# Structural origins of the optical properties of the La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub> phosphor

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#### Abstract

The structure of a phosphor materials for solid-state lighting is critically important to understanding its properties. Structure-property relations are elucidated here for  $La_{3-x}Ce_xSi_6N_{11}$  from synchrotron X-ray and neutron scattering, solid-state <sup>29</sup>Si nuclear magnetic resonance, and electron spin resonance. The site occupancy of Ce<sup>3+</sup> is deduced from Rietveld refinement of neutron scattering and solid-state <sup>29</sup>Si nuclear magnetic resonance measurements, revealing a non-random distribution of Ce in the lattice at low substitution levels. Rietveld refinement indicates the  $La_{3-x}Ce_xSi_6N_{11}$  to be quite rigid. For the first time, the luminescent properties of a Ce-based nitride phosphor with 100% Ce substitution are investigated. Emission spectra and decay time measurements suggest that both Ce sites have very similar emission properties, with a fast decay time of around 40 ns. It may be this fast decay time that prevents total self-quenching of luminescence, even with 100% substitution of Ce for La. Temperature-dependent quantum yield measurements demonstrate the remarkable stability of  $La_{2.82}Ce_{0.18}Si_6N_{11}$ , which shows little sign of thermal quenching, even at temperatures up to 503 K.

# Introduction

Solid-state lighting (SSL) based on bright-blue InGaN LEDs combined with an efficient down-converting phosphor<sup>1–5</sup> has attracted considerable attention in recent years due to the many advantages it offers. These solid-state white light-emitting devices possess advantages of high efficiency, a mercury-free design, long lifetimes, color stability, and physically robust devices.<sup>6,7</sup> Since the use of yellow-emitting  $Y_{3-x}Ce_xAl_5O_{12}$  (YAG:Ce) in solid-state white lighting devices in the mid-1990's,<sup>8</sup> many efforts have been put towards discovering new phosphors. Recently, researchers looking for new phosphors have tried materials containing different anions besides oxygen, resulting in many new host structures, such as oxysulfides and sulfides,<sup>9</sup> fluorosulfides,<sup>10</sup> oxyhalides such as  $Sr_3SiOF_4:Ce^{3+}$ ,<sup>11,12</sup> and oxynitrides and nitrides.<sup>13–16</sup> Nitrides have been a promising candidate for solid-state

lighting, due to their high quantum efficiencies and good thermal quenching characteristics.<sup>17</sup> This has led to development of highly efficient white LED devices based on nitride materials.<sup>13</sup> The smaller electronegativity of N compared with O increases the covalency of nitride host lattices compared with oxides, and shifts the center of gravity of the 5d energy levels to lower values (termed the nephelauxetic effect), red-shifting emission.<sup>18</sup> It has also been suggested that the red-shift in emission of nitrides is more strongly correlated with the anion polarizability,<sup>19</sup> or dielectric constant of the host lattice,<sup>20,21</sup> rather than simply the nephelauxetic effect. The higher formal charge of N compared with O also causes a larger crystal field splitting of the 5d levels of the activator ions in a nitride lattice, further red-shifting emission.<sup>22</sup> Some examples of recently-developed nitride phosphors include  $(Ca,Sr,Ba)_2Si_5N_8:Eu^{2+}, \frac{13}{(Ca,Sr,Ba)}YSi_4N_7:Eu^{2+}, \frac{23}{10}$  the  $Ca_3N_2$ -AlN-Si\_3N\_4:Eu^{2+} system, \frac{24}{10} (Sr,Ba)SiN<sub>2</sub>:Eu<sup>2+</sup>/Ce<sup>3+</sup>,<sup>25</sup> CaSiAlN<sub>3</sub>:Ce<sup>3+</sup>,<sup>26</sup> and LaSi<sub>3</sub>N<sub>5</sub>:Ce<sup>3+</sup>.<sup>27</sup> In phosphors such as  $(Ca,Sr,Ba)_2Si_5N_8:Eu^{2+}$ , Eu can be fully substituted for the Ca/Sr/Ba site; these compounds emit in the visible region. Activator ion substitution at 100% has also been previously shown for  $Ce^{3+}$  in  $CeF_3^{28}$  and  $CeMgAl_{11}O_{19}$ , <sup>29</sup> which both emit UV light. Additionally, blue luminescence of  $Ce^{4+}$  in  $Sr_2CeO_4$  has been reported with a long 65  $\mu$ s lifetime and poor thermal stability.<sup>30,31</sup> Full Ce<sup>3+</sup> substitution has not yet been reported for a nitride phosphor compound, or a visible-light-emitting phosphor, until now.

The host lattice structure of  $La_{3-x}Ce_xSi_6N_{11}$  was first discovered in 1983 as  $Sm_3Si_6N_{11}$ .<sup>32</sup> The structure, shown in Figure 1, is tetragonal and belongs to space group *P4bm* (#100). It has two rare-earth (RE) sites and two Si sites; the RE sites have the same coordination number with slightly different geometries, but the Si sites are nearly identical. After its discovery as  $Sm_3Si_6N_{11}$ , the compound was then extended to many other rare-earth ions in 1995, including  $Ce_3Si_6N_{11}$ , although the luminescent properties of this material were not studied at that time.<sup>33</sup> Schlieper *et al.* reported successful preparation of the  $Ce_3Si_6N_{11}$  compound, noting that it was yellow, but studied the structure by X-ray diffraction and the magnetic properties, not the optical properties.<sup>34</sup>  $La_{3-x}Ce_xSi_6N_{11}$ 

was first studied as a phosphor material in 2009,<sup>35,36</sup> when it was shown that doping  $La_{3-x}Ce_xSi_6N_{11}$  with small amounts of  $Ce^{3+}$  (on the order of 1 mole%) results in a compound with excitation in the blue around 450 nm that shows a bright, broad emission which ranges from nearly 500 nm to 700 nm. The emission intensity of  $La_{3-x}Ce_xSi_6N_{11}$  was shown to be very stable with temperature, an important characteristic of phosphors for use in practical devices. The emission intensity stability with temperature of  $La_{3-x}Ce_xSi_6N_{11}$  is so extraordinary that it even exceeds that of one of the most temperature-stable oxide phosphors, (Y,Gd)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce.<sup>35</sup>

Although the  $La_{3-x}Ce_xSi_6N_{11}$  crystal structure offers two La sites on which Ce can substitute, but the emission spectra appears similar to other compounds with emission from only one site, such as YAG:Ce. Previous studies on  $La_{3-x}Ce_xSi_6N_{11}$  have not elucidated the distribution of Ce substitution on these two sites. Here, we use the complementary techniques of neutron diffraction, nuclear magnetic resonance (NMR), and electron spin resonance (ESR), to investigate the site occupancy of Ce on the two different crystallographic RE sites, and connect this to the optical properties. Additionally, we use these techniques to explain the structural reasons for the remarkable thermal stability of emission intensity of  $La_{3-x}Ce_xSi_6N_{11}$ . We also, for the first time, investigate the optical and structural properties of a fully Ce-substituted nitride phosphor, Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub>.

# Materials and Methods

**Sample Preparation**  $La_{3-x}Ce_xSi_6N_{11}$  was prepared from  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder, LaN powder, CeO<sub>2</sub> powder, and CeN powder. CeN was prepared by nitridation of Ce metal under NH<sub>3</sub> flow. Two grams of total starting reagents were ground in an alumina mortar and pestle in a glove box with pure nitrogen gas, with oxygen and water vapor concentrations less than 1 ppm. The ground powders were then loaded into a BN crucible. The crucible was set in a high-pressure furnace with carbon heaters, and fired at 1580 °C to 2000 °C under

0.92 MPa nitrogen gas with purity greater than 99.9995 %. After the phosphor powders cooled to room temperature, they were ground into fine powders with an alumina mortar and pestle.

**X-ray and neutron scattering** High-resolution synchrotron powder diffraction data were collected using the 11-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory at 295 K and using an average wavelength of 0.4121540 Å. Additional details regarding the experimental setup can be found elsewhere.<sup>37–39</sup> Neutron powder diffraction was performed on the HIPD and NPDF instruments at the Los Alamos Neutron Science Center at Los Alamos National Laboratory. Samples were placed in vanadium sample containers, and time-of-flight neutron data was collected at 295 K on the HIPD instrument from 8 detector banks at  $\pm 45^{\circ}$ ,  $\pm 90^{\circ}$ ,  $\pm 119^{\circ}$  and  $\pm 148^{\circ} 2\theta$ . For the NPDF measurements, samples were placed in vanadium cans, and time-of-flight neutron data was collected at 295 K from 4 detector banks at  $14^{\circ}$ ,  $40^{\circ}$ ,  $90^{\circ}$  and  $153^{\circ}$  2 $\theta$ . Crystal structures were refined using the EXPGUI front end for the refinement program General Structure Analysis System (GSAS).<sup>40</sup> Simultaneous refinements to the X-ray and neutron scattering data were completed by adjusting the profile shapes and backgrounds (10-term Chebyshev polynomial functions) during initial LeBail fits,<sup>41</sup> refining neutron absorption coefficients, instrument parameters, and the unit cell, then refining the atomic positions, and finally the atomic displacement parameters and La/Ce occupancies. Occupancies and atomic displacement parameters are usually strongly correlated in Rietveld refinements, so these were refined in alternate cycles. Crystal structures were visualized using the software VESTA.<sup>42</sup>

**Solid-state** <sup>29</sup>**Si NMR and ESR** High-resolution solid-state NMR was used to investigate the local electronic environments of the  $La_{3-x}Ce_xSi_6N_{11}$  materials. The single-pulse <sup>29</sup>Si NMR experiments were performed at 300 K on a Bruker AVANCE IPSO NMR spectrometer, with an 18.8 T narrow-bore superconducting magnet, operating at a frequency of 158.99 MHz for <sup>29</sup>Si nuclei, which are about 5% naturally abundant. A Bruker 3.2 mm H-X-Y triple-resonance magic-angle spinning (MAS) probe head was used with zirconia rotors and Kel-F® caps, with a MAS rate of 20 kHz. Radio frequency (RF) pulse lengths and power levels were calibrated to achieve a 90° rotation of the net <sup>27</sup>Al magnetization (4  $\mu$ s) and were calibrated with respect to the longitudinal spin-lattice relaxation time (*T*<sub>1</sub>) to ensure the spectra were fully quantitative (recycle delay ranging from 300 s to 0.25 s depending on the Ce concentration). Due to the extremely fast relaxation of <sup>29</sup>Si in the Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub> material, a Hahn-echo pulse sequence was used. This pulse sequence was used for all materials, along with <sup>1</sup>H decoupling. The pulse sequence consisted of a  $\pi/2$  pulse, followed by a delay of 20 rotor periods, followed by a  $\pi$  pulse, and finally detection. The number of scans ranged from 128 (for samples with long relaxation times) to 16000 (for Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub>). The MAS for the Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub> material had to be initiated outside of the magnet, since the strong paramagnetism of the Ce<sup>3+</sup> in the structure prevented the rotor from initializing spinning inside the magnetic field. <sup>29</sup>Si chemical shifts were referenced to tetramethylsilane at -9.81 ppm.

<sup>29</sup>Si spin-lattice relaxation-time behaviors of the  $La_{3-x}Ce_xSi_6N_{11}$  samples were established by using 1D saturation-recovery MAS NMR spectra. 1D saturation-recovery <sup>29</sup>Si MAS NMR spectra were acquired for a range of times,  $\tau$ , between 0.01 s and 1 s for the  $Ce_3Si_6N_{11}$  material, and 0.01 s and 300 s for the  $La_{2.82}Ce_{0.18}Si_6N_{11}$  material, on the same spectrometer with the 18.8 T narrow-bore superconducting magnet used for the singlepulse <sup>29</sup>Si experiments. A RF pulse length of 4  $\mu$ s was calibrated with the power level for a 90° rotation of the net magnetization of <sup>29</sup>Si nuclei, and a 400-pulse saturation train with 2  $\mu$ s between saturation pulses with a 0.1 s recycle delay was used. Spectra were modeled using the simulation program DMFIT.<sup>43</sup> The  $T_1$  relaxation times of octahedral <sup>29</sup>Si nuclei were found by subsequently fitting the spectra from each delay time. The integrated intensity curves were then fitted with the curve fitting tool in MATLAB.

ESR spectra were collected on a Bruker X-band ESR spectrometer using an average

microwave frequency of 9.486 GHz. Samples were placed in quartz tubes, and data was acquired at a temperature of 10 K.

**Optical Measurements** Room temperature photoluminescence (PL) spectra were obtained on a Perkin Elmer LS55 spectrophotometer, scanning a wavelength range from 300 nm to 750 nm. The samples were thoroughly ground and subsequently mixed within a silicone resin. A small drop of the mixture was administered onto a small piece of glass and cured at 150°C for 15 minutes. Photoluminescence quantum yield (PLQY) was measured with 457 nm excitation using an argon laser and an experimental protocol as described by Greenham *et al.*<sup>44</sup> Further details describing the employed setup, as well as the protocol to determine the temperature-dependence of the photoluminescence properties can be found elsewhere.<sup>45,46</sup> Diffuse reflectance UV/vis spectra were recorded in the wavelength range 350 nm to 600 nm using a Shimadzu UV-3600 spectrometer equipped with an ISR-3100 integrating sphere. Samples were mixed with BaSO<sub>4</sub>. The absorbance spectrum was obtained by applying the Kubelka-Munk<sup>47</sup> relation  $F(R) = (1 - R)^2/(2R)$ . Luminescence life-time measurements were performed using Time-Correlated Single Photon Counting (TCSPC) technique,<sup>48</sup> further details can be found in the supporting information.

# **Results and discussion**

#### Compositional effects on crystal structure

The La<sub>3-*x*</sub>Ce<sub>*x*</sub>Si<sub>6</sub>N<sub>11</sub> material can be prepared with values of *x* ranging from 0 to 3, which concurrently modulates the optical and structural properties. The symmetry of the compound does not change with composition. La<sub>3-*x*</sub>Ce<sub>*x*</sub>Si<sub>6</sub>N<sub>11</sub> is tetragonal, crystallizing in the *P4bm* space group (#100). The structure consists of layers of eight-coordinate La–N<sub>8</sub> polyhedra and Si–N<sub>4</sub> tetrahedra, as shown in Figure 1. The La(1), La(2), and Si(2) sites lie in nearly the same plane parallel to the (001) plane, while the Si(1) sites are in

their own separate plane parallel to the (001) plane. The Si(1)-N<sub>4</sub> tetrahedra are fully corner-connected parallel to the (001) plane, and the  $Si(1)-N_4$  and  $Si(2)-N_4$  tetrahedra are corner-connected in the *c*-direction. This makes for a fully three-dimensionally cornerconnected Si-N<sub>4</sub> tetrahedral network. Most N atoms bridge two Si tetrahedra, the only N atom that bridges three Si tetrahedra is the N(3) site, which lies at the bottom of the Si(2) tetrahedra as shown in Figure 1. The La(2) atoms share four three-sided faces of their polyhedra with the La(1) sites in the *a*-*b* plane, and the La(1) sites share five corners of its polyhedra with other La(1) sites in the *a-b* plane. No La–La interconnectivity occurs in the *c*-direction. As shown in Figure 2, the two La sites have the same coordination number, but different polyhedral geometries. This manifests different site symmetries; La(1) has only a mirror plane (m), while La(2) has four-fold rotational symmetry (4). One site, referred to here as La(2)/Ce(2), has 4 N atoms above and 4 below in the a - b plane in a square antiprism configuration, similar to other phosphor crystal structures such as  $CaSc_2O_4$ .<sup>49</sup> The other site, La(1)/Ce(1), has 5 N atoms above and 3 below in the a - b plane, and an average La/Ce-N bond length that is around 2% larger than the La(2)/Ce(2) site. The standard deviation of bond length of the La(1) site is also about 10 to 20 times larger than La(2). Since the coordination numbers are identical and bond lengths quite similar, crystal field splitting of the Ce 5d levels on the two sites is expected to give similar emission properties. The effect of Ce substitution on the structure is investigated here by diffraction, and the results from Rietveld refinement are related to the  $La_{3-x}Ce_xSi_6N_{11}$  structure.

Rietveld refinement of synchrotron X-ray and neutron scattering from a single structural model enables one to probe the crystallographic parameters with a great deal of sensitivity. Synchrotron X-ray scattering is very sensitive to the unit cell parameters of materials, and the extremely high flux from the radiation source enables unprecedented sensitivity for detecting impurities and subtleties in the unit cell symmetry. Neutron scattering, on the other hand, has form factors that remain much larger with increasing Q than with X-rays, enabling a sensitive probe of atomic displacement parameters (ADPs). Addi-



Figure 1: The crystal structure of  $La_{3-x}Ce_xSi_6N_{11}$  looking down the *a*-axis. The atoms that compose the layers in the *a* – *b* plane have been labeled.



Figure 2: Simultaneous Rietveld refinement of  $La_{2.82}Ce_{0.18}Si_6N_{11}$  scattering data at 295 K, showing (a) time-of-flight neutron data acquired on the NPDF instrument, (b) time-of-flight neutron data acquired on HIPD instrument, and (c) synchrotron X-ray data. A small amount (~1%) of  $LaSi_3N_5$  impurity was included in the fit. The bars at the top of the figure show the expected reflection positions for the  $La_3Si_6N_{11}$  phase. The inset polyhedra show the La sites 1 and 2 with the 8 coordinating N atoms as ellipsoids representing 99% probability atomic displacement parameters. The polyhedra shown here are from the refinement of the x = 0.18 material.

tionally, neutron scattering intensity does not follow the same periodic trend as in X-ray scattering, but instead non-systematically varies with atomic number, enabling refinement of site occupancy of elements adjacent on the periodic table, such as La and Ce used in the materials here. Rietveld refinement of synchrotron X-ray and neutron scattering of



Figure 3: Unit cell parameters of  $La_{3-x}Ce_xSi_6N_{11}$  from Rietveld refinement of synchrotron powder X-ray diffraction data acquired at 295 K, showing (a) cell parameter *a*, (b) cell parameter *c*, and (c) unit cell volume, *V*. Best-fit lines have been added to guide the eye.

the phosphor La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub>, shown in Figure 2 for La<sub>2.82</sub>Ce<sub>0.18</sub>Si<sub>6</sub>N<sub>11</sub>, can therefore provide us with a sensitive probe to crystallographic parameters, impurities, ADPs, and site occupancy. For example, a small impurity (around 1 mol %) of LaSi<sub>3</sub>N<sub>5</sub> was observed in samples with low Ce content, while those with x = 1.2 and 2.1 had around 20 mol % of LaSi<sub>3</sub>N<sub>5</sub> impurity. A full table of the crystallographic data from the refinements, including unit cell parameters, site occupancies, and ADPs, is available in the supporting information. The unit cell parameters of La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub> analyzed through Rietveld refinement of synchrotron X-ray scattering, displayed in Figure 3, shows a linear decrease in unit cell parameter *a* and decreasing cell volume with increasing Ce content, indicating the La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub> solid solution obeys the Végard law. This suggests the nominal amount of Ce is indeed incorporated into the lattice. It also suggests the substitution is isovalent, meaning the Ce is in a 3+ state substituting for La<sup>3+</sup>. This is crucial for optical properties since Ce<sup>4+</sup> does not emit in the yellow region, and has even been known to quench luminescence.<sup>50</sup> The *c* cell parameter in Figure 3(b) essentially remains constant throughout the solid-solution series, showing that the contraction of the unit cell only occurs along the *a-b* plane.



Figure 4: (a) Ce site occupancy of  $La_{3-x}Ce_xSi_6N_{11}$  from Rietveld refinement of synchrotron X-ray and neutron scattering data acquired at 295 K, (b) bond-valence sums from Rietveld refinement, and (c) average La/Ce–N bond distance. Error bars represent estimated standard deviation from the refinements. Lines have been added to guide the eye.

The nature of the site preference of Ce was also investigated using Rietveld refinement of neutron data, and shows that Ce prefers to substitute on site 2 for low Ce concentrations. For a La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub> material with perfectly randomly distributed Ce atoms, the ratio of total Ce(1):Ce(2) would be 2:1 since the Wyckoff multiplicity of La(1) is twice that of La(2). Equivalently, the site fraction of Ce on both sites would be equal. The results from Rietveld refinements in Figure 4(a) show that this ratio is found to be 2:1.8 for the x = 0.18 material, 2:2.4 for the x = 0.3 material, and 2:1.3 for the x = 1.2 material. The refinements slightly overestimate the amount of Ce in the lattice, especially for the x = 0.18material. Preferential occupancy of the La site 2 by Ce is not surprising, since La site 2 has a slightly smaller average La–N distance compared to site 1 (2.70 Å for La site 1 compared to 2.64 Å for La site 2). The smaller ionic radii of 8-coordinate Ce<sup>3+</sup> (1.143 Å) compared to 8-coordinate La (1.16 Å)<sup>51</sup> is consistent with Ce favoring substitution on the smaller La site. Calculation of the bond-valence sums  $(BVS)^{52}$  for both Ce and La on sites 1 and 2, shown in Figure 4(b), also support Ce favoring La site 2. The bond lengths of the two La/Ce sites exhibited in Figure 4(c) demonstrate that Ce/La site 1 always has a larger bond length than site 2, regardless of Ce content. This results in a larger BVS for La/Ce site 2 that is much closer to the ideal value of 3 than for La/Ce site 1 as displayed in Figure 4(b). This indicates La and Ce may be more ideally bonded in La site 2. The BVS of La/Ce site 2 increases with Ce content, while the La/Ce site 1 BVS remains flat with increasing Ce substitution, a reflection of the variation in bond distances. The more ideal bonding environment of the La/Ce site 2 is consistent with the apparent preference of Ce to substitute on the La/Ce site 2.

A comparison of the La(1) and La(2) ADPs of  $La_{2.82}Ce_{0.18}Si_6N_{11}$  shows the La(1) site has a  $B_{iso}$  of 0.49(2), almost twice as big as that of La(2) [0.29(3)], which is consistent with the larger La(1)-N<sub>8</sub> bond distance and bond-length standard deviation compared to La(2)–N<sub>8</sub>. The refinement results also show the ADPs ( $B_{iso}$ ) of all atoms are on the order of 0.1 Å<sup>2</sup>, indicating La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub> has a very rigid and well-ordered lattice. The Debye temperature ( $\theta_D$ ), which is a rough estimate of the temperature at which the highest-energy phonon mode becomes populated, can be calculated from the isotropic displacement parameters.<sup>53</sup> Using the high-temperature approximation for calculation of  $\theta_D$ , we find  $\theta_D$ is at least 650 K for all materials investigated here (the high-temperature approximation is an underestimate of  $\theta_D$ ). The higher values of  $\theta_D$  for x = 2.1 (940 K) and x = 3 (933 K) are due to the small  $B_{iso}$  values in those refinements, which may be due to the contracted lattice compared with compositions with less Ce. The higher values of  $\theta_D$  may also be due to underestimated ADPs, since we have found synchrotron X-ray tends to underestimate ADPs compared with neutron scattering. The high  $\theta_D$  of 700 K indicates that at LED operation temperatures (273 K to 573 K), many high-energy phonon modes are not accessible. This decreases the amount of non-radiative pathways, lowering the rate of non-radiative recombination, and is one reason for the high quantum efficiency of the La<sub>2.82</sub>Ce<sub>0.18</sub>Si<sub>6</sub>N<sub>11</sub>

phosphor.



# Local structure near Ce<sup>3+</sup> and site preference from solid-state <sup>29</sup>Si NMR

Figure 5: Solid-state Hahn-echo <sup>29</sup>Si MAS NMR spectra of  $La_{3-x}Ce_xSi_6N_{11}$  acquired at 295 K, 20 kHz MAS, and 18.8 T, with *x* as indicated. The asterisks denote spinning sidebands. The spectra have been offset for clarity.

High-resolution solid-state MAS NMR enables investigation of the local structure around the activator ions in phosphors. The paramagnetic dopant (activator) ion,  $Ce^{3+}$  in this case, can be used as a contrast reagent for NMR experiments, as has been seen before in pyrochlores, <sup>54</sup> stannates, <sup>55</sup> YAG:Tb, <sup>56</sup> and YAG:Ce. <sup>57</sup> Here, the paramagnetic effects of the Ce<sup>3+</sup> ion on surrounding <sup>29</sup>Si nuclei in La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub> are used to evaluate the local structure around Ce<sup>3+</sup> and the site preference of its substitution. Since the relaxation time of an electron is very fast, interaction with a nearby paramagnetic ion causes the nuclear spins to relax quickly, and a Hahn-echo pulse sequence was used to enable detection of quickly relaxing Si<sup>29</sup> species. The spectra of *x* = 3 is the most simple to analyze, since there are only two <sup>29</sup>Si signals near –200 ppm and –38 ppm corresponding to the Si(1) and Si(2)

Table 1:	Populations,	chemical shi	ifts, FWHM	I, and $T_1$	relaxation	times for	<sup>29</sup> Si site	es in
$La_{3-x}Ce_x$	$Si_6N_{11}$ , with t	he different o	composition	ns labeled	l. Some of	the neares	t lantha	nide
ions are	given in parar	nthesis.						

$La_{2.82}Ce_{0.18}Si_6N_{11}$					
Si	Population	Chemical	FWHM	$T_1$	
site	(%)	Shift (ppm)			
1(6La)	65.7	-61.2	10.9	20.0	
2(3La)	24.6	-48.8	10.6	18.3	
1(1Ce(1))	5.4	-85.1	10.8	0.921	
2(1Ce(2))	2(1Ce(2)) 4.3		-99.5 11.8		
$La_{2.7}Ce_{0.3}Si_6N_{11}$					
Si	Population	Chemical	FWHM	$T_1$	
site	(%)	Shift (ppm)			
1(6La)	67.6	-60.5	14.6	19.84	
2(3La)	21.8	-47.1	11.4	16.76	
1(1Ce(1))	11.2	-84.5	11.7	0.8345	
2(1Ce(2))	8.5	-99.9	12.8	0.9651	
$Ce_3Si_6N_{11}$					
Si	Population	Chemical	FWHM	$T_1$	
site	(%)	Shift (ppm)			
1(6Ce)	67.6	-200.4	29.8	0.0572	
2(3Ce)	32.4	-37.7	29.0	0.105	



Figure 6: Solid-state Hahn-echo <sup>29</sup>Si MAS NMR spectra and multi-component fits of  $La_{3-x}Ce_xSi_6N_{11}$  acquired at 295 K, 20 kHz MAS, and 18.8 T, with *x* as indicated. Asterisks denote spinning sidebands. Peaks are labeled with the corresponding Si site in Table 1, with some of the nearest lanthanide atoms indicated in parenthesis. The spectra and fits have been offset for clarity.

sites, respectively, with the remaining peaks for x = 3 in Figure 5 and Figure 6 being due to spinning sidebands. The ratio of <sup>29</sup>Si site 1 to site 2 for the x = 3 material is 2.09 : 1, nearly the expected value of 2 : 1. The discrepancy may be due to different relaxation times of the two sites and non-uniform loss of signal intensity during the Hahn-echo pulse sequence. The high degree of crystallinity in the samples as seen in the X-ray and neutron scattering patterns should manifest as narrow peaks in the NMR spectra, but the peaks are somewhat broad. This is likely due to the paramagnetic broadening induced by the large amount of Ce<sup>3+</sup> in the lattice.<sup>58</sup>

As the amount of La is increased and the amount of Ce decreased, the Si(1) signal moves to a higher frequency at around -61 ppm, and the Si(2) signal moves to -49 ppm for the x = 0.18 material. The <sup>29</sup>Si spectra of La<sub>2.7</sub>Ce<sub>0.3</sub>Si<sub>6</sub>N<sub>11</sub> and La<sub>2.82</sub>Ce<sub>0.18</sub>Si<sub>6</sub>N<sub>11</sub> in Figure 5 are both very similar, with 2 main <sup>29</sup>Si signals at around -61 ppm and -49 ppm corresponding to the crystallographic Si sites Si(1) and Si(2), respectively. The other small

peaks near -85 ppm and -100 ppm are <sup>29</sup>Si nuclei near substituted Ce<sup>3+</sup> in the materials. These signals are displaced to lower frequencies (more negative ppm values), which is toward the Si(1) peak for the x = 3 material. Since the Si(2) signal is in the opposite direction (higher frequency or less negative ppm values), the displaced peaks near -85 ppm and -100 ppm are associated with <sup>29</sup>Si site 1 nuclei. Taking this into account, the ratio of <sup>29</sup>Si site 1 to site 2 for the x = 0.18 material is 3:1, which is much larger than the nominal 2:1 from the Wyckoff multiplicities. An overestimation of the Si(1) population is consistent with what was seen in the NMR spectra for the x = 3 material. This may be related to non-uniform signal loss from different <sup>29</sup>Si sites, due to the Hahn-echo pulse sequence.

Paramagnetic ions such as  $Ce^{3+}$  are known to displace the signal of NMR-active nuclei,<sup>54</sup> with the displacement dependent on the orientation of the nearby <sup>29</sup>Si nuclei with regard to a Ce<sup>3+</sup> atom in the lattice. To predict the directions and magnitudes of the paramagnetic displacements, one requires crystal-field splitting tensors of  $Ce^{3+}$ . However, these have not been measured or calculated for  $Ce^{3+}$  in  $La_{3-x}Ce_xSi_6N_{11}$ , so as a first approximation cylindrical symmetry of the crystal-field splitting tensors can be assumed. Since the mirror-plane and four-fold symmetries of the two La/Ce sites are parallel to the *c*-axis in the  $La_{3-x}Ce_xSi_6N_{11}$  unit cell, we assume the principle magnetic axis of symmetry for the Ce atoms in both sites lies along the c-direction. With this assumption, the angular factors that contribute to calculation of the paramagnetic displacements<sup>59</sup> would be equivalent for the eight Si atoms surrounding Ce on site 1, and would be equivalent for the eight Si atoms nearest Ce on site 2. Assuming the crystal-field splitting tensor values are nearly the same for Ce on the two sites, the only other parameter that will effect the paramagnetic displacement is the internuclear  $Ce^{3+}$ -Si distance. The magnitude of the paramagnetic displacement is related to the internuclear Ce<sup>3+</sup>–Si distance as  $1/r^3$ . Since the Si(1) distance to La/Ce(1) is 3.61 Å and to La/Ce(2) is 3.32 Å, the induced shift on Si(1) from a Ce(2) site is expected to be of greater magnitude than that from a Ce(1) site. The peaks in the fit in Figure 6 were assigned based on this inference, and the ratio of the two Ce sites can be

analyzed to understand the site preference of Ce. Combinatorial analysis with a random distribution of Ce in the lattice says the ratio of Ce site 1 to site 2 should be 2:1, since there are twice as many Ce 1 sites in the structure. The ratio from the NMR spectra here gives a ratio of 2:1.6 for the x = 0.18 material and 2:1.7 for the x = 0.3 material, showing Ce has a strong preference for site 2. This agrees with the Rietveld and BVS analysis, which gave a ratio of 2:1.8 for x = 0.18 and 2:2.4 for x = 0.3, slightly larger than the NMR result. Back-calculating the amount of substituted Ce from integration of the NMR spectra gives a result of 1.6% and 2.4% for the 6% (x = 0.18) and 10% Ce (x = 0.3) doped materials, respectively. The very low underestimate of total Ce substitution may be due to substantial loss of signal intensity from  $T_2$  relaxation of  ${}^{29}$ Si nuclei near substituted Ce<sup>3+</sup> ions.



Figure 7: Solid-state <sup>29</sup>Si MAS NMR saturation-recovery spectra of  $Ce_3Si_6N_{11}$  acquired at 295 K, 20 kHz MAS, and 18.8 T. Asterisks denote spinning sidebands. The traces at the top and bottom represent spectra from the longest and shortest delay times, respectively.

Fits of the x = 1.2 and x = 2.1 materials were infeasible, since a combinatorial analysis predicts 15 peaks from distinct <sup>29</sup>Si sites with different amounts of Ce ions nearby. These peaks would also have spinning sidebands that would convolute the fit, adding another 30 Gaussian peaks to the fit. Although we can see the gradual trend of the Si(1) signal moving to lower frequency, direct analysis of the Ce(2)/Ce(1) ratio from these spectra is challenging.

From the x = 0.18 spectra in Figure 5, the displacement of the Si(1) chemical shift from a nearby Ce(1) is found to be around -24 ppm, and -38 ppm from a nearby Ce(2) ion. These shifts are consistent with the -200 ppm position of the Si(1) in the x = 3 material, since there are 2 Ce(2) ions and 4 Ce(1) ions near each <sup>29</sup>Si(1) atom, for a total shift of -172 ppm, which would yield a signal around -233 ppm. However, since each Ce near a <sup>29</sup>Si atom is a distinct distance away, this generalized approach fails to perfectly predict the total displacement amount of the  ${}^{29}$ Si(1) signal, but appears to be a good approximation. The signal associated with the Si(2) site is not displaced as far as the Si(1) site as Ce substitution increases from x = 0.18 to 3, and is shifted toward higher frequency with addition of Ce in the lattice. This is because the Si(2) site is in the same plane as the 3 nearest Ce sites, which causes the anisotropic magnetic susceptibility of Ce to interact more weakly with the Si(2) site than the Si(1) site. In terms of the equation for the dipolar psuedocontact shift<sup>54,59</sup> this means the angle between the principle magnetic axis of symmetry of  $Ce^{3+}$  and the Ce–Si(2) internuclear distance is around 55° or 125°, which makes the paramagnetic NMR signal displacement nearly zero. In other words, the principle magnetic axis of symmetry of  $Ce^{3+}$  on site 2 is about 55° or 125° away from the *ab*-plane in the  $La_{3-x}Ce_xSi_6N_{11}$  unit cell.

The FWHM of the <sup>29</sup>Si peaks also increases with increased Ce content, as seen in Table 1. However, the FWHM of the paramagnetically-displaced peaks is not significantly greater than the bulk peaks in both the x = 0.18 and x = 0.3 Ce-doped samples, indicating uniform environments and a high amount of crystallinity around the substituted Ce<sup>3+</sup> ions. This likely relates to the high quantum efficiencies and resistance to thermal quenching seen in La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub>, as well as the high  $\theta_D$  calculated from the ADPs obtained from Rietveld analyses.

To further investigate the properties of the materials, saturation-recovery experiments were performed on the  $La_{3-x}Ce_xSi_6N_{11}$  materials. These experiments saturate the magnetization of NMR-active nuclei, then after a delay time perform a normal NMR experiment.



Figure 8: Integrated intensities from the saturation-recovery experiments for  $La_{3-x}Ce_xSi_6N_{11}$  with *x* as indicated in (a), (b), and (c). The signals from <sup>29</sup>Si nuclei near  $Ce^{3+}$  saturate much faster, indicating a dipolar interaction of the <sup>29</sup>Si nuclei with nearby  $Ce^{3+}$  ions.

This allows measurement of the  $T_1$  relaxation times of the different components in the spectra (by fitting the integrated areas as a function of time to an exponential function), and can separate the fast-relaxing components from the slow relaxing components. Figure 7, which shows a set of saturation-recovery experiments performed on Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub>, shows that the two Si sites have very fast relaxation times (around 0.05 s and 0.1 s for Si sites 1 and 2 in the structure, respectively). The fast  $T_1$ s are due to the large amount of Ce<sup>3+</sup> in the structure, which has an unpaired electron that interacts with the <sup>29</sup>Si nuclear spins and causes much shorter relaxation times. Figure 8(a) and (b) show that the La<sub>2.82</sub>Ce<sub>0.18</sub>Si<sub>6</sub>N<sub>11</sub> bulk <sup>29</sup>Si nuclei (around -49 ppm and -61 ppm) saturate much slower than the other peaks. The bulk <sup>29</sup>Si peaks correspondingly have long relaxation times (around 20 s) compared to the other peaks, which have relaxation times around 1 s. This further supports that the peaks near -85 ppm and -100 ppm are from <sup>29</sup>Si nuclei near Ce<sup>3+</sup>.

Local structure of Ce<sup>3+</sup> from electron paramagnetic resonance



Figure 9: Electron paramagnetic resonance of  $La_{3-x}Ce_xSi_6N_{11}$  with *x* as indicated. The top plot shows an expanded view of the  $La_{2.82}Ce_{0.18}Si_6N_{11}$  material, showing the  $g_y$  and  $g_z$  tensor components of Ce(1). The feature near 3400 G for the *x* = 2.1, 3 materials is an impurity. The spectra have been offset for clarity.

The site occupancy of Ce in  $La_{3-x}Ce_xSi_6N_{11}$  can also be explored through ESR, along with other structural details. The ESR spectra of the solid-solution series in Figure 9 shows that the sharp peaks in low Ce content samples broaden to nearly flat with increasing Ce content. This is due to Ce–Ce dipolar coupling, which decreases the unpaired electron relaxation time. Each site in the LSN structure has a different symmetry; the La/Ce site 1 has  $C_s$  symmetry (one mirror plane), and the La/Ce site 2 has  $C_4$  symmetry (4-fold rotational symmetry). From this it is expected that the La site 2 would exhibit a highersymmetry pattern than La site 1. The different peaks in the low-Ce content samples have been assigned to the two Ce sites as indicated in Figure 9 based on this assumption. The Ce(2) site has a much larger peak area, indicating that there is a preference for Ce to substitute on this site, consistent with the NMR and Rietveld results. Other small satellite peaks reside near the main Ce<sup>3+</sup> features, and are satellite peaks from Ce<sup>3+</sup> in slightly distorted lattice sites.

## La<sub>3-x</sub>Ce<sub>x</sub>Si<sub>6</sub>N<sub>11</sub> optical properties

Since  $La_{3-x}Ce_xSi_6N_{11}$  has been found to be an efficient yellow emitting phosphor under 450 nm excitation, <sup>35,60</sup> we have investigated the spectroscopic properties of the various samples. The room-temperature excitation spectra in Figure 10(b) exhibit two strong and broad bands, located at 460 nm and 395 nm with shoulders peaking around 500 nm and 345 nm, corresponding to the transitions from the ground state ( ${}^{2}F_{5/2}$ ) of the Ce<sup>3+</sup> ion to the lowest lying *d*-states. As the splitting of the ground state due to the spin orbit coupling (2000 cm<sup>-1</sup>) is much larger than the thermal energy  $k_BT$  at room temperature, absorption from the  ${}^{2}F_{7/2}$  state can be neglected. A comparison of the excitation and absorption properties (obtained from diffuse reflectance measurements) shows that the same features can be found in both types of spectra, as shown in Figure 10(a),(b). Only a slight shift in the absolute positions of the bands is observed if compared to the absorption data, which is mostly due to concentration and scattering effects, <sup>61</sup> since the absorption spectra have been collected from a sample diluted with BaSO<sub>4</sub>.

With increasing cerium concentration, *x* in  $La_{3-x}Ce_xSi_6N_{11}$ , a red shift of the position of the emission maximum is observed in the samples as shown in Figure 10(c) and Table 2. This can be explained in terms of the strength of the crystal field splitting (Dq or  $\Delta$ ), which can be approximated through a point-charge model as:<sup>62</sup>

$$Dq = \frac{1}{6}Ze^2 \frac{r^4}{R^5},$$
 (1)

with *Z* representing the valence of the coordinating anion, *e* the elemental charge and *r* the radius of the *d*-wave function. *R* is the bond length between the activator ion and the coordinating anion. We find that with increasing cerium concentration the Ce<sup>3+</sup>–N bond lengths decrease, leading to an increase in the crystal field splitting. A larger Dq or  $\Delta$  thus



Figure 10: Room-temperature (a) Kubelka-Munk absorption, (b) excitation spectra collected with the emission wavelength of maximum intensity, and (c) emission spectra collected with the excitation wavelength of maximum intensity of  $La_{3-x}Ce_xSi_6N_{11}$  materials, with the compositions *x* as indicated. The spectra have been offset for clarity.

means that the energy difference between the ground state(s) of cerium and the lowest *d*-state is reduced, shifting the emission maximum into the lower energy (*i.e.* red) part of the visible spectrum. More evidence for this increase in crystal field splitting strength can be found in the excitation/absorption spectra; with increasing cerium content (*i.e.* decreasing bond length), there is a significant shift towards lower energies in the position of the lowest energy excitation/absorption band, which can be seen in Figure 10(a) and (b).

The low-temperature (77 K) emission spectra in Figure 11(b) show the same shift towards lower energies with increasing cerium concentration as observed at room temperature. The splitting of the emission band, partially observed at room temperature, becomes more pronounced at lower temperatures, and two very distinct bands are observed. These two bands arise from the transitions of the lowest lying 5*d*-state to the  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$ 

states of the cerium ion. In order to further analyze these transitions, peak deconvolution for all cerium concentrations has been carried out. Although four Gaussian peaks can be used to fit the data, the data are represented well with only two Gaussians, suggesting emission from both sites is very similar. This is not surprising, since both Ce sites are eightcoordinate and have bond distances that only differ by about 2%. Other systems with two Ce sites that have similar coordination numbers, such as previously observed in lanthanum silicon oxynitride phosphors<sup>63</sup> and  $Sr_{2.975}Ce_{0.025}Al_{1-x}Si_xO_{4+x}F_{1-x}$ ,<sup>11</sup> also display an emission that can be fit well with two Gaussian curves. The fits yield two bands that are separated by about  $1900 \text{ cm}^{-1}$  in all samples, which is a measure of the magnitude of the spin-orbit coupling of the 4f levels. This result is consistent with the values of around  $2000 \text{ cm}^{-1}$  typically found for Ce<sup>3+</sup> in the literature.<sup>64</sup> The peak deconvolution also shows that with increasing cerium concentration, the emission band at higher energies decreased in intensity if compared to the low-energy band. The ratio of these two bands drops from 0.35 (x = 0.18) to about 0.23 (x = 3.00). This effect has been explained with more efficient re-absorption at higher cerium concentrations.<sup>28</sup> Additionally, Dorenbos<sup>65</sup> has shown that the Stokes shift, determined as the difference between the excitation band with the lowest energy and emission with the highest energy, can be considered as a feature of the host once a trivalent lanthanide ion is introduced into a host lattice. When taking the shoulder at around 495-520 nm as the excitation band with the lowest energy, we find values of about  $2975 \text{ cm}^{-1}$  for all samples, see Table 2.

To investigate the thermal robustness of the materials, temperature-dependent emission spectra have been recorded. The right column in Figure 11(b) displays the emission spectra (under 450 nm excitation) at a temperature of 503 K. It can clearly be seen that in the x = 0.18 material there is almost no sign of temperature quenching, see also Table 3. Materials with  $x \le 0.3$  show high emission intensities and a high quantum yield over the complete measured temperature range. If  $x \ge 1.2$ , the quenching effects become more pronounced, which is also evident in the quenching temperature  $T_{1/2}$  that has been calcu-



Figure 11: (a) Temperature-dependent normalized quantum yield for the x = 0.18 and  $x = 3 \text{ La}_{3-x}\text{Ce}_x\text{Si}_6\text{N}_{11}$  materials, and (b) emission spectra of the x = 0.18 and x = 3 materials at 77 K and 503 K with the fits to the data shown.

lated for the different compounds.  $T_{1/2}$  is usually defined as the temperature at which the emission intensity has dropped to 50% of the value obtained at low temperatures (4.2 K or 77 K). As can be seen in Table 3, for samples with *x* up to 1.2, we have not observed temperature quenching in the measured temperature range. For the samples with x = 2.1 and 3.0,  $T_{1/2}$  has been found to be 480 K and 450 K respectively. Even with full Ce substitution, a strong emission is still present. The Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub> material exhibits a quantum yield of about 1/4 of that of the La<sub>2.82</sub>Ce<sub>0.18</sub>Si<sub>6</sub>N<sub>11</sub> material at 503 K, which is remarkable for a stoichimetric cerium compound.

Composition (x)	$\lambda_{ex.}$ (cm <sup>-1</sup> )	$\lambda_{em.}$ (cm <sup>-1</sup> )	$\Delta S \text{ (cm}^{-1}\text{)}$
0.18	20120	17161, 19058	2959
0.30	20080	17116, 19015	2964
1.20	19801	16809, 18695	2992
2.10	19531	16552, 18461	2979
3.00	19342	16368, 18246	2974

Table 2: Spectroscopic properties of the various  $La_{3-x}Ce_xSi_6N_{11}$  materials.

Composition (x)	QY <sub>77<i>K</i></sub> (%)	$QY_{298K}$ (%)	$QY_{503K}$ (%)	$T_{1/2}$ (K)
0.18	0.94	1.00	0.95	> 503
0.30	0.96	0.98	0.86	> 503
1.20	0.65	0.63	0.38	> 503
2.10	0.71	0.62	0.30	480
3.00	0.77	0.61	0.25	450

Table 3: Temperature dependent spectroscopic properties (normalized quantum yield and quenching temperature) of the various  $La_{3-x}Ce_xSi_6N_{11}$  materials.

One very interesting feature of the  $La_{3-x}Ce_xSi_6N_{11}$  family of phosphors is the absence of complete concentration quenching at higher cerium concentrations. Usually, once a certain critical concentration is exceeded, non-radiative energy transfer mechanisms become more efficient (due to the increased probability of two emission centers being proximal) and the excitation energy is transfered between the activator ions until it has reached some kind of trap, such as defects or surface states. However, some cerium compounds, such as  $CeF_3^{28}$  and  $CeMgAl_{11}O_{19}^{29}$  also lack total concentration quenching. The lack of concentration quenching may be due to most of the  $Ce^{3+}$  sites have identical coordination environments. So even though the excited state electron could charge transfer to nearby  $Ce^{3+}$  ions, all of these ions would have the same probability of non-radiative transitions.

Blasse<sup>66</sup> has proposed a model which allows one to estimate the so-called critical distance ( $R_C$ ) of energy transfer, which has been described as the distance for which the transfer probability equals the emission probability of the emitting ion, from the concentration quenching.  $R_C$  can be calculated using:

$$R_C = 2 \cdot \left(\frac{3V}{4\pi x_c N}\right)^{\frac{1}{3}} \tag{2}$$

where *V* is the volume of the unit cell,  $x_c$  the critical quenching concentration and *N* the number of lattice sites in the unit cell. Using the obtained value for *V* of 502.8 Å<sup>3</sup> from the Rietveld refinement, and  $x_c = 0.06$  (the concentration for which the highest emission intensity was observed) and N = 6, we find a critical distance for energy transfer of about 13.9 Å. Since even in the stoichiometric cerium compound Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub>, the luminescence

is not quenched completely, we can use *V* of 497.6 Å<sup>3</sup> from the Rietveld refinement, and  $x_c = 1$ , which leads to a value of 5.4 Å. Typical Ce–Ce distances within the host lattice are 3.7 Å for Ce(1)–Ce(1) and Ce(1)-Ce(2) distances, and 4.8 Å for Ce(2)–Ce(2) pairs. Usually, the critical radius is much larger than typical next-nearest neighbor distances. However, if they are of the same order of magnitude, concentration quenching might be absent or very weak, as we find in the case of Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub>, thus, even this compound with full Ce substitution for La does not show complete quenching of the luminescence.

Another way of determining the concentration quenching effect is through the investigation of the concentration-dependence of the luminescence lifetime, therefore, the time resolved luminescence properties are displayed in Figure 12. The samples have been excited with 440 nm light and the emission between 530 and 560 nm was monitored. For all samples, decay times of about 40 ns are found, with a single exponential fit describing the data well. The single exponential fit suggests both Ce sites emit with a similar decay time. A similar result was found in an oxyfluoride phosphor with two separate Ce sites.<sup>11</sup> Only a very slight decrease is observed with increasing cerium concentration (from 42 ns in the sample with x = 0.18 to about 37 ns in Ce<sub>3</sub>Si<sub>6</sub>N<sub>11</sub>) pointing towards the fact that very little if any quenching due to concentration effects takes place. The obtained values are very comparable to typically observed decay times for 5d - 4f transitions in Ce<sup>3+</sup> and match very well the observations of Suehiro *et al.*<sup>60</sup>

#### Conclusions

Structural characterization of  $La_{3-x}Ce_xSi_6N_{11}$  through magnetic resonance and scattering has shown Ce prefers to substitute on site 2, which better satisfies its bond valence. Rietveld refinements have shown  $La_{3-x}Ce_xSi_6N_{11}$  to have a very rigid crystal structure, with small ADPs and high Debye temperatures, which is potentially a reason for the strong thermal robustness of luminescence observed for small Ce substitution, *x*. Optical excitation and emission spectra suggest both Ce sites emit at very similar energies with decay



Figure 12: Photoluminescence decay curves for the various  $La_{3-x}Ce_xSi_6N_{11}$  samples with different cerium concentrations under 440 nm pulsed laser excitation.

times of around 40 ns. The time decay of  $La_{3-x}Ce_xSi_6N_{11}$  only slightly decreases from x = 0.18 to x = 3, suggesting very little concentration quenching exists. The short lifetimes may help explain why Ce–Ce quenching does not fully quench luminescence, even at full Ce substitution for La.

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### Supporting Information Available

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