Cation Vacancy in Wide Bandgap III-Nitrides as Single-Photon Emitter: A First-Principles Investigation

Hang Zang, Xiaojuan Sun, Ke Jiang, Yang Chen, Shanli Zhang, Jianwei Ben, Yuping Jia, Tong Wu, Zhiming Shi,* and Dabing Li*
the same energy level $\langle \psi_i | H | \psi_j \rangle = E$ and inter-bond interaction $\langle \psi_i | H | \psi_j \rangle = -\Delta/4$. Due to the interaction between dangling bonds, the energy level splits into a nondegenerate $T_1$ state and a triple degenerate $T_2$ state with an energy difference of $\Delta$ under the $T_d$ symmetry. The relative position of $A_1$ and $T_2$ depends on the sign of $\langle \psi_i | H | \psi_j \rangle$ as shown in Figure 1, and it determines the relative energy level for different electronic configurations. For the case of $\langle \psi_i | H | \psi_j \rangle < 0$, the many-electron effect analysis shows that a ‘$5$-electron-8-orbital’ electronic configuration is suitable for single-photon emission. Whereas all the defect levels in the spin-up channel are occupied; in the spin-down channel, only the low energy $A_1$ level is occupied, and all the $T_2$ levels are empty, the optical emission corresponds to the transition of $A_1 \rightarrow T_2$ (details are described in the Supporting Information).

In this work, based on group theory analysis and first-principles computation, we present a comprehensive study of the single-photon emission property of Vcation in III-V compounds. We find that the charge-neutral Vcation in III-V compounds can meet the specific 5-electron-8-orbital electronic configuration. Moreover, the charge-neutral Vcation in wide bandgap III-nitrides including GaN, AlN, AlGaN, and low In component InGaN are thermodynamically stable and can serve as SPE. The corresponding defect energy level, formation energy, and photon energy of the proposed SPE are presented.

2. Experimental Section

It was first characterized whether charge-neutral Vcation in III–V (III = Al, Ga, In; V = N, P, As) compounds satisfy the 5-electron-8-orbital electronic configuration. The band structures calculated with HSE06 hybrid functional are shown in Figure 2 (the atomic structures are shown in Figure S3, Supporting Information). Taking the Fermi level as a reference, the VBM of the host material tends to increase as the group III component varies from Al to In when fixing the group V component or as the group V component varies from N to As when fixing the group III component. The orbital contribution of anions around Vcation shows the defect levels of Vcation in the spin-up channel are fully occupied, while in the spin-down channel the $A_1$ state lies below the $T_2$ states and only the $A_1$ state is occupied. This indicates a negative inter-bond interaction ($\langle \psi_i | H | \psi_j \rangle$) between the anion dangling bonds, the charge-neutral Vcation in III-V compounds thus satisfies the 5-electron-8-orbital electronic configuration.
Figure 2. Band structures for neutral V$_{cation}$ in III–V compounds calculated with HSE06 functional, here G (0.0, 0.0, 0.0), F (0.0, 0.5, 0.0), Q (0.0, 0.5, 0.5), Z (0.0, 0.0, 0.5), B (0.5, 0.0, 0.0) refer to the high-symmetry special points in the first Brillouin zone, the Fermi level is set to zero, the orbital contribution of four anions around V$_{cation}$ is represented by red dots.

The small and broad absorption of V$_{cation}$ in AlN in Figure 3e–3 includes the transition from VBM to T$_2$ and from A$_1$ to CBM, the calculated moment matrix $|\langle \psi_i | p_j | \psi_j \rangle|^2$ (see Equation S24, Supporting Information) shows that the corresponding magnitude of A$_1 \leftrightarrow T_2$ is about 3 times larger than VBM $\leftrightarrow T_2$ and A$_1 \leftrightarrow$ CBM, thus the broad absorption has little effect on the single-photon emission property. The absorption spectrum for V$_{cation}$ in strained GaN and AlN are shown in Figure S9, Supporting Information, the corresponding absorption peak of V$_{cation}$ blue (red) shifted under a compress (tensile) strain, consistent with the change of the energy difference between A$_1$ and T$_2$.

In addition to the binary GaN and AlN, III-nitride alloy is also widely investigated since it has a tunable bandgap. The single-photon emission property of V$_{cation}$ in III-nitride alloy is now calculated, the wurtzite structure of III-nitride alloy is built by cluster expansion method,[32] the corresponding unit cell structures are shown in Figure S1, Supporting Information. The structure of V$_{cation}$ in III-nitride alloy is determined by directly remove a cation from the perfect alloy, as indicated later, the formation energy of neutral V$_{cation}$ is high, such a non-equilibrium way is practical to generate V$_{cation}$ in the experimental condition.

For AlGaN alloy as a host material, the atomic structures with low, medium, and high Al composition of 0.25, 0.5, and 0.8 are chosen as representatives. The calculated band structures indicate that the CBM of AlGaN is contributed by the s orbital of the N atom (see Figure S2, Supporting Information). The VBM of AlGaN with low Al composition is contributed by the p$_x$ and p$_y$ orbital of the N atom. For AlGaN with high Al composition, the VBM is mainly contributed by the p$_z$ orbital of the N atom. This results in a different light emission mode in the electrically pumped light emission device,[33] this property can be used to separate the light signals from host material and V$_{cation}$ efficiently.

The calculated defect energy level and absorption spectrum of V$_{Al}$ in AlGaN with different Al compositions are shown in Figure 3b–d (the results for V$_{Ga}$ in AlGaN are shown in Figure S10, Supporting Information), the qualitative property of defect levels of V$_{cation}$ in AlGaN is the same as that of GaN and AlN. Due to the different interactions between the Al-N and Ga-N bond, the N atoms around V$_{cation}$ move unsymmetrically from their original position. Such a symmetry-low effect caused by the random alloy reduces the coupling between sp$^3$ dangling bonds and splits the degenerated T$_2$ states. Also, as shown in Figure 3, the optical transition is allowed between A$_1$ and T$_2$ for V$_{cation}$ in AlGaN, the moment matrix (see Equations S19 and S21, Supporting Information) of the broad absorption peak in Figure 3c, d is similar to the case of V$_{cation}$ in AlN, and it does not affect the single-photon emission property.

For InGaN alloy, previous calculation showed that V$_{cation}$ was suitable for single-photon emission in GaN but not InN, which is due to the low CBM position of InN. Since the bandgap of InGaN...
Figure 3. (a1–e1) The atomic supercell structures for V\textsubscript{Ga} in GaN, and V\textsubscript{Al} in Al\textsubscript{0.25}Ga\textsubscript{0.75}N, Al\textsubscript{0.5}Ga\textsubscript{0.5}N, Al\textsubscript{0.8}Ga\textsubscript{0.2}N, and AlN, the corresponding defect energy levels in the spin-down channel (the VBM is set to zero) and absorption spectrum for calculated with HSE06 functional areshown in (a2–e2) and (a3–e3), respectively.

decreases monotonically with the In component, there should be a maximum In component for V\textsubscript{cation} to serve as an SPE in In-GaN alloy. Therefore, the effect of different In compositions on the single-photon emission property of V\textsubscript{cation} is calculated, it is found that for V\textsubscript{cation} in In\textsubscript{0.25}Ga\textsubscript{0.75}N, the lowest T\textsubscript{2} state of V\textsubscript{cation} is nearly in resonance with the CBM, in this case, the insulation of the CBM is broken. While for a low In component case of In\textsubscript{0.125}Ga\textsubscript{0.875}N, all the defect energy levels in the spin-down channel are located within the bandgap (see Figures S4 and S6, Supporting Information). It was concluded that for V\textsubscript{cation} to realize single-photon emission in InGaN, a maximum component of In should not exceed about 25%. The calculated defect level and absorption spectrum of V\textsubscript{cation} in In\textsubscript{0.25}Ga\textsubscript{0.75}N are qualitatively the same as the case of GaN and AlN, the results are shown in Figure S8, Supporting Information.

To quantitatively characterize the single-photon emission property of V\textsubscript{cation}, the zero-phonon line (ZPL) was calculated, which is the optical transition energy without the phonon contribution. The excited-state structure was optimized with a constraint DFT method\cite{34} by restricting the excited-state electronic configuration. The results are listed in Table 1, and the corresponding interatomic distances between anions at ground (excited) state are listed in Table S2, Supporting Information. It can be seen that the ZPL of V\textsubscript{cation} in pure GaN and AlN shows a monotonic dependence on the strain, it increases (decreases) under the compress (tensile) strain. For AlGaN alloy, though the mixing of Al has a similar monotonic effect on the lattice constant, the local environment for V\textsubscript{cation} differs a lot, it affects the geometry of ground and excited states and then affects the ZPL. Even in the same AlGaN alloy, the ZPL of V\textsubscript{Al} and V\textsubscript{Ga} differs a lot, thus, the ZPL does not show an obvious dependence on the mixing ratio of AlGaN. In recent experimental investigations, the single-photon emission in GaN with ZPL from 1085 to 1340 nm has been observed\cite{21}, based on our ZPL results, the V\textsubscript{cation} should have contributions to the corresponding single-photon signal. The ZPL of V\textsubscript{cation} in these III-nitrides has a large overlap with the optimal range of $\approx 1.2–1.6 \mu$m that can reduce the attenuation\cite{35} for optical fiber telecommunication. Besides, the calculated radiative lifetime $\tau_{\text{rad}}$ of V\textsubscript{cation}, as listed in Table 1, are comparable to that of the NV\textsuperscript{-} center in diamond ($\approx 10–30$ ns)\cite{36}. These advantages indicate that V\textsubscript{cation} is suitable for practical quantum communication application.

As one of the key factors for the proposed SPE, the 5-electron-8-orbital electronic configuration should be stable in experimental conditions. Here, the thermodynamic stability of V\textsubscript{cation} in GaN, AlN, and AlGaN/InGaN alloy was assessed. The formation energies as a function of the Fermi level are shown in Figure 4. It is seen that different charge states of
configuration. Recently, through using superlattice doping, III-nitrides is requested to guarantee the 5-electron-8-orbital stable in the lower part in the bandgap, indicating the p-type based on V cation is thus achievable in experimental conditions. However, possible to take advantage of these carrier doping techniques to doping efficiency in III-nitrides can be effectively enhanced, it is long as the structure and local electronic configuration of V cation is maintained (see Figures S5 and S7, Supporting Information).

Table 1. Calculated moment matrix $|\langle \psi_i | p | \psi_j \rangle|^2$, transition energy $\Delta E$ between defect levels, radiative lifetime $\tau_{\text{rad}}$, and ZPL for V cation in GaN, AlN, AlGaN, and InGaN.

| Compound | $|\langle \psi_i | p | \psi_j \rangle|^2$ | $\Delta E$ [eV] | $\tau_{\text{rad}}$ [ns] | ZPL [eV] |
|----------|---------------------------------|----------------|----------------|--------|
| V cation in 95% strain-GaN | 1.90 × 10^{-2} | 1.97 | 14.23 | 1.49 |
| V cation in GaN | 1.05 × 10^{-2} | 1.45 | 35.18 | 0.70 |
| V cation in 105% strain-GaN | 6.06 × 10^{-3} | 1.08 | 81.56 | 0.57 |
| V cation in AlGaN | 9.22 × 10^{-1} | 1.22 | 48.59 | 0.68 |
| V cation in AlGaN | 1.31 × 10^{-2} | 1.30 | 32.04 | 0.92 |
| V cation in AlGaN | 1.61 × 10^{-2} | 1.35 | 25.80 | 0.76 |
| V cation in AI | 1.31 × 10^{-2} | 1.25 | 34.28 | 0.70 |
| V cation in AI | 1.60 × 10^{-2} | 1.46 | 24.72 | 0.84 |
| V cation in AI | 1.71 × 10^{-2} | 1.45 | 23.29 | 0.96 |
| V cation in AI | 2.59 × 10^{-2} | 2.10 | 10.83 | 1.96 |
| V cation in AlN | 2.24 × 10^{-2} | 1.64 | 16.03 | 0.94 |
| V cation in AlN | 8.54 × 10^{-1} | 1.36 | 50.63 | 0.72 |
| V cation in AlN | 7.38 × 10^{-1} | 1.14 | 62.78 | 0.62 |
| V cation in InN | 4.48 × 10^{-1} | 1.17 | 100.63 | 0.56 |

$\psi_i$ is an example was tested, the results show the major property of SPE will not be affected by the cation dopant as long as the structure and local electronic configuration of V cation is maintained (see Figures S5 and S7, Supporting Information). For practical application, since the atomic structure of V cation is simple, there are various techniques to achieve it such as electron irradiation[39] and pulse laser irradiation[40] the SPE based on V cation, is thus achievable in experimental conditions.

For the SPE in bulk material, refraction is an issue that strongly influences the signal extracting. In practice, recent structures of III-nitrides generally have a size of less than a few hundred nanometers, which is far less than the photon wavelength, the refraction issue is thus irrelevant. Since the mono vacancy structure possesses no inversion symmetry, the external field induces charge fluctuation and causes spectral diffusion,[41] however, its magnitude is not necessarily large for a single vacancy as indicated in a recent theoretical study.[42] The reported SPE here is only applicable in GaN and AlN among all the III-V compounds, where the inter-bond interaction $\langle \psi_i | H | \psi_j \rangle$ is negative, and the $A_1$ state lies below $T_2$. As indicated in Figure 1, when $\langle \psi_i | H | \psi_j \rangle > 0$ the $T_2$ states lies below $A_1$, which results in a different electronic configuration, further numerical calculations of vacancy with a $T_d$ symmetry in other material is a promising way to searching new SPE.

3. Conclusion

In summary, we have symmetrically investigated the single-phonon emission property of V cation in the III-V compound. Based on the group theory analysis and first-principles calculation with hybrid density functional, we predict that the charge-neutral V cation in III-V compounds has a unique 5-electron-8-orbital electronic configuration, which is suitable for single-phonon emission. Furthermore, we confirm that the charge-neutral V cation can only serve as SPE in wide bandgap III-nitrides among all the III-V (III = Al, Ga, In; V = N, P, As) compounds. The charge-neutral V cation in AlN, GaN, and III-nitride alloy is thermodynamically stable and the corresponding ZPL lies within the optimal range for low-loss fiber transmission, which makes this type of SPE particularly useful in practical applications. Our investigation also sheds light on the concept of designing an SPE with a precisely tuned electronic configuration.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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AlGaN, cation vacancy, density functional theory, group theory, single-phonon emitters

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