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# Density functional theory predictions for blue luminescence and nonlinear optical properties of carbon-doped gallium nitride

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ABSTRACT

The TD-B3LYP method and the plane-wave formalism of DFT method were applied to predict the blue luminescence and nonlinear optical effect of C-doped GaN, respectively. The introduction of carbon dopant will generate different acceptor or donor levels, which are mainly composed by *p* electronic state, within the energy gap of GaN. Exploring the calculated luminescence spectra based on the optimized excited-state structure, $C_N$:GaN exhibits high luminescence intensity and has nice monochromatic property. In addition, the corresponding second-order nonlinear optical coefficients are considerable, $\chi^{(2)}_{xzx} = -15.07$ pm/V and $\chi^{(2)}_{zzz} = 26.91$ pm/V, which are about 28 times and 50 times of the second-order optical coefficient of KDP crystal.

## 1. Introduction

Owing to the excellent luminescence performance, gallium nitride (GaN) has been applied in optical memory, high frequency and high power display, ocean communication, etc. [1]. In order to optimize the optical performance of GaN, doping becomes an importance means. Certain element of IVA, such as C, was found to be a good dopant for GaN [2–12]. Xu's groups have shown that under rich Ga or rich N condition, the formation energy of C dopant on gallium site ($C_{Ga}$) is 6.5 or 5.4 eV, respectively [2]. Nyk and Reshchikov found that C dopant would lead to yellow emission [3,4]. Additionally, Reshchikov, Seager and Armitage observed a blue band in the PL spectrum of the heavily carbon-doped GaN and speculated the electron transfer from $C_{Ga}$ donor to $C_N$ acceptor [4–7]. But the existence of some unintended impurities or some defects in crystal will always influence the optical property greatly. In that case, it is difficult to find out the luminescence mechanism of carbon-doped GaN. Furthermore, due to the lack of the inversion symmetry, wurtzite-type GaN presents strong polarization effect [8]. Corresponding researches have discovered the big second- and third-order nonlinear optical coefficient of GaN material [9–12]. To confirm the luminescence mechanism of C:GaN, especially its blue band, and to study the influence of C-doping on the nonlinear optical effect, the first-principles calculation was chosen to predict the optical properties. In research of optical performance, the energy gap is an important factor. Some research groups have calculated the possible energy gaps of GaN which agree with experiment data by using self-consistent norm-conserving pseudo-potential (NCPP) method, full linear augmented plane wave (FLAPW) method, B3LYP hybrid functional method, etc. [13–15]. In this work, the density functional theory (DFT) method [15–19] was chosen to calculate the energy gap, the main luminescence bands, and the second-order nonlinear optical coefficient of the wurtzite-type GaN doped with carbon.

## 2. Computational details

On the basis of previous study [15], the compositions of $Ga_{26}N_{26}$ were suitable as a computation model and hydrogen atoms were chosen to saturate the dangling bonds at the boundary of the clusters, shown as Fig. 1(a). The C dopant, such as carbon atom on gallium site ($C_{Ga}$), on nitrogen site ($C_N$), on interstitial site ($C_i$) or co-doped on gallium site and nitrogen site ($C_{Ga}$–$C_N$), was arranged in the central section. In the calculation, Hay and Wadt's relativistic effective core potentials (RECPs) were adopted for Ga atoms, in which 28 electrons were incorporated into pseudopotentials. A (6*s*6*p*/3*s*3*p*) basis set was employed for Ga atoms around the substitutional site and a (3*s*3*p*/1*s*1*p*) basis set was for the other Ga atoms. The standard 6-31G basis sets were chosen for the C atoms and N atoms closed to the substitutional site, while 3-21G basis sets were used for the rest N atoms and all H atoms. The structural optimizations for the

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clusters at ground state and the arrangements of the molecular orbitals (MOs) were performed by Becke's three-parameter hybrid functional (B3LYP). Moreover, singles configuration interaction (CIS) method was adopted to optimize the structures of the singlet excited state [15–18]. Then the luminescence spectra were obtained by using the TD-B3LYP method [15–19] with the energy error of $10^{-7}$ as the convergence criteria. In order to include the ultraviolet–visible region into spectra (about 300–800 nm), 150–180 excited states were taken into account. In this stage, all calculations with the cluster models were performed with Gaussian 03 package.

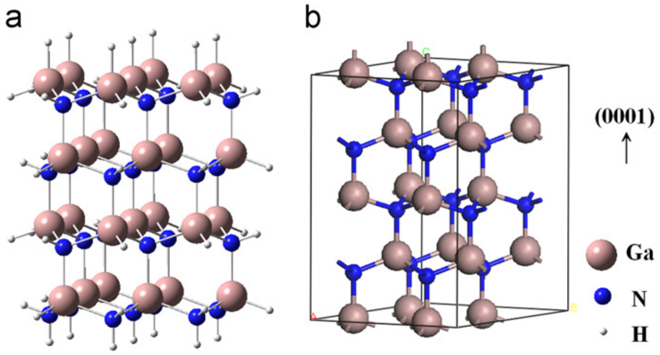


**Fig. 1.** GaN Models for the theoretical computation: (a) cluster models and (b) (2 × 2 × 2) cell models.

In addition, the partial density of states (PDOS) and the second-order nonlinear optical coefficient of C-doped GaN were calculated by using the plane-wave formalism of DFT as implemented with VASP package. Based on the following formula [20]:

$$\chi^{abc}(-2\omega,\,\omega,\,\omega)=\chi_e^{abc}(-2\omega,\,\omega,\,\omega)+\chi_i^{abc}(-2\omega,\,\omega,\,\omega) \tag{1}$$

A calculation module for the static second-order nonlinear optical coefficient of semiconductor was compiled by using Fortran 90 language and then was connected into VASP package. Where the contribution of the purely interband processes is given by the following equation:

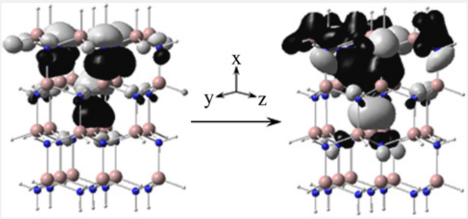
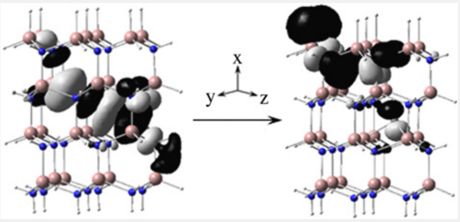
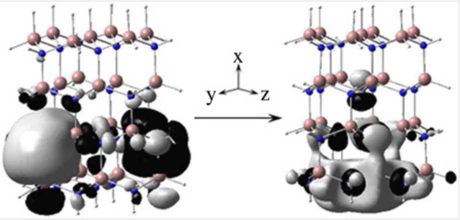
$$\chi_e^{abc}(-2\omega,\omega,\omega)=\frac{e^3}{\hbar^2\Omega}\sum_{nml,k}\frac{r_{nm}^a\{r_{ml}^b r_{\mathrm{ln}}^c\}}{\omega_{nm}\omega_{ml}\omega_{ln}}\left[\omega_n f_{ml}+\omega_m f_{ln}+\omega_l f_{nm}\right] \tag{2}$$

and the contribution of the mixed interband and intraband processes is defined as follows:

$$\chi_i^{abc}(-2\omega,\omega,\omega)=\frac{i}{4}\frac{e^3}{\hbar^2\Omega}\sum_{nm,k}\frac{f_{nm}}{\omega_{mn}^2}\Big[r_{nm}^a(r_{mn;c}^b+r_{mn;b}^c)+r_{nm}^b(r_{mn;c}^a+r_{mn;a}^c)$$
$$+r_{nm}^c(r_{mn;b}^a+r_{mn;a}^b)\Big] \tag{3}$$

As shown in Fig. 1(b), (2 × 2 × 2) cell was chosen to model C-doped GaN. The Perdew–Burke–Ernzerhof (PBE) type exchange-correlation was adopted. The Monkhorst-Pack k-point grid was

**Table 1**
Vertical emission excitation energy, oscillator strength, and main emission transition of the blue luminescence band.

| Material | $E_{emis}$ (eV) | $\lambda_{emis}$ (nm) | Main transition[a] and charge density figure | Electric transition dipole moments | | | $f$ |
|---|---|---|---|---|---|---|---|
| | | | | $x$ | $y$ | $z$ | |
| GaN | 3.52 | 352 | 155β[N2*p* Ga4*s*4*p*]→125β[N2*p* Ga4*s*] (95%) | 1.2346 | 0.0054 | −0.0073 | 0.1314 |
| $C_N$:GaN | 2.98 | 416 | 155β[N2*p* C2*p*]→130β[C2*p* N2*s*2*p* Ga4*p*] (88%)<br><br> | −0.8024 | −0.0160 | −0.0003 | 0.0472 |
| $C_i$:GaN | 2.76 | 449 | 161α[C2*p* N2*p* Ga4*p*]→150α[Ga4*p* C2*p* N2*p*] (74%)<br><br> | 0.3510 | −0.1835 | −0.2263 | 0.0141 |
| $C_{Ga}$-$C_N$:GaN | 2.74 | 453 | 170α[N2*s*2*p* C2*p* Ga4*p*]→157α[Ga4*s*4*p* C2*p* N2*s*] (95%)<br><br> | −0.0301 | −0.3803 | −0.2713 | 0.0147 |
| $Mg_{Ga}$:GaN | 3.08 | 403 | 155β[N2*p*]→131β[N2*p* Ga4*p*] (90%) | −0.4236 | −0.1359 | 0.0946 | 0.0156 |

[a] Main components of MOs are in the square brackets and the percent contribution of transition is in the parenthesis.

set at 7 × 7 × 7. The energy cutoff of the plane wave was set at 300 eV. The convergence criterion was the energy error of $10^{-4}$.

## 3. Results and discussions

### 3.1. Doping energy

In order to find out the optimal doping site, the doping energy ($E_{\mathrm{doping}}$) for carbon atom doped on different sites is calculated using the following expression [21]:

$$E_{\mathrm{doping}} = E_{\mathrm{C-doped}} - E_{\mathrm{GaN}} + E_X \text{-} E_{\mathrm{C}}$$

where $E_{\mathrm{C-doped}}$, $E_{\mathrm{GaN}}$, $E_X$, and $E_{\mathrm{C}}$ are the total energies of C-doped GaN, undoped GaN, free Ga atom or N atom replaced by C atom, and free C atom, respectively. The doping energies for carbon atom doped on gallium site ($C_{Ga}$), doped on nitrogen site ($C_N$), doped on interstitial site ($C_i$) and co-doped on both gallium site and nitrogen site ($C_{Ga}$–$C_N$) are 5.92, −7.73, −4.04 and −5.26 eV, respectively. Xu's groups mentioned that the formation energy of $C_{Ga}$ was 6.5 or 5.4 eV under rich Ga or rich N condition, respectively [2]. It is obvious that the doping energy of $C_{Ga}$ calculated here (5.92 eV) is close to the corresponding value in Ref. [2]. As the results, carbon atom may turn into $C_N$, $C_i$ or $C_{Ga}$–$C_N$ dopant and the priority would be the position of nitrogen atom. On the other hand, it is not easy for C atom to be introduced only into gallium site and then this case does not take into account in the following discussion.

### 3.2. Luminescence property

The luminescence spectra of C-doped GaN in the ultraviolet–visible region were predicted by the TDDFT method with the optimized structure of the singlet excited state [15–18]. The calculated results of the blue luminescence, such as the vertical emission excitation energy ($E_{\mathrm{emis}}$), the oscillator strength ($f$), the main transition, the related charge density figure, and the electric transition dipole moments are listed in Table 1. The simulated luminescence spectra range 300–800 nm are shown in Fig. 2, and the corresponding full width at half maximum (FWHM) is set as 1000 $\mathrm{cm}^{-1}$.

As shown in Fig. 2, the luminescence band of undoped GaN exists in ultraviolet region, the corresponding peak is at 352 nm (3.52 eV). While the luminescence spectra of C-doped GaN are different. The most significant distinguish is the strong luminescence band range 400–480 nm (about 2.6–3.0 eV) in C-doped GaN, which agrees with the experiment phenomenon [4–7]. As shown in Table 1, the inset charge density figure of the main transition about the dopant $C_{Ga}$–$C_N$ confirms the speculation of electron transition from $C_{Ga}$ donor to $C_N$ acceptor in Refs. [4–7]. As shown in Table 1, the electron transition occurs partially from $C_{Ga}$-$2p_y$ orbit to $C_N$-$2p_x$ orbit. But not completely agreeing with their point, this paper considers that the blue luminescence band should attribute to not only $C_{Ga}$–$C_N$ dopant but also $C_N$ or $C_i$ dopant. The luminescence spectrum of $Mg_{Ga}$:GaN, one of good blue luminescence materials, predicted by the same method is shown in Table 1 and Fig. 2 for comparing. The blue bands of C:GaN are stronger than that of $Mg_{Ga}$:GaN. It is worth notice that the electric transition dipole moments of the blue band of $C_N$:GaN are much greater, the oscillator strength reaches to $f$=0.0472, and the intensity is great. Moreover, the homochromatism of this blue band is best among three case of C:GaN mentioned in this paper.

Besides the blue band, there are other three bands to be mentioned. The first band is UV luminescence band at about 350 nm, which should attribute to the band-to-band emission. The second one is yellow band. In the spectrum experiment, GaN material exists an apparent yellow luminescence band, which was considered as a result of C impurity [3,4]. The spectrum simulation herein reveals that only the yellow-green luminescence band of $C_{Ga}$–$C_N$ dopant is visible. This band is at about 555 nm that agrees with the experimental study of Ref. [3]. The third one is red band (~700 nm) of $C_{Ga}$–$C_N$:GaN, which is similar to the broad red luminescence band observed at 1.64 eV in C-doped GaN [7].

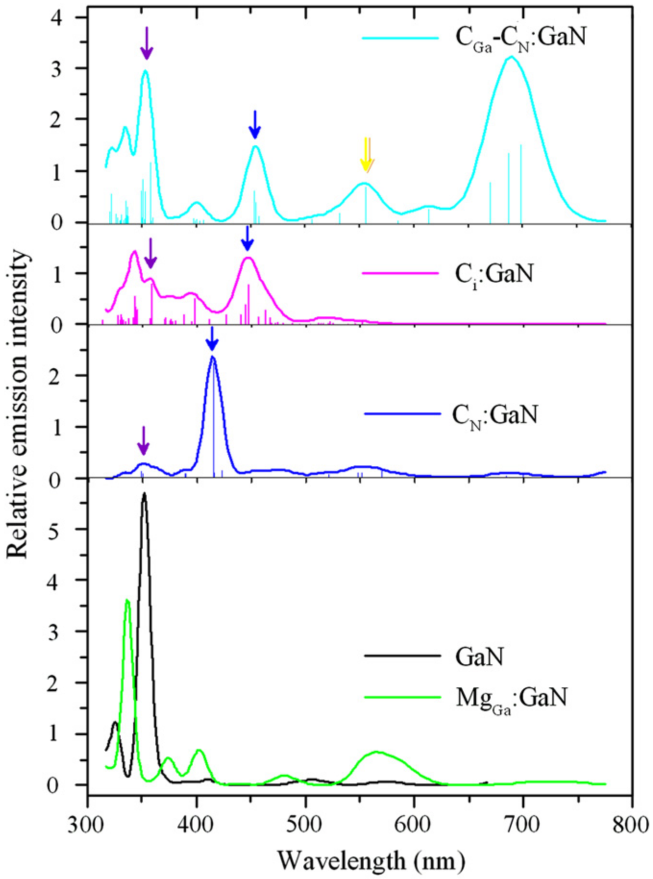


**Fig. 2.** Luminescence spectra of C-doped GaN clusters calculated by TDDFT method. The vertical lines refer to computed vertical peaks.

The arrangements of the molecular orbitals and the densities of states will affect the vertical excitation energy and the oscillator strength. In order to show the electron transition more clearly, the frontier molecular orbitals (MOs) of C-doped GaN and their partial densities of states (PDOS) were calculated. Fig. 3 shows MOs, PDOS and the main transitions of the blue luminescence of C:GaN and the UV luminescence of undoped GaN.

Carbon dopant introduces various acceptor or donor level, which results in the narrowing of the band gap of C:GaN, as well as the decrease of the predicted energy difference between HOMO and LUMO. Compare the PDOS of undoped GaN and $C_N$:GaN, the latter appears as a shallow acceptor. The corresponding level is around $E_{VB}$+0.1 eV, where $E_{VB}$ is the energy level of the top valence band. The dopant of $C_i$ tends to generate both the acceptor level and the donor level. The shallow and the deep acceptors distribute around $E_{VB}$+0.1 and $E_{VB}$+1.5 eV, respectively. The donor level distributes around $E_{CB}$–0.3 eV, where $E_{CB}$ is the energy level of the bottom conduction band. From the PDOS of $C_{Ga}$–$C_N$:GaN, a shallow acceptor level lies around $E_{VB}$+0.3 eV and a donor is around $E_{CB}$ − 0.6 eV. The narrowing of the band gap of C:GaN results in the blue luminescence band and other bands within the visible region.

According to the luminescence selection law $\Delta L \pm 1$ [22], the electron transition between *s* orbit and *p* orbit is allowable. If the quadratic term of the perturbation Hamiltonian is taken into account, the electron transition between *p* orbit and *p* orbit is also a valid route. The acceptor and donor levels are mainly originated from C-2*p* and/or C-2*s* electronic states. The addition of *p* electronic state of $C_N$:GaN is obvious, which is helpful to increase the probability of $s \rightarrow p$ or $p \rightarrow p$ transition, thus benefit the blue luminescence.

### 3.3. Second-order nonlinear optical coefficient

The stable structure of GaN belongs to hexagonal system. Due to the *Kleinman* total exchange symmetry, GaN has only two non-zero second-order nonlinear optical coefficient, namely $\chi^{(2)}_{xzx}$ and $\chi^{(2)}_{zzz}$. Herein, the energy cutoffs of the occupied orbit and the virtual orbit have been taken into account. Fig. 4 shows the relationship between the energy cutoff of the orbit and the calculated second-order optical coefficient. The calculated results tend to convergence if the energy cutoff of the occupied orbit is lower than −5 eV and that of the virtual orbit is higher than 20 eV. Here they are set as −10 and 30 eV, respectively. The calculated results are shown in Table 2. The non-zero second-order nonlinear optical coefficient can be determined to $\chi^{(2)}_{xzx} = -2.64$ and $\chi^{(2)}_{zzz} = 4.78$ pm/V for GaN, which is close to the experimental result in Refs. [9–12], and $\chi^{(2)}_{xzx} = -15.07$ pm/V and $\chi^{(2)}_{zzz} = 26.91$ pm/V for $C_N$:GaN that are about 28 times and 50 times of the second-order optical coefficient of potassium dihydrogen phosphate crystal (KDP, $\chi^{(2)}_{zxy} = 0.53$ pm/V) [23].

**Table 2**
Calculated second-order optical coefficient of GaN and $C_N$:GaN.

| Material | $\chi^{(2)}_{xzx}$ (pm/V) | $\chi^{(2)}_{zzz}$ (pm/V) | Ref. |
|---|---|---|---|
| GaN | −2.64 | 4.78 | This work |
| | 3 | | [9] |
| | 2.66 | −5.35 | [10] |
| | −2.1 | 3.5 | [11] |
| | −3.45 | 5.76 | [12] |
| $C_N$:GaN | −15.07 | 26.91 | This work |

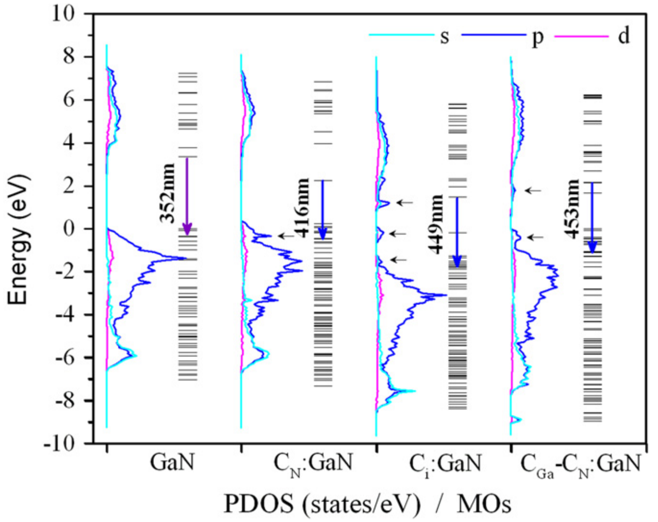


**Fig. 3.** The partial density of states and the frontier molecular orbitals of C-doped GaN. ↓ presents the main transition of the blue luminescence and ← stands out the position of the acceptor or donor.

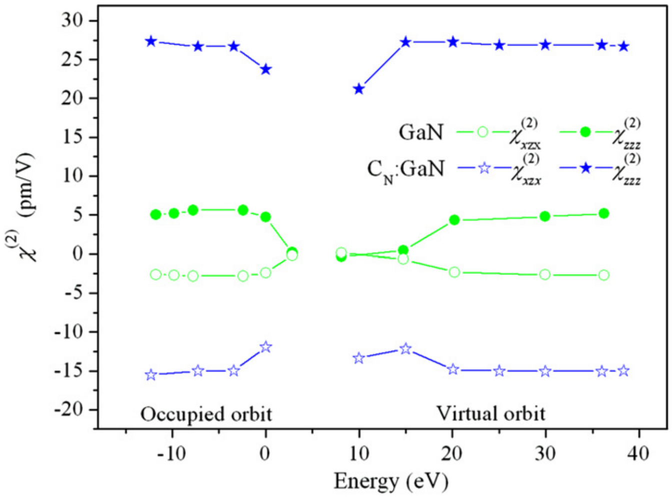


**Fig. 4.** Calculated second-order optical coefficient relate with the energy cutoff of the orbit taken into account.

## 4. Conclusion

We have proofed that carbon dopant could introduce different acceptor or donor levels, then narrow the band gap. The component of the acceptor or donor mainly generates from C-2*p* and/or C-2*s* electronic states. In three cluster models mentioned above, $C_{Ga}$–$C_N$ dopant is most likely to generate yellow and red luminescence. It is worth notice that the strong blue luminescence of GaN doped with C ranges 400∼480 nm (2.6–3.0 eV). Especially, the blue band of $C_N$:GaN is the strongest one with the best homochromatism. Furthermore, the calculated second-order nonlinear optical coefficients of $C_N$:GaN, $\chi^{(2)}_{xzx} = -15.07$ and $\chi^{(2)}_{zzz} = 26.91$ pm/V, are about 28 times and 50 times of the second-order optical coefficient of KDP crystal, respectively. In conclusion, GaN may be applied both as a blue laser semiconductor material and as a nonlinear optical material.

## Acknowledgments

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