{7/2}→⁶G_J excitation lines for Gd³⁺ under vuv excitation is approximately 1.5 times greater in the excitation spectrum for ⁵D₀ emission than for ⁵D₁ emission. This observation is consistent with the features of the emission spectra in Fig. 3(a) and also substantiates the presence of quantum cutting through downconversion.

The efficiency of cross relaxation between Gd³⁺ in the ⁶G_J state and Eu³⁺ in the ⁷F_J state can be calculated by evaluating the ⁵D₀ and ⁵D_{1,2,3} integrated emission intensities using the following equation:⁶

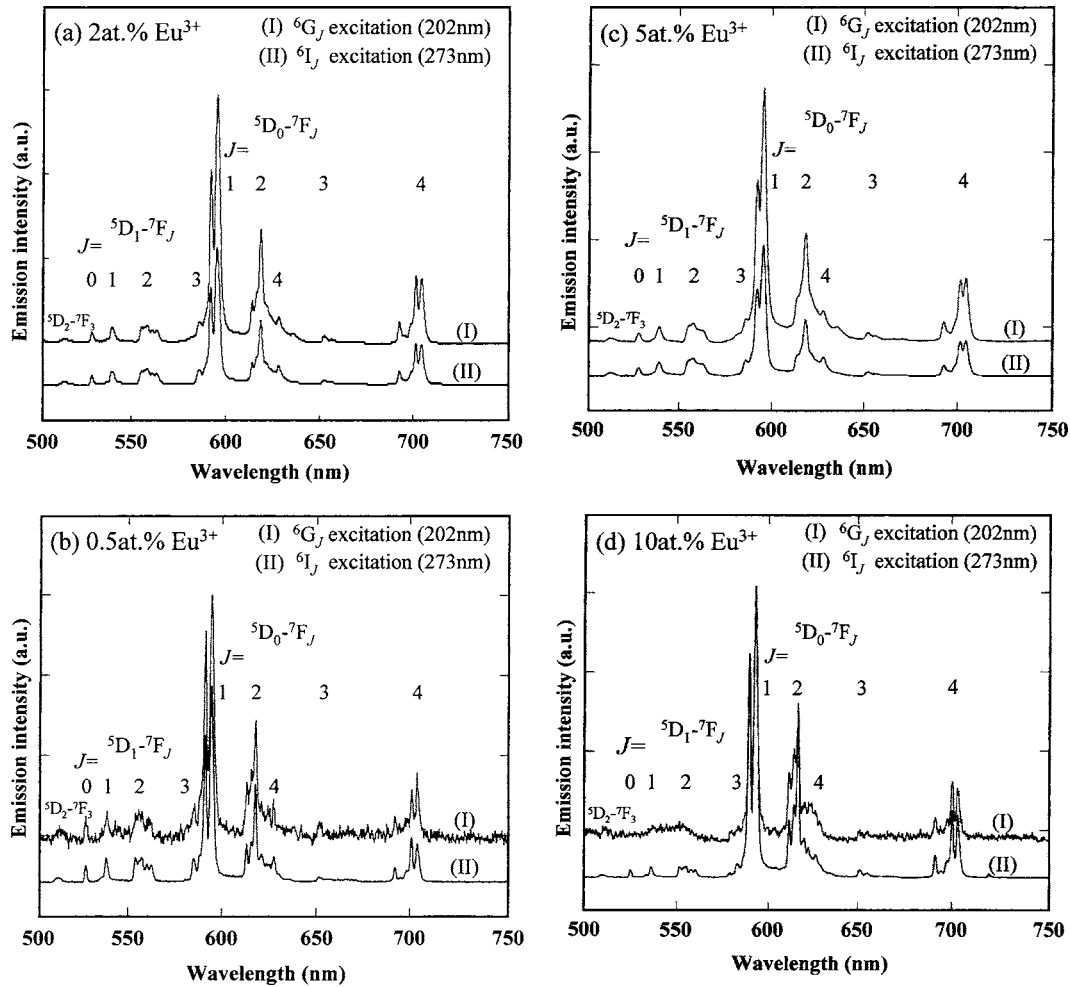


FIG. 3. Emission spectra of (a) KLiGdF₅ doped with 2 at. % Eu³⁺, (b) KLiGdF₅ doped with 0.5 at. % Eu³⁺, (c) KLiGdF₅ doped with 5 at. % Eu³⁺, and (d) KLiGdF₅ doped with 10 at. % Eu³⁺ upon excitation at (I) the ⁶G_J levels of Gd³⁺ (202 nm) and (II) the ⁶I_J levels of Gd³⁺ (273 nm). The spectra are scaled with respect to ⁵D₁→⁷F_J emission intensity.

$$\frac{P_{CR}}{P_{CR} + P_{DT}} = \frac{R(^5D_0/^5D_{1,2,3})_{6G_J} - R(^5D_0/^5D_{1,2,3})_{6I_J}}{R(^5D_0/^5D_{1,2,3})_{6I_J} + 1}. \quad (1)$$

Here, P_{CR} and P_{DT} are the probabilities of cross relaxation and direct energy transfer, and $R(^5D_0/^5D_{1,2,3})_{6G_J}$ and $R(^5D_0/^5D_{1,2,3})_{6I_J}$ are the intensity ratios of ⁵D₀ emission to ⁵D_{1,2,3} emission upon ⁶G_J excitation and ⁶I_J excitation, respectively. The efficiency of the cross-relaxation step in KLGF:Eu³⁺ was determined using the intensity ratios obtained from the emission spectra.

Figure 5 shows the dependence of the calculated efficiency of the cross-relaxation step on the Eu³⁺ doping concentration in KLGF:Eu³⁺. With increasing Eu³⁺ doping concentration, the cross-relaxation efficiency passes through a maximum of 0.4 at 2 at. % Eu³⁺, at which the Gd³⁺–Eu³⁺ (and/or Gd³⁺–Gd³⁺) interactions required for the cross relaxation may be strongest. If it is assumed that there are no nonradiative losses due to energy migration to quenching centers (defects and impurities), the quantum efficiency will be given by $P_{CR}/(P_{CR} + P_{DT}) + 1$. Using this expression, the visible quantum efficiency for KLGF with 2 at. % Eu³⁺ is approximately 140%. In optimized Eu³⁺-doped KLGF of high quality, the quantum efficiency may be even higher.

Although the absolute quantum efficiencies have not been determined and the nonradiative losses remain unknown, the very weak ⁶P_J→⁸S_{7/2} emission (311 nm) for Gd³⁺ under UV excitation compared to the total emission intensity suggests that energy transfer from Gd³⁺ to Eu³⁺ is highly efficient.

The energy transfer that takes place from Gd³⁺ to Eu³⁺ in quantum cutting can occur at any Eu³⁺ concentration, as Gd³⁺ and Eu³⁺ are always present as neighbor pairs. Nevertheless, the energy-transfer process clearly exhibits a strong dependence on the Eu³⁺ concentration, as shown in Fig. 5. This can be explained as follows. At low Eu³⁺ concentrations, the cross-relaxation probability between Eu³⁺ ions is small, resulting in Eu³⁺ emission from all excited ⁵D_J levels for the Eu³⁺ ion fed by the first step in the quantum cutting process and in emission from the ⁵D₀ level only in the second step. Energy migration over the Gd³⁺ sublattice in concentrated Gd compounds is also known to occur, providing efficient energy transfer at low Eu³⁺ concentrations through the efficient trapping behavior of Eu³⁺ in energy migration over the Gd³⁺ sublattice.¹¹

At higher Eu³⁺ concentrations, cross relaxation takes place between Eu³⁺ ions through direct energy transfer from Gd³⁺ to a Eu³⁺ level at ~50 000 cm⁻¹ or direct absorption of

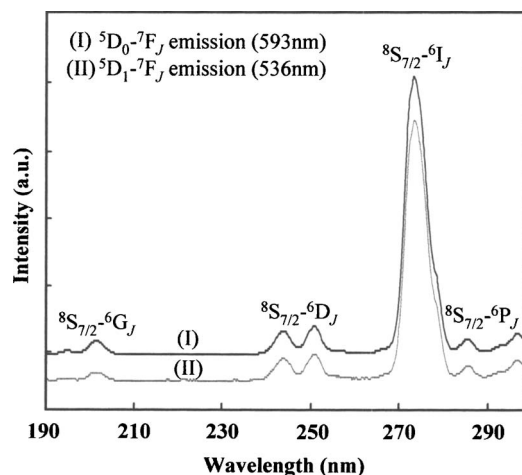


FIG. 4. Excitation spectra obtained by monitoring intensities for (I) the $^5D_0 \rightarrow ^7F_1$ (594 nm) emission and (II) the $^5D_1 \rightarrow ^7F_1$ (538 nm) emission of KLiGdF₅ doped with 2 at. % Eu³⁺. The spectra are scaled with respect to the $^8S_{7/2} \rightarrow ^6I_J$ excitation intensity.

Eu³⁺ instead of Gd³⁺. This process effectively reduces energy transfer due to cross relaxation between Gd³⁺ in the 6G_J state and Eu³⁺ in the 7F_J state, as can be proven by measuring the excitation spectra as a function of the Eu³⁺ concentration. After direct energy transfer to Eu³⁺ or direct absorption on Eu³⁺, fast relaxation occurs from the highly excited Eu³⁺ states to 5D_J ($J=1,2,3,4$) states. In such a case, the Eu³⁺ ions undergo cross relaxation between the $^5D_{J+1} \rightarrow ^5D_J$ ($J=0,1,2$) states in one Eu³⁺ ion and the $^7F_0 \rightarrow ^7F_{J'}$ ($J'=1-6$) states in another Eu³⁺ ion, resulting in intense emission from the 5D_0 state alone.¹² This suggests that less cross relaxation occurs between Gd³⁺ and Eu³⁺ than that required for quantum cutting, and thus the occurrence of quantum cutting via cross relaxation cannot be observed. To examine whether cross relaxation between Eu³⁺ ions increases with Eu³⁺ concentration, the decay curves of the Eu³⁺ $^5D_0 \rightarrow ^7F_1$ emission intensity were measured for KLGF:Eu³⁺ and the rise and decay times were evaluated for all samples.

Figure 6 shows the decay curves of Eu³⁺ $^5D_0 \rightarrow ^7F_1$ emission intensity for KLGF doped with 0.5–10 at. % Eu³⁺ upon excitation at 380 nm (i.e., the 5L_J , 5G_J , and 5D_4 levels of Eu³⁺). The decay curves fit well to a single exponential function, and the decay times decrease from 9.2 to 7.7 ms

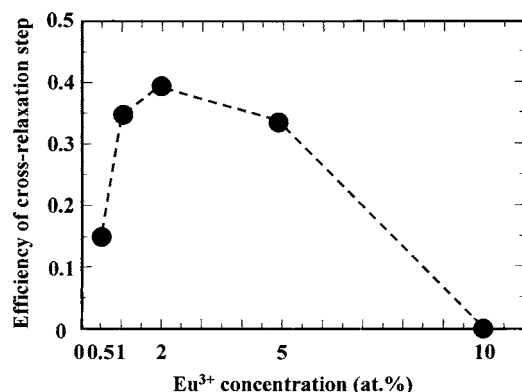


FIG. 5. Dependence of efficiency of cross-relaxation step on Eu³⁺ doping concentration in KLiGdF₅.

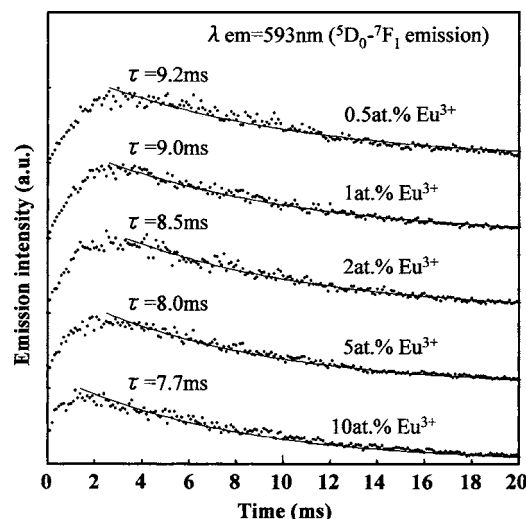


FIG. 6. Luminescence decay curves of the Eu³⁺ $^5D_0 \rightarrow ^7F_1$ emission in KLiGdF₅ doped with 0.5, 1, 2, 5, and 10 at. % Eu³⁺ after pulse excitation at 380 nm into the 5L_J , 5G_J , and 5D_4 levels of Eu³⁺.

with increasing Eu³⁺ doping concentration in this range. KLGF doped with 0.5 at. % Eu³⁺ exhibits a slow rise in Eu³⁺ emission intensity to a delay time of ~ 3 ms after pulse excitation, after which the emission also decays slowly. With increasing Eu³⁺ concentration, the intensity rises faster and the KLGF sample with 10 at. % Eu³⁺ exhibits a rise time of just ~ 1 ms. The decrease in rise time is brought about by a more rapid increase in the population of the 5D_0 level by cross relaxation between $^5D_{J+1} \rightarrow ^5D_J$ ($J=0,1,2$) and $^7F_0 \rightarrow ^7F_{J'}$ ($J'=1-6$).¹² As a result, intense 5D_0 emissions can be observed for KLGF with higher Eu³⁺ concentrations.

In the emission spectra for KLGF with 10 at. % Eu³⁺, similar increases in the 5D_0 emission are seen relative to the 5D_1 emission for excitation at both the 6G_J and 6I_J levels [Fig. 3(d)]. The fast rise and decay at Eu³⁺ concentrations greater than 5 at. % also suggest that fast relaxation occurs from the highly excited Eu³⁺ states to the 5D_J ($J=1,2,3,4$) states through VUV absorption by Eu³⁺ or direct energy transfer from Gd³⁺ to Eu³⁺ followed by cross relaxation between Eu³⁺. Therefore, in KLGF:Eu³⁺ with up to 2 at. % Eu³⁺, the probability of the transfer of excitation energy from Gd³⁺ to Eu³⁺ by cross relaxation becomes higher with increasing Eu³⁺ concentration, causing 5D_0 emission due to cross relaxation to occur more efficiently. However, the efficiency of cross relaxation between Gd³⁺ in the 6G_J state and Eu³⁺ in the 7F_J state, followed by energy transfer in quantum cutting process, decreases at Eu³⁺ concentrations higher than 5 at. %. Thus, there exists an optimum Eu³⁺ concentration in KLGF:Eu³⁺ with respect to the probability of cross-relaxation energy transfer, identified in the present study to occur at about 2 at. %. However, further experiments on the decay of 5D_0 and 5D_1 emissions upon excitation at the 6G_J and 6I_J levels of Gd³⁺ will be necessary to clarify the dynamic behavior of energy transfer in the quantum cutting process.

The number of neighbors N to which the excitation energy of a rare-earth ion can be transferred in the quantum cutting process has been reported to be related to the critical

concentration X_C at which the concentration quenching of rare-earth ion emission due to cross relaxation or energy transfer to defects begins.¹³ The relation is given as a simple approximation by $X_C=2/N$. Applying this relation to the present results reveals that cross relaxation and energy migration between $Gd^{3+}-Eu^{3+}$ and/or $Gd^{3+}-Gd^{3+}$ are strongest at 2 at. % Eu^{3+} . Thus, from Fig. 5, $N \cong 100$ for $KLGF:Eu^{3+}$ with 2 at. % Eu^{3+} . On the basis that every rare-earth ion (Gd^{3+} or Eu^{3+}) in the $KLiGdF_5$ lattice has three first-nearest rare-earth neighbors, every rare-earth ion has three rare-earth first-nearest neighbors at 3.8 Å, 15 second-nearest neighbors at 7.7 Å, 45 third-nearest neighbors at 11.5 Å, and 141 fourth-nearest neighbors at 15.3 Å. It can therefore be concluded from the number of rare-earth neighbors that effective energy transfer from Gd^{3+} excited to the 6G_J level in the quantum cutting process extends out to the fourth-nearest Eu^{3+} neighbors. The distance of the effective energy transfer is evaluated to be about 15 Å based on the nearest-neighboring $Gd^{3+}-Gd^{3+}$ interatomic distance (~ 3.8 Å) and the $KLiYF_5$ structure and lattice constants determined by x-ray diffraction.¹⁰ In $KLGF:Eu^{3+}$, the efficiency of cross-relaxation energy transfer from Gd^{3+} to Eu^{3+} is not particularly high (maximum efficiency, ~ 0.4), despite the existence of energy-conserving pathways. The probability of cross relaxation by dipole-dipole interaction may therefore be competitive with the radiative transition probability ($4f-4f$ transitions), as in $LiGd_{1-x}Eu_xF_4$.¹⁴ For sufficient energy transfer to occur by cross relaxation, it is considered necessary to invoke exchange interactions and energy migration. Taking into account that the distance of effective energy transfer in $KLGF:Eu^{3+}$ (~ 15 Å) is quite large for direct exchange interactions, which operate only over short distances (e.g., nearest-neighbor distances),¹² there is a possibility that superexchange interactions contribute to the energy transfer in $KLGF:Eu^{3+}$. Further experiments are therefore necessary to verify whether energy transfer over such long distances is possible and to identify the applicable cross-relaxation process.

IV. CONCLUSIONS

Visible quantum cutting through downconversion was observed for the $Gd^{3+}-Eu^{3+}$ couple in $KLGF:Eu^{3+}$. The dependence of the efficiency of the cross-relaxation step in downconversion on the Eu^{3+} doping concentration was discussed in terms of the probability of energy transfer between the rare-earth ions and the decay property of 5D_0 emission for Eu^{3+} . The highest cross-relaxation efficiency was found to be 0.40, obtained for $KLGF$ crystal doped with 2 at. % Eu^{3+} . Based on the number of nearest-neighbor rare-earth ions and the 5D_0 emission intensity, the transfer of energy from excited Gd^{3+} ions in $KLGF:Eu^{3+}$ appears to extend to the fourth-nearest Eu^{3+} neighbors in the quantum cutting process.

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¹G. Blasse and B. C. Grabmaier, *Luminescent Materials* (Springer-Verlag, Berlin, 1994).

²C. R. Ronda, *J. Alloys Compd.* **225**, 534 (1995).

³J. L. Sommerdijk, A. Bril, and A. W. de Jager, *J. Lumin.* **8**, 341 (1974).

⁴W. W. Piper, J. A. DeLuca, and F. S. Ham, *J. Lumin.* **8**, 344 (1974).

⁵R. T. Wegh, H. Donker, and J. Holsa, *Phys. Rev. B* **56**, 13841 (1997).

⁶R. T. Wegh, H. Donker, K. D. Oskam, and A. Meijerink, *Science* **283**, 663 (1999).

⁷R. T. Wegh, E. V. D. Van Loef, and A. Meijerink, *J. Lumin.* **90**, 111 (2000).

⁸A. N. Belsky, N. M. Khaidukov, J. C. Krupa, V. N. Makhov, and A. Philippov, *J. Lumin.* **94-95**, 45 (2001).

⁹N. Kodama and Y. Watanabe, *Appl. Phys. Lett.* **84**, 4141 (2004).

¹⁰A. V. Goryunov, A. I. Popov, N. M. Khaidukov, and P. P. Fedorov, *Mater. Res. Bull.* **27**, 213 (1992).

¹¹B. Henderson and G. F. Imbuh, *Optical Spectroscopy in Inorganic Solids* (Clarendon, Oxford, 1989).

¹²S. Tanabe, K. Hirao, and N. Soga, *J. Non-Cryst. Solids* **142**, 148 (1992).

¹³P. A. M. Berdowski and G. Blasse, *J. Solid State Chem.* **63**, 86 (1986).

¹⁴J. P. M. van Vliet, G. Blasse, and L. H. Brixner, *J. Electrochem. Soc.* **135**, 1574 (1988).