Ab Initio Calculations of the Structural, Elastic, Electronic and Optical Properties of Copper Nitride Compounds Doped with La, Eu and Yb

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Abstract—In order to examine the characteristics of copper nitride (Cu₃N) doped with transition metals, total-energy calculations from scratch utilizing the full-potential linearized augmented plane wave (FP-LAPW) approach. It enabled us to calculate theelastic constants, best structural parameters, density of states, bulk modulus, and band structure for Cu₃NM compounds, where M represents La, Eu, and Yb. In this study, we employed the precise configuration of the Cu₃N anti-ReO₃ type cell, by introducing a transition metal atom into the vacant position within the cell. Specifically, our computations have determined that the arrangement of electrons in the 3d orbit of doped atoms significantly affects the Cu₃NM system. The introduction of a transition metal atom-doped Cu₃N unit cell, with an additional rare earth (RE) atom positioned at the center of the cube, results in an initial expansion in volume, followed by a subsequent contraction when the atomic number of the doped atoms increases. All of the substances possess mechanical stability and should be classified as brittle substances. The absorption spectrum results show that the absorption edge of metal-doped copper nitride Cu₃NM has a blue shift compared with the absorption edge of Cu₃N, indicating that Cu₃NM can be used in ultraviolet photodetectors.

Index Terms—Copper nitride, first-principles, rare earth metal, physical properties

I. INTRODUCTION

As a transition metal nitride, copper nitride (Cu₃N) has attracted extensive research for its application in optical storage and integrated circuits [1]. In 1938, Juza and Hahn [2] first obtained polycrystalline Cu₃N grains in ammonia (NH₃) by high-temperature and high-pressure method with a molecular weight of 204.63 for bulk Cu₃N and a crystal density of 5.84 g/cm³ at room temperature. Subsequently, Terao and Acad's team [3] measured the structure of Cu₃N crystal for the first time by X-ray diffraction (XRD) in the mid-1970s. The results indicate that Cu₃N possesses an anti-ReO₃ type structure, characterized by a space group of 221 Pm-3m [4]. The nitrogen (N) atoms are situated at the

Manuscript received March 22, 2023; revised September 21, 2023.

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vertex of the cubic crystal, while the copper (Cu) atoms are positioned at the midpoint of the edges of the cubic crystal. The Cu atoms are bound to the N atoms through covalent bonds, as seen in Figure 1. Cu₃N has a high resistivity and low decomposition temperature, and around 350-450 °C will be decomposed into Cu and N₂ [2,5]. Using the low-temperature thermal breakdown features of Cu₃N, Asano's team successfully conducted a one-time optical recording test on Cu₃N film for the first time [6]. Nosaka et al. decomposed the Cu₃N film by electron beam etching, leaving Cu spots and Cu lines on the substrate surface [7]. After that, Li's team calculated the thermodynamic properties of Cu₃N [8]. The findings indicate that the lattice constant of Cu₃N diminishes as the pressure P rises and expands as the temperature T increases within the range of 0-700K and 0-5GPa. [9,10].

Due to the widespread application of Cu₃N optical storage [11], solar cells, lithium batteries [12], and other domains, several experimental and theoretical studies on Fe [9], Sc [12], Li [13], La [14], and In [15] have been conducted. However, there are few studies on the properties of Cu₃N doped with rare earth metals. This study employs the first-principles calculation methodology. The WIEN2k software system was employed to investigate the impact of doping with rare earth metals La (4f05d16s2), Eu (4f76s2), and Yb (4f146s2) on the electrical, elastic, structural and optical properties of Cu₃N.

II. METHOD OF CALCULATION

This research calculated the structure and electrical characteristics of Cu₃N and Cu₃NM using the WIEN2k software package and the first-principles calculation approach. The muffin-tin radii of M, N and Cu in the computation are 1.8 atomic units (a.u.), 1.6 a.u., and 1.9 a.u., respectively. The spherical harmonic basis of the wave function in each muffin-tin sphere is truncated at an angular momentum of 56 k points in the decreased Brillouin zone. The determination of the plane-wave truncation of the function is based on the value of K_{max}, which is calculated as 9 divided by the minimum radius of the muffin-tin sphere (RMT) within the unit cell, $K_{max} = 9/RMT$. K_{max} represents the maximum reciprocal lattice vector in the plane-wave expansion. The cut-off energy for splitting the core and valence states is -9.0Ry. In the Fourier expansion of charge density, $G_{max} = 17 \exp(Ry)$. In this article, the self-consistent loop operation selects a $12 \times 12 \times 12$ grid, with 2000 as the selected k point and 0.0001 Ry energy convergence as the

This work was supported in part by the Natural Science Foundation of Hunan Province under grant number 2022JJ50276, and the Scientific Research Fund of Hunan Provincial Education Department under grant number 20B107, and the Yiyang Science and Technology Plan Project under grant number 2021133.

convergence criterion.

III. RESULTS AND DISCUSSION

A. Constitutive property

The Birch-Murnaghan equation of state [18] was employed in this study to establish the correlation between crystal volume and total energy. It allowed us to compute the equilibrium volume of the compounds under investigation.

$$E(V) = E_0 + \frac{BV}{B'} \left[\frac{(V_0 / V)^B}{B'} + 1 \right] - \frac{BV_0}{B' - 1}$$
(1)

when E_0 represents the equilibrium energy, B and B denote the bulk modulus and its initial pressure derivative, respectively.

The structure of Cu_3NM (M= La, Eu and Yb) and Cu_3N is seen in Fig.1. Table 1 details the lattice characteristics, elastic constants, and formation energy of Cu_3N and Cu_3NM



Fig. 1. Unit cells for (a) pure Cu_3N and (b) Cu_3N have been doped with M, where M stands for the elements La, Eu, and Yb.

The examination of the unit cell volume of the compound reveals that the volume of the Cu₃N unit cell increases as a result of the introduction of the M atom through doping. From $La \rightarrow Eu \rightarrow Yb$, the expansion degree of the unit cell volume of Cu₃N gradually decreases. The main reason is that as the number of electrons on the 4f orbital of the rare earth element gradually increases, the bonding with the 3d electrons of the Cu atom is enhanced, making it more closely bonded. It can be observed from the table that the formation energy of Cu₃N and Cu₃NM compounds is lower than -19eV, and the formation energy of Cu₃N becomes decreased after doping with M atoms, which implies that Cu₃NM compounds are easier to make in the laboratory. A negative formation energy indicates that the molecules Cu₃N and Cu₃NM are both stable. Furthermore, doping Cu₃N with M atoms improves the stability of the system.

B. Electrical properties

With the enhancement of preparation technology, Cu_3N can be prepared by a variety of processes, such as DC reactive sputtering, DC magnetron sputtering [17], chemical vapour deposition [19], plasma nitriding [20] and so on. It is found that the optimal growth direction of copper nitride is (100) [19, 21]. With the increase of the N₂ flow rate, the optimal growth direction changes from (100) to (111). Therefore, the charge density distribution of (100) and (111) crystal planes of Cu_3N and Cu_3NM is studied in this paper.

In the Cu_3N (100) crystal plane (Fig.2a), the vertex of the cube frame and the center of the cube edge line are N atoms and Cu atoms, respectively. It is evident that there is a charge distribution around both atoms. There is almost no charge density distribution at the center of the cube frame, confirming that Cu_3N indeed has a body center vacancy.

 $\label{eq:constant} \begin{array}{c} TABLE \ I \\ THEORETICAL CALCULATION OF UNIT CELL VOLUME (V), LATTICE \\ CONSTANT (a), ELASTIC COEFFICIENT (C_{jj}) AND FORMATION ENERGY (\Delta H) \\ OF Cu_3N AND Cu_3NM COMPOUNDS \end{array}$

Because the N atom's extra-nuclear electron distribution is [He]2s22p3 and the Cu atom's extra-nuclear electron distribution is [Ar]3d104s1, that is, the extra-nuclear electron of the Cu atom is much more than that of the N atom, and the charge density diagram can also reflect the covalent bond between Cu atom and N atom. After doping M atoms, the charge density of each atom in the Cu₃N unit cell changed accordingly. The extra-nuclear electrons of M atoms begin to interact with Cu atoms, and even form covalent connections with Cu atoms, which weakens the interaction of extra-nuclear electrons between Cu-N atoms. The charge density distribution of the (110) crystal plane of the Cu₃NM combination (Fig.2 j-l) reveals the presence of charge density at the body-centered vacancy. It suggests that all M atoms have been effectively absorbed into the body-centered emptiness of Cu₃N. Figure 3 and Figure 4 display the overall density of states for Cu₃N and Cu₃NM, as well as the partial density of states for specific atomic orbitals, respectively.

Based on the data presented in Figure 3, it is evident that Cu_3N possesses a band gap of 0.3 eV. This value aligns with the theoretical determination of 0.23 eV by Weber and Hahn [19], as well as the experimental range of 0.25 to 0.83 eV reported by Pierson [22]. It also illustrates the semiconductor nature of Cu_3N .

By comparing the overall density of states of Cu₃N in Figure 3a with that of Cu and N in Figure 3b, the apex of hybridization between Cu-3d and N-2p orbital electrons is clearly seen, which occurs at $-8 \sim 0 \text{eV}$, is primarily responsible for the hybridization peak in the total density of states of Cu₃N. The small peak at -16eV is contributed primarily by N-2s orbital electrons. Analysis of Figure 3 b reveals that the N atom's total DOS value is lower than the Cu atom's total DOS value. This is because fewer outer electrons bonded to the N nucleus than Cu atoms. It can also be seen from the total density of states of Cu₃N (Fig. 3a) that the N-2s orbital electrons are rarely bonded to the Cu orbital electrons, indicating that the N-2s orbital is very stable. The hybridization of the Cu-3d orbital electrons and the N-2p orbital electrons primarily govern the bonding process of the Cu₃N crystal.

Figure 4 illustrates the cumulative density of states for Cu_3NM , as well as the density of states for each atom (a: Cu_3NLa ; b: Cu_3NEu ; c: Cu_3NYb). Inferring from the fact that the Fermi level line crosses the total density of states line in Fig. 4, Cu_3NM compounds display conductor qualities, i.e., doping Cu_3NM with M atoms transforms it from a semiconductor to a conductor. After examining the cumulative density of states of Cu_3N (as depicted in Figure 3), it is evident that the 4s and 4p orbitals of Cu in Cu3N are unoccupied. However, when the M atom is doped into its



Fig. 2. The charge densities in two dimensions are measured for the (100) (a), (111) (e), and (110) (i) planes of Cu_3N , the (100) (b), (111) (f), and (110) (j) planes of Cu_3NLa , the (100) (c), (111) (g), and (110) (k) planes of Cu_3NEu , and the (100) (d), (111) (h), and (110) (l) planes of Cu_3NYb .



Fig. 3. The density of states (DOSs) for Cu₃N, both total (a) and partial (b), were determined using the FP-LAPW method.

body-centered location, the two empty orbitals are gradually filled with M atoms, resulting in Cu₃N with metallic characteristics. An investigation of the density of states of Cu₃NLa in Fig.4a shows three prominent peaks, of which La-p orbital electrons and N-2s orbital electrons, respectively, contribute to two small peaks at-17eV and-16eV. The central peak observed in the energy range of $-4 \sim 4$ eV can be attributed to the robust hybridization between the La-5d orbital and Cu-3d orbital electrons. The prominent peak in the $-4 \sim 4eV$ energy region of the density of states diagram of Cu₃NEu is caused by the hybridization effect between the Eu-4f orbital and the Cu-3d orbital. The peak near 20 eV results from the interaction between Eu-p orbital electrons and N-2s orbital electrons. There is no peak in the low-energy region of Cu₃NYb. The electron hybridization between Yb-4f and Cu-3d orbitals produces the peak in the $-4 \sim 4 \text{ eV}$ energy region. However, this peak is weaker than those of Cu₃NLa and Cu₃NEu.

Fig. 5 shows the band structures of Cu_3N and Cu_3NM . Figure 5 demonstrates that the valence band in Cu_3N has its maximum energy level at point R, which is a position of high symmetry within the Brillouin zone. Conversely, the conduction band's lowest energy level is located at point M, which is also a position of high symmetry within the

Brillouin zone. The lack of alignment between the valence band's highest energy level and the conduction band's lowest energy level at the same symmetry point indicates that the Cu₃N crystal has an indirect band gap, classifying it as a semiconductor. The picture also reveals that the band gap value for Cu₃N is 0.3 eV, which is consistent with the DOS finding. The band diagram can be divided approximately into three sections: One energy band is located near 14 electron volts (eV), significantly distant from the Fermi level. The electrons primarily influence this band in the N-2s orbital; The second part is the valence band in the range of 0 eV to -8 eV below the Fermi level. There are 12 forbidden bands within this region, separating three bonding bands and three antibonding bands; The third component is the conduction band above the Fermi level, which contributes marginally to the interaction between orbiting electrons. The DOS values for Cu₃N correspond to the energy range corresponding to these three components. The energy band structure diagram further reveals that the N-2s orbital electrons are far from the Fermi level line and contribute little to bonding. In the second component, the energy bands in the valence band region cross closely, demonstrating a significant hybridization effect between the Cu-3d and N-2p orbital electrons.

The gap disappears when Cu₃N is doped with M atoms,



Fig. 4. The FP-LAPW approach was employed to calculate the total densities of states and partial densities of states (DOSs) for three compounds: (a) Cu_3NLa , (b) Cu_3NEu , and (c) Cu_3NYb .



Fig. 5. Energy band structure diagrams of Cu₃N and Cu₃NM. (a) pure Cu₃N, (b) La-doped Cu₃N, (c) Eu-doped Cu₃N and (d) Yb-doped Cu₃N.

confirming that Cu_3NM is a conductor. M atoms and Cu atoms have a significant hybridization in the Fermi level area; hence the Fermi level energy band structure of Cu_3NM is highly dense. Compared to La doping, Eu and Yb atoms influence the low energy region (-18 to -24 eV) of Cu_3N .

C. Elastic properties

The only three independent elastic constants in copper nitride, which is a cubic solid, are C_{11} , C_{12} , and C_{44} . If the value of the elastic constant fulfills the following (2), the mechanical stability of the system can be determined [25]:

$$\begin{cases} C_{44} > 0 \\ C_{11} > | C_{12} | > 0 \\ C_{11} > B > C_{12} \\ B = (C_{11} + 2C_{12}) / 3 > 0 \end{cases}$$
(2)

The bulk modulus, denoted as B, quantifies the correlation between the change in volume and the average stress applied to an object.

$$B = (C_{11} + 2C_{12}) / 3 \tag{3}$$

The shear modulus G, calculated using the following formula (4), reflects the system's capacity to resist shear strain.

$$G = (G_v + G_R) / 2 \tag{4}$$

 $G_V=(C_{11}-C_{12}+3C_{44})/5$ is the Voigt shear modulus, which corresponds to the upper limit of *G*; $G_R=5(C_{11}-C_{12})/4C_{44}+3(C_{11}-C_{12})$ is the Reuss shear modulus,

TABLE II VARIOUS PHYSICAL PROPERTY PARAMETERS OF $\rm Cu_3N$ and $\rm Cu_3NM$

| | Cu ₃ N | Cu ₃ NLa | Cu ₃ NEu | Cu ₃ NTb |
|----------------|-------------------|---------------------|---------------------|---------------------|
| B/GPa | 114.9 | 52.9 | 107.8 | 81.9 |
| G/GPa | 24.5 | 20.0 | 16.1 | 16.8 |
| E/GPa | 68.6 | 53.2 | 46.0 | 47.2 |
| ξ | 0.319 | 0.730 | 0.880 | 0.813 |
| Å | 0.176 | 2.031 | 2.341 | 1.506 |
| \overline{v} | 0.400 | 0.332 | 0.429 | 0.404 |
| B/G | 4.69 | 2.65 | 6.69 | 4.87 |

which corresponds to the lower limit of *G* in formula (4). B/G can determine whether the system is ductile or brittle. Material is brittle if B/G < 1.75 and vice versa.

Young's modulus *E* and Poisson's ratio values can be calculated from *B* and *G* as follows:

$$E = \frac{9BG}{3B+G} \tag{5}$$

$$\overline{v} = \frac{3B - 2G}{2(3B + G)} \tag{6}$$

According to the calculation data in TABLE I and TABLE II, it can be seen that the three elastic parameters and elastic modulus B values of Cu₃N and Cu₃NM compounds satisfy formula (2), demonstrating that the compounds of Cu₃N and Cu₃NM are mechanically stable throughout the range of elastic deformation, and the elastic modulus of Cu₃NM is less than that of Cu₃N, meaning that Cu₃NM crystal is more accessible to compress than Cu₃N crystal. The computed B/G values of Cu₃N and Cu₃NM are significantly more significant



Fig. 6. Calculated (a) absorption coefficients and (b) energy-loss functions for Cu₃N and Cu₃NM



Fig. 7. Calculated (a) reflectivities and (b) refractive indices for Cu₃N and Cu₃NM

than the crucial value of 1.75, indicating that all four compounds are ductile; The Zener anisotropy factor A for an isotropic compound is 1, and the calculated Zener anisotropy factor values depart from 1. Therefore, both Cu_3N and Cu_3NM are anisotropic.

D. Optical property

Cu₃N and Cu₃NM were analyzed for their refractive index $n(\omega)$, absorption spectrum $\alpha(\omega)$, reflectivity $R(\omega)$ and energy loss spectrum $L(\omega)$. The complex dielectric function, denoted by $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$, can be used to analyse the optical characteristics of the crystal. Here, $\varepsilon_1(\omega)$ refers to the real component of the complex dielectric function, $\varepsilon_2(\omega)$ represents the imaginary part, and ω denotes the frequency of the electromagnetic wave. The function $\varepsilon_2(\omega)$ is closely linked to the interband transition inside the energy band in which the electronic transition energy between the valence band and the conduction band is the determining factor. Its value can be calculated using the formula (7) [25]:

$$\varepsilon_{2}(\omega) = \left(\frac{4\pi^{2}e^{2}}{m^{2}\omega^{2}}\right) \sum \int \langle i|M|j\rangle^{2} f_{i}(1-f_{i}) \times \delta(E_{f}-E_{i}-\omega)d^{3}k$$

$$(7)$$

where *i* is the initial energy level state, *j* is the final energy level, *M* is the dipole transition matrix, f_i is the Fermi distribution function, and E_i is the electron energy of the 1th ground state.

The Kramers-Kroning dispersion relation yields the real portion of the complex dielectric function.

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\varepsilon_2(\omega)}{\omega^2 - \omega^2} d\omega d\omega$$
(8)

The compounds' optical characteristics are derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. Absorption spectrum function:

$$\alpha(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_1^2(w) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}$$
(9)

The reflectivity function:

$$\begin{array}{c} \textbf{33} \textbf{2.4} \\ \textbf{33} \textbf{2.0} \\ \textbf{1.6} \\ \textbf{1.2} \\ \textbf{0.8} \\ \textbf{0} \\ \textbf{10} \\ \textbf{20} \\ \textbf{20} \\ \textbf{30} \\ \textbf{40} \\ \textbf{Energy (eV)} \end{array}$$

$$R(\omega) = \left| \frac{\sqrt{\varepsilon_1(\omega) + j\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + j\varepsilon_2(\omega)} + 1} \right|$$
(10)

Refractive index function:

$$n(\omega) = \frac{\left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)\right]^{\gamma_2}}{\sqrt{2}}$$
(11)

Energy-loss function:

$$L(\omega) = \frac{\varepsilon_2(w)}{\left[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)\right]}$$
(12)

According to Figure 6(a), the absorption edge of Cu_3N is observed at an energy level of 0.35 eV, indicating a band gap width of 0.30 eV. The short band gap and comparatively low absorption edge are mainly attributable to the p-d repulsion in the valence band, which is a result of the low energy difference between the Cu-3d and N-2p orbitals. Cu₃N has a first absorption peak at 4.5 eV. This peak is caused, according to the DOS diagram and energy band structure of Cu₃N, by the transition from N-2p (-7.7 eV) to Cu-3d (-2.4 eV). It is evident from Fig.6a that Cu₃N's highest absorption peak occurs at 8.0 eV. The DOS diagram and energy band structure of Cu_3N reveals that the transition from the 2s (-14 eV) orbital of N to the 3d (-2.4 eV) orbital of Cu is responsible for this significant absorption peak. In comparison to Cu₃N, the spectral lines of Cu₃NM exhibit a clear blue shift, while Cu₃NLa's absorption edge is 12.2 eV. Based on the total density of states, it can be deduced that the La-p orbital (-17 eV) transitions to the Cu-3d orbital (-2.4 eV). Cu₃N's energy loss spectrum reveals that the first loss peak is centered at 11.8 eV, where Cu₃N's reflectivity drops (Fig. 7a). At 14.4 eV, where Cu₃N reflectivity is at its lowest, the loss peak is the highest. By comparing the energy loss spectra of Cu₃NM and Cu₃N, it can be seen that all of Cu₃NM's spectral lines have a blue shift, with Cu₃NYb having the bluest shift, which corresponds to the reflectivity spectrum of Cu₃NM.

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 Cu_3N doped with rare earth metals can be utilized in ultraviolet detectors and other applications, as indicated by the blue shift of Cu_3NM .

It can be seen from Fig. 7 that the refractive index and reflectivity of Cu₃N are greatly affected by the incorporation of M atoms. For the 0~5.5 eV energy region of Cu₃N, the refractive index is high, but the reflectivity is low; in the region of 5.5 ~ 15 eV, the reflectivity is enhanced, and there are several small reflection peaks. On the contrary, the refractive index begins to decrease. The reflectivity and refractive index have opposite trends in the high energy region (15~42 eV). When La is doped, the energy area with a strong refractive index is 12.8~16.5 eV, whereas the reflectivity in the same region is relatively low. In the area of 16.5~23 eV, the reflectivity began to grow, and there were multiple reflection peaks, while the refractive index began to drop. In the 23~42 eV energy region, the reflectivity starts to change opposite the refractive index. The reflectivity and refractive index of Eu and Yb doped with Cu₃N are similar to the spectral line trend of Cu₃NLa but are more shifted to the region with high energy.

IV. CONCLUSION

The elastic, optical, structural, and electrical properties of Cu₃N with an anti-ReO₃ structure and doped with the rare earth metals La, Eu, and Yb are estimated in this study using the whole potential linear augmented plane wave method. According to the research results, the value of the lattice constant for Cu₃N is 3.834 Å. When rare earth elements are doped, the lattice constant of Cu₃N increases to 4.299 Å (Cu₃NLa), 4.228 Å (Cu₃NEu) and 4.212 Å (Cu₃NTb), respectively. The charge density distribution results show that the rare earth metal is successfully doped into the body center vacancy of Cu₃N. The band structure and density of states indicate that Cu₃N undergoes a transition from being an indirect band gap semiconductor to a conductor upon rare earth metal doping. The rare earth metal is hybridized with the Cu-3d orbital, thus weakening the covalent interaction between Cu and N. The elastic results show that Cu₃N is mechanically stable before and after doping. The analysis of optical properties shows that when rare earth elements are doped, the spectral lines of optical spectra, such as absorption spectra have an apparent blue shift, indicating that Cu₃N can be used in ultraviolet detectors and other fields after doping rare earth elements.

REFERENCES

- Sieberer M, Khmelevskyi S, Mohn P. Magnetic instability within the series TCu₃N (T= Pd, Rh, and Ru): A first-principles study[J]. *Physical Review B*, vol.74, no.1, pp 014416, 2006.
- [2] Juza R, Hahn H. Über die kristallstrukturen von Cu₃N, GaN und InN metallamide und metallnitride[J]. Zeitschrift für anorganische und allgemeine Chemie, vol.239, no.3, pp 282-287, 1938.
- [3] Kanoun-Bouayed N, Kanoun M, Goumri-Said S. Structural stability, elastic constants, bonding characteristics and thermal properties of zincblende, rocksalt and fluorite phases in copper nitrides: plane-wave pseudo-potential ab initio calculations[J]. *Open Physics*, vol.9, no.1, pp 205-212, 2011.
- [4] Asano M, Umeda K, Tasaki A. Cu₃N thin film for a new light recording media[J]. *Japanese Journal of Applied Physics*, vol.29, no.10R, pp 1985, 1990.

- [5] Nosaka T, Yoshitake M, Okamoto A, et al. Thermal decomposition of copper nitride thin films and dots formation by electron beam writing[J]. *Applied Surface Science*, vol.169, pp 358-361, 2001.
- [6] Li Shina, Liu Yong. First-principles study on elastic and thermodynamic properties of Cu₃N [J]. *Journal of Physics*, vol.59, no.10, pp 6882-6888, 2010.
- [7] Maruyama T, Morishita T. Copper nitride and tin nitride thin films for write - once optical recording media[J]. *Applied Physics Letters*, vol.69, no.7, pp 890-89, 1996.
- [8] Pereira N, Dupont L, Tarascon J M, et al. Electrochemistry of Cu₃N with lithium: A complex system with parallel processes[J]. *Journal of the Electrochemical Society*, vol.150, no.9, pp A1273, 2003.
- [9] Yang J, Huang S, Wang Z, et al. Synthesis of copper nitride films doped with Fe, Co, or Ni by reactive magnetron sputtering[J]. *Journal* of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, vol.32, no.5, pp 051510, 2014.
- [10] Bocharov D, Anspoks A, Timoshenko J, et al. Interpretation of the Cu K-edge EXAFS spectra of Cu₃N using ab initio molecular dynamics[J]. *Radiation Physics and Chemistry*, vol.175, pp 108100, 2020.
- [11] Li S, Hao J, Yu S. Mechanical properties of cubic Cu₃N and Cu₄N: A theoretical investigation[J]. Vacuum, vol.191,pp 110366, 2021.
- [12] Wu Z, Chen H, Gao N, et al. Ab initio calculations of the structural, elastic, electronic and optical properties of Cu3N as well as Cu₃NLa and Cu₃NCe compounds[J]. *Computational materials science*, vol.95, pp 221-227, 2014.
- [13] Kuzmin A, Anspoks A, Kalinko A, et al. Origin of Pressure-Induced Metallization in Cu₃N: An X-ray Absorption Spectroscopy Study[J]. *Physica status solidi* (b), vol.255, no.11,pp 1800073, 2018.
- [14] Wu Z, Chen H, Gao N, et al. Ab initio calculations of the structural, elastic, electronic and optical properties of Cu₃NM compounds doped with M= Sc, Y and La[J]. *Solid State Communications*, vol.201,pp 9-14, 2015.
- [15] Zervos M, Othonos A, Pavloudis T, et al. Impact of Oxygen on the Properties of Cu₃N and Cu₃-x N1-x O x[J]. *The Journal of Physical Chemistry C*, vol.125, no.7, pp 3680-3688, 2021.
- [16] Birch F. Finite elastic strain of cubic crystals[J]. *Physical review*, vol.71, no.11, pp 809, 1947.
- [17] Sahoo G. Manipulating elastic and mechanical properties of Cu₃N through site selective Ag doping: First principles investigation[J]. *Materials Today Communications*, vol.29, pp 102950, 2021.
- [18] Blucher J, Bang K, Giessen B C. Preparation of the metastable interstitial copper nitride, Cu₄N, by dc plasma ion nitriding[J]. *Materials Science and Engineering: A*, vol.117, pp L1-L3, 1989.
- [19] Pinkas J, Huffman J C, Baxter D V, et al. Mechanistic Role of H₂O and the Ligand in the Chemical Vapor Deposition of Cu, Cu₂O, CuO, and Cu₃N from Bis (1, 1, 1, 5, 5, 5-hexafluoropentane-2, 4-dionato) copper (II)[J]. Chemistry of materials, vol.7, no.8, pp 1589-1596, 1995.
- [20] Mukhopadhyay A K, Momin M A, Roy A, et al. Optical and Electronic Structural Properties of Cu₃N Thin Films: A First-Principles Study (LDA+ U)[J]. ACS omega, vol.5, no.49,pp 31918-31924, 2020.
- [21] Hahn U, Weber W. Electronic structure and chemical-bonding mechanism of Cu₃N, Cu₃NPd, and related Cu (I) compounds[J]. *Physical Review B*, vol.53, no.19, pp 12684, 1996.
- [22] Pierson J F. Structure and properties of copper nitride films formed by reactive magnetron sputtering[J]. *Vacuum*, vol.66, no.1, pp 59-64, 2002.
- [23] Hill R. The elastic behaviour of a crystalline aggregate[J]. Proceedings of the Physical Society. Section A, vol.65, no.5, pp 349, 1952.
- [24] Yoo M H. On the theory of anomalous yield behavior of Ni/sub 3/Al-Effect of elastic anisotropy[J]. Scr. Metall.;(United States), vol.20, no.6, 1986.
- [25] Sharma S, Ambrosch-Draxl C, Khan M A, et al. Optical properties and band structure of 2 H– WSe 2[J]. *Physical Review B*, vol.60, no.12, pp 8610, 1999.