Temperature Quenching of Yellow Ce^{3+} Luminescence in YAG:Ce

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Yttrium aluminum garnet (YAG) doped with Ce^{3+} is the phosphor of choice for the conversion of blue to yellow light in the rapidly expanding market of white light LEDs, but it is generally thought to suffer from a low luminescence quenching temperature. The luminescence quenching temperature is an important parameter, especially in high-power LEDs, but surprisingly no systematic research has been done to measure and understand the temperature quenching of the yellow Ce luminescence in YAG:Ce. Here we report on the luminescence temperature quenching in YAG:Ce. For a wide range of Ce concentrations (between 0.033% and 3.3%) the temperature dependence of the emission intensity and the luminescence lifetimes are reported. The intrinsic quenching temperature of the Ce luminescence is shown to be very high (>700 K). The lower quenching temperatures reported in the literature are explained by thermally activated concentration quenching (for highly doped systems) and the temperature dependence of the oscillator strength (for low doping concentrations). In addition, high-resolution spectra are reported, which provide insight into the position of the zero-phonon transition (20450 cm^{-1}), the Stokes shift (2400 cm^{-1}), the energy of the dominant phonon mode (200 cm^{-1}), and the Huang–Rhys parameter ($S = 6$). These parameters are compared with ab initio calculations on the position of and relaxation in the excited 5d state of Ce^{3+} in YAG, which can aid in providing a better theoretical understanding of the temperature quenching.

1. Introduction

Yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$ or YAG) doped with Ce^{3+} is a luminescent material with a rich history and a wide variety of applications. Recently, there is a renewed interest in this material due to its application in white light LEDs. The story of the garnet dates back to ancient times when garnets were used as gemstones due to their beautiful colors or as abrasives because of their hardness. The scientific history starts in 1928 when Menzer assigned the garnet structure to the space group *Ia*3*d*.[1] The unit cell consists of four formula units with a single type of Y-site. Eight oxygen atoms in a distorted dodecahedron coordinate the Y atom, giving it D_2 symmetry. Blasse and Bril were the first to report on Ce^{3+}-doped YAG as a new phosphor for flying-spot cathode ray tubes (CRT). The combination of a high luminescence efficiency, a short luminescence lifetime and a relatively long wavelength (visible) emission made this material ideally suited for this application. A good estimate of the luminescence decay time was given (0.07–0.08 μs).[2] The fast emission was shown to be most efficiently excited in the blue (at 460 nm) but it was not until later that this feature was exploited. In a second publication Blasse and Bril reported more detailed spectroscopic results like the position of the first four (of the expected five) f–d excitation bands, emission bands in the visible and the UV spectral

range, the quantum efficiency for the emission from the lowest excited d-level, and the Stokes shift.[3] The use of the long wavelength excitation band centered around 460 nm was reported by Van Kemenade et al.[4] They described the application of YAG:Ce in low-pressure mercury vapor discharge lamps to absorb the Hg-plasma lines in the blue/violet part of the spectrum, viz. 405 and 436 nm. The conversion of the violet and blue emission lines into yellow light adds to the white light emitted by the halophosphate phosphor (the commonly used phosphor in those days) to create a warmer white light. In the late 1970s some excellent papers were published by Robbins et al. on the fundamental aspects of the luminescence and luminescence quenching for Ce^{3+} in YAG.[5−7] In the 1990s YAG:Ce and the higher density analog LuAG:Ce were proposed as fast and efficient scintillator materials, which again triggered interest in this material. Here, the research was focused on the response time as a scintillator material and energy transfer from a self-trapped-exciton (STE) state to Ce^{3+}. Another recent application of the luminescence of YAG:Ce is the use of single-crystalline disks of YAG:Ce to monitor and control the dose

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of VUV radiation in wafer steppers. The dose applied for photoetching is measured by converting a small part of the VUV radiation from an excimer laser pulse into visible light.

In recent years YAG:Ce has received renewed interest related to yet another application: the use as color converter in (In,Ga)N-based phosphor-converted LEDs (pc-LEDs). At present, YAG:Ce is the most widely applied phosphor in white light LEDs.[8] Part of the blue light from the (In,Ga)N LED is absorbed by a thin layer of YAG:Ce and is converted into yellow light. The combination of blue and yellow gives a bright white light source with an overall energy efficiency that is approaching that of the compact fluorescent lamp. For low-power cool-white LEDs efficiencies higher than those for fluorescent tubes have been realized. One can observe the yellow phosphor when looking into the LED (turned off). In spite of the success of YAG:Ce, the rapidly expanding market for solid-state lighting has an urgent need for new phosphors with a higher conversion efficiency, a better coverage of the spectrum (including the orange/red spectral region), and an improved thermal quenching behavior. This becomes even more evident when one takes the fast development in the market of *high-power* LEDs into account.[8,9] For general lighting applications, high-power LEDs are needed but by increasing power consumption the heat created at the p−n junction increases as well, and the temperature of the phosphor layer reaches temperatures well above 450 K in commercially available products. At these high temperatures thermal quenching has been observed for YAG:Ce. For example, Tamura et al. give temperature-dependent emission spectra of an InGaN white LED.[10] For increasing chip temperatures they observe an intensity decrease of the blue emission from the LED combined with a shift of the emission maximum to longer wavelength. They also observe a decrease of the YAG:Ce emission band.[10] The same observation has been reported by Sakuma et al.[11] Setlur et al. reported on the temperature dependence of the Ce^{3+} emission intensity and observed a steady decrease above 400 K.[12,13] New luminescent materials with a better spectral coverage and temperature behavior are thoroughly investigated and the work has resulted in an impressive number of papers and patents in the past 3 years. Especially the Ce^{3+}- and Eu^{2+}-doped nitrides and oxynitrides are promising candidates to replace YAG:Ce.[8,14−16]

In spite of the general realization that the efficiency of YAG:Ce decreases at the high temperatures that are reached in high-power LEDs, the understanding of the temperature quenching is limited. The work of Robbins was focused on the behavior between 4 and 400 K.[7] The variation of the light output was shown to be complex and to involve changes in the absorption strength of the (different) f−d absorption bands and the (temperature-dependent) energy transfer to defects. After this work, research on the fundamental understanding of the temperature quenching of the luminescence in YAG:Ce is limited. It is the aim of this paper to provide a better understanding of the temperature quenching of the Ce^{3+} emission in YAG:Ce in the high-temperature regime (above 400 K), which is especially relevant for application in high-power LEDs. To establish the intrinsic quenching temperature for the Ce luminescence, temperature-dependent measurements are performed on systems down to very low Ce^{3+} concentrations (0.033%) in the temperature range 5−700 K. For the isolated centers thermally activated crossover to the ground state is probably responsible for the temperature quenching and the temperature dependence of the luminescence of isolated Ce^{3+} ions (i.e., no energy transfer) provides insight into the intrinsic thermal quenching for Ce^{3+} in YAG. It is shown that the intrinsic quenching temperature for the emission is high (>700 K). The lower luminescence quenching temperature observed in the commercial (highly doped) YAG:Ce LED phosphors is explained by concentration quenching, which becomes more pronounced at elevated temperatures. In addition to establishing the intrinsic luminescence quenching temperature, low-temperature studies are reported on the luminescence properties of the YAG−Ce samples. The observation of zero-phonon lines and vibrational structures makes it possible to accurately determine the true Stokes shift (which is smaller than the Stokes shift reported in the literature for more concentrated systems) and is related to theoretical work (ab initio calculations) on luminescence properties and the configurational coordinate diagram for Ce^{3+} in YAG.[17]

2. Experimental Section

Research on YAG:Ce has been conducted on single crystals, ceramics, and powders. A good overview of the different synthesis methods for crystalline powders is provided by Pan et al.[18] Four methods are described: solid-state reaction, coprecipitation method, sol−gel method, and the combustion method. We used a coprecipitation method to prepare crystalline powder samples of YAG: Ce with 0.033, 0.33, and 1.0 at. % Ce^{3+} (relative to Y^{3+}). $YCl_3 \cdot 6H_2O$ (Aldrich, 99.99%), $AlCl_3$ (Aldrich, 99.99%), $(NH_4)_2SO_4$ (Aldrich, 99.999%), urea (Aldrich, 99+%), and $CeCl_3 \cdot 7H_2O$ (Aldrich 99.999%) were dissolved in water. The solution was heated slowly to 90−100 °C until the precipitation started because of evaporation of water. The solution was kept constant at this

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temperature for 2−3 h. The precipitate was filtered, washed with water, and dried at 100 °C. For the firing the crucible was placed in a bed of active carbon to create a reducing atmosphere. It was fired twice, at 1300 and 1700 °C, respectively, each time for 2 h with a milling step in between. Additionally, a commercially available sample of YAG:Ce containing 3.33% Ce³⁺ (made by Philips Lighting Components) was used for this study. XRD analysis was done on a Philips diffractometer PW 1729 at room temperature, using Cu Kα radiation. All samples under investigation were single phase.

Luminescence spectra were recorded between 300 and 600 K on a modified spectrofluorometer system FL900 of Edinburgh Instruments using a Xe lamp as the excitation source. The spectra were measured with a spectral resolution of 0.5−1.0 nm. Luminescence spectra between 4 and 300 K were recorded on a Spex Fluorolog 2 spectrofluorometer equipped with a helium flow cryostat. Luminescence lifetimes were obtained using a Pico Quant picosecond laser (λ_{exc} = 406 nm, pulse width 65 ps) with a repetition rate of 1 MHz using pulse height analysis (PHA) and time-to-amplitude conversion (TAC). The emitted photons were detected using a fast Hamamatsu photomultiplier. The emission wavelength was selected using a 0.1 m monochromator with a grating blazed at 536 nm. For measurements up to 700 K a homemade heating cell connected to a temperature controller was used.

3. Results

3.1. Luminescence Spectra. The normalized room temperature (RT) excitation and emission spectra of the YAG samples with the four different Ce concentrations are depicted in Figure 1a. Emission spectra were recorded for λ_{exc} = 450 nm, which corresponds to excitation into the lowest energy d-level of Ce³⁺. For increasing Ce³⁺ concentrations a significant red shift in the emission spectrum and its maximum is observed, viz. 536 nm for 0.033% to 558 nm for 3.33% Ce³⁺. The emission is ascribed to the 5d to 4f transition on Ce³⁺. Excitation spectra were taken for emission at 536 nm (for 0.033% and 0.33% Ce³⁺), 546 nm (for 1% Ce³⁺), and 558 nm (for 3.33% Ce³⁺), respectively. The spectra show two excitation bands which are assigned to transitions to the two lowest energy levels of the five crystal field levels expected in D_2 symmetry. The two bands are centered around 460 and 342 nm, which is in agreement with the observations reported in the literature.[2−7] The relative intensity of the two bands changes with increasing Ce concentration because of saturation of the absorption. Saturation sets in at lower concentrations for the stronger absorption band around 460 nm and as a result the relative intensity of the weaker absorption band increases. This is also observed in the diffuse reflection spectra (Figure 1b) of the same four samples. The position of the absorption bands does not change with increasing Ce³⁺ concentration. In the diffuse reflection and excitation spectra also a third absorption band centered around 260 nm is observed. The origin of this band is under discussion in the literature and it is not clear whether it is a transition to the third 5d level or a transition related to a defect or impurity in the YAG host lattice. For the present work the origin of this band is not important. The reflection spectrum of the sample with 1% Ce³⁺ shows a shoulder for wavelengths shorter than 400 nm. The origin of this absorption is not clear and may be related to a difference in the preparation conditions, even though the
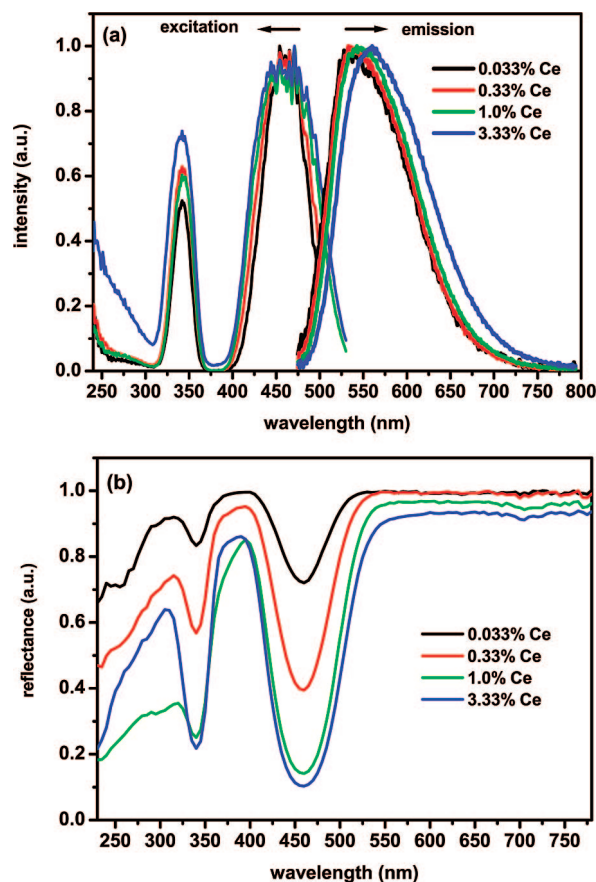
Figure 1. (a) Excitation and emission spectra of Y₃Al₅O₁₂:Ce 0.033%, 0.33%, 1.0%, and 3.33%; (b) diffuse reflection spectra of Y₃Al₅O₁₂:Ce 0.033%, 0.33%, 1.0%, and 3.33% (all spectra recorded at room temperature).

same synthesis procedure was followed as for the other samples. The lower baseline for the samples with 1% and 3.33% Ce in the 550−750 nm spectral range may be due to the presence of small amounts of Ce⁴⁺, which causes absorption in the visible due to charge-transfer transitions. Luminescence quantum yields (QYs) of the samples were determined for excitation at 450 nm. The quantum yields are high: ~89% for the sample with 1% Ce and 81% for the sample doped with 3% Ce. For the lower doped samples QYs around unity were measured but the accuracy is lower because of the relatively high reflectivity.

The luminescence spectra are studied as a function of temperature in the ranges from 5 to 295 K (in a cryostat) and from 300 to 600 K (in a high-temperature cell). Note that the emission spectra for the two temperature ranges were recorded on different spectrofluorometers (an Edinburgh FL900 for the high-temperature range and a SPEX Fluorolog 2 for the low-temperature regime) and the difference in the spectral response between the two setups explains the differences between the 300 K emission spectra in parts (a) and (b) of Figure 2. Because we are interested in the luminescence properties of the isolated Ce ions, the spectra for the lowest Ce concentration are studied in detail. For higher concentrations energy transfer and reabsorption of the emission can occur. This will influence the temperature dependence of the luminescence spectra and decay curves. As a result, the observations will not reflect the intrinsic luminescence properties of the isolated Ce ions in YAG (vide
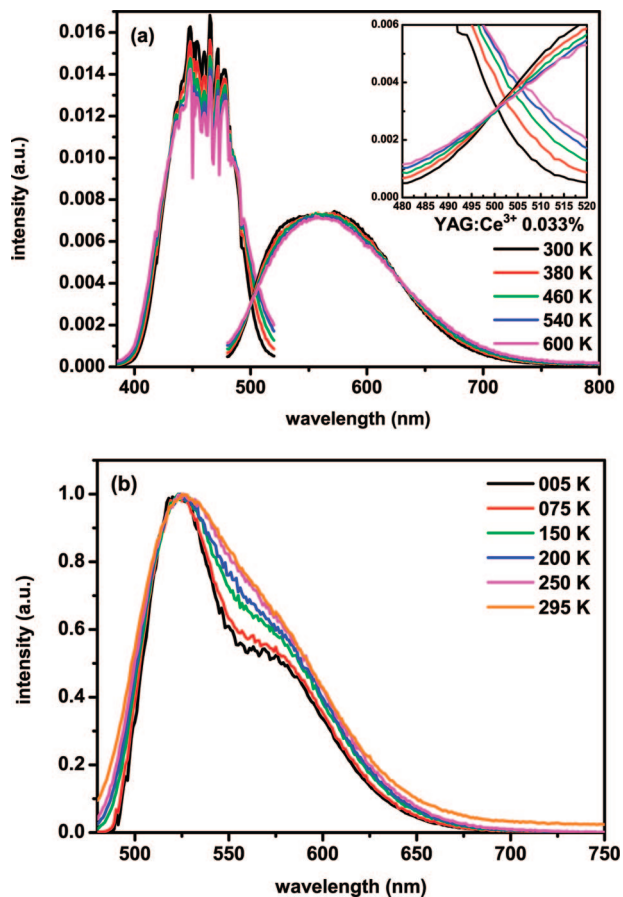
Figure 2. (a) Excitation and emission spectra for YAG:Ce 0.033% for λ_{exc} = 450 nm recorded at the temperatures indicated; (inset) magnification of the area of spectral overlap. The structure observed in the excitation spectrum between 440 and 475 nm is an artifact due to imperfect correction for strong variations in the Xe-lamp intensity. (b) Emission spectra at temperatures indicated for YAG:Ce 0.033%.

infra). In Figure 2a a selection of excitation and emission spectra is shown for the sample containing 0.033% Ce^{3+} in the range between 300 and 600 K. For this low Ce concentration, interaction between the Ce^{3+} ions and reabsorption will be negligible. The inset in Figure 2a depicts a close-up of area around the zero-phonon origin and shows the spectral overlap as a function of temperature. For the excitation spectra only the 460 nm band is shown. For both types of spectra the area of each spectrum was normalized to unity. The following is observed: both excitation and emission spectra broaden with increasing temperature, which because of the area normalization lead to a decrease in height. Clearly, the spectral overlap between the excitation and emission band increases as the temperature is raised. In the excitation spectra the position of the band does not change with increasing temperatures. The structure between 440 and 475 nm in the excitation bands is due to the variation in intensity of the Xe lamp and results in some sharp features in spite of the fact that the excitation spectrum is corrected for changes in the lamp intensity, which should in principle eliminate structure because of variations in the lamp intensity.

To accurately determine the Stokes shift and the energy of the 5d excited state, luminescence spectra were recorded at 5 K. At low temperatures the emission spectrum shows the well-known double band structure of the Ce^{3+} emission
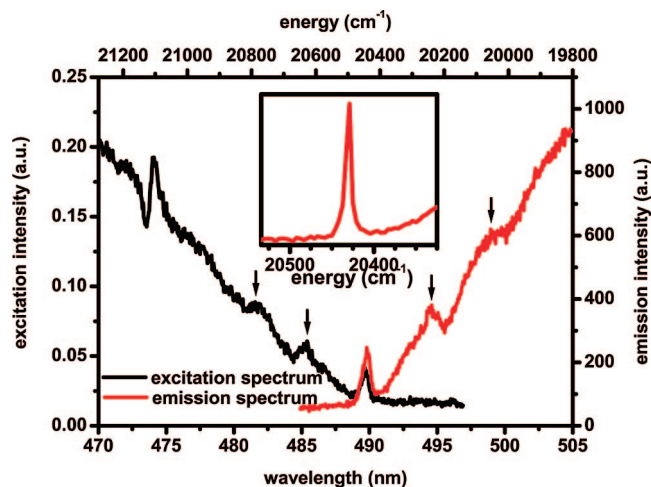
Figure 3. Emission spectrum for YAG:Ce 0.033% for λ_{exc} = 450 nm taken at 7 K; (inset) detail of the emission spectrum measured with higher resolution showing the zero-phonon line.

(Figure 2b). When the temperature is raised, the two emission bands, $5d^1 \rightarrow {}^2F_{5/2}$ and $5d^1 \rightarrow {}^2F_{7/2}$, broaden and start to overlap, resulting in one broad emission band at 600 K. At the lowest temperatures, fine structure is observed. In Figure 3 the zero-phonon line and vibrational structure are shown in more detail for the excitation and emission spectrum at 4 K. The spectra show a zero-phonon line at 489 nm (20450 cm^{-1}). The inset shows the zero-phonon line in more detail. On the low-energy side of the zero-phonon line, vibronic structure is observed in emission with phonon sidebands at 20259, 20065, and 19866 cm^{-1}. This indicates that there is a coupling with a 200 cm^{-1} vibrational mode. In the excitation spectrum a similar vibronic structure is observed. The present results on the fine structure compare well with the low-temperature spectra reported by Robbins et al.[5−7]

From the high-resolution low-temperature spectra we can accurately determine the Stokes shift for the Ce^{3+} emission as well as the Huang−Rhys parameter S. The Stokes shift can be determined by different methods. The simplest way is to determine the Stokes shift from the energy difference between the excitation and emission maximum. It is important to realize that a reliable value is only obtained for low Ce^{3+} concentrations; at higher Ce concentrations reabsorption of the high-energy part of the emission occurs and the resulting red shift of the Ce-emission band results in a calculated Stokes shift that is larger than the actual shift. Also, it is important to use the low-temperature spectra where the double band structure is observed for the Ce^{3+} emission and the position of the reverse of the electronic transition in absorption ($^2F_{5/2} \rightarrow$ 5d) can be observed as a separate band rather than the position of the emission band corresponding to transitions to both the $^2F_{5/2}$ and the $^2F_{7/2}$ levels. The luminescence spectra for the 0.033% Ce sample at 5 K show an excitation maximum at 460 nm whereas the maximum of the higher energy emission band is at 520 nm. This yields a Stokes shift of 2500 cm^{-1}. A slightly lower number is obtained by taking the Stokes shift as twice the energy difference between the zero-phonon line (∼489 nm) and the maximum of the emission band (520 nm) (SS = 2440 cm^{-1}). Finally, the Stokes shift can be obtained by taking the Stokes shift as ($2S\hbar\omega$) and determining the Huang−Rhys parameter
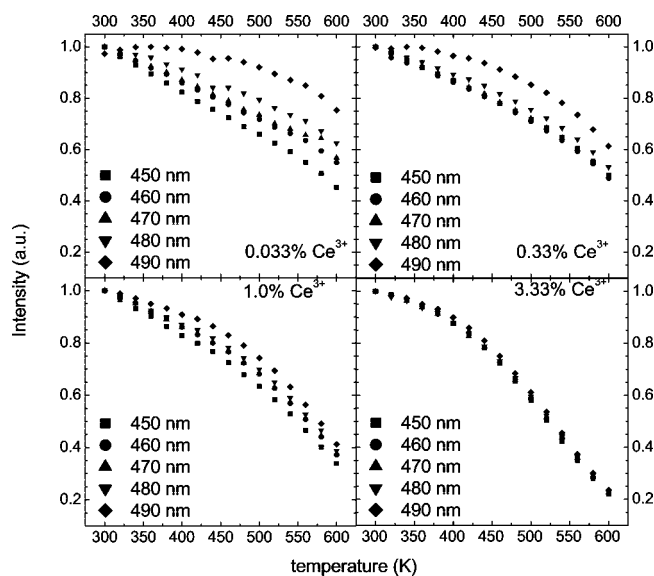
Figure 4. Temperature dependence of the integrated emission intensity for YAG:Ce 0.033%, 0.33%, 1.0%, and 3.33% taken at the five excitation wavelengths indicated.

S from the relative intensity of the zero-phonon line. The Huang−Rhys parameter S characterizes the electron−phonon coupling for an electronic transition. The intensity of the zero-phonon line (I_{ZPL}) with respect to the total emission intensity I_0 is given by $I_{ZPL} = I_0*\exp(-S)$.[19] The relative intensity of the zero-phonon line is 0.27% of the total intensity of the higher energy emission band, giving a value of 6 for S. From SS $= 2S\hbar\omega$ and $\hbar\omega = 200$ cm⁻¹ the Stokes shift is determined to be 2400 cm⁻¹. The values obtained here with the various methods are consistent and show that for Ce³⁺ in YAG the Huang−Rhys factor S is 6 and the Stokes shift is about 2400 cm⁻¹.

Now that the optical properties for isolated Ce³⁺ ions in YAG have been described, we turn to the temperature dependence of the luminescence with a focus on understanding the luminescence temperature quenching. The integrated emission intensity was measured as a function of temperature for all four Ce³⁺ concentrations and for different excitation wavelengths. The results are shown in Figure 4. For all concentrations temperature quenching is observed. The quenching is most pronounced for higher doping levels. For the commercially applied sample with 3.33% Ce³⁺ quenching sets in immediately above RT and at 520 K the intensity has dropped to half the intensity at 300 K. For the higher dopant concentrations (3.33%) the temperature quenching is the same for the different excitation wavelengths, whereas for the systems with low Ce concentrations the temperature dependence of the emission intensity depends on the excitation wavelength. Below we will explain this complex behavior. Because of the complexity of the various factors that contribute to the temperature dependence of the luminescence intensity (e.g., temperature dependence of the absorption strength and temperature dependence of energy migration and reabsorption), luminescence lifetime measure-
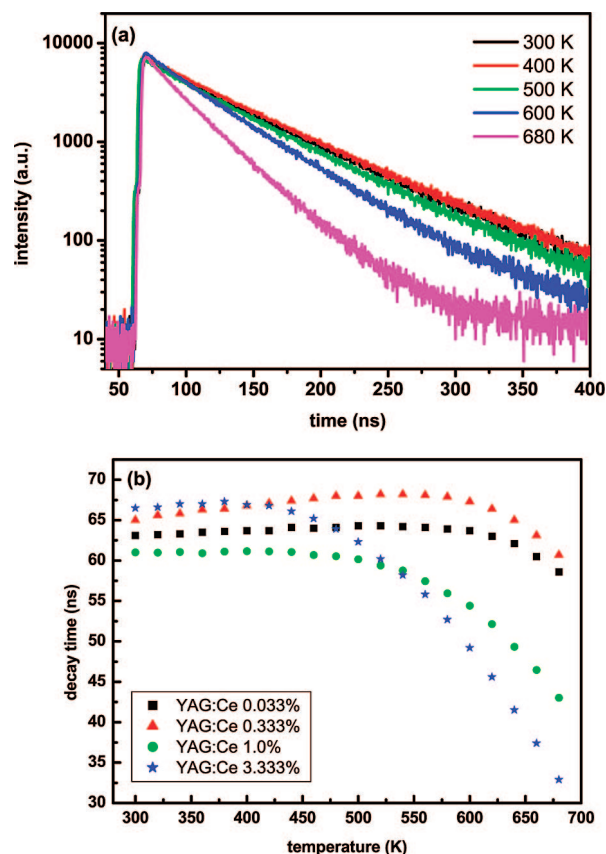
Figure 5. (a) Luminescence decay curves for YAG:Ce 3.33% for $\lambda_{exc} = 406$ nm and $\lambda_{em} = 580$ nm, taken at the temperatures indicated; (b) decay times determined from single-exponential fits of the luminescence decay as a function of temperature for YAG:Ce 0.033%, 0.33%, 1.0%, and 3.33%.

ments are performed to provide better insight into the quenching temperature for the 5d−4f emission of Ce³⁺ in YAG.

3.2. Luminescence Lifetime Measurements. For an allowed transition the radiative lifetime usually does not change strongly with temperature.[20,21] A well-established method to determine the temperature quenching is therefore to measure the luminescence lifetime of an emission band as a function of temperature. As quenching sets in, the luminescence lifetime shortens because of an additional nonradiative contribution to the decay process.[20,21] To determine the luminescence quenching temperature for the Ce³⁺ luminescence in YAG, luminescence lifetime measurements were performed as a function of temperature for the four different Ce³⁺ concentrations. As an example, luminescence decay curves are shown in Figure 5a for the 560 nm emission of Ce³⁺ in YAG doped with 3.3% Ce³⁺ for different temperatures between 300 and 700 K. All decay curves are (close to) single exponential. In Figure 5b the decay times (determined from a fit of the experimental data to a single exponential function) are plotted as a function of temperature for all four samples. Some interesting differences are observed. At room temperature the luminescence decay time is around 65 ns for all Ce concentrations. There seems

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to be a slight increase in the experimentally determined luminescence lifetime upon increasing the Ce concentration (from 63 ns for 0.033% Ce to 67 ns for 3.33% Ce). Most probably this is caused by reabsorption of the emission at the higher Ce concentrations. It is well-known that reabsorption of emission gives rise to a longer decay time.[22,23] It is hard to estimate the fraction of emission that is reabsorbed because the optical path length through the sample is not well-defined in a crystalline powder. The lengthening of the lifetime due to reabsorption means that the true radiative lifetime of the d−f emission from Ce in YAG is 63 ns, the lifetime measured for the lowest Ce concentration. This compares well with the commonly reported value of 65−70 ns. Note that in most reports the lifetimes have been measured for relatively high Ce concentrations (1−5%) or for single scintillator crystals where reabsorption may influence the experimentally observed decay time and this can explain the higher values reported in the literature (65−70 ns vs 63 ns).

The most important observation in Figure 5b is that the lifetime of the Ce^{3+} emission for the low dopant concentrations does not change in the temperature regime up to 600 K. Above 600 K the lifetime starts to decrease. Experimental limitations prevent the measurements of the lifetime at temperatures above 700 K and the quenching temperature $T_{50\%}$ cannot be determined. The present results show that the thermal quenching temperature for the Ce^{3+} emission in YAG:Ce is well above 600 K and is much higher than previously reported.[10−12] For the higher Ce concentrations (1% or 3.3%) a shortening of the lifetime sets in above 400 K. The origin will be discussed below.

4. Discussion

The temperature- and concentration-dependent luminescence and luminescence decay time measurements provide new insights into the luminescence properties of Ce ion in YAG and on the potential of this material to be applied as a phosphor in (high-power) white light LEDs. These various aspects will be discussed below.

4.1. Luminescence Spectra. From the low-temperature luminescence measurements on the YAG samples with the lowest Ce concentration (0.033%) information is obtained on the Huang−Rhys parameter S for the electron−phonon coupling and the phonon energy. S is approximately 6, the energy of the dominant phonon mode coupling to the electronic f−d transition is 200 cm^{-1}, and the Stokes shift of the emission is 2400 cm^{-1}. This Stokes shift is smaller than Stokes shifts that have previously been reported for the Ce^{3+} emission in YAG:Ce, viz. 3800 cm^{-1},[3] 3316 cm^{-1},[7,21] or 3770 cm^{-1} [12]. The discrepancy is explained by differences in the energy for the maximum of the emission band used to determine the Stokes shift. In earlier work the maximum of the combined emission bands to the $^2F_{5/2}$ and $^2F_{7/2}$ levels was used or the emission maximum used was the value for the red-shifted emission band in a YAG:Ce sample with a

higher (1−5%) Ce^{3+} concentration. The presently measured emission spectra show a shift of the emission maximum to longer wavelengths with increasing concentrations. Reabsorption of the high-energy part of the emission and nonradiative energy transfer to Ce^{3+} ions, which emit at a slightly lower energy, can explain the continuous red shift with increasing Ce concentration. For more accurate determination of the Stokes shift, the measurements for the lowest Ce concentrations are used and the present data provide therefore a more accurate value for the Stokes shift. Comparison with data in the literature, as collected by Dorenbos,[21] shows that the Stokes shift for the Ce emission in YAG:Ce is smaller than that for the Ce^{3+} emission in most other systems. Typically, Stokes shifts between 1000 and 8000 cm^{-1} are observed (although one has to keep in mind that not all the Stokes shifts have been determined correctly; just as for YAG:Ce, the Stokes shifts are often overestimated). In view of the small Stokes shift a high luminescence quenching temperature can be expected for the Ce^{3+} emission. This is in-line with the high luminescence quenching temperature observed.

The present results on the phonon energy of the dominant vibrational mode coupling with the f−d transition are in agreement with a recent paper by Grinberg et al.[22] where, based on the photoacoustic spectra of YAG:Ce, the phonon energy was estimated to be 200 cm^{-1}, in good agreement with the dominant vibrational frequency observed in the low-temperature luminescence spectra and the high-resolution spectra reported by Robbins,[7] which show even more detail. Four phonon modes were observed, weaker phonon sidebands around 130 and 160 cm^{-1} and stronger sidebands around 185 and 211 cm^{-1}. The Huang−Rhys parameter, deduced from the photoacoustic spectra, was however much higher, around 10, than the presently determined value of S = 6. From the parameters on the electron−phonon coupling a configurational coordinate diagram can be constructed for the f and d states of Ce^{3+} in YAG.

The presently obtained data on the luminescence of Ce^{3+} in YAG are more accurate than some of the data reported in the literature and can serve to validate results from theoretical calculations. Comparison of the presently reported Stokes shift with ab initio calculations on the excited 5d state of Ce^{3+} in YAG[17] show that the Stokes shift is underestimated in the calculations (700 cm^{-1} vs 2400 cm^{-1} experimentally), but the discrepancy is smaller than assumed in ref 17 based on the Stokes shifts reported in the literature on YAG:Ce (Stokes shifts over 3000 cm^{-1}). The relative intensities for the absorption bands involving transitions to the two lowest energy d states calculated in ref 17 is 2, the lower energy band being the stronger absorbing. This is in good agreement with the ratio observed in the excitation spectra for the lowest doped sample (YAG:Ce^{3+} 0.033%) where saturation effects do not play a role and the intensities reflect the true absorption strengths. Note that for higher concentrations the experimentally observed ratio becomes less than 2 because of saturation of the absorption in the lower energy band. The position of the zero-phonon line is overestimated in the ab initio calculations where it situated around 23700 cm^{-1} whereas the experimentally observed position is 20450 cm^{-1}.

(22) Grinberg, M.; Sikorska, A.; Kaczmarek, S. *J. Alloys Compd.* **2000**, *300−301*, 158.
(23) Bachmann, V.; Juestel, T.; Meijerink, A.; Ronda, C.; Schmidt, P. J. *J. Lumin.* **2006**, *121*, 441.

4.2. Temperature Dependence Luminescence Decay Time. Now that we have determined the intrinsic luminescence properties of the Ce^{3+} ion in YAG, it is interesting to discuss the luminescence quenching behavior. At first sight the results are confusing: the observed temperature quenching behavior is different as a function of Ce concentration, measuring technique (intensity or decay time) and excitation wavelength. To explain the various results shown in Figures 4 and 5, first the intrinsic quenching temperature is established and second the temperature dependence observed in the various experiments will be discussed. The most straightforward method to determine the luminescence quenching temperature is to measure the integrated luminescence intensity as a function of temperature under identical experimental conditions as has been done for the results contained in Figure 5. This method, however, has drawbacks, for example, if the absorption strength is strongly temperature-dependent. From the work of Robbins it is known that the absorption strength of the lower energy absorption band around 460 nm decreases with increasing temperature because of a redistribution over the different crystal field components of the $^2F_{5/2}$ ground state because the transition from the second crystal field level of the $^2F_{5/2}$ level to lowest d-level is symmetry forbidden. The energy splitting between these crystal field components is 285 cm^{-1}.[7] This energy difference is consistent with the temperature regime where thermal population of the higher crystal field component is expected and observed to affect the absorption strength (around room temperature).

A more accurate determination of the intrinsic luminescence quenching temperature is possible by considering the temperature dependence of the luminescence decay time. The results in Figure 5b show that for the sample with the lowest Ce concentration the luminescence decay time is constant up to 600 K for the lowest doping level (0.033% Ce). This shows that indeed the luminescence decay time of this allowed d−f emission band is not strongly temperature-dependent and can be used to accurately determine the luminescence quenching temperature. Note that in this case thermal population of a higher crystal field component will not occur because the next higher d state is 8000 cm^{-1} higher in energy. The fact that the luminescence decay time is constant up to 600 K shows that the intrinsic quenching temperature for the Ce^{3+} in YAG is very high (well above 600 K) and is comparable or even better than that of the Eu^{2+} emission in Eu-doped oxynitride and nitride phosphors which have been introduced to replace YAG:Ce.[8,14−16]

For the sample with 0.33% Ce, the luminescence decay time shows a small increase between 300 and 600 K and the decay time is slightly longer than that for the 0.033% sample (65 ns vs 63 ns). These observations are explained by reabsorption. Because of the strongly allowed character of the f−d transition, reabsorption may occur for the light emitted in the wavelength region where Ce^{3+} can reabsorb the emission (see the spectral overlap region in Figure 2a). Reabsorption of emission leads to a lengthening of the experimentally measured lifetime. Because the spectral overlap increases with temperature, the reabsorption will also slightly increase with temperature and this can explain the

small increase of the experimentally observed lifetime for the YAG sample doped with 0.33% of Ce^{3+} in the temperature regime between 300 and 600 K. For the samples with 1% and 3.33% of Ce^{3+} the luminescence quenching temperature is lower and quenching starts around 480 K (for the 1% sample) or 440 K (for the 3.33% sample). The lower quenching temperatures are explained by thermally activated concentration quenching. Thermal activation results from an increase of the spectral overlap with increasing temperature (faster energy migration), on the one hand, and from a thermally activated trapping of the migrating excitation energy by defects (faster trapping), on the other hand. A quantitative analysis of the concentration quenching process is beyond the scope of the present paper. Qualitatively, the observations are well-explained by this model. The lower quenching temperatures are observed for the more concentrated samples. The temperature dependence of the quenching due to thermally activated energy transfer to defects is also consistent with the work of Robbins et al.[5−7]

4.3. Temperature Dependence Luminescence Intensity. The measurements depicted in Figure 4 show that the temperature dependence of the luminescence is complex: it varies as a function of both the Ce concentration and excitation wavelength. On the basis of the discussion above, it is clear that the intrinsic quenching temperature of the Ce emission is well above 600 K. To explain the decrease in the emission intensity below 600 K, several factors need to be considered.

For the lowest concentration the main contribution is from the temperature dependence of the oscillator strength. At higher temperatures the absorption strength of the 460 nm absorption band decreases due to thermal population of the higher crystal field components of the $^2F_{5/2}$ ground state (vide supra). The lower absorption strength results in a lower light output, even though the quantum efficiency is constant. This explanation is consistent with both the excitation wavelength dependence and the concentration dependence of the emission intensity as a function of temperature. For the lower concentrations the temperature quenching is less pronounced for excitation at longer wavelengths. (As the excitation shifts from the maximum of the absorption band to the wings, from 450 to 490 nm, the "quenching temperature" increases.) This is explained by the fact that, in the center of the band, the absorption strength decreases (as discussed above), but for the longer wavelengths this decrease is partially compensated by thermal broadening of the absorption band (see also Figure 2), which increases the absorption strength in the tails of the absorption band. The influence of the excitation wavelength is strongest for the lowest concentrations where the fraction of the light absorbed is proportional to the oscillator strength. For higher concentrations we move into the saturation regime where the fraction of absorbed light increases, no longer linear with the oscillator strength. For the highest concentration (3.33% of Ce) there is hardly any wavelength dependence observed, indicating that for this concentration there is (almost) complete saturation and the fraction of excitation light that is absorbed is close to 100%. The presently observed decrease of the luminescence intensity with increasing temperature is the opposite of the

increase of the intensity that has been reported by Robbins for excitation in the higher energy 5d absorption band (excitation at 340 nm) upon increasing of the temperature. Indeed, for this transition (to the higher energy 5d level) the oscillator strength increases upon increasing of the temperature and for a low-concentration YAG:Ce crystal an increase of the luminescence intensity is expected and observed. The present findings are also consistent with the temperature dependence measured for scintillation efficiency of YAG-Ce under X-ray excitation.[24] For low dopant concentrations, a stable scintillation output is measured in the temperature regime 300−600 K, confirming the absence of temperature quenching. Note that in case of X-ray excitation, there is no temperature-dependent oscillator strength involved.

In addition to the influence of the oscillator strength, a second process is responsible for the decrease in luminescence intensity upon raising the temperature: thermally activated concentration quenching. This gives rise to temperature quenching of the emission for the higher doped samples where energy migration to defects occurs. This observed decrease in luminescence intensity is in-line with the decrease in luminescence lifetime observed for the higher doped (1 and 3.33% Ce) samples in this temperature regime. For these higher concentrations the temperature quenching due to thermally activated concentration quenching dominates.

From the discussion above it is clear that the low quenching temperature reported in the literature[10−12] for the commercial YAG:Ce phosphor is not related to the intrinsic quenching temperature of the Ce^{3+} luminescence. For commercial YAG:Ce phosphors with relatively high Ce^{3+} concentration (1−5%) the mechanism behind the temperature quenching is thermally activated concentration quenching and is observed at temperatures above 400 K. For example, the temperature quenching reported by Setlur et al.[12] is very similar to the temperature dependence of the luminescence intensity shown in Figure 2 for the sample with 3.3%. The fact that the temperature quenching of the luminescence in commercial YAG:Ce is due to thermally activated concentration quenching has important implications for industrial applications. With its intrinsic quenching temperature above 600 K for low activator concentrations, the temperature quenching behavior of YAG:Ce compares favorably with those of rare-earth activated nitride and oxonitride materials.[8,14−16] In ref 23 we reported on the thermal quenching

(24) Zych, E.; Brecher, C.; Glodo, J. *J. Phys.: Condens. Matter* **2000**, *12*, 1947.

behavior of Eu^{2+}-activated $SrSi_2O_2N_2$. The onset of thermal quenching was determined to be around 500 K. In the class of nitride materials the system $M_2Si_5N_8:Eu^{2+}$ (M = Ca, Sr, Ba) plays an important role.[8] In these materials the emission intensity at 470 K was thermally quenched to about 90% of the initial emission intensity at RT.[8] Both the oxonitride and the nitride materials are proposed for use in an all-nitride white LED.[8,14−16] The present results show that the intrinsic quenching temperature of the Ce luminescence is in fact higher than that for some of the alternative LED phosphors suggested. In commercial YAG powder phosphors with Ce^{3+} concentrations above 1 at. %, thermal quenching by energy migration occurs. The same may be true for nitride and oxonitride phosphors doped with relatively high Eu^{2+} concentrations. To make use of the high thermal quenching temperature of YAG:Ce, one may use translucent ceramic YAG:Ce plates for color conversion. Here, one can choose lower concentrations of activator ions and compensate for the loss in absorption strength by a longer optical pathway, e.g., by increasing the thickness of the YAG:Ce ceramic disk.

5. Conclusions

Systematic research on the temperature dependence of the intensity and lifetime of the Ce^{3+} luminescence is reported for the widely applied YAG:Ce phosphor. Temperature-dependent luminescence lifetime measurements for low Ce concentrations (0.033%) show that the intrinsic quenching temperature of the Ce^{3+} is high (well above 700 K). The lower quenching temperatures reported for the commercial YAG:Ce phosphor is explained by thermally activated concentration quenching. The high luminescence quenching temperature offers possibilities for YAG:Ce to be applied in high-power LEDs, provided that lower Ce^{3+} concentrations are used. In addition, low-temperature luminescence spectra are reported. For YAG doped with low Ce^{3+} concentrations zero-phonon lines and vibrational structure are observed in the excitation and emission spectra. On the basis of these measurements, the Stokes shift ($\sim$2400 cm^{-1}), Huang−Rhys parameter ($S = 6$), and phonon energy ($\sim$200 cm^{-1}) have been determined for the f−d luminescence and compared with the results from theoretical calculations on the 5d excited state for Ce^{3+} in YAG.