

Article

First-Principles Calculation of Mechanical Properties and Thermal Conductivity of C-Doped AlN

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Abstract

Due to its good thermal conductivity and small thermal expansion coefficient, aluminum nitride (AlN) is an excellent material for thermal shock resistance. Recently, carbon (C) doping has emerged as a potential strategy for tailoring the properties of AlN, but its effects on the mechanical properties and thermal conductivity of AlN remain unclear. In the present study, the mechanical properties and thermal conductivity of C-doped AlN (C@AlN) with various C-doping densities were investigated using first-principles calculations based on density functional theory. The results suggest that C doping often leads to an increase in the *c* lattice constant. When the C-doping concentration reaches 12.5%, the structural symmetry of 4C@AlN is fully broken. In addition, as the C-doping density increases, the strength and stiffness of C@AlN generally decrease while the ductility increases. Moreover, the thermal conductivity of C@AlN generally decreases as the C-doping density increases, mainly because of the structural distortion. Meanwhile, as the C-doping density reaches 12.5%, the thermal conductivity of 4C@AlN anomalously increases, due to the symmetry breakage.

Keywords: C-doped AlN; thermal conductivity; first-principles calculation; mechanical properties



Academic Editor: Dawei Wang

Received: 13 July 2025

Revised: 15 September 2025

Accepted: 17 September 2025

Published: 19 September 2025

Citation: Shao, H.; Wang, Y.; Song, J.; Lei, L.; Liu, X.; Hou, X.; Zhang, J. First-Principles Calculation of Mechanical Properties and Thermal Conductivity of C-Doped AlN. *Ceramics* **2025**, *8*, 117. <https://doi.org/10.3390/ceramics8030117>

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1. Introduction

The rapid advancement of electronic information technology demands a new generation of power electronic devices. Aluminum nitride (AlN), a representative ceramic material, exhibits outstanding physical and chemical properties, including high thermal conductivity, non-toxicity, corrosion resistance, high-temperature stability, an ultra-wide bandgap (~6.2 eV) [1], and excellent thermochemical stability. Consequently, it has been widely employed as an ideal packaging material, heat dissipation substrate, circuit component, and interconnect carrier in large-scale integrated circuits, semiconductor modules, and high-power devices [1–4]. Furthermore, AlN serves as a key additive for enhancing the thermal and mechanical properties of polymer composites [5–7]. At room temperature (300 K), the theoretical thermal conductivity of single-crystal AlN can reach 319 W·m^{−1}·K^{−1}, while commercially available polycrystalline AlN ceramic substrates typically exhibit thermal conductivities between 150 and 180 W·m^{−1}·K^{−1}, significantly lower

than the theoretical value. Thus, enhancing the thermal conductivity of polycrystalline AlN remains crucial for practical applications [8].

Multiple factors influence the thermal conductivity of AlN ceramics, including material purity, intrinsic defects (e.g., dislocations, vacancies, impurities, and lattice distortions), grain orientation, and sintering conditions [9–11]. Doping represents a common strategy for microstructural tuning for modifying AlN's properties. Recent experimental studies indicate that carbon (C) doping can effectively substitute nitrogen sites within the AlN lattice [12], involving both p-type and n-type substitutions. For instance, Lee et al. [13] used AlN powder with varying oxygen contents, doped 0.5 weight percent of C powder, sintering at 1820 °C under atmospheric pressure, and reported a notable improvement in thermal conductivity, attributing the enhancement to thermodynamic and kinetic mechanisms. In contrast, Peng et al. [14] observed that introducing Si₃N₄ into AlN reduced its thermal conductivity by approximately 50% at a doping level of 3%. Similarly, using density functional perturbation theory (DFPT) and Debye modeling, Cai et al. [15] demonstrated that Cu doping drastically reduces thermal conductivity, with values dropping to 75 W·m^{−1}·K^{−1} at 1% doping and 300 K. Zhang and Hou [16] constructed a 3 × 3 × 2 supercell model of wurtzite AlN and concluded that all defect types reduce lattice thermal conductivity, with oxygen impurities and aluminum vacancies having the most pronounced effect, followed by carbon or silicon impurities.

Doping also significantly affects mechanical properties. Jia et al. [17] performed density functional theory (DFT) calculations on La-doped AlN and reported reductions of 12% in bulk modulus (*B*) and 14% in Young's modulus (*E*). Elhamra et al. [18] studied Fe-doped AlN (Al_{0.75}Fe_{0.25}N) and found decreases of 20% in shear modulus (*G*), 16% in *E*, and 35% in Vickers hardness (*H_v*). Su et al. [19] reported that C doping reduced the bulk modulus by 8% in AlN, and C-Na co-doping further intensified lattice distortion, leading to an additional reduction in *E*. Qi et al. [20] experimentally measured the elastic constants of Sc_xAl_{1-x}N films and noted a 39% decrease in *C*₃₃ when Sc doping exceeded 20%, indicating substantial degradation in mechanical performance.

In summary, carbon doping influences both the thermal and mechanical properties of AlN. Table 1 summarizes the recent literature about AlN for clarity. However, the effect of C-doping concentration on these properties remains insufficiently understood. Therefore, this study employs first-principles calculations based on DFT to systematically evaluate the mechanical properties and thermal conductivity of C-doped AlN (C@AlN) across various doping concentrations. The results indicate that an increasing C-doping concentration generally reduces strength and stiffness but enhances ductility. In addition, doping foreign elements into AlN may enhance its ductility; it thus can be employed in applications requiring good ductility, such as thermal cycling and impact resistance [21]. Notably, a doping concentration of 6.25% induces a transition from isotropic to anisotropic mechanical behavior. Moreover, while thermal conductivity generally decreases with increased doping, an anomalous increase occurs at 12.5% doping, attributed to symmetry breaking. These insights may guide the application of AlN in contexts requiring tailored thermomechanical properties.

Table 1. Summary of recent studies on doped AlN systems.

Material	Doping Type	Method	Key Findings	Ref.
AlN	/	Experimental	Thermal conductivity: 150–180 W·m ^{−1} ·K ^{−1} (polycrystalline)	[8]
AlN-C	C (0.5%)	Experimental	Thermal conductivity increased	[13]
AlN-Si ₃ N ₄	Si ₃ N ₄ (3%)	Experimental	Thermal conductivity reduced by ~50%	[14]
AlN-Cu	Cu (1%)	DFPT/Debye	Thermal conductivity: 75 W·m ^{−1} ·K ^{−1} at 300 K	[15]
AlN-(O,C,Vac)	Point defects	DFT	O impurities and Al vacancies most detrimental to κ	[16]
AlN-La	La	DFT	B decreased by 12%, E by 14%	[17]
Al _{0.75} Fe _{0.25} N	Fe	DFT	G decreased by 20%, E by 16%, H_v by 35%	[18]
AlN-C/Na	C, C-Na	DFT	B decreased by 8%; co-doping further reduced E	[19]
Sc _x Al _{1-x} N	Sc (>20%)	Experimental	C_{33} decreased by 39%	[20]

2. Calculation Method

2.1. Theoretical Model

AlN exhibits a hexagonal wurtzite structure with a space group of P6₃mc and a point group of C6v [1–3]. There are four atoms in the AlN unit cell, which is composed of a hexagonal close-packed structural sub-lattice of Al and N that is translated along the *c*-axis. Due to the large computational cost of disorder defects in large periodic supercells, we expanded the unit cell into a supercell of 2 × 2 × 2 with a total of 32 atoms. Then, we selected one, two, or four N sites to be replaced by C atoms in the doping structure. For simplicity, we mainly focus on simple periodic C-doped AlN models to illustrate the effect of C doping on the properties of AlN. C-doped AlN with random doping positions will be considered in our future work. Although this simplification may lead to a nonrandom structure in the *c*-axis or other special circumstances, we think that the results still include the common characters. Figure 1 provides the structures of AlN (Figure 1a) and C@AlN with various C-doping densities, i.e., 1C@AlN (Figure 1b), 2C@AlN (Figure 1c), and 4C@AlN (Figure 1d). It should be noted that, to demonstrate the C doping's effect on the properties of AlN, the computational models are ideal models due to their limited model size, which may differ from experiments.

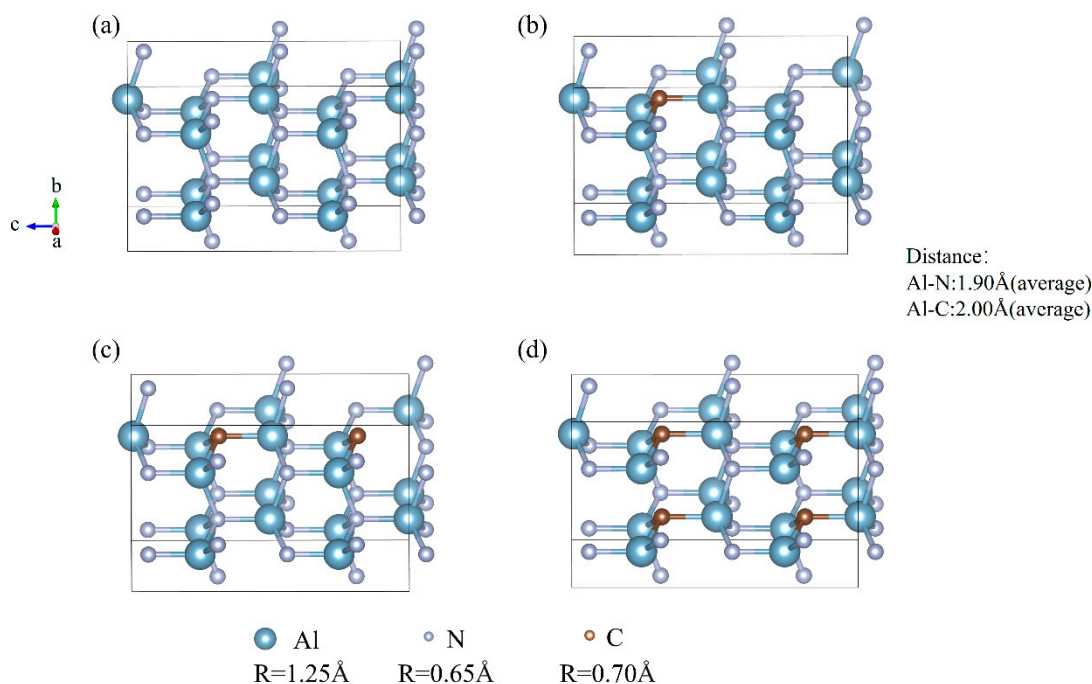


Figure 1. (a) AlN, (b) 1C@AlN, (c) 2C@AlN, and (d) 4C@AlN cell structures. The atomic radius of aluminum (Al) is 1.25 Å, the atomic radius of nitrogen (N) is 0.65 Å, and the atomic radius of carbon (C) is 0.70 Å. The average bond length between Al and N is 1.90 Å, while the average bond length between Al and C is 2.00 Å.

2.2. Calculation Parameters

This study utilized VASP (Vienna ab initio simulation package) software [22], based on DFT [23] combined with the projected augmented wave (PAW) method [24], to simulate these systems. The general gradient approximation (GGA) [25] was used to describe the exchange correlation potential between electrons, and the PBE (Perdew–Burke–Ernzerhof) functional [26] was employed for processing. Here, we employed the GGA exchange–correlation functional in all the DFT simulations rather than hybrid functionals, due to its much lower computational costs and relatively high accuracy [27–29]. The valence electron configurations of atoms in AlN and C@AlN systems are Al $3s^2 3p^1$, N $2s^2 2p^3$, and C $2s^2 2p^2$. The plane wave cutoff energy was 520 eV, and a $2 \times 2 \times 1$ Monkhorst–Pack-type K-point grid was selected for the integral calculation of the Brillouin zone. In the present study, we did not consider spin polarizations in the DFT simulations, because AlN and C-doped AlN do not exhibit magnetic properties. Here, C-doped AlN structures are considered as insulators or semiconductors rather than metals, so we set ISMEAR to 0 and SIGMA to 0.05, which means that we employed the Gaussian smearing method with a width of 0.05 eV to account for electron partial occupancies. Structural optimization and property calculations set a cutoff standard for ion relaxation where the force between ions was less than $2 \times 10^{-2} \text{ eV} \cdot \text{Å}^{-1}$ with an energy difference less than $1 \times 10^{-8} \text{ eV}$. We employed periodic boundary conditions in all the simulations. In addition, we introduced the Born–Oppenheimer approximation [30] to separately address the motions of electrons and nuclei in a material system in all the DFT simulations.

The lattice vibration and phonon properties of these systems were calculated using PHONOPY software [31], which utilizes first-principles calculation software (such as VASP and Quantum ESPRESSO) to calculate the phonon dispersion relationship and phonon density state of the material based on the atomic force constant matrix and atomic position information obtained. The lattice thermal conductivity was calculated by solving the phonon Boltzmann transport equation using the ShengBTE code [32]. This code is

completely parameter-free and based only on the information of the chemical structure. In this code, the lattice thermal conductivity κ can be obtained as [33]

$$\kappa^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0(f_0 + 1) (\hbar \omega_{\lambda})^2 v_{\lambda}^{\alpha} F_{\lambda}^{\beta} \quad (1)$$

In Equation (1), k_B is the Boltzmann constant, T is the temperature, Ω is the volume of the unit cell, $N = N_1 \times N_2 \times N_3$ is the number of $\mathbf{q}$ grids, λ comprises both a phonon branch index p and a wave vector $\mathbf{q}$, and ω_{λ} and v_{λ} are the angular frequency and group velocity of the phonon mode, respectively. At thermal equilibrium, in the absence of a temperature gradient or other thermodynamic forces, phonons are distributed according to Bose–Einstein statistics f_0 . And $f_0 = \frac{1}{e^{\hbar \omega_{\lambda}/k_B T} - 1}$, where the Bose–Einstein factor f_0 is always calculated using the phonon mode energy ω_{λ} as the independent variable. F_{λ} is a vector that represents the ‘effective transport quantity’ of the phonon mode λ . It is often used for calculating heat flow and thermal conductivity, which is defined as $F_{\lambda} = \tau_0^{\lambda} (v_{\lambda} + \Delta_{\lambda})$. τ_0^{λ} is the relaxation time, which refers to the time required for the phonon mode λ to return to an equilibrium state under the condition of an approximate relaxation time (RTA), and Δ_{λ} is a vector correction term representing the contribution of the RTA.

The individual software versions used in the calculation process are as follows: VASP version 5.4.4, PHONOPY version 2.17.1, and ShengBTE version 1.1.1. The calculation were performed using MPI parallelism, the CPU was a $2 \times$ Intel® Xeon® Processor E5-2687W v4, with a total of 24 cores and 48 threads, the memory capacity was 256 GB, and the total computing time was about a month.

3. Results and Discussion

3.1. Geometry Optimization

Before performing any property calculations, the structures of the AlN, 1C@AlN, 2C@AlN, and 4C@AlN systems were optimized. As shown in Table 2, C doping may cause structural distortion. Critically, increasing the C-doping concentration often leads to a progressive elongation of the unit cell along the c -axis direction, resulting in a significantly larger c -direction lattice constant. This expansion is also accompanied by a slight compression in the a - and b -axis directions. In addition, it is evident that, when the C-doping density reaches 12.5%, the a and b lattice parameters are unequal, suggesting large structural distortion and thus the breakage of symmetry. Moreover, the overall unit cell volume increases in all doped systems, mainly due to the increased c lattice constant.

Table 2. The unit cell parameters of AlN, 1C@AlN, 2C@AlN, and 4C@AlN.

System	C-Doping Concentration	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
AlN	0	6.257	6.257	10.030	340.092
AlN(Exp) [34]	0	6.220	6.220	9.960	333.711
1C@AlN	3.125%	6.257	6.257	10.032	340.172
2C@AlN	6.25%	6.257	6.257	10.222	346.598
4C@AlN	12.5%	6.260	6.121	10.365	351.357

Exp = experimental data.

3.2. Structural Stability

Then, to evaluate the structural stability of AlN and C@AlN, we calculated the phonon dispersion relations for these systems. The relevant phonon spectra are shown in Figure 2.

In the present study, the model for calculating the phonon spectrum of pure AlN is a $2 \times 2 \times 2$ supercell. The phonon spectrum appears to have only 12 lines due to degeneracy. Although the number of atoms in the AlN supercell is large, it still maintains a high degree of symmetry consistent with the AlN unit cell, resulting in many vibrational modes being degenerate in both energy (frequency) and momentum [35]. Consequently, some bands in the phonon spectrum overlap, making it appear as if there are only 12 bands. This is consistent with previous studies [35]. However, after doping C into AlN, the crystal symmetry of the AlN supercell is disrupted, and the originally degenerate vibrational modes are split, resulting in a significant increase in the number of bands in the phonon spectrum.

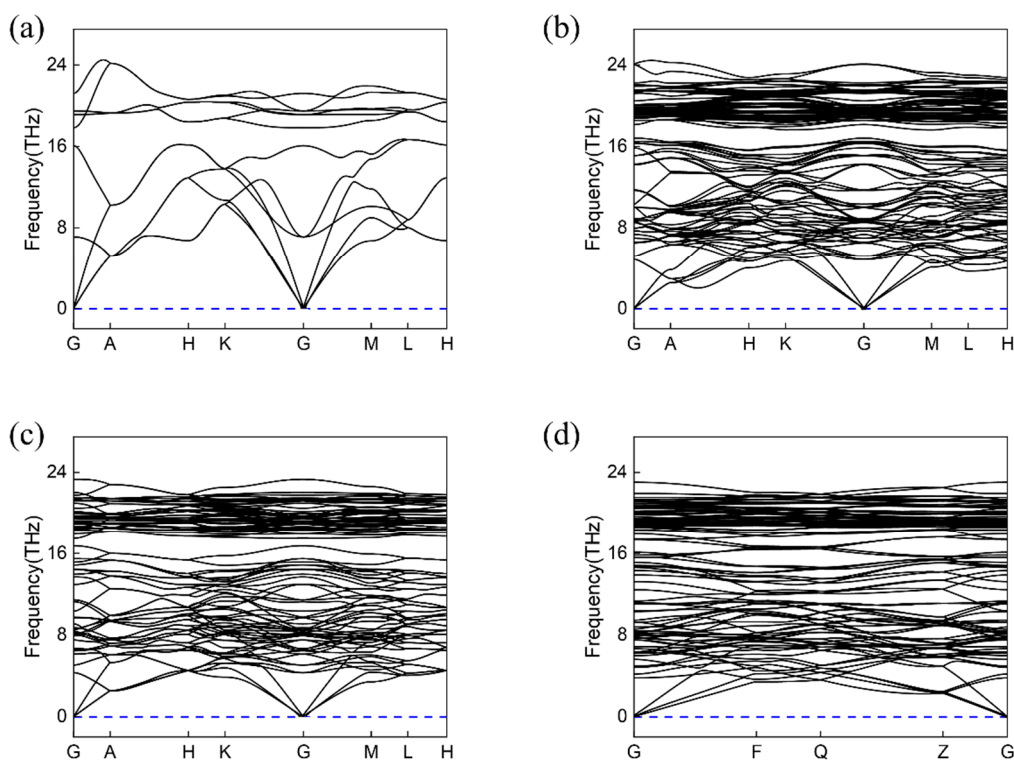


Figure 2. Phonon spectra of (a) AlN, (b) 1C@AlN, (c) 2C@AlN, and (d) 4C@AlN. There are no imaginary frequencies, demonstrating good dynamic stability in these systems.

In addition, the phonon spectrum is primarily used to assess structural stability here. The results suggest that their phonon spectra show no imaginary frequencies at the origin, indicating that structure optimization was achieved. Moreover, there are also no imaginary frequencies at other positions, demonstrating good dynamic stability in these systems. The vibration of the center of mass of the unit cell is reflected by the acoustic branch, whereas the relative vibration of particles in the unit cell is reflected by the optical branch. The phonon mean free path is a key factor affecting the lattice thermal conductivity. As the phonons in AlN have a long mean free path, the associated thermal conductivity is relatively high. The phonon spectra in Figure 2b–d are not as well resolved as the spectrum in Figure 2a. This may be due to the cell expansion-induced overlap of some phonon spectral curves. The symmetry is greatly reduced upon incorporating C elements, with a decrease in the structural degree of freedom, resulting in a markedly increased number of spectral curves. Particularly, the severe structural distortion of the 4C@AlN collapses the degenerate phonon branches (Figure 2d), altering the phonon dispersion and phase space for Umklapp scattering [36]. In 4C@AlN, the flattened acoustic branches near the G point (Figure 2d) may enhance phonon group velocities in specific directions, partially offsetting

scattering losses [37]. These features suggest that the thermal conductivity of AlN may be affected through C doping, which will be discussed in future studies.

3.3. Mechanical Properties

To examine the effect of C-doping density on the mechanical properties of AlN, we then calculated the elastic constants of AlN and C@AlN, as shown in Table 3. The results suggest that, as the C-doping density increases, the general trend of C_{11} , C_{44} , and C_{66} decreases, while C_{33} remains constant, except for 4C@AlN. Particularly, the C_{33} of 4C@AlN decreases by ~20%. This is mainly attributed to symmetry breaking-induced lattice distortions. Due to the crystal symmetry, atomic arrangement, and covalent bonding directionality, pure AlN generally exhibits anisotropic mechanical properties.

Table 3. The elastic constants of AlN, 1C@AlN, 2C@AlN, and 4C@AlN.

System	C-Doping Concentration	C_{11} /GPa	C_{12} /GPa	C_{13} /GPa	C_{33} /GPa	C_{44} /GPa	C_{66} /GPa
AlN	0	382	133	107	344	116	124
AlN(Exp) [38]	0	400	138	98	378	120	/
1C@AlN	3.125%	339	157	108	344	99	91
2C@AlN	6.25%	281	197	107	348	87	42
4C@AlN	12.5%	241	140	184	273	86	97

Exp = experimental data.

Additionally, the structural stability of all configurations was verified using the Born stability criteria, as defined by the following equations [39]:

$$C_{11} > |C_{12}| \quad (2)$$

$$2C_{13}^2 < C_{33}(C_{11} + C_{12}) \quad (3)$$

$$C_{44} > 0; C_{66} > 0 \quad (4)$$

This confirms that all configurations satisfy the Born stability criteria, indicating that these structures are mechanically stable. Next, the polycrystalline bulk modulus (B) and shear modulus (G) for these systems were computed using the Voigt model (Equations (5) and (6)) and the Reuss model (Equations (7) and (8)), respectively [40].

$$B_v = \frac{C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{23} + C_{31})}{9} \quad (5)$$

$$G_v = \frac{C_{11} + C_{22} + C_{33} - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66})}{15} \quad (6)$$

$$B_R = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{31})} \quad (7)$$

$$G_R = \frac{1}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66})} \quad (8)$$

where $[S_{ij}]$ denotes the inverse matrix of $[C_{ij}]$, specifically the compliance matrix.

To mitigate uncertainty, the bulk modulus (B) and shear modulus (G) values calculated via the Voigt and Reuss models were averaged prior to subsequent calculations. And the Young's modulus (E) and Poisson's ratio (ν) were derived using the following expressions:

$$E = \frac{27GB}{9B + 3G} \quad (9)$$

$$\nu = \frac{1}{2} \left[1 - \frac{3G}{3B + G} \right] \quad (10)$$

Moreover, we also employed Pugh's ratio (B/G) to quantify material toughness. The Vickers hardness (H_v) and anisotropy index (A^U) can also be calculated using the following expressions:

$$H_v = 0.151G \quad (11)$$

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \quad (12)$$

The mechanical properties of AlN and 4C@AlN are summarized in Table 4. The bulk modulus (B), shear modulus (G), Young's modulus (E), and hardness (H_v) generally decrease as C-doping density increases, suggesting that doping C atoms into AlN may decrease its strength and stiffness. Meanwhile, we found that the Pugh's ratio (B/G) exceeds the threshold of 1.75 after doping, implying a brittle-to-ductile transition in material behavior.

Table 4. The mechanical properties of AlN, 1C@AlN, 2C@AlN, and 4C@AlN.

System	C-Doping Concentration	B/GPa	G/GPa	E/GPa	B/G	ν	H_v/GPa	A^U
AlN	0	199.7	122.0	304.0	1.638	0.246	18.417	0.021
1C@AlN	3.125%	195.8	100.4	257.3	1.950	0.281	15.164	0.079
2C@AlN	6.25%	192.5	69.9	187.1	2.752	0.338	10.559	1.057
4C@AlN	12.5%	188.2	70.8	188.8	2.657	0.333	10.698	1.180

In addition, we also selected 2C@AlN as an example to examine the effect of C-doping positions on the properties. As shown in Figure 3, we constructed four 2C@AlN models with different C-doping positions. Their structural and mechanical properties were then calculated, as shown in Table 5. The results suggest that structures with more randomly distributed doping positions (Figure 3b–d) exhibit lower elastic moduli and less pronounced anisotropy than the highly ordered structures (Figure 3a). This indicates that periodic ordered doping may lead to a larger elastic modulus of the AlN structure. However, for simplicity, we considered the periodic structure of C-doped AlN with various C-doping concentrations in the present study. In future work, we will perform systematic theoretical studies to illustrate the effect of random C-doping positions on the properties of AlN.

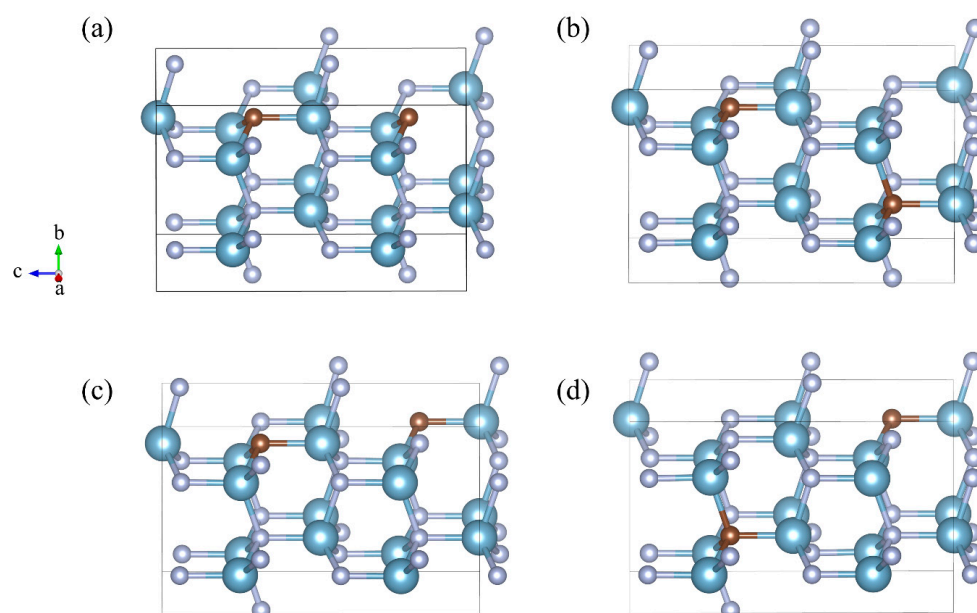


Figure 3. Four 2C@AlN models with different C-doping positions. (a) The structure in Figure 1c, (b–d) The structures with more random doping positions of C.

Table 5. Four 2C@AlN models' structural and mechanical properties.

Model	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$	B_H/GPa	G_H/GPa	E/GPa
(a)	6.257	6.257	10.222	346.598	192.4578	69.92453	187.1128
(b)	6.257	6.225	10.086	341.975	194.2918	58.83744	160.3282
(c)	6.257	6.257	10.075	341.611	194.8536	57.39972	156.8023
(d)	6.257	6.272	10.079	341.755	194.7237	57.3242	156.6051

To examine the elastic anisotropy of the material more clearly, the change in elastic modulus with crystal orientation can be represented by three-dimensional graphics. The change in Young's modulus with crystal orientation in the hexagonal crystal system is shown in Equation (13) [41].

$$\frac{1}{E} = (1 - l_3^2)^2 S_{11} + l_3^4 S_{33} + l_3^2 (1 - l_3^2) (2S_{13} + S_{44}) \quad (13)$$

where l_1 , l_2 , and l_3 denote the directional cosines, and $[S_{ij}]$ denotes the inverse matrix of $[C_{ij}]$. It should be noted that, when the shape of the Young's modulus tends to a sphere, the material generally exhibits isotropy. This is due to the fact that, in polycrystalline materials that are composed of some small grains with random orientations, each grain with a single-crystal structure may exhibit anisotropy at the microscale, but the overall polycrystalline material manifests isotropy at the macroscale. Equation (9) mainly describes the macroscopic Young's modulus of polycrystalline materials at the microscale. In contrast, Equation (13) describes how the Young's modulus of an anisotropic single crystal varies with the crystallographic direction. The Young's modulus calculated with Equation (9) is an average of the Young's modulus at the tensor level obtained from Equation (13), while taking into account two reasonable mechanical boundary conditions (Voigt and Reuss) [42]. Thus, Equation (9) calculates the volume average or mechanical average across all possible directions.

Doping always leads to anisotropy by altering the crystal symmetry, bonding, and electronic structure of the crystals [43,44]. In the present study, doping C into AlN can induce local strains due to different ionic radii, thereby lowering or even breaking crystal

symmetry. And doping C into AlN may change its charge distribution and electronic properties, which also induce significant anisotropy in C-doped AlN. In addition, the C-doped AlN structures with a more random distribution of C-doping sites often exhibit less pronounced anisotropy. However, for simplicity, we selected the periodic structure of C-doped AlN with various C-doping concentrations in the present study. In future work, we will perform systematic theoretical studies to illustrate the effect of random C-doping positions on the properties of AlN. We found that the anisotropy coefficient abruptly changed from almost 0 to 1.057 at 6.25 at% C doping, so we plotted a three-dimensional graph of the Young's modulus (E) and crystal orientation of the structure at 3.125 and 6.25 at% C-doping concentrations. Figure 4 reveals a quasi-spherical profile of the Young's modulus (E) directional dependence at 3.125 at% C doping, conforming to isotropic behavior. Conversely, at 6.25 at% doping, 3C@AlN exhibits an elongated ellipsoidal distribution of E versus orientation (Figure 5), demonstrating pronounced elastic anisotropy. This mainly arises from the doping-induced structural distortion.

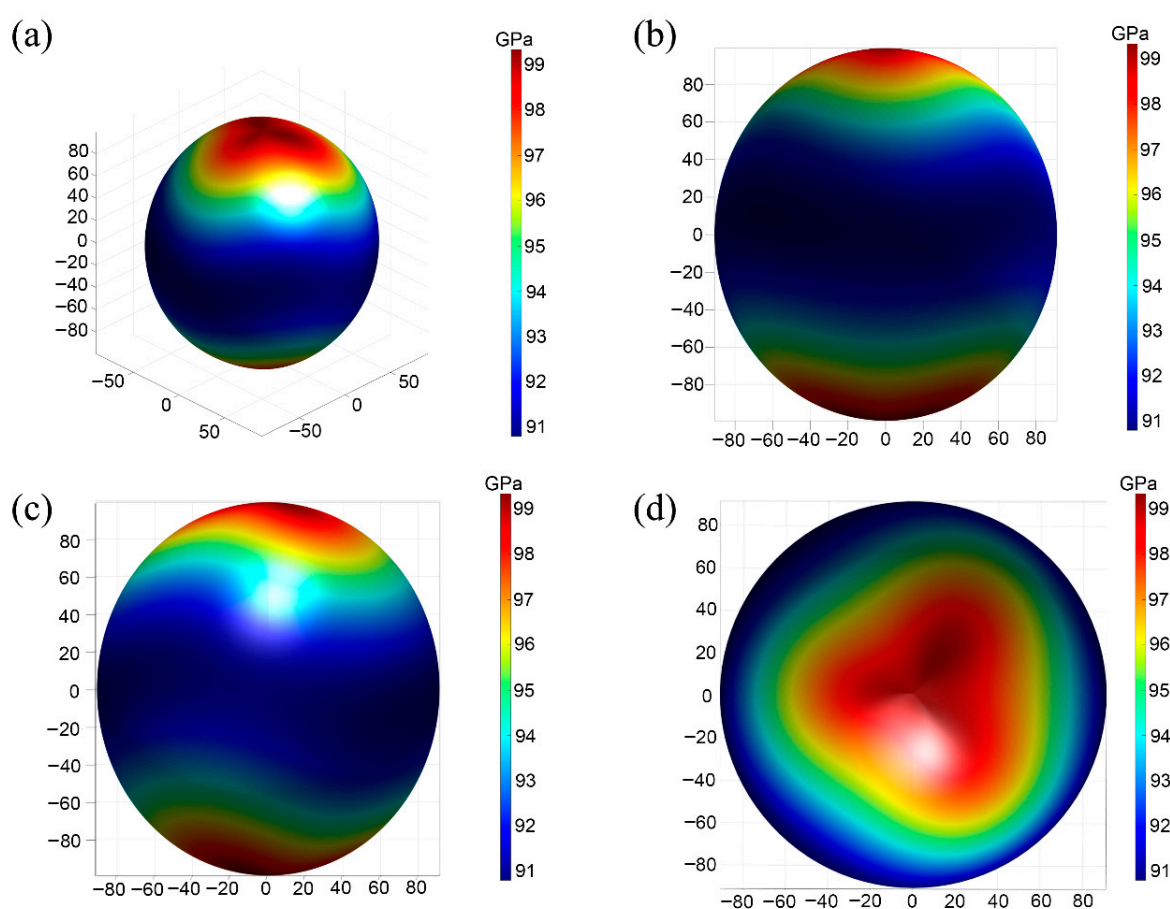


Figure 4. Directional dependence of Young's modulus (E) at 3.125 at% C-doping concentration: (a) overview; (b) XZ plane; (c) YZ plane; (d) XY plane. The change in Young's modulus with crystal orientation is close to a sphere, indicating approximate isotropy at a 3.125 at% C-doping concentration.

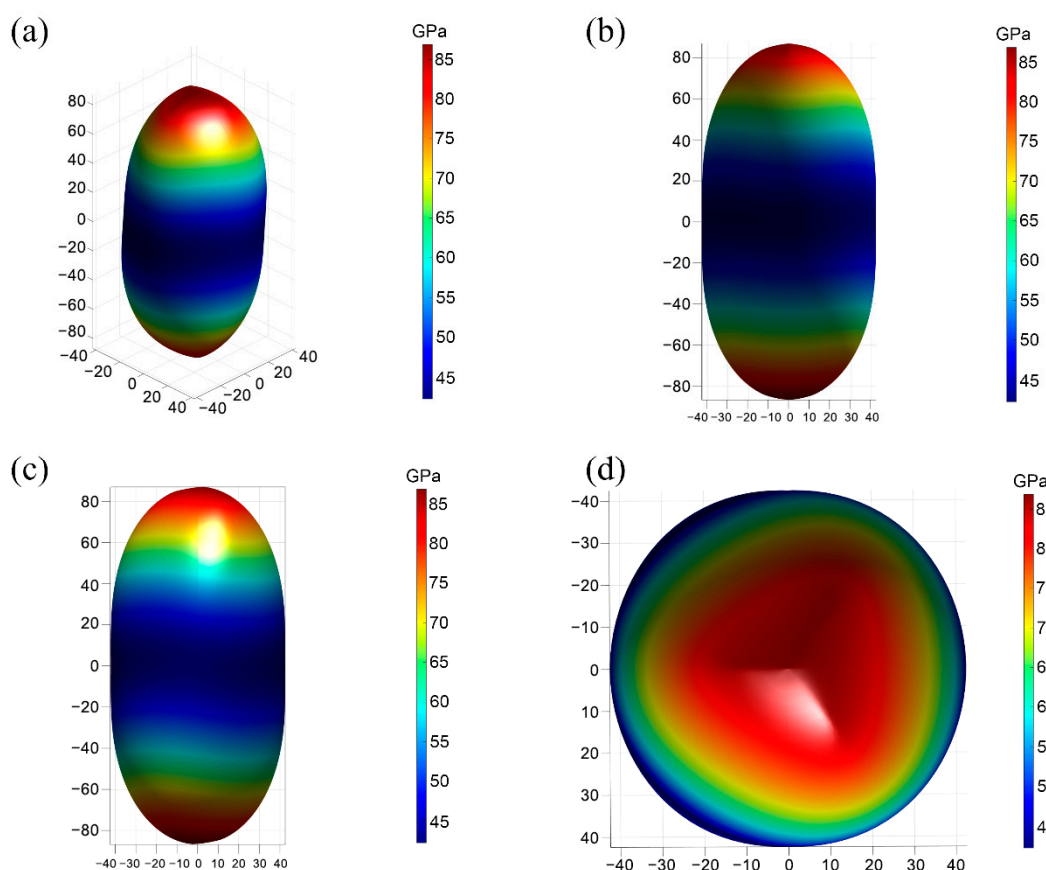


Figure 5. Directional dependence of Young's modulus (E) at 6.25 at% C-doping concentration: (a) overview; (b) XZ plane; (c) YZ plane; (d) XY plane. The change in Young's modulus with crystal orientation deviates from a sphere, indicating significant anisotropy at a 6.25 at% C-doping concentration.

3.4. Thermal Conductivity

The total thermal conductivity (κ_{total}) of a material is composed of electronic (κ_e) and lattice (κ_L) components. The lattice component (κ_L) is the main contributor to the κ_{total} of ceramic materials at lower temperatures [45,46]. The electronic component (κ_e), on the other hand, has a significant impact at higher temperatures and can be directly calculated using the Wiedemann–Franz law [31]. ShengBTE is an open-source computational software package for calculating the lattice thermal conductivity of crystalline materials by solving the phonon Boltzmann Transport Equation (BTE). The electron thermal conductivity is not considered in the ShengBTE software [33]. Therefore, we mainly focus on the lattice thermal conductivity of materials while ignoring the electron contributions in the present study. And the electron thermal conductivity of AlN and C-doped AlN will be examined in future work.

Here, the lattice thermal conductivity (κ_L) mentioned is closely related to phonon scattering. We utilized the ShengBTE code [47] to calculate the lattice thermal conductivity for these systems with temperatures ranging from 300 K to 1800 K using the second-order force constant matrix and Grüneisen parameters obtained from the PHONOPY software [48], based on the improved Debye–Callaway model. As shown in Figure 6, the thermal conductivity of the four systems decreases with increasing temperature, which may be attributed to the associated increase in phonon scattering. Each system shows an initial strong dependence on temperature with a decrease in the range 300–800 K and a subsequent lower decline with increasing temperature to reach a limiting value. As the temperatures increase above 800 K, the heat capacity, phonon velocity, and

mean free path are invariant, and the lattice thermal conductivity approaches a constant value [49]. In addition, we obtained a thermal conductivity of $212.04 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for pure AlN at room temperature (300 K), which is consistent with previous experimental results ($170\text{--}320 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [50].

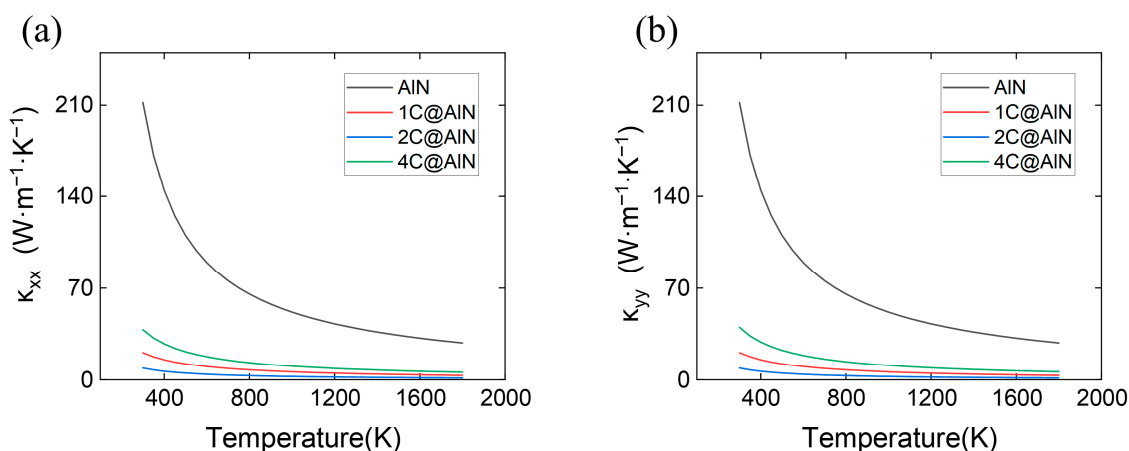


Figure 6. Temperature dependence of the AlN, 1C@AlN, 2C@AlN, and 4C@AlN lattice thermal conductivity in the (a) XX direction and (b) YY direction. It can be found that the thermal conductivity is always $\text{AlN} > 4\text{C@AlN} > 1\text{C@AlN} > 2\text{C@AlN}$.

Comparing the lattice thermal conductivities of AlN, 1C @ AlN, 2C@AlN, and 4C@AlN, it can be found that the order is always $\text{AlN} > 4\text{C@AlN} > 1\text{C@AlN} > 2\text{C@AlN}$. At room temperature (300 K), the thermal conductivity values of the four materials in the YY direction are $212.04 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (AlN) $> 40.164 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (4C@AlN) $> 20.9 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (1C@AlN) $> 8.9798 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (2C@AlN), while in the XX direction, the order is $212.04 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (AlN) $> 38.351 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (4C@AlN) $> 20.9 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (1C@AlN) $> 8.9798 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (2C@AlN). At 1800 K, the thermal conductivity values of the four in the YY direction are $28.315 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (AlN) $> 6.1264 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (4C@AlN) $> 3.3879 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (1C@AlN) $> 1.39058 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (2C@AlN), while in the XX direction, the values of κ_{xx} are $28.315 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (AlN) $> 5.7972 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (4C@AlN) $> 3.3879 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (1C@AlN) $> 1.39058 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (2C@AlN). It is evident that the general trend is that C doping drastically reduces the lattice thermal conductivity of the material system. In addition, the thermal conductivity of 4C@AlN is no longer equal in the XX and YY directions, mainly arising from the significant breakage of symmetry. Therefore, the abnormal increase in the lattice thermal conductivity of 4C-AlN is mainly attributed to the breakage of crystal symmetry. However, the thermal conductivity's variation with C-doping concentration is non-monotonic. As illustrated in Figure 7, a notable reversal in thermal conductivity trend is observed beyond a doping concentration of 12.5 at%. Specifically, the thermal conductivity increases anomalously from $8.978 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $40.164 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. This unexpected rise is likely attributed to symmetry breaking within the 4C@AlN configuration, which fundamentally alters phonon-scattering dynamics.

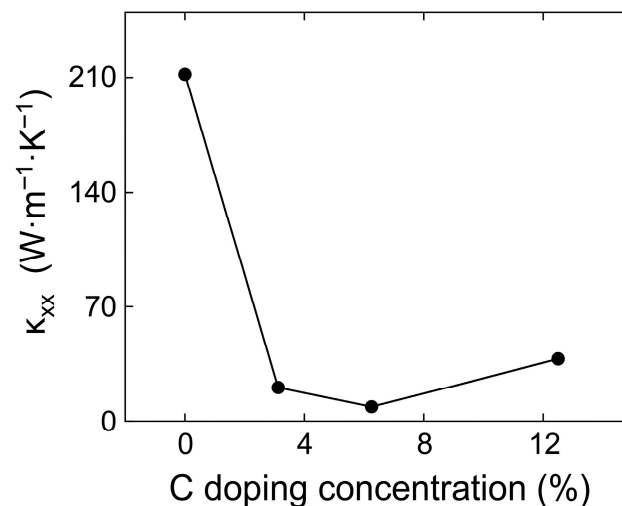


Figure 7. Evolution of thermal conductivity (κ_{xx}) with C-doping concentration at 300 K. As the C-doping concentration increases, the thermal conductivity generally decreases.

To further illustrate the drastic decrease in thermal conductivity in C-doped AlN, we analyzed the phonon lifetimes (the relaxation time τ_0^λ in Equation (1)) and group velocities of these structures. The contribution to the phonon lifetime consists of three parts, as shown in Equation (14) [51,52]:

$$\frac{1}{\tau_0^\lambda} = \frac{1}{\tau_{anh}^\lambda} + \frac{1}{\tau_{iso}^\lambda} + \frac{1}{\tau_B^\lambda} \quad (14)$$

where τ_{anh}^λ is the phonon lifetime due to the intrinsic anharmonic phonon–phonon scattering process, τ_{iso}^λ is the phonon lifetime due to the phonon–impurity scattering process, and τ_B^λ is the phonon lifetime due to the phonon–boundary scattering process.

Figures 8 and 9 show the group velocity and phonon lifetime of AlN and C-doped AlN. The results suggest that, as the C-doping concentration increases, the phonon lifetimes significantly decrease (Figure 9a) while the group velocities vary slightly (Figure 8). This indicates that the phonon lifetimes serve as an important factor for the drastic decline in thermal conductivity. Additionally, the intrinsic anharmonic phonon–phonon scattering process is the primary contributor to the total phonon lifetime. Meanwhile, the contributions from the phonon–impurity scattering process and the phonon–boundary scattering process are not significant.

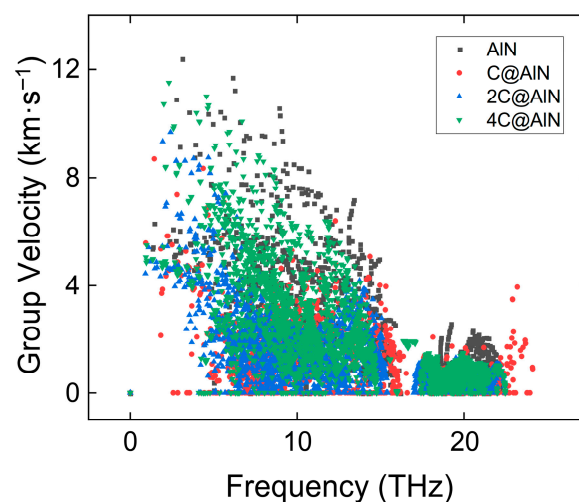


Figure 8. Group velocities of AlN and C@AlN structures. It can be found that the group velocities vary slightly after C doping.

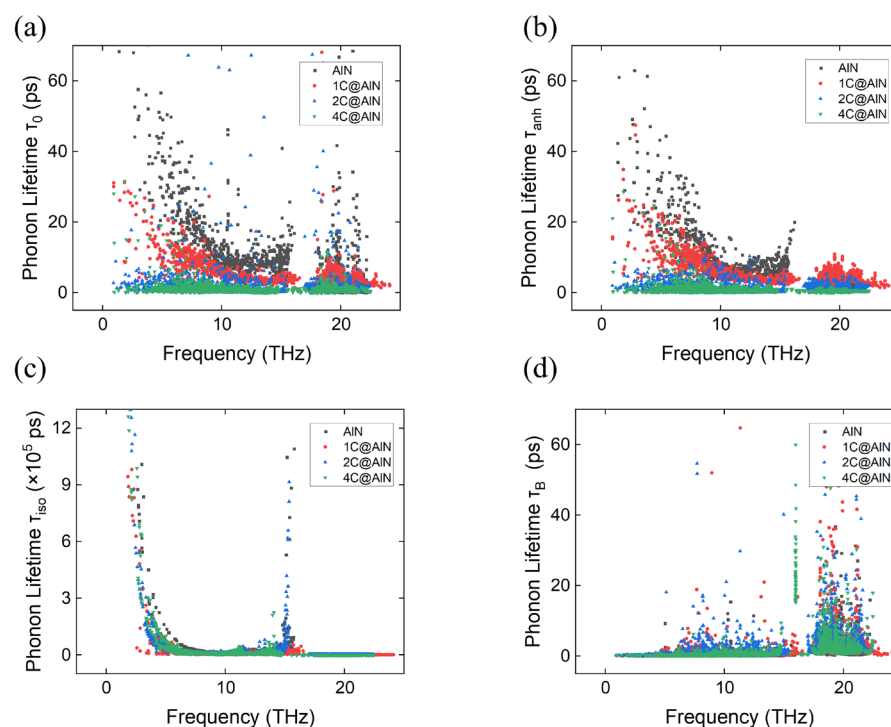


Figure 9. Phonon lifetimes (a) τ_0^λ , (b) τ_{anh}^λ , (c) τ_{iso}^λ , and (d) τ_B^λ of AlN and C@AlN structures. These results suggest that τ_{anh}^λ is the primary contributor to the phonon lifetimes.

3.5. Discussion

In the present study, we systematically explore the effect of C doping on the mechanical properties and thermal conductivity of AlN through first-principles calculations. First, the results suggest that, as the C-doping content increases, the elastic moduli (B , G , E) generally decrease (Table 3). This is consistent with previous studies about the La-doped AlN [17], in which a 12–14% decrease in B and E is observed due to lattice softening. In addition, C doping also decreases the stiffness of AlN, which may be attributed to the weak Al-C bonds. Notably, the brittle-to-ductile transition for all C-doped systems suggests that C doping is an effective strategy for increasing the ductility of AlN.

The general suppression of thermal conductivity at low-to-moderate C-doping (Figure 5) is consistent with phonon-scattering theories. Here, carbon dopants act as point defects that disrupt periodicity, scattering high-frequency phonons and reducing the mean free path. This aligns with Zhang and Hou's findings [16], where point defects (O, C, vacancies) generally degraded the lattice thermal conductivity in AlN. However, the lattice thermal conductivity with 12.5% doping (4C@AlN) unexpectedly increases, which may originate from symmetry-breaking-induced phonon engineering.

4. Conclusions

Using first-principles calculations based on DFT, the mechanical properties and thermal conductivity of C@AlN with various C-doping densities were examined and compared with those of AlN. The results suggest that C doping often leads to an increase in the c lattice constant, and particularly when the C-doping concentration reaches 12.5%, the symmetry is significantly broken, resulting in unequal lattice parameters along the a and b directions. Meanwhile, C doping can also cause a decrease in the strength and stiffness of the structure, while there is an increase in the ductility. And when the C-doping concentration reaches 6.25%, the material changes from isotropic to anisotropic. In addition, a decrease in the thermal conductivity of C@AlN is observed as the C-doping density increases, due to C-doping-induced structural distortion. Particularly, when the C-doping concentration is

12.5%, the thermal conductivity of 4C@AlN anomalously increases, due to the destruction of the symmetry. In future work, we will consider the doping effect of other elements, such as O, on the mechanical and thermal properties of AlN, which may provide significant guidance for the application of AlN.

Author Contributions: Writing—original draft preparation: H.S. and Y.W.; Writing—review and editing: J.S.; Formal analysis: L.L.; Software: X.L.; Methodology: X.H.; Supervision: J.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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