Structural origins of the optical properties of the La_{3-x}Ce_xSi₆N₁₁ phosphor

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Supporting information

Materials and Methods

Optical Measurements Approximately 200 fs excitation pulses with a wavelength of 440 nm were generated by doubling the fundamental frequency of a Ti:Sapphire laser

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(Coherent Mira 900) pulses in a commercial optical harmonic generator (Inrad). The laser repetition rate was reduced to 200 KHz by a home-made acousto-optical pulse picker in order to avoid saturation effects. The TCSPC system is equipped with an ultrafast microchannel plate photomultiplier tube detector (Hamamatsu R3809U-51) and electronics board (Becker and Hickl SPC-630) and has an instrument response time of about 60 ps to 65 ps. A triggering signal for the TCSPC board was generated by sending a small fraction of the laser beam onto a fast (400 MHz bandwidth) Si photodiode (Thorlabs Inc.). The fluorescence signal was dispersed in an Acton Research SPC-500 monochromator after passing through a pump blocking, long wavelength-pass, autofluorescence-free, interference filter (Omega Filters, ALP series). The monochromator is equipped with a CCD camera (Roper Scientific PIXIS-400) allowing for monitoring of the time-averaged fluorescence spectrum. Luminescence transients were not deconvolved with the instrument response function since their characteristic time-constants were much longer than the width of the system response to the excitation pulse.

Luminescence life-time measurements were performed using Time-Correlated Single Photon Counting (TCSPC) technique.¹ Approximately 200 femtosecond (fs) excitation pulses with wavelength 440 nm were generated by doubling the fundamental frequency of fs Ti:Sapphire laser (Coherent®Mira 900) pulses in a commercial optical harmonic generator (Inrad®). The laser repetition rate was reduced to 200 KHz by a home-made acousto-optical pulse picker in order to avoid saturation of the chromophore. The TCSPC system was equipped with an ultrafast microchannel plate photomultiplier tube detector (Hamamatsu Photonics®R3809U-51) and electronics board (Becker & Hickl®SPC-630) and has instrument response time about 60 ps to 65 ps. The triggering signal for the TCSPC board was generated by sending a small fraction of the laser beam onto a fast (400 MHz bandwidth) Si photodiode (Thorlabs Inc.®). The fluorescence signal was dispersed in an Acton Research®SPC-500 monochromator after passing through a pump blocking, long wavelength-pass, autofluorescence-free, interference filter (Omega Filters®, ALP series). The monochromator is equipped with a CCD camera (Roper Scientific®PIXIS-400) allowing for monitoring of the time-averaged fluorescence spectrum. Luminescence transients were not de-convolved with the instrument response function since their characteristic time constants were much longer than the width of the system response to the excitation pulse.

Further discussion To investigate whether or not charge transfer occurs between Ce(1) and Ce(2), a similar time-decay experiment was done with 400 nm excitation. However, no change in the decay time behavior was found, suggesting neither Ce site emits in another range besides the observed emission.

2.1 refinements. The P4bm space group was used for the La_{3-x}Ce_xSi_{6-y}Al_yN₁₁ phase. Estimated standard deviations are given Table 1: Crystallographic parameters and Debye temperatures (θ_D) calculated from atomic displacement parameters from Rietveld refinement of 295 K 11-BM synchrotron powder X-ray diffraction (SPXD) and HIPD and NPDF powder neutron diffraction (ND) data of $La_{3-x}Ce_xSi_6N_{11}$. 2.5% O was included on the N sites in the refinements, and a small (~1 mol %) amount of LaSi₃N₅ impurity was included in the x = 0.18, 0.3, and 3 refinements. About 20 mol % was included in the x = 1.2, in parenthesis.

x	0.18	0.3	1.2	2.1	33
	SPXD	SPXD	SPXD	SPXD	SPXD
data	NPDF	NPDF	NPDF		
	HIPD				
SPXD R_{wp} (%)	7.38	8.23	9.51	6.89	6.56
ND R_{wp} (%)	1.77	1.34	2.16		
Total \vec{R}_{wp} (%)	4.29	6.97	7.73		
a (Å)	10.190730(4)	10.187324(5)	10.16841(1)	10.153044(7)	10.138464(6)
<i>c</i> (Å)	4.841257(3)	4.840409(4)	4.840461(8)	4.840329(5)	4.841018(5)
V (Å ³)	502.7693(4)	502.3452(5)	500.487(1)	498.9619(7)	497.6008(7)
θ_D (K)	665	748	646	940	933
Cel F	0.066(5)	0.05(3)	0.38(3)		
Ce2 F	0.120(7)	0.12(4)	0.50(4)		
total x	0.25(1)	0.22(7)	1.26(3)		

x	0.18	0.3	1.2	2.1	3
La1/Ce1					
x	0.68097(8)	0.68107(1)	0.68113(2)	0.68118(2)	0.68112(1)
V	0.18097(8)	0.18107(1)	0.18113(2)	0.18118(2)	0.18112(1)
N	0.0134(3)	0.0052(2)	0.0116(3)	0.0108(2)	0.0095(2)
B_{iso} (Å ²)	0.49(2)	0.49(6)	0.53(6)	0.439(5)	0.401(3)
La2/Ce2 ^a					
N	0.9963(4)	0.9839(3)	0.994833(5)	0.993694(3)	0.993332(4)
B_{iso} (Å ²)	0.29(3)	0.20(7)	0.61(8)	0.297(6)	0.270(5)
Si1					
ĸ	0.2093(1)	0.21012(6)	0.2109(1)	0.20954(8)	0.20994(6)
2	0.0779(2)	0.07775(7)	0.0773(1)	0.07795(8)	0.07804(7)
•	0.5306(4)	0.5240(3)	0.5334(5)	0.5312(4)	0.5313(3)
B_{iso} (Å ²)	0.19(2)	0.12(3)	0.24(2)	0.19(2)	0.12(2)
Si2					
K	0.1165(2)	0.11683(7)	0.1171(1)	0.11687(9)	0.11698(7)
2	0.6165(2)	0.61684(7)	0.6171(1)	0.61688(9)	0.61699(7)
N	0.0415(5)	0.0312(4)	0.0422(6)	0.0408(4)	0.0413(3)
B_{iso} (Å ²)	0.26(3)	0.07(5)	0.21(4)	0.18(3)	0.11(2)

x	0.18	0.3	1.2	2.1	S.
N1					
x	0.08039(7)	0.0796(2)	0.0795(2)	0.0786(3)	0.0804(2)
y	0.17843(6)	0.1786(1)	0.1785(2)	0.1787(3)	0.1790(2)
2	0.636705(6)	0.6283(4)	0.6423(5)	0.6414(6)	0.6426(4
B_{iso} (Å ²)	0.47(2)	0.52(4)	0.49(3)	0.13(5)	0.17(4)
N2					
x	0.23249(6)	0.2326(1)	0.2322(2)	0.2322(3)	0.2309(2)
y	0.07413(7)	0.0746(2)	0.0736(2)	0.0729(3)	0.0737(2)
. 27	0.1765(2)	0.1679(4)	0.1786(5)	0.1766(5)	0.1764(4)
B_{iso} (Å ²)	0.40(2)	0.44(4)	0.39(3)	0.13(5)	0.17(4)
N3					
x	0.15324(6)	0.1538(1)	0.1532(2)	0.1531(3)	0.1536(2)
y	0.65324(6)	0.6538(1)	0.6532(2)	0.6531(3)	0.6536(2)
2	0.6936(2)	0.6832(5)	0.6910(7)	0.6898(8)	0.6923(6)
B_{iso} (Å ²)	0.37(1)	0.39(4)	0.38(3)	0.06(6)	0.19(6)
$N4^{a}$					
X	0.0665(4)	0.0593(7)	0.0681(9)	0.061(1)	0.0687(9)
B_{iso} (Å ²)	0.54(2)	0.56(6)	0.58(3)	0.06(6)	0.36(7)

Table 2: Crystallographic parameters and Debye temperatures (θ_D) calculated from atomic displacement parameters from Rietveld refinement of 295 K 11-BM synchrotron powder X-ray diffraction (SPXD) and HIPD and NPDF powder neutron diffraction (ND) data of La_{3-x}Ce_xSi_{6-y}Al_yN₁₁. 2.5% O was included on the N sites in the refinements, and a small (~1%) amount of LaSi₃N₅ impurity was included. The *P4bm* space group was used for the La_{3-x}Ce_xSi_{6-y}Al_yN₁₁ phase. Estimated standard deviations are given in parenthesis.

x	0.18	0.3	1.2
La1/Ce1			
U_{11}	0.51(2)	0.89(7)	0.55(6)
U_{22}	0.51(2)	0.89(7)	0.55(6)
U_{33}	0.86(3)	0.10(9)	0.90(9)
U_{12}	-0.02(2)	0.26(7)	0.07(6)
U_{13}	0.01(2)	-0.20(6)	-0.25(5)
U_{23}	0.01(2)	-0.20(6)	-0.25(5)
La2/Ce2			
U_{11}	0.40(3)	0.13(8)	1.1(1)
U_{22}	0.40(3)	0.13(8)	1.1(1)
U_{33}	0.31(4)	0.50(14)	0.1(1)
U_{12}	0	0	0
U_{13}	0	0	0
U_{23}	0	0	0
Si1			
U_{11}	0.31(3)	0.15(4)	0.30(3)
U_{22}	0.28(3)	0.15(4)	0.30(3)
U_{33}	0.13(3)	0.15(4)	0.30(3)
U_{12}	-0.04(3)	0	0
U_{13}	-0.03(3)	0	0
U_{23}	0.03(3)	0	0
Si2			
U_{11}	0.20(3)	0.09(6)	0.27(5)
U_{22}	0.20(3)	0.09(6)	0.27(5)
U_{33}	0.57(5)	0.09(6)	0.27(5)
U_{12}	-0.15(4)	0	0
U_{13}	0.01(3)	0	0
U_{23}	0.01(3)	0	0

x	0.18	0.3	1.2
N1			
U_{11}	0.43(2)	0.37(5)	0.51(4)
U_{22}	0.71(2)	0.38(5)	0.75(4)
U_{33}	0.63(2)	1.21(7)	0.62(4)
U_{12}	0.10(1)	-0.13(4)	0.30(3)
U_{13}	-0.04(2)	0.11(5)	-0.08(4)
U_{23}	0.01(1)	0.17(5)	0.03(4)
N2			
U_{11}	0.45(2)	0.48(5)	0.26(3)
U_{22}	0.75(2)	0.65(5)	0.75(4)
U_{33}	0.31(2)	0.54(6)	0.46(4)
U_{12}	-0.09(1)	-0.35(4)	-0.18(3)
U_{13}	-0.01(1)	0.05(5)	-0.14(3)
U_{23}	0.04(2)	0.12(6)	0.07(4)
N3			
U_{11}	0.54(1)	0.46(4)	0.52(3)
U_{22}	0.54(1)	0.46(4)	0.52(3)
U_{33}	0.34(2)	0.56(7)	0.40(5)
U_{12}	0.15(2)	0.22(5)	0.10(4)
U_{13}	0.02(1)	-0.04(5)	0.07(4)
U_{23}	0.02(1)	-0.04(5)	0.07(4)
N4			
U_{11}	0.59(2)	0.43(7)	0.41(5)
U_{22}	0.59(2)	0.43(7)	0.41(5)
U_{33}	0.88(4)	1.3(1)	1.4(1)
U_{12}	0.13(3)	-0.27(9)	0.10(7)
U_{13}	0	0	0
U_{23}	0	0	0



Figure 1: Solid-state Hahn-echo 29 Si static NMR spectra of Ce₃Si₆N₁₁ acquired at 295 K and 18.8 T. The spectra have been offset for clarity.



Figure 2: Solid-state ²⁹Si MAS NMR saturation-recovery spectra of $La_{2.82}Ce_{0.18}Si_6N_{11}$ acquired at 295 K, 20 kHz MAS, and 18.8 T. The traces at the top and bottom represent spectra from the longest and shortest delay times, respectively.



Figure 3: Solid-state ²⁹Si MAS NMR saturation-recovery spectra of $La_{2.7}Ce_{0.3}Si_6N_{11}$ acquired at 295 K, 20 kHz MAS, and 18.8 T. The traces at the top and bottom represent spectra from the longest and shortest delay times, respectively.

References

(1) Becker, W. *Advanced Time-Correlated Single Photon Counting Techniques*; Springer Series in Chemical Physics; Springer: Berlin, Heidelberg, New York, 2005; Vol. 81.