Electronic And Nonlinear Optical Features of Inorganic Ga₁₂N₁₂ Nanocage Decorated With Alkali Metals (Li, Na and K)

Azadeh Jamshidi

Lorestan University

Zeinab Biglari (✉ biglariz@gmail.com)

Lorestan University <https://orcid.org/0000-0003-1874-7041>

Research Article

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**Electronic and nonlinear optical features of inorganic Ga₁₂N₁₂ nanocage
decorated with alkali metals (Li, Na and K)**

Azadeh Jamshidi, Zeinab Biglari*

Chemistry Department, Faculty of Science, Lorestan University, Khorram Abad, Lorestan, Iran

Corresponding author information:

Chemistry Department,
Faculty of Science,
Lorestan University, Khorram Abad, Lorestan, Iran
Email: biglari.z@lu.ac.ir; biglariz@gmail.com
ORCID ID: 0000-0003-1874-7041

Abstract

The effect of alkali metals (Li, Na and K) interaction on the nonlinear optical response (NLO) of $\text{Ga}_{12}\text{N}_{12}$ nanocage has been performed using density functional theory (DFT) calculations. The results show that the $\text{exo-M@Ga}_{12}\text{N}_{12}$ structures are energetically favorable with negative interaction energies in the range of -1.50 to -2.28 eV. The electronic properties of decorated structures are strongly sensitive to interaction with the alkali metals. The HOMO-LUMO gap of $\text{Ga}_{12}\text{N}_{12}$ is reduced by about 70% due to the decoration with alkali metals. It is obtained that the adsorption of alkali metals over the tetragonal ring of $\text{Ga}_{12}\text{N}_{12}$ nanocage remarkably enhances the first hyperpolarizability up to 6.5×10^4 au. The results display that decorating $\text{Ga}_{12}\text{N}_{12}$ nanocage with alkali metals can be introduced it as a novel inorganic nanomaterial with significant NLO properties.

Keywords: $\text{Ga}_{12}\text{N}_{12}$ nanocage; Alkali metals; nonlinear optical properties; Hyperpolarizability

1. Introduction

Since the discovery of C_{60} fullerene in 1985 by Kroto et al. [1], many theoretical and experimental researches have been done on fullerene carbon systems. Carbon fullerenes C_n ($20 < n < 60$) have been synthesized experimentally and have attracted much attention. Detailed studies of the carbon clusters are important in many applied fields, such as astrophysics, interstellar chemistry, electronics, and combustion processes [2-5]. The discovery of interesting properties and applications of carbon fullerenes led to extensive research in the design and synthesis of inorganic fullerenes

Therefore, a variety of different inorganic-based fullerene-like nanocages have been reported. Among them, the most attractive nanocages with the general formula $X_{12}Y_{12}$ are the most stable nanocages. Because of unique applications of fullerene-like structures in electronic devices, imaging materials, magnetic recording and environmental processes, investigating of them is one of the most important topics in nanotechnology [6-12]. Theoretical studies have confirmed that the $X_{12}Y_{12}$ clusters have two structures including a cubic quasi-structure consisting of square and hexagonal rings, and a quasi-fullerene structure having pentagonal and hexagonal rings. It has been confirmed that the cubic structure of $B_{12}N_{12}$ (made of square and hexagonal rings) is more stable than its fullerene structure (made of pentagonal and hexagonal rings) [13,14]. The group III nitrides ($B_{12}N_{12}$, $Al_{12}N_{12}$ and $Ga_{12}N_{12}$) nanocages are have been attracted considerable attention due to their remarkable chemical and physical properties [9-21]. More studies and references have been made about $B_{12}N_{12}$ and $Al_{12}N_{12}$ [9-17], but less researches have been done on the $Ga_{12}N_{12}$ nanostructure and fewer references are available [18-21].

The design and synthesis of novel materials with excellent nonlinear optical (NLO) properties has attracted great interest in experimental and theoretical fields over the past several decades due to

their potential application in optical, electro-optical devices, optical switching and other laser devices [22-29]. Among many strategies for enhancing the NLO response of materials, introducing the diffuse excess electron, such as alkali metals, proposed an efficient approach to improve the NLO properties of different systems. The excess electron is a kind of special anion with dispersivity, which plays an important role to improve the NLO properties of different systems and the first hyperpolarizability (β_0) [30, 31]. In addition to their various other applications, they are potential candidates for materials with large nonlinear optical response [32-41].

In this paper, we study the decorated Ga₁₂N₁₂ structures with alkali metals both exohedrally and endohedrally. The effect of decorating in different sites of the nanocage on NLO properties is investigated in detail.

2. Computational Details

All calculations are performed using Gaussian 09 quantum chemistry code [42] with default convergence criteria; the SCF convergence criteria are set to 10^{-8} Hartree on the density (SCF=Tight) as well as the convergence of geometric optimizations are adjusted to maximum force and root-mean-square (RMS) force of 4.5×10^{-4} and 3.0×10^{-4} Hartree.Bohr⁻¹, respectively, and maximum and RMS displacements of 1.8×10^{-3} and 1.2×10^{-3} Bohr, respectively. The geometries of all considered structures are fully optimized at B3LYP/6-31+G(d) level of theory and the nature of the stationary points are checked by frequency analysis at the same computational level. The spin-unrestricted approach is applied to describe the geometry optimization, electronic structure and NLO properties of M@Ga₁₂N₁₂ (M=Li, Na, K); whereas the restricted approach is used for the isolated clusters. The corresponding $\langle S^2 \rangle$ values for spin-unrestricted approach are in the range of 0.752–0.754 for these mentioned structures, which are very close to the value 0.750 for the pure

doublet state, indicating that the spin contamination is negligible and the computational results are reliable. The first static hyperpolarizability is evaluated using an analytical density functional Coulomb-attenuated hybrid exchange-correlation functional CAM-B3LYP approach and 6-31+G(d) basis set. The magnitude of the applied electric field is chosen as 0.001 au for calculation of the hyperpolarizability.

The interaction energy (E_{int}) between the alkali metal and nanocage is computed as:

$$E_{int} = E_{M@nanocage} - (E_{nanocage} + E_M) \quad (1)$$

$E_{M@nanocage}$ is the total energy of the M@nanocage as well as $E_{nanocage}$ and E_M are the energies of the isolated nanocage and alkali atoms, respectively. Energies of the frontier molecular orbitals (FMOs), the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, are ε_H and ε_L . The energy gap (E_g) and the percentage of change in energy gap ($\% \Delta E_g$) values are considered to explore electronic properties of the considered systems defined as follow:

$$E_g = \varepsilon_L - \varepsilon_H \quad (2)$$

$$\% \Delta E_g = \frac{E_g^{M@Ga_{12}N_{12}} - E_g^{Ga_{12}N_{12}}}{E_g^{Ga_{12}N_{12}}} \times 100 \quad (3)$$

The energy of a system in the weak and homogeneous electric field can be defined as [43, 44]:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \dots \quad (4)$$

where E^0 is the molecular total energy without the electric field and F_α is the electric field component along α direction. The, μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ denote dipole, polarizability, and the first hyperpolarizability, respectively. The dipole moment (μ), main polarizability (α), anisotropy of polarizability ($\Delta\alpha$) and first hyperpolarizability (β_0) are noted as:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (5)$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (6)$$

The polarizability (α) is a second rank tensor or a 3×3 matrix with 9 elements. The diagonal elements describe the response parallel to the applied electric field and their eigenvalues α_{ii} ($i = x, y$, and z) are used to calculate the mean polarizability α (isotropic of polarizability Eq. (6)). Some materials also become polarized in directions perpendicular to the applied electric field. Anisotropy of polarizability ($\Delta\alpha$) is calculated from diagonal and off-diagonal elements of polarizability tensor according to the following equation:

$$\Delta\alpha = \left[\frac{1}{2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2) \right] \right]^{\frac{1}{2}} \quad (7)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (8)$$

$$\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk}); \quad i, j, k = x, y, z. \quad (9)$$

The first hyperpolarizability (β_0) is a third rank tensor or a $3 \times 3 \times 3$ matrix with 27 components and known as nonlinear optical response (NLO) coefficient. Time-dependent density functional theory (TD-DFT) calculations were performed at the CAM-B3LYP/6-31+G(d) method to obtain the crucial excited states, and the differences of dipole moments between the ground state and crucial excited state.

3. Results and Discussions

3.1. Optimized structures

The optimized geometry of inorganic $\text{Ga}_{12}\text{N}_{12}$ nanocage at B3LYP/6-31+G(d) level of theory are depicted in **Fig. 1**. This nanocage consisted of six tetragonal (R4) and eight hexagonal (R6) rings. It is clear from this figure that two kinds of individual Ga-N bonds (b66, b64) are distinguishable for the considered structures. These different bonds are presented in **Fig. 1**. The bond lengths (l) of b66

and b64 are 1.844 and 1.916 Å, respectively in good agreement with the earlier reports (1.85, 1.93 Å) [19]. The bond lengths of b64 bonds are larger than b66 ones, it indicates that more p orbital participation is responsible for such increasing of b64-bonds than b66-ones. The distance between the nitrogen atoms (I_{N-N}) and the gallium atoms (I_{Ga-Ga}), that is, the diameters of the four-membered rings in $Ga_{12}N_{12}$, is 2.755 and 2.621 Å, indicating that the four rings are rhombic, not square. The HOMO and LUMO distribution pictures of the pristine $Ga_{12}N_{12}$ nanocage are also shown in **Fig. 1**. It is clear that HOMO orbitals are on nitrogen atoms and LUMO orbitals are on gallium atoms. In other words, nitrogen atoms are electron donors due to having non-bonded electron pairs and gallium atoms are electron acceptors due to having empty orbitals.

The present computational study is performed to understand the influence of alkali metals interaction with $Ga_{12}N_{12}$ nanocage on its electronic and nonlinear optical properties. For this purpose, the alkali atoms (Li, Na, K) are located in several different positions of $Ga_{12}N_{12}$ including; a front of gallium and nitrogen atom (M@fGa and M@fN), top of hexagonal and tetragonal rings (M@R6 and M@R4) and above the different types of Ga-N bonds (M@b66 and M@b64) as well as inside (M@inside) the $Ga_{12}N_{12}$ nanocage. The geometries of the considered structures are optimized at B3LYP/6-31+G(d) level of theory. The obtained stable structures with all real vibrational frequency are presented in **Fig. 2**. The results indicate that four stable decorated structures are obtained with Li and Na alkali metals and three stable structures with K atom. The alkali metals encapsulation (M@inside), adsorption on top of hexagonal (M@R6) and tetragonal (M@R4) rings for all alkali metals; and adsorption of Li and Na alkali metals in front of the N atom of the $Ga_{12}N_{12}$ nanocage lead to stable structures (see **Fig. 2**).

The most important atomic distance (I) and bond lengths of all structures are listed in **Table 1**. The bond lengths of b64 and b66 in K@inside, Na@inside and Li@inside are elongated to 1.930, 1.925,

1.923 Å and 1.862, 1.857, 1.852 Å compared to the pristine Ga₁₂N₁₂ (1.916, 1.844 Å), which shows that by placing a larger atom inside the nanocage, the bond lengths of nanocage increase and the nanocage size becomes larger than pristine Ga₁₂N₁₂.

The b₆₄ and b₆₆ bond lengths of other decorated structures (M@R₄, M@R₆, and M@fN) are also longer than the corresponding bond lengths in the pristine Ga₁₂N₁₂. The geometry of M@R₄ is such that the M atoms are directed toward two Ga atoms of the four-membered ring, and in M@R₆ the M atoms are directed toward three Ga atoms of the six-membered ring. The atomic distance of M–Ga are 2.485, 2.880, 3.178 Å; and M–N are 2.090, 2.608, 2.877 Å in Li@R₄, Na@R₄ and K@R₄, respectively. While, the distance of M–Ga are 2.510, 3.005, 3.257 Å and the bond length of M–N are 2.285, 2.823, 3.078 Å in Li@R₆, Na@R₆ and K@R₆, respectively. In Li@fN and Na@fN structures, the M–Ga distances is about 3 Å, the M–N distances are 1.809, 3.631 Å in Li@fN and 2.317, 3.071 Å in Na@fN.

The interaction energies (E_{int}) of alkali metals decorated Ga₁₂N₁₂ nanocage are computed as **Eq. (1)**. The obtained interaction energy values are listed in **Table 1**. Negative interaction energy indicates the formed complex is stable and positive one belongs to the local minimum in which the interaction of alkali atom with the nanocage is prevented by a barrier. The obtained values are $-2.28 > -2.11 > -1.91 > -1.73$ eV, which are related to Li@fN > Li@R₄ > Li@R₆ > Li@inside, respectively. The interaction Energy of the other decorated structures are -1.62 (Na@fN) > -1.60 (Na@R₄) > -1.50 (Na@R₆) > -0.72 (Na@inside) as well as -1.691 (K@R₄) > -1.679 (K@R₆) > $+0.281$ eV (K@inside). The results show that the most stable complexes of lighter alkali metals (Li, Na) are formed by the interaction of their adsorption with the electronegative N atom of the Ga₁₂N₁₂ nanocage.

However, in comparison with similar complexes of all three alkali atoms, the occupation of the R4 and R6 positions by the alkali atom leads to the formation of more stable structures and their order of stability are -2.11 (Li@R4) $>$ -1.691 (K@R4) $>$ -1.60 (Na@R4); and also -1.91 (Li@R6) $>$ -1.691 (K@R6) $>$ -1.60 (Na@R6). The E_{int} results show that encapsulation of alkali metals in the nanocage is energetically favorable (exothermic) except K@inside. The E_{int} values of them are -1.73 (Li@inside) $>$ -0.72 (Na@ inside) $>$ $+0.28$ (K@ inside). The large size of the K atom causes the K@inside complex to become unstable, and the energy of the interaction in this structure is positive.

3.2. Electronic properties

The obtained frontier molecular orbital energies (ϵ_L and ϵ_H), energy gap (E_g), percentage of variation of E_g ($\% \Delta E_g$) and dipole moment of all studied structures are listed in **Table 1**. Energy gap (E_g) of the pristine Ga₁₂N₁₂ nanocage is 3.2 eV, while for all doped structures is about 0.8 eV, in other words it is reduced by about 70%. The results show that the interaction of the alkali metals with the inorganic Ga₁₂N₁₂ nanocage significantly narrows the energy gap.

The LUMO energy level of the pristine Ga₁₂N₁₂ and the decorated complexes are about $-3.4 \sim -3.8$ eV. But the HOMO energy level of the pristine Ga₁₂N₁₂ is -6.6 eV and it is about $-4.3 \sim -4.6$ for decorated structures. To have a clear picture of the electronic behavior of the decorated nanocages, density of state analysis was performed and the total densities of states (TDOS) spectrum of all nanocages are given in **Fig. 3**. The TDOS spectra indicate that HOMO of doped nanocages appeared at higher levels of energy and shifted from -6.6 to ~ -4.5 eV. The contribution of alkali metals in the formation of these new HOMOs can be observed, and this reduction in E_g of doped nanocages can be attributed to the excess electrons induced by alkaline metals in the nanocages.

Therefore, it can be concluded that the interaction of alkali metals with Ga₁₂N₁₂ leads to the formation of a higher energy level as the location of the new HOMO level between the original HOMO and LUMO of the pristine Ga₁₂N₁₂, which is responsible for significant narrowing of energy gap. The picture of FMOs is displayed in **Fig. 4**. In these pictures, the presence of the LUMOs on the alkali metal is observed and it shows that the charge transfer (CT) from the alkali metal atoms to the nanocage has taken place.

3.3. Linear and nonlinear optical properties

The calculated dipole moment (μ), polarizability (α), the first hyperpolarizability (β_0) and its components (β_x , β_y , and β_z), anisotropy of polarizability ($\Delta\alpha$) and the Bader charge of metal atom of considered structures are listed in **Table 3**. The μ value of the pristine Ga₁₂N₁₂ and M@inside structures are about zero, and it can be due to the symmetrical distribution of electrons on structures. The obtained values for μ , α , $\Delta\alpha$ and β_0 of all decorated structures are shown in **Fig. 5**. The trend of μ values are Li@fN (9.149 D) > Li@R4 (7.337 D) > Li@R6 (4.947 D) > Li@inside (0.056 D); Na@fN (10.074 D) > Na@R4 (9.890 D) > Na@R6 (8.490 D) > Na@inside (0.032 D) and K@R4 (13.231 D) > K@R6 (11.409 D) > K@inside (0.013 D). Also, decorated structures with different atoms and the same position of alkali metals show that the dipole moment increases with increasing atomic number and atom size, i.e., Na@fN (10.074 D) > Li@fN (9.149 D); K@R4 (13.231 D) > Na@R4 (9.890 D) > Li@R4 (7.337 D) and K@R6 (11.409 D) > Na@R6 (8.490 D) > Li@R6 (4.947 D). Therefore, in dipole moment plot according to the type of alkali atoms and their position (μ /decorated structures), the curve of related to K@Ga₁₂N₁₂ is at the highest and the Li@Ga₁₂N₁₂ is at the lowest level (**Fig. 5**).

The polarizability (α) of decorated structures is: 514.6 (Li@fN) > 462.5 (Li@R4) > 446.4 (Li@R6) > 441.9 (Li@inside); 533.9 (Na@fN) > 521.6 (Na@R4) > 485.1 (Na@R6) > 443.9 (Na@inside) and 515.2 (K@R4) > 482.8 (K@R6) > 445.3 au (K@inside). As shown in **Fig. 5**, in studying the anisotropy of polarizability ($\Delta\alpha$) values, a similar trend is observed in α value. Investigation of obtained values of all decorated structures shows that the order M@fN > M@R4 > M@R6 > M@inside is confirmed for μ , α and $\Delta\alpha$ and are shown in **Fig. 5**. According to the results of **Table 3** and **Fig. 5**, the adsorption of alkali metals over the tetragonal and N atom of Ga₁₂N₁₂ nanocage induces outstanding first hyperpolarizability. The calculated β_0 of Na@R4 > K@R4 > Na@fN > Li@fN > Na@R6 > K@R6 > Li@R4 > Li@R6 structures are 64723.4 > 61447.1 > 61385.7 > 47523.2 > 37079.5 > 30823.1 > 18418.9 > 4267.7 au, respectively; whereas for the pristine Ga₁₂N₁₂ nanocage it is 1.5 au. The β_0 value of Li@inside, Na@inside and K@inside structures are 18.0, 8.9 and 14.8 au, respectively. The calculated polarizability (α) values indicate that structures with a significant NLO response have larger α values and structures with an insignificant NLO response have smaller α values.

The diffuse excess electron release from alkali metals into the Ga₁₂N₁₂ causes a large NLO response. And this diffuse of electrons from outside the nanocage is much more effective in the position of the R4 ring and front of nitrogen atom. It is noteworthy that the interaction in these two positions causes the highest amounts of negative interaction energy (E_{int}) and increased the first hyperpolarizability. In other words, complexes with significant NLO response have the highest polarizability (α) and the most interaction energy among the studied complexes. Therefore, it can be confirmed that a more stable system can show remarkable first hyperpolarizability.

The ionization potential energy (IPE) of alkali metal atoms (Li, Na, and K), the interaction distance and the position of them with the Ga₁₂N₁₂ nanocage are important factors in the diffuse excess

electron to the nanocage. Heavier alkali metals have easier electron diffusion into the nanocage and cause a large NLO response. And also, the interaction distance between the alkali atom and the nanocage, plays a very important role in the amount of electron transfer, and the shorter the interaction distance leads to a greater NLO response. These factors challenge with each other. The interaction distances of the structures considered in **Table 1**. Among studied structures, some of them lead to insignificant NLO response (M@inside). The results of this table indicate that the shortest interaction distance is belonged to Li metal, but the greatest values of β_0 are related to Na@R4, K@R4, Na@fN and Li@fN structures. Therefore, the ionization potential, interaction distance and the position of alkali metals with Ga₁₂N₁₂ play an essential role in changing the NLO response of structures.

3.3. TD-DFT calculations

To investigate the decorating effect of an alkali atom and its position on β_0 value of Ga₁₂N₁₂, the time-dependent density functional theory (TD-DFT) computations were performed to obtain the crucial excited states of the all systems and the two levels of expression can be used [45-47]:

$$\beta_0 \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3} \quad (10)$$

where ΔE , f_0 , and $\Delta\mu$ are the crucial transition energy, the largest oscillator strength, and the difference of dipole moment between the ground state and the crucial excited state (the excited state with the largest oscillator strength), respectively. Our computed results are listed in **Table 4**. The maximum absorption wavelength ($\lambda_{\max}$) and dominant transitions of all studied systems are also given in **Table 4**. Pristine Ga₁₂N₁₂ nanocage has an electron excitation with 3.18 eV which its wavelength appear at 390.1 nm in near-UV region as displayed in **Fig. 6**. The transition energies (ΔE) of decorated nanocage are in the range of 1.13 to 1.75 eV and are much smaller than the value

of the $\text{Ga}_{12}\text{N}_{12}$ structure. According to eq. 5, the β_0 value is inversely proportional to the third power of transition energy, so the β_0 value increases with decreasing transition energy. Also, the β_0 value is proportional to the values of f_0 and $\Delta\mu$. The data in Table 4 show that the f_0 and $\Delta\mu$ for all decorated structures are larger than the pristine $\text{Ga}_{12}\text{N}_{12}$. The UV-Visible spectrum of all structures is plotted in **Fig. 6**. As expected, due to the reduced transition energy of doped structures, the UV-Visible absorption peaks shift to larger wavelengths in the visible or IR region.

The maximum wavelength (λ_{max}) changes according to the type of doped structures and the position of the alkali atom are shown in **Fig. 7**. Study of the obtained absorption wavelength of dominant transitions values shows that the decorated structures have similar behavior and trends such as dipole moment (μ), polarizability (α) and anisotropy of polarizability ($\Delta\alpha$) of the structure. In other words, for the λ_{max} of structures, there is a trend $\text{M@fN} > \text{M@R4} > \text{M@R6} > \text{M@inside}$.

Therefore the obtained results show that the decoration of $\text{Ga}_{12}\text{N}_{12}$ nanocage with alkali metals could be introduced as an effective strategy to induce remarkable first hyperpolarizability and it could be considered as promising innovative nonlinear optical inorganic-based nanomaterial.

3.4. Compare with previous reports

In the study of the effect of alkali metals on the nonlinear optical properties of nitride of other elements of this group ($\text{B}_{12}\text{N}_{12}$ and $\text{Al}_{12}\text{N}_{12}$), several references can be mentioned [15-17]. In 2014, Niu et al. investigated the effect of alkali metals on NLO properties of inorganic $\text{Al}_{12}\text{N}_{12}$ nanocage [15], and they reported that the excess electron play a key role in enhancing the static first hyperpolarizability of $\text{Al}_{12}\text{N}_{12}$ nanocage. In 2016, Hou et al. [16] and Shakerzadeh et al. [17] separately studied the interaction of alkali metals with $\text{B}_{12}\text{N}_{12}$ nanocage on NLO properties of M-doped structures. For comparison, significant values of β_0 from the three references are listed in

Table 5. Based on the data in Table 5, the interaction of alkali metals with the group (III) nitride nanocages ($B_{12}N_{12}$, $Al_{12}N_{12}$ and $Ga_{12}N_{12}$) has significantly increased the nonlinear optical response. Depending on the type of alkali atom, nanocages and the location of the alkali atom, in some structures the β_0 value has increased by about 10^4 - 10^5 au. Decoration of the inorganic nanocages with alkali metal atoms has improved the NLO properties of the decorated inorganic nanocages. This increase is due to the charge transfer and excess electron from the alkali metal atom to the nanocages.

4. Conclusion

The present DFT study on interaction of alkali metals with $Ga_{12}N_{12}$ nanocage shows that the electro-optical properties of $Ga_{12}N_{12}$ are remarkably sensitive to interaction with alkali metals. It is found these decorations narrow the HOMO-LUMO gaps of $Ga_{12}N_{12}$ nanocage. The results display that the interaction process are energetically favorable with negative interaction energies in the range of -1.50 to -2.28 eV. Indeed, it is found that the adsorption of alkali metals over the tetragonal ring of $Ga_{12}N_{12}$ nanocage remarkably enhances their first hyperpolarizability.

Exohedrally adsorption of alkali atoms on $Ga_{12}N_{12}$ nanocage leads to significant increases in dipole moment, polarizability and remarkable NLO response. In particular, the adsorption of Na atom on nanocage (Na@R4) with $E_{int} = -1.62$ eV leads to outstanding NLO response of 64723.4 au. causes a dramatic response to NLO. It is indicated that the ionization potential of alkali metal atoms, interaction distance and the position of them with $Ga_{12}N_{12}$ nanocage are important factors in NLO response. It seems that it can be concluded that decorated $Ga_{12}N_{12}$ nanocage with alkali metals can be promising for the design and synthesis of novel NLO nanomaterial.

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Declarations

The authors declare that they have no conflict of interest.

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Fig. 1. The optimized structure and HOMO-LUMO distribution of $\text{Ga}_{12}\text{N}_{12}$ nanocage

Fig. 2. The stable decorated structures of $\text{M}@\text{Ga}_{12}\text{N}_{12}$ ($\text{M}=\text{Li}, \text{Na}, \text{K}$)

Fig. 3. The total density of states (TDOS) spectrum of all studied nanocages

Fig. 4. The picture of FMOs of obtained $\text{Na}@\text{Ga}_{12}\text{N}_{12}$ and $\text{K}@\text{Ga}_{12}\text{N}_{12}$ structures

Fig. 5. The obtained values for μ , α , $\Delta\alpha$ and β_0 of all decorated structures in terms the position and type of alkali atom

Fig. 6. The UV-Visible spectrum of all studied structures

Fig. 7. The maximum wavelength (λ_{max}) of all studied structures in terms the position and type of alkali atom

Table 1. The obtained bond lengths ($\text{\AA}$) of $\text{Ga}_{12}\text{N}_{12}$ and all decorated $\text{M@Ga}_{12}\text{N}_{12}$

Table 2. The interaction energy (E_{int}), HOMO and LUMO energies (ε_H and ε_L) and energy gap (E_g) in eV, percentage of variation of E_g ($\% \Delta E_g$) and dipole moment in Debye of optimized structures

Table 3. The calculated dipole moment (μ), polarizability (α), the first hyperpolarizability (β_0) and the Bader charge of metal atom in the considered structures

Table 4. The calculated transition energy (ΔE), the difference of dipole moment ($\Delta\mu$) between the ground state and the crucial excited state, the largest oscillator strength (f_0), maximum absorption wavelengths (λ_{max}) and the dominated transition of all studied structures

Table 5. The β_0 values of $\text{M@B}_{12}\text{N}_{12}$, $\text{M@Al}_{12}\text{N}_{12}$ and $\text{M@Ga}_{12}\text{N}_{12}$ nanocages ($\text{M}=\text{Li}$, Na and K)

Figures

Figure 1

The optimized structure and HOMO-LUMO distribution of Ga₁₂N₁₂ nanocage

Figure 2

The stable decorated structures of $M@Ga_{12}N_{12}$ ($M=Li, Na, K$)

Figure 3

The total density of states (TDOS) spectrum of all studied nanocages

Figure 4

The picture of FMOs of obtained Na@Ga₁₂N₁₂ and K@Ga₁₂N₁₂ structures

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The maximum wavelength (λ_{max}) of all studied structures in terms the position and type of alkali atom

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