

Host sensitization of Gd³⁺ ions in yttrium and scandium borates and phosphates: Application to quantum cutting

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Energy transfer from host excitation at $\lambda \sim 160$ nm to Gd³⁺ impurity ions was observed in yttrium and scandium borates and phosphates. The fluorescence and excitation spectra, as well as time-resolved fluorescence data were obtained. For ScPO₄:1% Gd³⁺ efficient energy transfer to the Gd³⁺ ⁶G state was observed followed by the cascade emission of the visible and ultraviolet photons, yielding quantum cutting. For ScBO₃:Ge and ScPO₄:Gd, absolute quantum yields approach unity making these potential vacuum ultraviolet excited phosphors. A comparison of estimated dipole-dipole energy-transfer rates with observations supports the importance of energy migration of the intrinsic excitations.

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I. INTRODUCTION

Several schemes have now been demonstrated for implementing quantum cutting as a means to obtain from a luminescent material two or more emitted photons for each absorbed photon. It, therefore, serves as a down-converting mechanism that offers the prospect for developing materials with quantum efficiency greater than unity, and it offers the prospect of providing improved energy efficiency in lighting devices. For example, a new class of fluorescent lamps could be developed by replacing the mercury discharge with xenon provided that phosphors with quantum efficiencies in excess of 150% under vacuum ultraviolet (VUV) excitation could be discovered. Examples of materials that emit two visible photons per absorbed ultraviolet photon were demonstrated in the early 1970s, when it was shown that photon cascade emission from the high energy ¹S₀ level of Pr³⁺ can yield two visible photons in a sequential two-step radiative process.^{1,2} Detailed experimental studies of the quantum efficiency showed that the actual visible (380–750 nm) quantum efficiency was 127%. It has been shown that Gd³⁺ ions can also exhibit photon cascade emission in YLiF₄ (Ref. 3) and GdBaB₉O₁₆ (Ref. 4) provided Gd³⁺ is excited to its ⁶G state.

In a second method using a combination of two lanthanide ions, cross relaxation resonant energy transfer (CRET) in which each ion shares a portion of the energy of the initially absorbed photon, was shown to yield two visible photons. For the Gd³⁺-Eu³⁺ couple, an internal quantum efficiency as high as 190% was demonstrated.⁵ The relevant energy levels of Gd³⁺ are shown in Fig. 1. After initial excitation of the ⁶G state of Gd³⁺ at about 50 000 cm⁻¹, a CRET occurs whereby the Gd³⁺ ion undergoes a nonradiative transition to its ⁶P state, while the Eu³⁺ ion undergoes a transition from its thermally populated ⁷F₁ state to its ⁵D₀ state.⁶ The excited Eu³⁺ is responsible for the first visible photon. Resonant energy migration among excited Gd³⁺ ions occurs from within the ⁶P state until the energy resides nearby another Eu³⁺ ion to which it can transfer its energy. The second excited Eu³⁺ ion produces the second visible photon, achiev-

ing the quantum cutting. The quantum cutting, therefore, requires that Gd³⁺ be excited into its ⁶G excited state at about 50 000 cm⁻¹. However, because of the weak absorption by Gd³⁺ resulting from the parity-forbidden and spin-forbidden character of transitions from the ground state to excited states of the 4f⁷ configuration, the direct absorption of this state is weak. Thus a successful phosphor using the Gd-Eu couple will require sensitization of the Gd³⁺ excitation.

Sensitization of the ⁶G state of Gd³⁺ using the 4fⁿ⁻¹5d states of other rare earth ions has been examined. Allowed f-d transitions of many of the rare-earth ions occur in the VUV.⁷ Tm³⁺ and Nd³⁺ have both been shown to sensitize Gd³⁺ in GdLiF₄ but they each also provide an alternate cross relaxation pathway for energy transfer that is more efficient than the Gd-Eu CRET.^{8,9} As a result, after the CRET, the

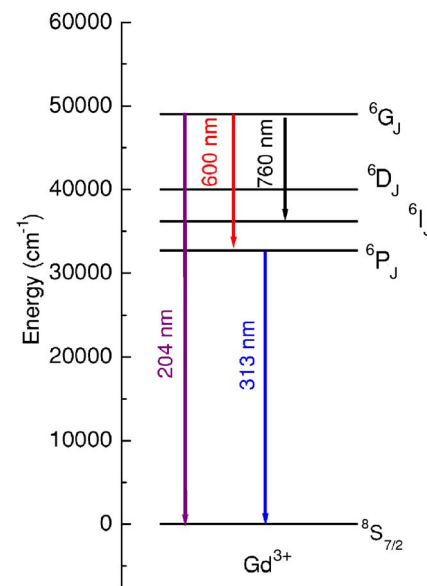


FIG. 1. (Color online) Energy levels of Gd³⁺. The arrows and associated labels indicate the wavelengths of the relevant transitions.

Tm³⁺ and Nd³⁺ ions are left in low-lying excited states which yield, for the first photon, infrared emission. This, of course, defeats the goal of a visible quantum cutter. While sensitization of the ⁶G state of Gd³⁺ by Pb²⁺ has also been examined, it was concluded that sensitization of the ⁶G state will be difficult with this and other heavy *ns*² ions.¹⁰

Sensitization of Gd³⁺ using the intrinsic excited states of the host would be most desirable since it does not require additional doping of ions into the system, and the host provides very strong absorption of the VUV excitation light. It requires that the host excited state transfers its energy effectively to ⁶G of Gd³⁺. This could occur either if the host emission were to overlap the Gd³⁺ absorption to ⁶G at about 204 nm (or higher-lying states of Gd³⁺ which relax predominantly to ⁶G) or via some efficient intersystem crossing between the self-trapped exciton and the Gd³⁺ ⁶G potential surface. Excitation of ⁶G has been demonstrated in a number of hosts, including GdPO₄, using x-ray excitation.¹¹ In some sense, this is an example of host sensitization of the ⁶G state of Gd³⁺.

Host sensitization of Gd³⁺ to its ⁶P levels has been demonstrated in a number of systems.¹² In the present paper we study several materials in which the absorption of light by the host may have the potential for efficient transfer of energy to Gd³⁺ ions in the ⁶G state, as required for quantum cutting. The main feature that distinguishes these kinds of materials is that they should exhibit intense fluorescence from the intrinsic excitations in the undoped materials. This emission is usually ascribed to self-trapped excitons (STE).¹³ The spectral overlap of the host emission with the absorption of Gd³⁺ (or another) ion is the necessary condition of the nonradiative energy transfer according to the Förster-Dexter energy transfer processes.¹⁴ It is also important that the rate of energy transfer from the host to the acceptor ions be faster than the host excitation decay rate. Yttrium and scandium borates and phosphates (YBO₃, ScBO₃, YPO₄, ScPO₄) are interesting materials for sensitizing Gd³⁺ ions because they have relatively large band gaps and they emit intrinsic short-wavelength UV fluorescence efficiently when excited in the VUV. Using emission and excitation spectroscopy along with time-resolved emission, we demonstrate host sensitization of the ⁶G level of Gd and obtain its efficiency, estimate the absolute quantum yields of both the undoped and Gd-doped samples, and examine the dynamics of both the host-to-Gd³⁺ energy transfer and the dynamics of the photon-cascade emission of Gd³⁺.

II. EXPERIMENTAL

Samples of doped and undoped YBO₃, ScBO₃, YPO₄, ScPO₄ were prepared in powder form by using Y₂O₃ (99.999%, Standard Material Corporation), B₂O₃ (99.99%, Alfa Aesar), Sc₂O₃ (99.999%, Standard Material Corporation), (NH₄)₂HPO₄ (99.99%, Sigma-Aldrich), and Gd₂O₃ (99.99%, Standard Material Corporation.) The oxides were mixed according to the desired stoichiometric ratios of each sample, including a 15 mol % excess of B₂O₃ or a 10 mol % excess of (NH₄)₂HPO₄. The mixtures were thoroughly ground and fired in alumina crucibles at 1150 °C for 3 h.

For the phosphate samples, the resulting products were ground a second time with an additional 10 mol % excess of the phosphate reagent. This mixture was then heated at 1350 °C for 3 h. For the borate compounds, the resulting products were ground and mixed two additional times with a 10 mol % excess of B₂O₃ and fired twice at 1330 °C for 4 h.

All spectra were obtained at room temperature. Emission spectra were obtained by exciting the sample, contained in vacuum, with a deuterium lamp spectrally filtered with an Acton VM-502 VUV monochromator. The visible and UV emission was dispersed with an Acton Spectrapro-150 spectrometer and was detected with a Santa Barbara Instrument Group ST-6I charge-coupled device (CCD) camera. All emission spectra were corrected for the wavelength-dependent response of the detection system.

Excitation spectra were obtained by scanning the VUV monochromator, illuminated by the deuterium lamp, while detecting the emission with a photomultiplier tube (PMT) after passing the luminescence through colored glass or interference filters. The excitation spectra of each sample were compared to that of a reference sample of sodium salicylate whose quantum efficiency is assumed to be about 58% and constant over the excitation wavelength range from 140 to 320 nm.¹⁵

For the time-resolved data, the samples were excited with a model EX5 GAM pulsed laser (pulse width 10 ns), operating at 157 or 193 nm with F₂ or ArF, respectively. The laser emission was passed through Acton Research VUV interference filters in order to eliminate other wavelengths from the emission of the laser discharge. The emission was selected with a 0.25-m monochromator and additional colored glass or interference filters. The bandwidth of the instrument was ~3 nm. The emission was detected with a PMT and was averaged and stored in a digital oscilloscope. A temporal resolution of 1–2 ns was obtained.

III. RESULTS

A. ScBO₃

Undoped ScBO₃, under excitation in the VUV at 160 nm, emits a broad emission centered at 238 nm, which is shown by the bold solid curve in Fig. 2. This emission may be assigned to recombination of self-trapped excitons (STE) that could be associated with band-gap excitations or molecular transitions within the BO₃³⁻ group.¹⁶ When ScBO₃ is doped with Gd³⁺ the broad UV emission decreases with an increase in Gd³⁺ concentration as shown by the dotted and dot-dashed curves in Fig. 2. Accompanying the decrease of the broad emission is a dramatic increase in the ⁶P → ⁸S emission of Gd³⁺ at 313 nm, suggesting efficient energy transfer from the host states to Gd³⁺. The energy-transfer efficiency is so great that even the undoped sample shows a weak Gd³⁺ ⁶P emission due to residual Gd³⁺ impurities. As seen in Fig. 3, there is also evidence for weak ⁶G → ⁶P emission around 600 nm (see Fig. 1) which has been previously identified in other materials containing Gd³⁺.^{3,4} The time-resolved emission data described later add support to this assignment. This suggests that there is some energy transfer from the host states to ⁶G of Gd³⁺, although weak direct

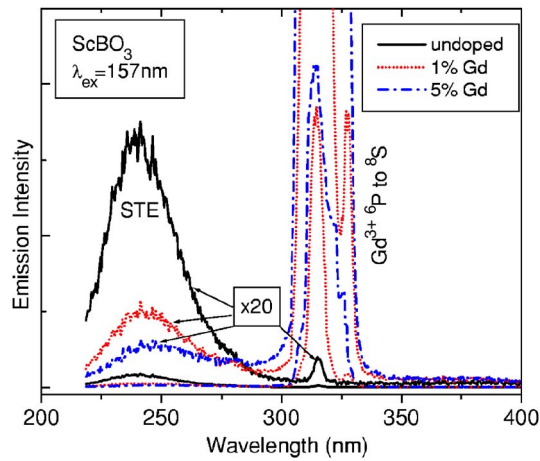


FIG. 2. (Color online) Emission spectra of ScBO₃ excited at 157 nm. The intrinsic STE emission is shown amplified by a factor of 20.

excitation of Gd³⁺ into one of the states of the 4f⁷ above ⁶G at 157 nm is also possible.

The excitation spectra of undoped and 1% Gd and 5% Gd doped samples of ScBO₃ fluorescence (detected at wavelengths longer than 305 nm) are shown in Fig. 4. All three samples show the same spectral excitation features. The quantum yields, measured relative to sodium salicylate, indicate very high quantum efficiencies. Since the absolute quantum yield of sodium salicylate is 0.58, one sees that the ⁶P emission of the 5% Gd³⁺ sample has an absolute quantum yield of 0.8±0.15. Thus, if efficient energy transfer occurs from Gd³⁺ in the ⁶P state to another ion that is a good visible emitter, this material could be a highly efficient VUV-excited phosphor. While the broad intrinsic UV emission of the undoped sample has a considerably lower quantum yield, it is still about 0.3.

The intrinsic emission decay is shown in Fig. 5. In undoped ScBO₃ the decay time is 195 ns, and it becomes much shorter in the Gd³⁺-doped samples. The data are fitted with exponential curves with the best fitted results shown on the

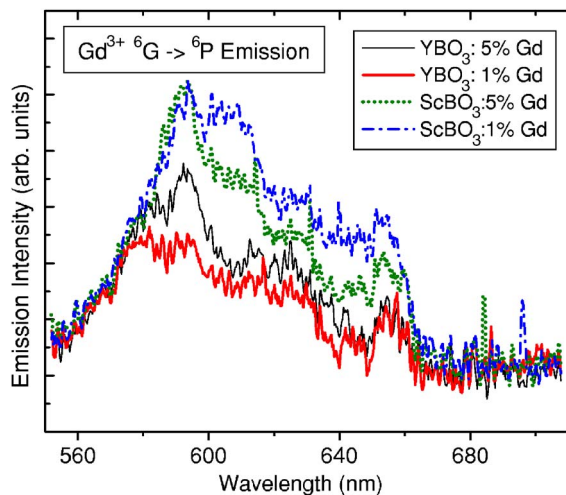


FIG. 3. (Color online) Emission spectra of the Gd³⁺-doped borates in red showing the weak Gd³⁺ ⁶G→⁶P emission.

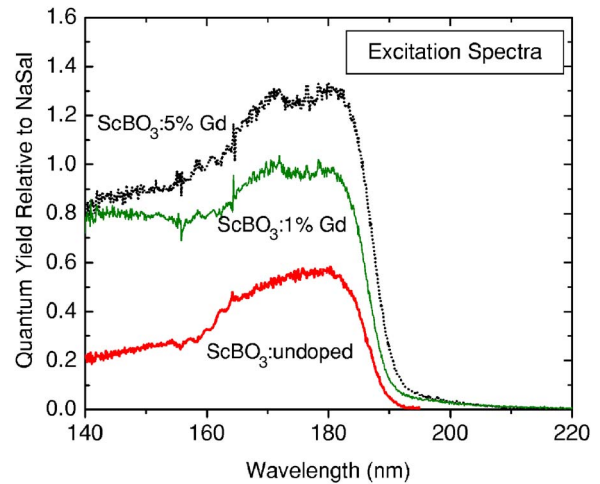


FIG. 4. (Color online) Excitation spectra of undoped and Gd³⁺-doped ScBO₃ detecting the total emission and measured relative to that of sodium salicylate.

figure. The instrumental response (laser and PMT), determined from studies of ZnO, which is known to have a subnanosecond lifetime, yields a 5 ns contribution to any measured decay. Thus, the actual estimated decay time of the 1% and 5% Gd³⁺ samples is 15 and 3 ns, respectively. These shortened decay times are consistent with the fact that the time-averaged intrinsic emission intensities decrease with Gd³⁺ concentration (see Fig. 2). The increased quantum yield in the Gd³⁺-doped samples supports this assertion. The weak emission around 600 nm has a lifetime of 450 and 320 μs in the 1% Gd and 5% Gd samples, respectively, as seen in Fig. 6. This is consistent with expectations for the lifetime of the ⁶G state. The ⁶G decay is dominated by radiative emission to ⁸P and is spin allowed, in contrast to the spin-forbidden ⁶P→⁶S emission whose lifetime is typically milliseconds. The large energy gap of 5000 cm⁻¹ between ⁶G and the next lower manifold, ⁶D, leads to low multiphonon relaxation rates and hence to radiative decay.

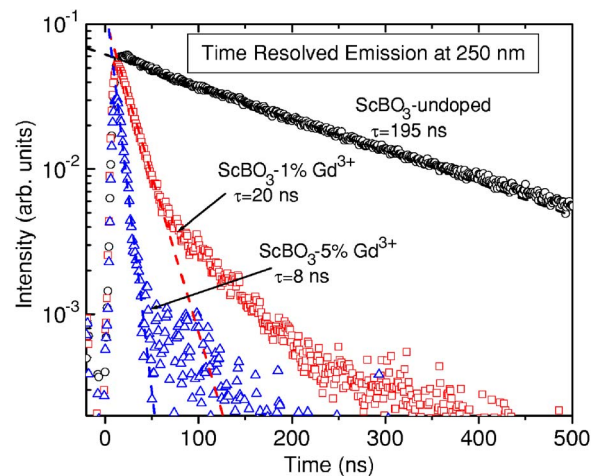


FIG. 5. (Color online) Time-resolved intrinsic emission of undoped and Gd³⁺-doped ScBO₃. The emission was excited at 157 nm and detected at 250 nm. Fitted decay curves are shown by the dashed lines. The fitted values have a 5 ns instrumental contribution.

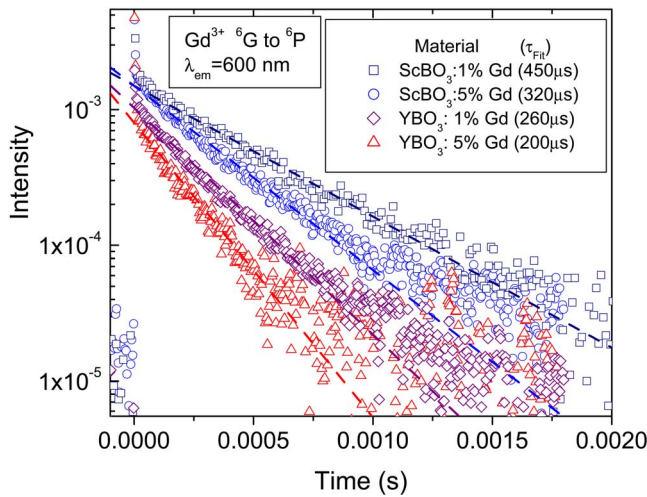


FIG. 6. (Color online) Observed decay of the $Gd^{3+} \ ^6G \rightarrow \ ^6P$ emission in the Gd^{3+} -doped borates. The fitted decay curves are shown by the dashed lines with the decay values shown in the legend.

The relatively weak 6G emission shows that the Gd^{3+} ions are mostly excited to the 6P state; the excitation to 6G state is much less efficient in $ScBO_3$. This may be explained by the insufficient energy of the host excitations. The excitation of the $^8S \rightarrow \ ^6G$ transition is at $\lambda = 205$ nm and corresponds only to the high-energy wing of the host emission so that spectral overlap with the host emission is not ideal. The spectral overlap between host emission and Gd^{3+} absorption favors excitation of 6D and 6I at 254 and 276 nm, respectively. These states undergo rapid multiphonon relaxation to 6P . Despite the strong 6P emission, it is not possible to study its population buildup with nanosecond resolution as the long lifetime limits the photon emission rate; thus, the details of the initial state distributions resulting from the energy transfer from the host states have not been determined.

B. YBO_3

The case of YBO_3 shows some similarities to that of $ScBO_3$. The emission spectra of the doped and Gd^{3+} -doped samples excited at 157 nm are shown in Fig. 7. One sees a broad emission in the undoped sample (bold solid line) peaking at about 325 nm, which is considerably weaker than the emission in $ScBO_3$. In the Gd^{3+} -doped samples a strong 6P emission appears. The broad emission is not quenched in the 1% Gd^{3+} -doped samples, but in the 5% Gd^{3+} it is reduced significantly.

The time-resolved emission exhibits a fast and slow component for all samples, as shown in Fig. 8. The decay time of the fast component is very short, less than 2 ns, but this is not shown in this figure because of the larger input impedance used to obtain these data, which limits the time resolution to about 1 μs . The slow component has a decay time of about 36 μs in the undoped sample. The addition of 1% Gd^{3+} has very little effect on the dynamics of the slower decay component, but with 5% Gd^{3+} it does decrease somewhat (31 μs). This is in sharp contrast to $ScBO_3$ which ex-

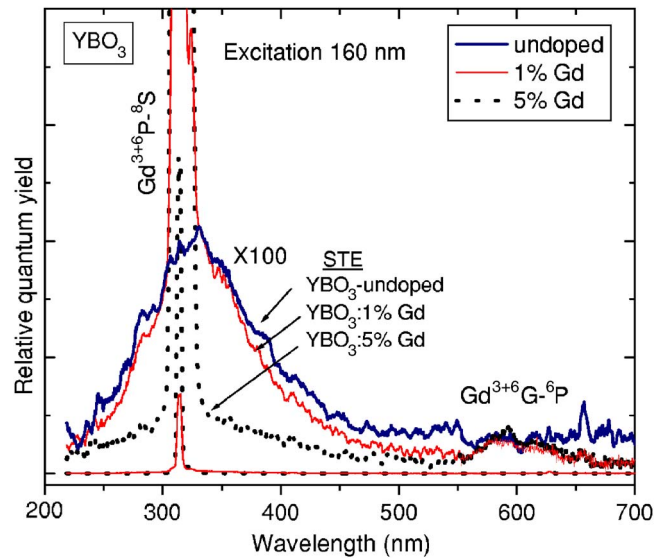


FIG. 7. (Color online) Fluorescence spectra of YBO_3 excited at 160 nm. The intrinsic emission is shown expanded by a factor of 100.

hibited a single exponential decay which became much faster with the addition of Gd^{3+} . The spectra of the fast and slow components, shown in Fig. 9, reveal that there are two independent emission features associated with the two decays peaking at 285 nm (fast) and 325 nm (slow). We suggest that the fast component is the intrinsic emission whereas the slow component, which dominates the intensity of the undoped sample, arises from some defect center. The peak of the fast (intrinsic) component occurs at a slightly longer wavelength than that of the intrinsic emission of $ScBO_3$, for which it occurred at 240 nm.

The excitation spectra, shown in Fig. 10, indicate that the total emission intensity grows with the introduction of Gd^{3+} and that the 5% sample shows an estimated absolute quan-

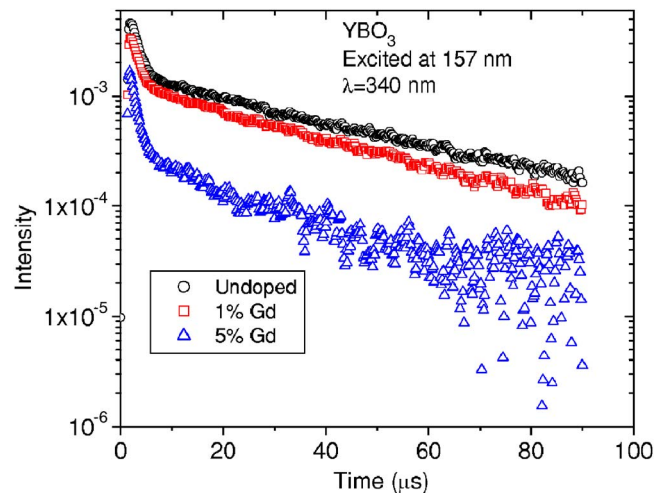


FIG. 8. (Color online) Time-resolved emission excited at 157 nm and detected at 340 nm. The decay is a double exponential. The short decay component in the figure is lengthened by the 5.9 k Ω oscilloscope input impedance. Its actual decay time is < 2 ns.

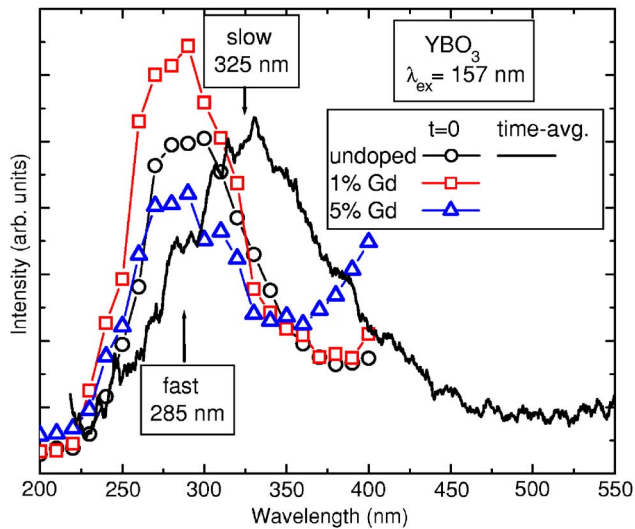


FIG. 9. (Color online) Time-resolved emission spectra excited at 157 nm. The $t=0$ spectrum is obtained from the initial intensity of the fast decay component. The spectrum of the slow decay component was obtained from the intensity at 400 ns after the fast component had decayed. It is identical to the time-averaged emission spectrum.

tum yield of about 0.5 for excitation at 172 nm, about 60% that of ScBO₃ containing 5% Gd³⁺. The spectral features in the excitation spectra are similar for the doped and undoped samples. Reflectance measurements indicate that the band gap of YBO₃ is at 7.65 eV (163 nm).¹⁷ This is just the spectral region where the quantum yield drops. It is likely that this is related to the onset of very strong absorption resulting in excitation close to the phosphor particle surface where nonradiative processes can cause a decrease in quantum yield. The peak at 170 nm may be identified with an exciton state just below the band-gap transition. Calculations of the electronic states for YBO₃ indicate that the low-lying conduction-band states are dominated by metal d -like states.¹⁸

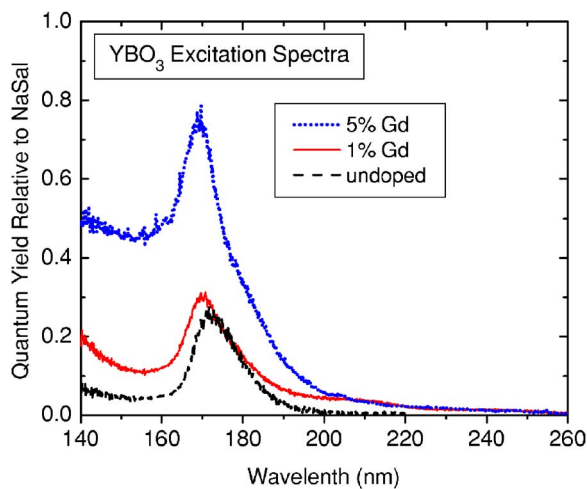


FIG. 10. (Color online) Excitation spectra of undoped and Gd³⁺-doped YBO₃ detecting the total emission and measured relative to that of sodium salicylate.

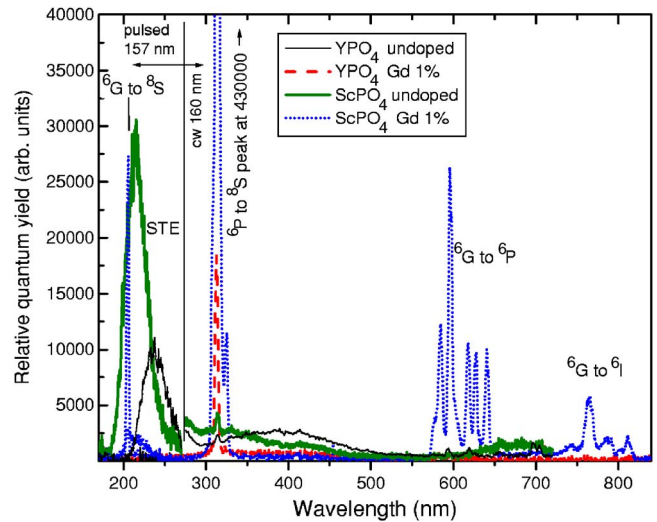


FIG. 11. (Color online) Emission spectra of undoped ScPO₄ and YPO₄ and samples doped with 1% Gd³⁺. For detection wavelengths $\lambda_{\text{det}} < 270$ nm, excitation was with the pulsed laser at 157 nm; for $\lambda_{\text{det}} > 270$ nm excitation was with a cw source at 160 nm.

For excitation at 157 nm the total absolute quantum yield of the undoped sample is about 0.03. Since approximately 10% of this occurs in the fast-emission component, it can be assumed that the short-lifetime results from energy transfer to nonradiative killer centers. The radiative lifetime would then be about 300 times the < 2 ns measured lifetime. Thus, the radiative rate of the intrinsic emission in YBO₃ is less than 600 ns. Because the quantum yield increases with Gd³⁺ concentration due to energy transfer to Gd³⁺ (evidenced by the appearance of ⁶P emission from Gd³⁺), the Gd³⁺ must compete effectively with the killer centers. Thus, the energy transfer to Gd³⁺ appears to be faster than in ScBO₃, i.e., at room temperature it is likely that energy migration of the exciton is more rapid in YBO₃ than in ScBO₃. It is possible that the killer centers are associated with the slow component of the emission, but this cannot be proven.

As seen in Fig. 3, there is evidence for some excitation of the ⁶G level of Gd³⁺ as evidenced by the weak emission at 600 nm, as was the case for ScBO₃:Gd³⁺. The decay of this emission is also shown on Fig. 6 and is similar to that of ScBO₃ with decay times of 260 and 200 μ s in the 1% Gd and 5% Gd samples, respectively. This is consistent with the poor overlap of the fast component of the emission with the ⁶G absorption, which occurs for $\lambda < 204$ nm.

C. ScPO₄

The ScPO₄:Gd³⁺ samples are definitely the most interesting of all studied in the present paper from the point of view of energy transfer to the high-energy excited states of Gd³⁺ and for enabling quantum cutting. In contrast to the borates, ScPO₄ phosphate does sensitize the ⁶G state of Gd³⁺ with considerable efficiency. The emission spectra of ScPO₄, undoped and doped with 1% Gd³⁺, are shown in Fig. 11. The host emission has been ascribed to STEs (Ref. 19) which are derived from intramolecular transitions of the phosphate

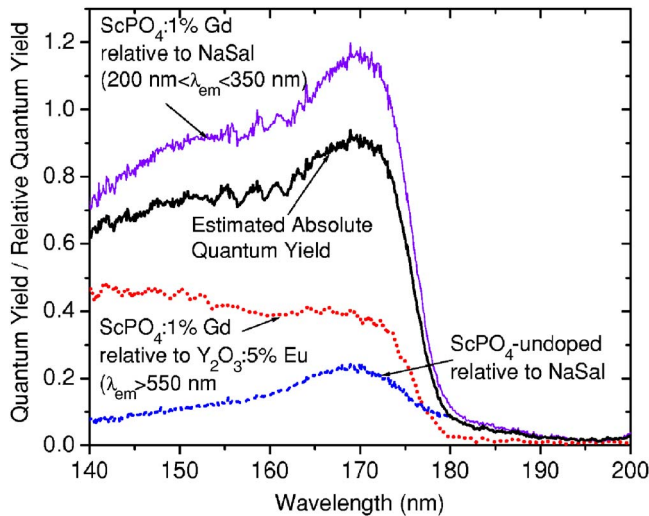


FIG. 12. (Color online) Excitation spectra of undoped and Gd^{3+} -doped ScPO_4 . The doped sample is referenced to sodium salicylate (dashed curve). For the Gd^{3+} -doped sample, the excitation of the UV portion of the emission is measured relative to sodium salicylate (the thin solid curve) while the red portion of the emission is referenced to $\text{Y}_2\text{O}_3:5\% \text{Eu}^{3+}$ (the dotted curve). The estimated absolute quantum yield is shown by the bold solid curve.

group.^{20,21} Intrinsic emission from the host excitations, seen in the undoped sample, consists of two broad features whose maxima are at 215 and 330 nm; the latter extends out to 470 nm. Emission from undoped ScPO_4 under 140 nm excitation at 10 K has been reported at 211, 350, and 470 nm.²² The 211-nm emission can only be excited with excitation energies above the band gap whereas the other bands can be excited at longer wavelengths, supporting their assignment to impurities or defects. Indeed, single crystals of ScPO_4 have been reported to exhibit emission from a variety of impurities.¹⁹ Energy transfer from the intrinsic excitations to Yb^{3+} has been observed.²² In a sample doped with 1% Gd^{3+} , strong quenching of the host emission with the appearance of intense emission from Gd^{3+} suggests efficient energy transfer from the host to Gd^{3+} ions. Even in the undoped sample, weak 6P emission from Gd^{3+} is observed due to some residual impurity level. In the 1% Gd^{3+} sample a very weak intrinsic luminescence persists. Note that in addition to the 6P emission, strong ${}^6G \rightarrow {}^8S$ emission is observed at 204 nm along with ${}^6G \rightarrow {}^6P$ and ${}^6G \rightarrow {}^6I$ emission near 600 and 770 nm, respectively, indicating considerable sensitization of 6G . The integral 6G emission intensity is of the same order of magnitude as ${}^6P \rightarrow {}^8S$ emission at 313 nm.

The excitation spectra of Gd^{3+} -doped and undoped ScPO_4 samples are shown in Fig. 12. Since the emission consists of contributions through the UV, visible, and near IR, the excitation spectra were obtained separately in the different spectral regions. The UV and blue emission was isolated with filters and referenced to the sodium salicylate emission, and the red and near IR emission was compared to that of $\text{Y}_2\text{O}_3:\text{Eu} 5\%$ whose absolute quantum yield as a function of wavelength is well established.¹⁵ All excitation spectra exhibit the same general features with a sharp onset at about 180 nm, indicating that they all result from the same initial-

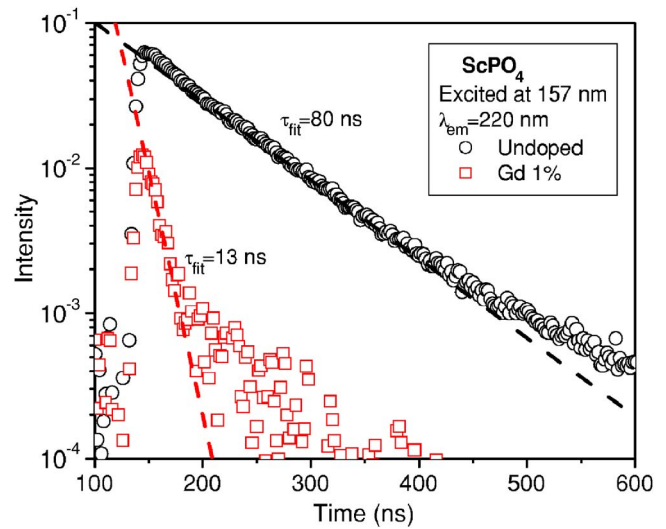


FIG. 13. (Color online) Time-resolved emission of undoped and Gd^{3+} -doped ScPO_4 excited at 157 nm. The fits are shown by the dashed lines and include a 5 ns instrumental contribution.

excitation centers and that the intrinsic-center transfers its energy to Gd^{3+} . The undoped sample (the dashed curve in Fig. 12) produces a quantum yield whose maximum value is 0.23 relative to sodium salicylate at 170 nm, or an absolute quantum yield of 0.14. For the 1% Gd^{3+} -doped ScPO_4 , the UV emission from 6P and 6G (a light solid line) shows a maximum quantum yield of 1.16 relative to sodium salicylate, or an absolute quantum yield of 0.68. The quantum yield of the red and near IR emission relative to that of $\text{Y}_2\text{O}_3:\text{Eu} 5\%$ (dotted line) is about 0.4. The maximum absolute quantum yield of 0.24, based on the known absolute quantum yield of $\text{Y}_2\text{O}_3:\text{Eu} 5\%$ at 170 nm of 0.6,¹⁵ also occurs at 170 nm. The total absolute quantum yield (bold solid line) is then obtained as the sum of these two contributions. It reaches a maximum value of 0.92 ± 0.2 . Thus, this could be an excellent phosphor if the Gd^{3+} ions can transfer their energy to a visible emitting activator.

The relative contributions of the 6G and 6P emission can be estimated from the ratio of their absolute quantum yields. In the ideal circumstance for photon cascade emission, all Gd^{3+} ions would be excited to 6G and would radiate in two steps, first to 6P and then from 6P to the 8S ground state, producing equal contributions in the two spectral regions. If one assumes no nonradiative losses, the observed relative contributions indicate that only about 35% of the Gd^{3+} ions start from the 6G state; the remainder are excited to 6P , 6I , or 6D , where the latter two states rapidly decay to 6P through multiphonon emission. Indeed, as noted above, the 215-nm broad intrinsic emission band overlaps both the 6G and 6D Gd^{3+} absorptions. In addition, the 320-nm feature is strongly resonant with the 6P and perhaps the 6I absorptions. Therefore, it is to be expected that energy transfer will populate all of these states.

The results of time-resolved fluorescence measurements in $\text{ScPO}_4:1\% \text{Gd}^{3+}$ confirm the above conclusions. The decay of the intrinsic emission is shown in Fig. 13 along with an exponential fit to the data. The decay of the intrinsic emission at 215 nm in the undoped sample is 75 ns after subtract-

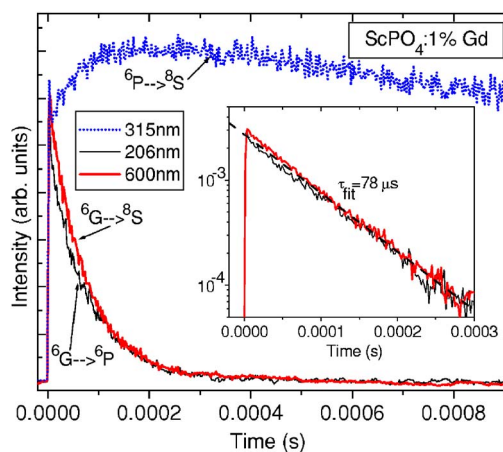


FIG. 14. (Color online) Time-resolved emission of ScPO₄:1% Gd excited at 157 nm and detected at 206 and 600 nm (Gd³⁺ ⁶G emission) and 315 nm (Gd³⁺ ⁶P emission). The inset shows the fit of the ⁶G decay.

ing the instrumental contribution. This value is slightly less than that previously reported in nominally undoped single crystals prepared by flux growth.¹⁹ The decay at 220 nm has been remeasured in these single crystals that were supplied by Lynn Boatner of Oak Ridge National Laboratory and a decay time of 130 ns was observed. Therefore, an additional nonradiative process may be active in the powder samples. In the sample containing 1% Gd³⁺ the fitted decay time is 13 ns, yielding an actual measurable decay time of 8 ns. This is assumed to arise from energy transfer to Gd³⁺ but the buildup of the Gd³⁺ emission cannot be obtained with sufficient resolution. The dynamics of the ⁶G and ⁶P states of Gd³⁺ are shown in Fig. 14 where ⁶G is obtained from emission detected at both 206 and 600 nm while the dynamics of ⁶P is determined from the emission at 313 nm. The 78 μs decay of Gd³⁺ ⁶G state is due to radiative transitions to the ⁶P state; the corresponding buildup of ⁶P population may be seen in the ⁶P → ⁸S fluorescence kinetics which can be described by the same rate as the ⁶G decay. This buildup makes up about 25% of the total ⁶P → ⁸S emission intensity; 75% of the excited population goes to ⁶P much faster (nanosecond time scale). This means that the ratio of the numbers of ions excited by energy transfer to ⁶G and ⁶P states is about 1:3; most of the ions are excited by energy transfer from the host excitations directly to ⁶P or to ⁶P via ⁶D and ⁶I. This is in reasonable agreement with the conclusions based on the excitation spectra where the ratio was determined to be 1:2.

The experimental results show that ScPO₄:1% Gd³⁺ exhibits quantum cutting due to the Gd³⁺ cascade emission process ⁶G → ⁶P (or ⁶I) → ⁸S. It is favorable for quantum cutting that the dominant transition from ⁶G occurs to the ⁶P state, yielding visible emission in the red. However, it is unfortunate that the majority of Gd³⁺ ions are excited by energy transfer from the host states directly to ⁶P (or perhaps ⁶D or ⁶I), preventing the occurrence of a quantum yield exceeding unity. In order to obtain a more efficient phosphor material it will be necessary to find a material with a better branching ratio for the transfer of energy to ⁶G rather than ⁶P population. Since the second photon in the cascade emission occurs

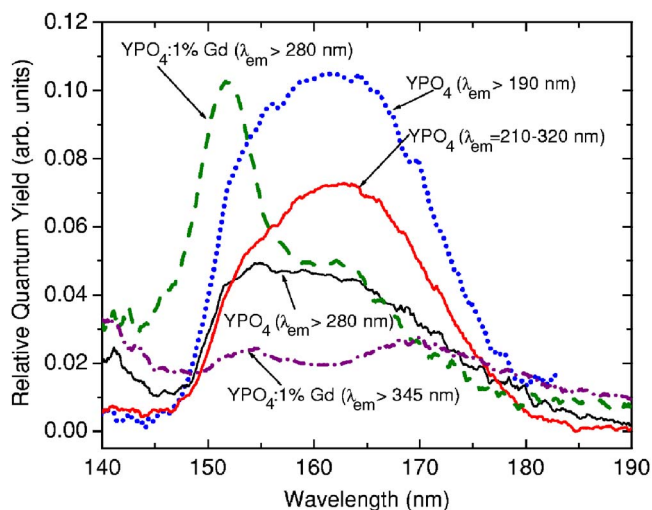


FIG. 15. (Color online) Excitation spectra of undoped and Gd³⁺-doped YPO₄ for detection in different wavelength regions showing the dependence of the spectra on detection wavelengths.

in the UV from ⁶P, it will also be necessary to incorporate a second ion that emits in the visible which can receive the ⁶P energy via an energy transfer process.

D. YPO₄

YPO₄ also emits intrinsic emission in the UV and deep UV as shown in Fig. 11. As for ScPO₄ there are two broad emission bands, one centered at 240 nm and the other at 400 nm. The emission is considerably weaker than that of ScPO₄. Doping YPO₄ with 1% Gd³⁺ completely quenches the 240 nm emission feature and a strong ⁶P emission from Gd³⁺ is evident. A very weak ⁶G emission is observed at 600 nm (to ⁶P) and 204 nm (to ⁸S_{7/2}) whose lifetime is 72 μs. The excitation spectra of the doped and undoped samples, under various detection conditions are reported in Fig. 15. All the excitation spectra show an onset beginning at 180 nm. The excitation spectra for the undoped sample differ somewhat depending on the detection wavelength range. There appear to be two bands whose relative strengths are such that the shorter wavelength excitation feature dominates for detection at longer wavelengths and vice versa for detection at shorter wavelengths. Thus there appear to be two independent sources in the excitation spectrum. Two features are also observed in the Gd³⁺-doped YPO₄ fluorescence excitation spectrum. The excitation spectrum of Gd³⁺-doped YPO₄ is in agreement with that reported by Nakazawa²³ who assigned the feature at 152 nm to the host lattice absorption. The 4f⁶5d and charge-transfer bands of Gd³⁺ are at much higher energies. For detection wavelengths greater than 280 nm in the Gd³⁺-doped sample, which includes essentially all of its emission, the 152-nm band is stronger; for detection of the weak emission only at wavelengths greater than 345 nm, two features of nearly equal relative intensity are seen. The two peaks in the excitation spectra probably correspond with the two distinct host states observed in the fluorescence spectra. The strong peak at 152 nm, observed in excitation spectra of the total (Gd³⁺+host) emission may

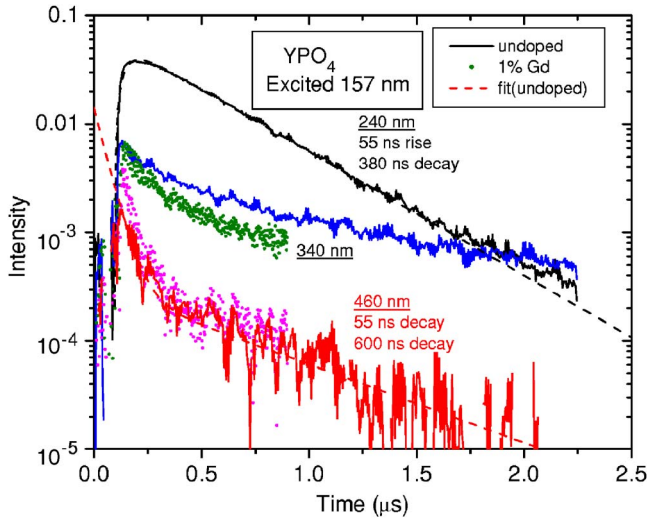


FIG. 16. (Color online) Time-resolved emission of undoped (solid curves) and Gd³⁺-doped (dotted curves) YPO₄. The 240 nm emission shows a 55 ns buildup and 380 ns decay while the emission at longer wavelengths (340 and 460 nm shown in the figure) exhibit a decay with two components. The dashed curves show fits to the 240 and 460 nm data for the undoped sample.

suggest a more efficient energy transfer from the higher energy host excitations to Gd³⁺. However, the total quantum yield relative to sodium salicylate is below 0.1 for both the doped and undoped samples.

The dynamics of the host emission is shown in Fig. 16. The dynamics are quite unusual. First, consider the undoped sample (solid curves). The decay of the emission detected at 240 nm is exponential with a decay time of 380 ns as shown by the fit to the data. This is about five times greater than the lifetime in ScPO₄. However, it does not appear immediately but rather has a rise time of 55 ns as shown by the fit to the time dependence of the 240 nm emission (dashed curve).

The longer wave-length emission feature peaking at 400 nm (detected at 460 nm to minimize contributions from the shorter wavelength bands) exhibits a double-exponential decay and does not display any detectable rise time. The faster decay component is described by a 55 ns decay time, the same as the 240 nm emission rise time; this is shown by the fit (dashed curve). The longer decay time is 600 ns. The nearly identical dynamics of the 240-nm buildup and 400-nm fast decay component suggest that the center responsible for the 400-nm feature feeds the center corresponding to the 240-nm feature. This does not violate energy conservation provided that the 400 nm emission results from a very large Stokes shift. In this way, its excited-state energy may still be above that of the center producing the 240-nm emission. Second, the dynamics of the Gd³⁺-doped sample is nearly identical to that of the undoped sample, except that the 240-nm feature is totally absent. This can occur if the center responsible for the 240-nm emission transfers its energy very efficiently to the Gd³⁺ ions. The small effect of Gd³⁺ on the 400 nm emission implies that energy transfer from this center to Gd³⁺ is inefficient.

IV. ENERGY TRANSFER RATES

The decay rates of the intrinsic and Gd³⁺ emission for the undoped and doped samples are summarized in Table I. It should be possible to compare the observed energy transfer rates from the host to the Gd³⁺ ions to estimates based on dipole-dipole mediated Förster-Dexter energy transfer theory. The Förster-Dexter energy transfer rates can be represented by the expression^{24,9}

$$P_{AB}^{dd} = (1.4 * 10^{24} f_{host} f_{Gd} S) / (\Delta E^2 R^6), \quad (1)$$

where ΔE is the transition energy in eV, f_{host} and f_{Gd} are the oscillator strengths of the host emission and Gd³⁺ absorptions, respectively, S is the spectral overlap of the host emission with the Gd³⁺ absorption expressed in units of cm⁻¹, and

TABLE I. Wavelengths and decay times of the emission of undoped and Gd³⁺ doped scandium and yttrium borates and phosphates.

	Host emission wavelength	Host emission (STE) decay time			Gd ³⁺ Decay time		
		Undoped	Gd doped		⁶ P	⁶ G	
			1%	5%		1%	5%
ScBO ₃	238 nm	195 ns	15 ns	3 ns	4.0 ns	450 μs	320 μs
YBO ₃	285 nm	<2 ns	<2 ns	<2 ns	4.5 ms	260 μs	200 μs
ScPO ₄	215 nm (powder)	75 ns	8 ns		4.8 ms	78 μs	
	215 nm (crystal)	130 ns					
YPO ₄	320 nm						
	240 nm	55 ns rise 380 ns decay	absent		3.2 ms	72 μs	
	400 nm	55 ns decay 600 ns decay	55 ns decay 900 ns decay				

R is the distance between the host excitation and Gd³⁺ expressed in angstroms.

An upper limit of the radiative decay rate of the intrinsic emission is given by its observed decay rate. However, since the quantum yield of the intrinsic emission is of order 1 in all but YPO₄, the observed decay rate must, in fact, be close to the radiative rate, typically 10⁶–10⁷ s⁻¹, based on the data in Table I. Such a decay rate corresponds to an oscillator strength $f_A \sim 10^{-3}$ –10⁻². For Gd³⁺ the absorptive transitions are spin-forbidden so that oscillator strengths of about 10⁻⁶ to 10⁻⁷ are to be expected. The overlap can be estimated as 2×10^{-4} cm⁻¹ based on the observation that the host broadband emission has a bandwidth that is much greater than that of Gd³⁺ and is about 5000 cm⁻¹. Dipole-dipole-mediated energy-transfer rates for typical nearest-neighbor cation distances of 3.7 Å are then estimated from Eq. (1) to lie between 5×10^5 to 5×10^7 s⁻¹. For a 1% Gd³⁺ concentration, the typical nearest-neighbor distance between a localized host excitation and Gd³⁺ ion is about 7 Å yielding estimated energy-transfer rates of 10⁴–10⁶ s⁻¹. Since there are a number of Gd³⁺ ions in the vicinity of a host excitation, these estimates should probably be increased to the range 10⁵–10⁷ s⁻¹. The observed rates in these borates and phosphates doped with 1% Gd³⁺ are at least 10⁸ s⁻¹, a value that is one to three orders of magnitude greater than the rate estimated based on dipole-dipole Förster-Dexter energy transfer. This suggests that the host excitations are mobile, allowing them to sample the whole lattice such that they spend a fraction of their time as a nearest neighbor of the Gd³⁺ where the dipole-dipole interactions will be about a factor of 100 larger or where much larger exchange interactions can provide an additional energy-transfer mechanism.

V. CONCLUSIONS

The simple binary yttrium and scandium borates and phosphates have all been found to exhibit intrinsic emission in the UV, and the lifetimes of these intrinsic emissions have been determined. Efficient energy transfer from the host excitations to Gd³⁺ was observed, showing that host sensitization occurs in these materials. A comparison of the observed and estimated theoretical rates suggests that the host excitations are mobile at room temperature. For ScPO₄:1% Gd³⁺ about 30% of the energy transfer from the host excitations to Gd³⁺ occurs to the ⁶G state, demonstrating for the first time host sensitization of the ⁶G state of Gd³⁺. This excitation is followed by a cascade emission of photons, making possible quantum cutting in which one visible and one UV photon are emitted. Absolute quantum yields were determined for all samples with measured values of 0.92 and 0.8 in ScPO₄:Gd and ScBO₃:Gd, respectively. If the Gd³⁺ ⁶P excitation can be transferred efficiently to another ion emitting visible radiation, these Gd³⁺-doped materials could be competitive with existing VUV excited phosphors.

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