I. INTRODUCTION

Phosphors are essential components of white light-emitting-diodes (LEDs). In particular, phosphors activated by the Ce$^{3+}$ ion, presenting a $4f \rightarrow 5d$ spin-allowed transition, have attracted much attention from academia and industry. A large effort has been devoted to the development of novel Ce$^{3+}$ doped systems in the last decades. However, most of these have been found thanks to a semi-empirical method that can only provide trends and qualitative predictions. Especially, the prediction on emission property and Stokes shift is limited since the structure geometry of excited state is difficult to measure experimentally. A typical example beyond the expectation of the semi-empirical method is the emission color of Ce$^{3+}$ ion in two closely related lanthanum silicon nitrides (LSN), LaSi$_3$N$_5$ and La$_2$Si$_6$N$_{11}$. In particular, the latter is a blue-convertible yellow phosphor, with a great potential to replace commercial YAG:Ce, while the former gives a blue emission under the UV excitation.

The crystal structure of LaSi$_3$N$_5$ was studied by Inoue in 1980. Its structure is built up of Si$_4$ tetrahedra, which are linked by shared corners. In this compound, there is only one non-equivalent La$^{3+}$ crystallographic site. The crystal structure of La$_2$Si$_6$N$_{11}$ (La: lanthanide element) was reported by Woike and Jeitschko in 1995, and that of La$_2$Si$_6$N$_{11}$ has recently determined by Yamane’s group. Similar to the structural character of LaSi$_3$N$_5$, the crystal structure of La$_2$Si$_6$N$_{11}$ also consists of corner-sharing Si$_4$ tetrahedra. La$_2$Si$_6$N$_{11}$ crystallizes in a tetrahedral structure with the space group of P4bm. In this compound, there are two non-equivalent La$^{3+}$ crystallographic sites. Both sites are coordinated with eight nitrogen atoms, and we call them La$_{2a}$ and La$_{4c}$ according to their Wyckoff positions. The La$_{2a}$ site has a four-fold local symmetry, while the symmetry at the La$_{4c}$ site is lower (As seen in Figure 1).

In recent years, Ce$^{3+}$ doped LSN samples have been synthesized to examine their potential in solid state lighting applications. The optical performance of LaSi$_3$N$_5$:Ce was experimentally studied in detail. These results show that the Ce$^{3+}$ ion occupies the La$^{3+}$ crystallographic site, and gives the above-mentioned blue emission under UV excitation. On the other hand, the properties of La$_2$Si$_6$N$_{11}$:Ce were investigated by Seto et al. who found the yellow emission of La$_2$Si$_6$N$_{11}$:Ce. This experimental observation has been recently confirmed by Seshadri’s group. According to these facts, some preliminary discussions based on crystal structure and dielectric properties have been given to understand the difference between LaSi$_3$N$_5$:Ce and La$_2$Si$_6$N$_{11}$:Ce. However, there are still two main questions existing now, which the semi-empirical method cannot answer: (1) Why do Ce$^{3+}$ ions emit different colors in the two LSN phosphors? (2) Which site is the luminescent center in the La$_2$Si$_6$N$_{11}$:Ce phosphor?

At present, first-principle calculations have been widely used in material science, as they provide an useful insight in the chemical and electronic properties of materials and hence can aid in the search for better materials or guide modification of existing ones. Compared to the semi-empirical model, they might also have advantages in the design of phosphors: first, such theoretical simulations can provide a detailed understanding of interactions and effects involved in the optical processes; second, without relying on empirical information they have the potential to precisely simulate $4f \rightarrow 5d$ neutral transition in new potential materials, not only for the absorption process but also for the emission process.
ABINIT package. The generalized gradient approximation (GGA) exchange-correlation (XC) effects were treated within the generalized density functional theory (DFT) using the projector augmented wave (PAW) method as implemented in the ABINIT package. To obtain the Ce$^{3+}$ states below the conduction band, the Ce$^{5d}$ states are considered, yielding the Stokes shift and characterization of the Ce$^{3+}$ luminescence. In this work, the calculations were performed within DFT+U method, allowing the Ce$^{3+}$ ion to be located inside the gap, following the hybrid functional study of LaSi$_3$N$_5$:Ce$^{3+}$ [22] because of the similar composition of the two nitrides, the same U (J) value was also used in the study of La$_5$Si$_6$N$_{11}$:Ce$^{3+}$.

Most of the PAW atomic datasets were directly taken from the ABINIT website. [23] The nitrogen dataset, with 2s$^2$2p$^3$ valence electrons, has a 1.3 Bohr radius and two projectors per angular momentum channel. The silicon PAW dataset, with 3s$^2$3p$^2$ valence electrons, has a 1.71 Bohr sphere radius and two projectors per angular momentum channel. The cerium dataset, with 5s$^2$5p$^6$6s$^2$5d$^1$4f$^1$ valence electrons, has a 2.5 Bohr radius and two projectors per angular momentum channel.

For La, we tested two different PAW atomic datasets. The normal ABINIT La PAW dataset, with 5s$^2$5p$^6$6s$^2$5d$^1$4f$^0$ as valence electrons, has a 2.5 Bohr sphere radius and two projectors per angular momentum channel. Here, we call this La PAW atomic dataset 'La$_{4f}$-semicore'. In order to test the effect of La$_{4f}$ orbitals, we have generated a PAW atomic dataset with the valence configuration 5s$^2$5p$^6$6s$^2$5d$^1$ (freezing the unoccupied 4f orbital in the core). Here we denote this PAW atomic dataset as 'La$_{4f}$-core'. The PAW atomic dataset was generated using the ATOPAW software with the same input parameter as the other La PAW GGA-PBE atomic dataset, but with frozen 4f states.

With these PAW atomic datasets, we performed the structural relaxation and band structure calculations. The convergence criteria have been set to $10^{-5}$ Hartree/Bohr (for residual forces) and 0.5 mHa/atom (for the tolerance on the total energy). In these calculations, cutoff kinetic energies of 30 Ha and 25 Ha for the plane-wave basis set were used for the LaSi$_3$N$_5$:Ce and La$_5$Si$_6$N$_{11}$:Ce compounds, respectively. The Monkhorst-Pack sampling of the primitive cells (36 atoms for LaSi$_3$N$_5$ and 40 atoms for La$_5$Si$_6$N$_{11}$) for the same tolerance criteria were determined to be 3x3x2 and 3x3x3 for the two nitrides, respectively.

FIG. 1: Coordination environment of (a) the La$^{3+}$ crystallographic site in LaSi$_3$N$_5$; (b) the La$_{2a}$ site in La$_5$Si$_6$N$_{11}$; (c) the La$_{4c}$ site in La$_5$Si$_6$N$_{11}$. Green and gray spheres stand for La and N atoms, respectively.

Still, a routine use of first-principle methods might not yield the sought understanding. As an example, a recent first-principle study of LaSi$_3$N$_5$, doped with Ce as well as some other dopant ions, has been published [23]. The hybrid functional HSE06 has been used. They point out that, in their scheme, simply based on the Kohn-Sham band structure, the Ce$^{3+}$ states are in the conduction band, at variance with experimental data.

With this background, in the present study, we have performed an ab-initio study of these two LSN phosphors, aiming at answering the above-mentioned questions. Our methodological approach differs from the previous ab-initio study [23] at three levels: (1) Constrained DFT allows us to obtain the Ce$^{5d}$ state below the conduction band, in agreement with experimental data; (2) $\Delta$SCF method is used to get the $4f \rightarrow 5d$ transition energy of the Ce$^{3+}$ ion; (3) The lattice relaxation in the excited state is considered, yielding the Stokes shift and characterization of the Ce$^{3+}$ luminescence. Our paper is structured as follows. In Sec. [II] we summarize the calculation method. The study of the undoped LSN bulk materials is presented in Sec. [III]. The Ce$^{3+}$ doped calculations are shown in Sec. [IV], and we give the conclusion in Sec. [V].

II. NUMERICAL APPROACH

A. Computational details

In this work, the calculations were performed within density functional theory (DFT) using the projector augmented wave (PAW) method as implemented in the ABINIT package. [24,25] Exchange-correlation (XC) effects were treated within the generalized gradient approximation (GGA). [26] For the Ce$^{3+}$ doped calculation, DFT+U was used, allowing the Ce$^{4f}$ states to be located inside the band gap. [26] The U value has been optimized to 4.6 eV ($J = 0.5$ eV), in order to reproduce the location of the $4f$ inside the gap, following the hybrid functional study of LaSi$_3$N$_5$:Ce$^{3+}$ [22]. Because of the similar composition of the two nitrides, the same U (J) value was also used in the study of La$_5$Si$_6$N$_{11}$:Ce$^{3+}$. For La, we tested two different PAW atomic datasets. The normal ABINIT La PAW dataset, with 5s$^2$5p$^6$6s$^2$5d$^1$4f$^0$ as valence electrons, has a 2.5 Bohr radius and two projectors per angular momentum channel. Here, we call this La PAW atomic dataset ‘La$_{4f}$-semicore’. In order to test the effect of La$_{4f}$ orbitals, we have generated a PAW atomic dataset with the valence configuration 5s$^2$5p$^6$6s$^2$5d$^1$ (freezing the unoccupied 4f orbital in the core). Here we denote this PAW atomic dataset as ‘La$_{4f}$-core’. The PAW atomic dataset was generated using the ATOPAW software with the same input parameter as the other La PAW GGA-PBE atomic dataset, but with frozen 4f states.

With these PAW atomic datasets, we performed the structural relaxation and band structure calculations. The convergence criteria have been set to $10^{-5}$ Hartree/Bohr (for residual forces) and 0.5 mHa/atom (for the tolerance on the total energy). In these calculations, cutoff kinetic energies of 30 Ha and 25 Ha for the plane-wave basis set were used for the LaSi$_3$N$_5$:Ce and La$_5$Si$_6$N$_{11}$:Ce compounds, respectively. The Monkhorst-Pack sampling of the primitive cells (36 atoms for LaSi$_3$N$_5$ and 40 atoms for La$_5$Si$_6$N$_{11}$) for the same tolerance criteria were determined to be 3x3x2 and 3x3x3 for the two nitrides, respectively.
B. Supercell calculations

The Ce$^{3+}$ doped LSN calculations have been conducted using the supercell method. The cluster approach based on Hartree-Fock theory was not considered since previous studies have shown this method may lead to the deficiencies of the local geometry around the rare earth site. Moreover, the obvious demerit of the cluster method is the lack of the electronic information about the host lattice. We will see that the position of the conduction band minimum (CBM) of the host is important in the luminescent center identification. Therefore, a 72-atom 2x1x1 supercell for LaSi$_3$N$_5$ and a 80-atom 1x1x2 supercell for La$_3$Si$_6$N$_{11}$ have been used for the study of Ce$^{3+}$ doped phosphor. In the calculations, one cerium atom substitutes one lanthanum atom, which leads to La$_7$Ce$_{24}$Si$_{24}$N$_{40}$ for LaSi$_3$N$_5$:Ce, and two different cases, La$_{11}$Ce$_{20}$Si$_{22}$N$_{44}$ and La$_{11}$Ce$_{24}$Si$_{24}$N$_{44}$, for La$_3$Si$_6$N$_{11}$:Ce. Such supercells have a Ce$^{3+}$ doping concentration of 12.5% and 8.3% for the two LSN phosphors, respectively, which is reasonable compared to the experimental data.

C. Neutral excitations

At present, the Bethe-Salpeter Equation (BSE) is the best approach to study the optical properties of solids. It describes neutral excitations as coherent superpositions of electron-hole pairs. However, the computational burden of such approach is quite heavy, and not feasible with supercells of nearly one hundred atoms. Instead of BSE, we simulated the 4$f$ → 5$d$ neutral excitation of Ce$^{3+}$ ion on the basis of the constrained DFT method (CDFT). The electron-hole interaction, an essential contribution in the BSE, is mimicked by promoting the Ce$_{4f}$ electron to the Ce$_{5d}$ state, by constraining the seven 4$f$ bands to be unoccupied, while occupying the lowest 5$d$ state lying higher in energy. The CDFT method has been used for the search of novel scintillators, proposed by Canning, Chaudhry and coworkers. However, the previous works aimed at the qualitative description of the RE$_{5d}$ state. Compared to these results, we observe the CDFT ability to yield quantitative predictions following the ∆SCF method, that is, relying on total energy differences of the different constrained configurations. Through the combination of CDFT and ∆SCF, the 4$f$ → 5$d$ neutral excitation of Ce$^{3+}$ ion is correctly described within the DFT framework, which has a much lower computational cost than the BSE method. In practice, the calculations are performed by setting manually the energy-ordered occupation numbers (optional independent input variables in ABINIT) to one or zero. For both the ground state and the excited state, all valence levels, spin up as well as spin down, are occupied. For the ground state, additionally, the lowest spin-up level found in the band gap (clearly identified as a predominantly Ce-4f level) is occupied, while for the excited neutral state, the seven spin-up predominantly Ce-4f levels that are found in the band gap are unoccupied, and the next spin-up level is occupied. In most cases, the latter level is detached from the conduction band, and exhibits Ce-5d character, as will be seen later.

D. Configurational coordinate diagram

Following the proposed method to describe the neutral excitation of Ce$^{3+}$ ion, we will use the configuration coordinate diagram to analyze the absorption/emission process and Stokes shift of the two Ce$^{3+}$ doped lanthanum silicate nitride phosphors, as shown in Figure 2.

Here, we briefly explain its physical meaning. This configurational coordinate diagram depicts the total energy of a system containing Ce$^{3+}$ ion in its ground state and of a system containing Ce$^{3+}$ ion in its excited state, curve 4$f$ and 5$d$, respectively, as a function of the generalized configuration coordinate Q, which can be made up of any relevant combination of ionic degrees of freedom in the system. Q$_0$ and Q represent the equilibrium configuration coordinates, for the system with Ce$^{3+}$ in its ground state and in its excited state, respectively. The horizontal lines inside the curves 4$f$ and 5$d$ denote the energy levels of the system in which the quantization of vibrational motion is taken into account. When a photon is absorbed by the Ce$_{4f}$ electron, the Ce$^{3+}$ ion will be excited from the ground state to the excited state, corresponding to A$_0$ → A$_0^*$. After the absorption, the system will be out of equilibrium due to the change of electronic configuration of the Ce$^{3+}$ ion. The atomic positions are then relaxed following the forces, which is represented by the process A$_0^*$ → A$^*$ in Figure 2. After this lattice relaxation, the system reaches the new equilibrium state, at which the emission process A$^*$$\rightarrow$A occurs. The cycle is finished by the lattice relaxation A$\rightarrow$A$_0$ process in the ground state. Based on this idea, the absorption/emission energy and
the Stokes shift of Ce$^{3+}$ doped phosphors can be determined as below:

$$E_{\text{abs}} = E_0^* - E_0$$  \hspace{1cm} (1)  

$$E_{\text{em}} = E^* - E$$  \hspace{1cm} (2)  

$$\Delta S = E_{\text{abs}} - E_{\text{em}}$$  \hspace{1cm} (3)  

These values can be directly compared with experimental data, which can validate the proposed method and yield the identification of the luminescence site.

### III. THE PRISTINE HOSTS

In this section, we focus on the results for bulk LaSi$_3$N$_5$ and La$_3$Si$_6$N$_{11}$: relaxed crystal structure, electronic band structure, and the role of the La$_{4f}$ state in the calculation.

#### A. Crystal structure

In Section I, we have briefly mentioned that LaSi$_3$N$_5$ is built of SiN$_4$ tetrahedra, which are linked by shared corners. The La atom is centrally located between the pentagonal holes along the c-axis, and is coordinated with nine nitrogen atoms at a distance between 2.6-3.2˚Å. LaSi$_3$N$_5$ crystallizes in the orthorhombic crystal system with space group P2$_1$2$_1$2$_1$.

The space group of La$_3$Si$_6$N$_{11}$ is more symmetric, P4/bm. La$_3$Si$_6$N$_{11}$ is isostructural with Ce$_3$Si$_6$N$_{11}$. Similar to the structural character of LaSi$_3$N$_5$, the crystal structure of La$_3$Si$_6$N$_{11}$ also consists of corner-sharing SiN$_4$ tetrahedra. The experimental data [10] have been used to start the initial optimization of the crystal structure (with the La$_{4f}$-semicore PAW atomic dataset). Table I lists the relaxed lattice parameters for the two nitride compounds. The theoretical results for LSN bulk are consistent with the experimental value, within 2% relative difference. This small difference might be attributed to the GGA exchange and correlation functional.

![LaSi$_3$N$_5$ and La$_3$Si$_6$N$_{11}$ crystal structures](image)

FIG. 3: Crystal structure of (a) LaSi$_3$N$_5$, view from a direction; (b) La$_3$Si$_6$N$_{11}$, view from c direction. Green, blue and gray spheres stand for La, Si and N atoms, respectively.

#### Table I: Lattice parameters of LSN bulk.

|                | a (Å) | b (Å) | c (Å) |
|----------------|-------|-------|-------|
| LaSi$_3$N$_5$  | 4.834 | 7.891 | 11.387|
| LaSi$_3$N$_5$  | 4.807 | 7.838 | 11.236|
| La$_3$Si$_6$N$_{11}$ | 10.246 | 10.246 | 4.887 |
| La$_3$Si$_6$N$_{11}$ | 10.199 | 10.199 | 4.841 |

and two non-equivalent La$^{3+}$ sites, La$_{2a}$ and La$_{4c}$ sites in La$_3$Si$_6$N$_{11}$. When doped, the Ce$^{3+}$ ion is expected to substitute these crystallographic sites, which results in one case of Ce$_{La}$ for LaSi$_3$N$_5$, and two cases (Ce$_{2a}$ and Ce$_{4c}$) for La$_3$Si$_6$N$_{11}$ with the Ce ion occupying the La$_{2a}$ and La$_{4c}$ sites, respectively. Table II lists the relaxed La-N bond lengths for the three La$^{3+}$ crystallographic sites. Through these results, the average distance of La-N has been determined to be 2.819 Å for the La site in LaSi$_3$N$_5$, and 2.711/2.655 Å for the La$_{2a}$/La$_{4c}$ site in the La$_3$Si$_6$N$_{11}$ compound.

The nomenclature for the neighboring nitrogen atoms is presented in Figure 3. This will help understand the different types of bonds presented in Table II. In LaSi$_3$N$_5$, there are five types of nitrogen atoms, while the lanthanum atom has nine neighbors. Some symmetry operations do not leave the lanthanum site unchanged. So, among the nine nearest-neighbor atoms of lanthanum, there are four pairs of equivalent nitrogen atoms (by symmetry), whose distance to the specific nitrogen atom dif-
fers. The local geometry of La$^{3+}$ site can be represented as a tricapped trigonal prism. In the more symmetric La$_3$Si$_6$N$_{11}$, there are four types of nitrogen atoms. The tetragonal symmetry leaves the La$_{2e}$ site unchanged, and the eight nearest neighbors nitrogen atoms of this site are split in two groups of four, where the La-N distances in each are equal. The La$_{4e}$ site is left unchanged by a mirror plane, so that five distances characterize the locations of the eight nearest-neighbour atoms. The local geometry of La$_{2e}$ and La$_{4e}$ sites can be seen as a square antiprism and a bicapped trigonal prism, respectively.

### B. Electronic band structure

With the relaxed crystal structure of the two nitrides, we have calculated the corresponding electronic band structure within the DFT framework, as it might have a bearing on the different luminescent behaviors. Figure 4 shows the calculated results for the La$_4$-core PAW atomic dataset. LaSi$_3$N$_5$ has a 3.21 eV Γ − X indirect band gap, and La$_3$Si$_6$N$_{11}$ belongs to the direct-transition class of compounds with a 2.99 eV band gap at the Z point. At present, there is no experimental data for the band gap of the two compounds. However, we can expect that our calculation suffers from the well-known ‘band gap problem’ of DFT, with sizeable under-

![FIG. 4: Kohn-Sham DFT electronic band structure of LSN bulk with converged lattice parameters. LaSi$_3$N$_5$ (left) La$_3$Si$_6$N$_{11}$ (right)](image)

estimation compared to experimental results. Recently, Ibrahim et al. have investigated the electronic structure of LaSi$_3$N$_5$ using the HSE06 functional, for which the band gap problem is much reduced compared to our GGA approach, giving a band gap of 4.8 eV. In Ref. 14, a similar work for La$_3$Si$_6$N$_{11}$ was conducted by Seshadri’s group. A band gap of about 4 eV was obtained for this compound. Thus, the band gap seems consistently smaller in La$_3$Si$_6$N$_{11}$ than in LaSi$_3$N$_5$. A previous work of one of us was devoted to understand the origin of the change of band gaps, and tried to link it with the optical performance of Ce$^{3+}$ ion in the two compounds. Here, we continue the study, aiming at providing a quantitative description about the performance of the two phosphors.

The composition of the valence band maximum (VBM) and conduction band minimum (CBM) might also be important to understand the luminescence. We have examined the partial density of states, as shown in Figure 5. The results show that for both compounds, the CBM consists of a mixture of La$_{4f}$ and La$_{5d}$ states, while the VBM mainly comes from N$_{2p}$ states. Such similarity again does not help to quantitatively explain the observed different optical properties of LSN phosphors.

To confirm the CBM composition of LSN bulk, the pseudopotential La$_{4f}$-core has been used in band structure calculations. Figure 6 depicts the obtained band structure with the La$_{4f}$-core PAW atomic dataset (still with the relaxed geometry from the lattice relaxation based on La$_{4f}$-semicore PAW dataset). Through comparison of the Figures 4 and 6, it can be seen that the 4f freezing does not modify the valence band, but clearly impacts the conduction band because of the missing 4f state in the La$_{4f}$-core case. The modification of the conduction band leads to small changes of band gap, the one of LaSi$_3$N$_5$ becomes 3.34 eV and the one of La$_3$Si$_6$N$_{11}$ becomes 2.91 eV. From these results, it can be deduced

### Table II: Relaxed La-N bond lengths [Å] of the La crystallographic site in LaSi$_3$N$_5$ and La$_3$Si$_6$N$_{11}$.

| Bond              | GGA-PAW | Exp |
|-------------------|---------|-----|
| La-N1             | 3.151   | 3.134 |
| La-N1             | 3.140   | 3.067 |
| La-N2             | 2.443   | 2.421 |
| La-N2             | 2.724   | 2.697 |
| La-N3             | 2.884   | 2.832 |
| La-N4             | 2.577   | 2.553 |
| La-N4             | 2.898   | 2.884 |
| La-N5             | 2.693   | 2.645 |
| La-N5             | 2.860   | 2.830 |

| La$_3$Si$_6$N$_{11}$ |
|----------------------|
| La$_{2e}$-N1(x4)     | 2.652   | 2.650 |
| La$_{2e}$-N2(x4)     | 2.659   | 2.644 |
| La$_{4e}$-N1(x2)     | 2.528   | 2.551 |
| La$_{4e}$-N2*(x2)    | 2.674   | 2.674 |
| La$_{4e}$-N2*(x2)    | 2.893   | 2.853 |
| La$_{4e}$-N3         | 2.823   | 2.863 |
| La$_{4e}$-N4         | 2.640   | 2.623 |
Energy [eV]

on the ground state properties. Table III lists the redinate diagram. Therefore, we first focus our attention luminescence will be based on the configurational coordinate. The supercells used in this part, namely in the excited state and the luminescent center iden-
cation for the two LSN compounds. In this section, the above bulk study has provided the basic infor-
mation for the two LSN compounds. In this section, the results of Ce$^{3+}$ doped calculations will be presented, including the ground state of the supercell, the exci-
tated state description, the effect of lattice relaxation in the excited state and the luminescent center identification. The supercells used in this part, namely La$_7$CeSi$_{24}$N$_{10}$, La$_{11}$Ce$_2$Si$_{24}$N$_{44}$ and La$_{11}$Ce$_4$Si$_{24}$N$_{44}$, will be simply denoted as LaSi$_3$N$_5$:Ce, La$_3$Si$_6$N$_{11}$:Ce$_2$a and La$_3$Si$_6$N$_{11}$:Ce$_{4c}$.

A. Ground state

As mentioned in Section II, the analysis of the Ce$^{3+}$ luminescence will be based on the configurational coordinate diagram. Therefore, we first focus our attention on the ground state properties. Table IV lists the relaxed lattice parameters of the supercells. The data for the corresponding LSN bulk supercell is also shown for comparison, which is obtained from the calculation results for the LSN primitive cell but doubled in the $a$ direction for LaSi$_3$N$_5$, and in the $c$ direction for La$_3$Si$_6$N$_{11}$. From these results, we see that the Ce$^{3+}$ doping leads to a slight shrinkage of the crystal cell. The reason for the contraction can be ascribed to the relatively smaller ionic radius of Ce$^{3+}$ ion than the one of La$^{3+}$ ion. The ionic radius of Ce$^{3+}$ is determined to 1.143 Å and 1.196 Å for the coordination number of 8 and 9, respectively, while the corresponding values for the La$^{3+}$ ion are 1.16 Å and 1.216 Å for the La$^{3+}$ ion.$^{[22]}

With the relaxed geometry obtained above, the ground state electronic band structures for LaSi$_3$N$_5$:Ce, La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ and La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ have been calculated. The corresponding total energies are listed in Table V. The values of La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ and La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ are quite similar, with La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ being favored only by 0.3 mHa (less than 10 meV), which indicates that the Ce$^{3+}$ ions should nearly equally occupy the La$_{2a}$ and La$_{4c}$ sites in La$_3$Si$_6$N$_{11}$ at firing temperature (1500 - 2000°C). Moreover, there are twice more asymmetric sites than symmetric sites in La$_3$Si$_6$N$_{11}$. Hence, there should be twice more Ce$^{3+}$ lying in La$_{4c}$ sites than in La$_{2a}$. This result is consistent with experimental observation that shows the Ce$^{3+}$ can equally substitute on the La$_{2a}$ and La$_{4c}$ site at high Ce concentration.$^{[10]}

Figure 7 (Left-hand, upside) shows the Kohn-Sham DFT band structure results, in the ground state (super-
cell). Compared with the bulk results shown in Figure 4 for the primitive cell, a localized Ce$^{4f}$ state occurs in the band gap. In this case, no Ce$^{4f}$ state appears into the band gap, as indicated in Figure 7 (Right-hand,
Ce$^{4f}$ and Ce$^{5d}$ states. Similar to the result of the corresponding LSN bulk, this result is not consistent with the experimental fact that both LSN phosphors give an intense emitting light, for which a localized Ce$^{5d}$ state, inside the band gap, is expected. The reason for this failure is an incorrect identification of the levels in a ground-state electronic band structure, provided by DFT (or even quasiparticle band structure) with the experimentally observed neutral excitation of the system.

### TABLE III: Relaxed lattice parameters [Å] and Volume [Å$^3$] of LSN:Ce supercell.

| LSN                  | Volume (Å$^3$) | a (Å)  | b (Å)  | c (Å)  |
|----------------------|----------------|--------|--------|--------|
| LaSi$_3$N$_5$        | 868.77         | 9.668  | 7.891  | 11.387 |
| LaSi$_3$N$_5$:Ce     | 867.32         | 9.662  | 7.890  | 11.376 |
| La$_3$Si$_6$N$_{11}$ | 1026.16        | 10.246 | 10.246 | 9.774  |
| La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ | 1025.78   | 10.244 | 10.244 | 9.774  |
| La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ | 1025.37   | 10.243 | 10.243 | 9.772  |

As shown in Figure 7(a)-(c), the composition of CBM for the LSN phosphors has been determined to be a hybrid state of La$^{4f}$ and La$^{5d}$, similar to the result of the corresponding LSN bulk. This result is not consistent with the experimental fact that both LSN phosphors give an intense emitting light, for which a localized La$^{5d}$ state, inside the band gap, is expected. The reason for this failure is an incorrect identification of the levels in a ground-state electronic band structure, provided by DFT (or even quasiparticle band structure) with the experimentally observed neutral excitation of the system.

### B. Excited state

As shown by the ground-state calculations, the electron-hole interaction is necessary to describe the excited state of the LSN phosphor. In our work, the electron-hole interaction is described in the constrained DFT method. Figure 7(A$^*$ case) depicts the results for LSN phosphors. When one hole is created in the 4f band, the Ce$^{5d}$ state successfully appears below the CBM of the LSN host. Eigenergies from the DFT calculations cannot be identified as the optical transition levels for the neutral excitation. Instead of comparing eigenergies, the neutral excitation energy can be calculated from the ∆SCF method through the total energy difference of the ground state and excited state. The calculated absorption energies for LaSi$_3$N$_5$:Ce, La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ and
FIG. 8: Partial density of state of LSN:Ce phosphors: (a) LaSi$_3$N$_5$:Ce$_{A0}$ case; (b) La$_3$Si$_6$N$_{11}$:Ce$_{2a}$,A$_0$ case; (c) La$_3$Si$_6$N$_{11}$:Ce$_{4c}$,A$_0$ case; (d) LaSi$_3$N$_5$:Ce,A$^*$ case; (e) La$_3$Si$_6$N$_{11}$:Ce$_{2a}$,A$^*$ case; (f) La$_3$Si$_6$N$_{11}$:Ce$_{4c}$,A$^*$ case.

La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ are shown in Table IV, and will be used to identify the luminescent center in the two LSN phosphors.

**C. Lattice relaxation in the excited state**

Following the configuration coordinate diagram in Figure 2 after absorption, the system will be out of equilibrium due to the change in electronic configuration, leading to the relaxation of atomic position in the excited state. Accordingly, we have conducted geometry optimization of doped LSN phosphors. The constrained DFT has been used to keep the electronic configuration of Ce$^{3+}$ ion in its excited state. In the geometry optimization, the lattice parameters have been fixed to the value from the ground state, because the time scale of atomic position relaxation is much shorter than the change of the macroscopic state (strain) of the crystal. Figure 7 (A$^*$ case) shows the band structure for the excited state of emission process, and the corresponding partial density of states are depicted in the Figure 8(d)-(f). Also, the charge density at the $\Gamma$ point of the lowest band over the Ce$_{4c}$ state is shown in Figure 9. For the case of La$_3$Si$_6$N$_{11}$:Ce$_{4c}$, the lowest conduction band has La$_{5d}$ character, while those of LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ are composed of Ce$_{5d}$ state. Based on the above calculation, we have obtained the theoretical emission energies and Stokes shifts for the LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce, that are listed in Table IV. Through the comparison with the experimental value for the LSN phosphor, we can deduce that the luminescence center for the LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce phosphors is from the Ce$_{La}$ and Ce$_{2a}$ site, respectively.

| Case         | LaSi$_3$N$_5$:Ce | La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ | La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ |
|--------------|------------------|-------------------------------|-------------------------------|
| A$_0$        | -763.4608 Ha     | -932.1088 Ha                  | -932.1091 Ha                  |
| A$^*$        | -763.3333 Ha     | -932.0062 Ha                  | -932.9887 Ha                  |
| A             | -763.3379 Ha     | -932.0129 Ha                  | -932.0924 Ha                  |
| $\Delta E_{\text{abs}} (A_0$-$A_0$) | 3.50 eV         | 2.79 eV                       | 3.28 eV                       |
| $\Delta E_{\text{abs}} (\text{Exp.})$ | 3.43 eV         | 2.58 eV                       | -                            |
| $\Delta E_{\text{em}} (A^*-A)$ | 3.12 eV         | 2.40 eV                       | 2.60 eV                       |
| $\Delta E_{\text{em}} (\text{Exp.})$ | 2.95 eV         | 2.25 eV                       | -                            |
| $\Delta S (\text{Cal.})$ | 3080 cm$^{-1}$ | 3160 cm$^{-1}$ | 5456 cm$^{-1}$ |
| $\Delta S (\text{Exp.})$ | 3815 cm$^{-1}$ | 2717 cm$^{-1}$ | - |

TABLE IV: The calculated absorption, emission and Stokes shift of LSN phosphors, compared with the experimental data [13,15].
the case of La₃Si₆N₁₁:Ce⁺, we tentatively assign this Ce site as non-luminescent center with the Ce⁵d states inside the conduction bands, as we discussed in our work for other phosphors. Although more advanced methods like the GW approximation might be needed to precisely determine the relative position of Ce⁵d and the CBM, this is out of the scope of this work. Here, it is worthy to note that the calculated Stokes shift for La₃Si₆N₁₁:Ce is underestimated compared to the experimental data, while the calculated value for La₃Si₆N₁₁:Ce is overestimated. The reason for the above difference is due to the relative accuracy of the theoretical method, which gives an error about 0.2eV for the transition energies, while the accurate value of Stokes shift is smaller than 0.5eV.

We observe that, with such excited structure geometry, the Stokes shift and emission energy are in reasonable agreement with experimental data. At this stage, the effect of the excited state relaxation of atomic positions can be analyzed. One can focus on the change of Ce⁵⁺ coordination environment in the La₃Si₆N₅ and La₃Si₆N₁₁, as listed in Table V. The change of Ce-N bond length is due to the movement of ions in the crystal structure. For La₃Si₆N₅, an anisotropic distortion occurs around the Ce⁵⁺ ion. Four bond lengths are increased (by up to 6% for Ce-N₁¹) while five bond lengths are decreased (by up to 5% for Ce-N₂⁰ and Ce-N₅⁰). For La₃Si₆N₁₁:Ce₂⁺ there is a slight shortening of the Ce-N₁ bond length, and a larger shortening of the Ce-N₂ bond length (3%). Finally, for La₃Si₆N₁₁:Ce₄⁺, all bond lengths contract, by up to nearly 7% for Ce-N₄. These information can be useful for the analysis of emission color of Ce⁵⁺ ion in the two LSN compounds.

Now, we can come back to the analysis of the behaviour of the eigenenergy difference between the Ce⁵d band and the bottom of the conduction band. We will show that it can increase as well as decrease upon relaxation, depending on the behaviour of the energy difference between the Ce₄f band and the bottom of the conduction band, and the bonding or anti-bonding character of the Ce⁵d orbital. For this purpose, we first define the total energy \( E(\mathbf{R}, f_{5d}) \) as a function of the Ce⁵d occupation number, denoted \( f_{5d} \), and at atomic positions symbolically denoted as \( \mathbf{R} \). Note that the occupation of the Ce₄f levels decreases at the same rate as the occupation of the Ce⁵d increases. Due to Janak’s theorem, the derivative of the total energy with respect to the Ce⁵d occupation number is directly linked to the difference between Ce⁵d and Ce₄f eigenvalues, as well as to their differences with respect to the conduction band minimum. \( \frac{\partial E(\mathbf{R}, f_{5d})}{\partial f_{5d}} = \epsilon_{5d} - \epsilon_{4f} = \epsilon_{5d} - \epsilon_{CBM} - (\epsilon_{4f} - \epsilon_{CBM}) \). In the exact density-functional theory, the eigenenergies themselves should not depend on the occupation numbers, while in semi-local approximations, a convexity is observed. Actually, this convexity is quite important, and we have argued in the previous subsection that the difference of total energies is more reliable than eigenenergies to predict excited states and their relaxation. Still, if the eigenenergies were constant, \( E(\mathbf{R}, f_{5d} = 1) - E(\mathbf{R}, f_{5d} = 0) \) = \( (\epsilon_{5d} - \epsilon_{CBM}) - (\epsilon_{4f} - \epsilon_{CBM}) \). Comparing the relaxed and unrelaxed geometries, we see that the Stokes shift is approximately equal to the change of \( \epsilon_{5d} - \epsilon_{CBM} \) minus the change \( \epsilon_{4f} - \epsilon_{CBM} \) upon relaxation. Thus, if the Ce₄f eigenenergy increases significantly with respect to the conduction band, due to the relaxation, and in particular, if this increase is bigger than the Stokes shift, it might be that the Ce⁵d raises with respect to the conduction band. We have checked that this is indeed the case for La₃Si₆N₁₁:Ce₄⁺. Physically, we know that the electronic negative charge that is present on the Ce₄f in the ground state repels the negatively charge N ions. When the Ce₄f gets unoccupied, a large contraction of the N cage is observed, as described in the previous subsection. If the Ce⁵d is more anti-bonding than the La₅d states at the bottom of the conduction band, the eigenenergy difference between them will decrease.

| TABLE V: Ce-N bond lengths [Å] of the Ce site. The bold characters highlight the biggest change of local geometry of three Ce³⁺ sites, as mentioned in the text. |
| --- |
| Bond | Ground | Excited | Geometry |
| Ce-N₁ᵃ | 3.151 | 3.178 |  |
| Ce-N₁ᵇ | 3.137 | 3.324 |  |
| Ce-N₂ᵃ | 2.430 | 2.380 |  |
| Ce-N₂ᵇ | 2.717 | 2.601 |  |
| Ce-N₃ | 2.874 | 2.955 |  |
| Ce-N₄ᵃ | 2.553 | 2.416 |  |
| Ce-N₄ᵇ | 2.898 | 2.835 |  |
| Ce-N₅ᵃ | 2.690 | 2.792 |  |
| Ce-N₅ᵇ | 2.850 | 2.712 |  |
| La₃Si₆N₁₁:Ce₂⁺ |
| Ce-N₁ (x4) | 2.657 | 2.645 |  |
| Ce-N₂ (x4) | 2.638 | 2.555 |  |
| La₃Si₆N₁₁:Ce₄⁺ |
| Ce-N₁ (x2) | 2.512 | 2.389 |  |
| Ce-N₂ᵃ (x2) | 2.670 | 2.596 |  |
| Ce-N₂ᵇ (x2) | 2.901 | 2.895 |  |
| Ce-N₃ | 2.802 | 2.718 |  |
| Ce-N₄ | 2.641 | 2.472 |  |
TABLE VI: Dorenbos model analysis of the [Xe]5d state of Ce$^{3+}$ ion in LSN phosphors. GS: ground state; EX: excited state.

|                | LaSi$_3$N$_5$:Ce | La$_3$Si$_6$N$_{11}$:Ce$_{2a}$ | La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ |
|----------------|------------------|-------------------------------|-------------------------------|
| $\chi_{av}$    | 1.74             | 1.68                          | 1.68                          |
| $\sigma_{av}^N$| 7.97             | 7.52                          | 7.52                          |
| $\varepsilon_c$, GS | 21380 cm$^{-1}$ | 25166 cm$^{-1}$               | 23671 cm$^{-1}$               |
| $\varepsilon_c$, EX  | 23950 cm$^{-1}$ | 28242 cm$^{-1}$               | -                             |
| $\beta$        | 5.67×10$^8$      | 1.20×10$^9$                   | 1.20×10$^9$                   |
| $R_{av}$, GS    | 281 pm           | 265 pm                        | 270 pm                        |
| $R_{av}$, EX    | 280 pm           | 260 pm                        | -                             |
| $\varepsilon_{cfs}$, GS | 7181 cm$^{-1}$ | 17088 cm$^{-1}$               | 16461 cm$^{-1}$               |
| $\varepsilon_{cfs}$, EX | 7232 cm$^{-1}$ | 17751 cm$^{-1}$               | -                             |

D. Analysis based on the Dorenbos model with first-principles geometry data

The Dorenbos model described in the Appendix has been used to analyse the different luminescent behaviour of LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce. The structural geometries of the ground and excited state, as depicted in Table VI were adopted to obtain the $R_i$ and $R_{av}$ in the corresponding formula. The results about the centroid shift of the 5d energy, $\varepsilon_c$, are listed in Table VI. At present, the $\varepsilon_c$ analysis of La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ in the emission state was not conducted, since this site was determined to be non-luminescent. For the cases of LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce$_{2a}$, the obtained results indicate that the difference in $\varepsilon_c$ is 0.47eV and 0.5eV, for the ground and excited state, respectively.

Qualitative analysis also has been performed on the crystal field splitting, $\varepsilon_{cfs}$. In our cases, the coordination environment of Ce$^{3+}$ ion in LaSi$_3$N$_5$:Ce is in the form of tricapped trigonal prism, while those of Ce$_{2a}$ and Ce$_{4c}$ in La$_3$Si$_6$N$_{11}$:Ce can be seen as distorted cubic (square antiprism and bicapped trigonal prism, respectively). Following this idea, the $\varepsilon_{cfs}$ in the two nitrides can be calculated through the $\beta$, fitted according to Ref.8. The corresponding results are also listed in Table VI. Similar with the situation of $\varepsilon_c$, the analysis of La$_3$Si$_6$N$_{11}$:Ce$_{4c}$ in the emission state was not conducted. If we assume $r$(LSN) to be equal to 2.4, the effect of $\varepsilon_{cfs}$ on the cases of LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce$_{2a}$, give an energy difference of 0.51eV and 0.53eV, for the ground and excited state, respectively.

Through the analyses above, the difference of red-shift between the LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce$_{2a}$, is calculated to be 0.98eV and 1.03eV for the ground and excited state that compares reasonably with the experimental data of 0.81eV and 0.72eV, respectively. The calculated Stokes shift is 2600cm$^{-1}$ and 3466cm$^{-1}$ for the LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce$_{2a}$. Considering the qualitative character of Dorenbos model, these values are quite reasonable. Based on the above consistence, we can give the conclusion in two aspects: firstly, the structural geometry for LSN phosphor are accurately described, not only for the ground state, but also for the excited state. Second, the difference of luminescence in LaSi$_3$N$_5$:Ce and La$_3$Si$_6$N$_{11}$:Ce$_{2a}$, could be ascribed to the larger spectroscopic polarization of N$^{3-}$ ion in La$_3$Si$_6$N$_{11}$ and the stronger crystal field splitting of Ce$_{2a}$ site.

V. CONCLUSION

In this paper, an ab-initio study has been conducted to accurately describe the neutral excitation of Ce$^{3+}$ ions in two nitrides, LaSi$_3$N$_5$ and La$_3$Si$_6$N$_{11}$. The analysis of Ce$^{3+}$ luminescence follows from the configurational coordinate diagram, in which the ground state and excited state descriptions rely on the DFT+U and the con-
strained DFT approach. The absorption and emission energies are calculated with the ∆SCF method. Following these methods, the Stokes shift can be obtained. The luminescent centers (CeLa and Ce2a) can be identified from the agreement between the theoretical calculation and experimental results. It remains to be seen whether the same method can be applied successfully to other phosphors. For this purpose, other materials for which experimental data are known should be analyzed. This should be followed by large-scale computations for new dopant-hosts combinations.

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Appendix: The Dorenbos model

To explain the different optical performance between LaSi3N5:Ce and La3Si6N11:Ce2a, a qualitative analysis has been performed based on the semi-empirical model proposed by Dorenbos, and the corresponding structural geometry obtained from this work, including the consideration of ground state as well as the excited state.

First, it is worthy to briefly introduce the Dorenbos model here. Figure A1 shows the basic idea. The red-shift of the first 4f→5d transition D(A) in the compound A, can be written as:

\[ D(A) = \varepsilon_c(A) + \frac{1}{r(A)} \varepsilon_{cfs}(A) - 1890 \text{cm}^{-1} \]  

(A.1)

in which the \( \varepsilon_c(A) \) is the centroid shift of the 5d energy relative to the free ion, defined as follows:

\[ \varepsilon_c(A) = 1.44 \times 10^{17} \Sigma_i N_i \frac{\alpha_{sp}^i}{R_i^6} \]  

(A.2)

In the above formula, \( \alpha_{sp}^i \) is the spectroscopic polarization of anion \( i \) located at distance of \( R_i \) from the Ce3+ ion in the relaxed structure. The summation is over all anions \( N \) in the coordinated environment. For nitrides, the qualitative relationship between \( \alpha_{sp}^i \) and electronegativity of the cations is demonstrated as

\[ \alpha_{sp}^N = 0.87 + \frac{18.76}{\chi_{av}} \]  

(A.3)

where the electronegativity is

\[ \chi_{av} = \frac{1}{N} \Sigma_{i=1}^N Z_i \chi_i \]  

(A.4)

This formula is obtained from the reason that a cation of formal charge \( +Z_i \) will bind on average with \( Z_i/\gamma \) anions of formal charge of \( -\gamma \). The summation is over all cations \( M \) in the compound, and \( N \) is the number of anions.

Another parameter affecting the spectroscopic red-shift is the contribution from the crystal field shift, \( 1/r(A) \varepsilon_{cfs}(A) \). The crystal-field splitting \( \varepsilon_{cfs}(A) \) is defined as the energy difference between the lowest and highest 5d level. A fraction \( 1/r(A) \) contributes to the red-shift, where \( r(A) \) usually varies between 1.7 and 2.4. The \( \varepsilon_{cfs}(A) \) is determined as

\[ \varepsilon_{cfs} = \frac{\beta}{R_{av}^2} \]  

(A.5)

in which \( \beta \) is a parameter related to the shape and size of the anion polyhedron coordinated to the Ce3+ ion, and \( R_{av} \) is average distance between the Ce3+ ion and anions in the relaxed structure.

In our work, the Dorenbos model has been used to analyse the different luminescent behaviour of LaSi3N5:Ce and La3Si6N11:Ce.
