

Artificial intelligence-assisted tuning dielectric property of two-dimensional hexagonal boron nitride via doping

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ABSTRACT

Hexagonal boron nitride (h-BN) offers an atomically flat surface and excellent stability at the ultrathin limit as a van der Waals dielectric material. However, the doping design space for tuning its dielectric constant is inherently high-dimensional, involving multiple substitution sites, concentrations, and elemental species, which makes exhaustive first-principles calculations prohibitively costly. Here, we established an efficient research framework that integrates density functional theory (DFT) with machine learning (ML) to investigate the dielectric properties of doped h-BN. We constructed a dielectric property database containing 648 doping configurations for monolayer h-BN doped with different atoms (Fe, Co, Cu, Ti, Pd, Rh, Ag, Pt, Au, C, Si, Ge, Sn). The Atomistic Line Graph Neural Network (ALIGNN) was employed in this work to establish a direct mapping from atomic structures and local environments to the dielectric constant, yielding superior predictive performance. The binding-energy analysis shows that all examined dopants bind favorably to pre-existing B vacancies, with C@B exhibiting the strongest binding. It is revealed that h-BN co-doped with C-Si@2B shows significant dielectric enhancement, with its in-plane and out-of-plane two-dimensional (2D) polarizabilities reaching approximately 4.78 and 1.50 times the corresponding values of pristine h-BN, respectively. In contrast, 3Si@3B exhibits substantially lower 2D polarizabilities in both directions, resulting in a comparatively weak dielectric response. Our work further reveals that Born effective charges, phonon mode softening, and enhanced orbital hybridization collectively govern the dielectric properties. The ALIGNN-based doping research method proposed in this work provides theoretical insights into the modulation of the dielectric properties of h-BN and facilitates the prioritization of candidate structures within the high-dimensional doping design space.

1. Introduction

Van der Waals (vdW) two-dimensional (2D) materials offer ultimate thickness scaling, tunable electronic structures, and flexible hetero-integration [1–3], which help address lattice mismatch and interface defects encountered when conventional three-dimensional semiconductors are integrated with gate dielectrics [4–6]. They have become key materials for 2D semiconductor microchips. Dielectric materials that perform essential functions such as gate control and electrical isolation are indispensable in high-performance miniaturized devices [7]. Hexagonal boron nitride (h-BN) has attracted considerable research interest as a 2D material in recent years [8–10]. The crystal structure of h-BN consists of alternating B and N atoms that form an in-plane honeycomb

network, while vdW interactions bind the adjacent layers [11]. Compared with conventional dielectric materials (SiO₂, HfO₂, TiO₂, and Al₂O₃), h-BN has superior mechanical, thermal, and electrical insulation properties [12]. Specifically, it delivers an ultrahigh fracture strength of approximately 100 GPa, a high Young's modulus of approximately 0.8 TPa, excellent thermal stability in air up to 800 °C, a high thermal conductivity of 300–2000 W m⁻¹ K⁻¹, and notably low dielectric loss [13–15]. h-BN is also compatible with many 2D materials and can form high-quality heterostructures, making it suitable as an ultrathin dielectric in atomically scaled microchips [16–18]. The dielectric constant is a key parameter for evaluating dielectric performance [19]. Gate dielectrics generally require high-*k* materials to improve electrostatic control and reduce gate leakage current [20]. By contrast, interconnect

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insulating layers use low- k materials to minimize parasitic capacitance between adjacent metal lines and reduce resistance capacitance delay [21]. Recent studies have demonstrated a broad range of dielectric responses in 2D materials. For example, single-crystalline vdW layered Bi_2SeO_5 exhibits a high dielectric constant of approximately 16.5 [22], whereas fluorine-rich 2D polymer films exhibit ultralow in-plane and out-of-plane dielectric constants of 1.85 and 1.82, respectively [23]. Reported dielectric constants of h-BN are approximately 3–5, which limits its use as a 2D dielectric material [24]. This value falls between the ideal regimes for interconnect and gate dielectrics, being neither sufficiently low to minimize parasitic capacitance nor sufficiently high to provide strong gate coupling. Recent experiments have demonstrated that integrating h-BN with high- k HfO_2 enhances gate coupling and enables low-voltage optoelectronic doping in MoTe_2 transistors [25]. These advances highlight the importance of dielectric engineering in h-BN-based heterostructures and motivate the tunable control of the dielectric response and related electronic properties of h-BN to broaden its device applications.

Doping is a direct means of changing the local bonding, electronic states, and lattice vibrations of h-BN and can therefore improve its properties [26]. Asif et al. [27] found that P doping at a B site converted pristine h-BN from an insulator into a semiconductor, while substitution of B by F or Cl and substitution of N by O tuned the band gap of h-BN. Etou et al. [28] experimentally investigated C doping in BN films. They prepared BCN films at different temperatures by plasma-enhanced chemical vapor deposition (PECVD) and found that the dielectric constant could be reduced to 2.4. Other researchers have also examined interstitial doping with several elements [29–34], including Be, Mg, Zn, Si, F, S, C, and O. Direct introduction of these elements into interstitial sites of h-BN can tune its band gap and produce desirable electronic properties. These studies provide useful references for doping control of h-BN, but most focus on improving electrical or magnetic properties. Systematic investigation of its dielectric response is still lacking. In addition, current doping schemes are largely designed on the basis of experience and are often limited to specified elements and sites [35–38]. Within a high-dimensional design space involving different dopants, concentrations, and sites, both experiments and first-principles calculations have limitations in cost and efficiency [39].

Materials informatics provides a new route to this problem by using data-driven methods and machine learning (ML) to extract patterns and relationships from materials data [40,41]. ML can learn nonlinear mappings among composition, structure, and properties from existing computational or experimental data, thereby focusing expensive calculations on the most valuable candidate regions [42–44]. Conventional ML methods require manually engineered features describing composition and local structural environments [45,46]. Subsequent graph neural network (GNN) methods represent crystals directly through atoms and their adjacency relations and show good transferability across different prediction targets [47–49]. GNN models include the Crystal Graph Convolutional Neural Network (CGCNN), Materials Graph Network (MEGNet), Global Attention Graph Neural Network (GATGNN), Atomistic Line Graph Neural Network (ALIGNN), and Bond Dissociation Network (BondNet). ALIGNN introduces an atomistic line graph in addition to the atomistic graph, allowing message passing to include atomic species, interatomic distances, and bond-angle information [50]. It can therefore capture complex geometries and topological relations in atomic structures more accurately and is particularly suitable for representing local coordination distortions caused by doping [51].

In this work, we established a framework for doping design that integrates first-principles calculations with ML to predict the dielectric properties of doped h-BN. Different doping combinations were designed using metallic dopants (Fe, Co, Cu, Ti, Pd, Rh, Ag, Pt, and Au) and nonmetallic dopants (C, Si, Ge, and Sn). Binding energy was calculated to examine the binding of dopant atoms to pre-existing vacancies. All examined elements show negative binding energies for pre-existing B

vacancies, and doping systems involving two B vacancies exhibit stronger binding than those involving one B vacancy and one N vacancy. We then used density functional perturbation theory (DFPT) to construct a database of dielectric properties containing 648 relaxed h-BN structures with different doping configurations. An ALIGNN model was trained to learn the nonlinear relationship between local atomic structures and dielectric responses, achieving a test-set R^2 of 0.876. It also enabled visualization of atom-resolved representation intensities that highlight the local environments encoded by the model. Notably, among the doped configurations in the DFPT-calculated dataset constructed in this work, C-Si@2B emerges as a particularly promising high- k candidate, while 3Si@3B drives the dielectric constant to the ultralow value. To investigate the physical mechanisms governing the dielectric response of doped systems, we also calculated the Born effective charges and phonon modes of representative doped materials. The electronic contribution to the dielectric response was further analyzed through the band structures and density of states (DOS). These factors have pronounced effects on the regulation of polarizability. This study provides an efficient method for predicting dielectric candidates in doped h-BN and offers important guidance for optimizing its dielectric properties. The findings also provide a theoretical basis and technical support for doping studies of 2D dielectric materials.

2. Methods

2.1. First-principles calculations

The first-principles calculations based on density functional theory (DFT) in this work were performed using the Vienna *Ab initio* simulation package (VASP) [52]. The projector augmented wave (PAW) [53] pseudopotentials were adopted to describe electron-ion interactions, with the exchange-correlation functional treated at the Perdew-Burke-Ernzerhof (PBE) level of the generalized gradient approximation (GGA) [54]. The primitive cell of h-BN was used as the repeating unit and contained one B atom and one N atom. Its lattice constants were $a = b = 2.51 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. On this basis, a $3 \times 3 \times 1$ supercell containing nine B atoms and nine N atoms was constructed. A $15 \text{ \AA}$ vacuum layer was introduced perpendicular to the material surface to isolate periodically repeated images and avoid nonphysical interactions caused by periodic boundary conditions. The plane wave cutoff energy was 520 eV, and the Brillouin zone (BZ) was sampled using a Γ -centered $5 \times 5 \times 1$ k-point mesh. The electronic self-consistent energy convergence threshold was 10^{-6} eV, and geometric optimization continued until the force on each atom was below $0.01 \text{ eV \AA}^{-1}$. The doping configuration space comprised single-atom substitution at B or N sites, interstitial doping, and multi-dopant configurations involving nonmetallic elements. The dopants were Fe, Co, Cu, Ti, Pd, Rh, Ag, Pt, Au, C, Si, Ge, and Sn. The element combinations, substitution sites, and numbers of dopant atoms were varied to cover different sites and concentrations. In this work, a multi-dopant configuration contains two or three dopant atoms and is accordingly classified as a two-dopant or three-dopant configuration. The term co-doped configuration refers to a structure containing two or more different dopant species. The configuration notation is defined as follows: X@B and X@N indicate single substitution of a B or N atom by one X atom, respectively. X-Y@2B denotes one X atom and one Y atom substituting two B atoms; and 3X@3B denotes three X atoms substituting three B atoms. Bond lengths, bond angles, and other structural parameters of the doped systems were analyzed using the electronic-structure visualization software VESTA [55]. To evaluate the binding strength of dopant atoms in h-BN, the binding energy was defined as follows:

$$E_b = E_{\text{total,doped}} - (E_{\text{total,undoped}} + E_K) \quad (1)$$

Here, $E_{\text{total,doped}}$ denoted the total energy of h-BN after doping, $E_{\text{total,undoped}}$ was the total energy of undoped h-BN containing the

corresponding N or B vacancy, and E_K was the spin-polarized total energy of the corresponding free dopant atom. The binding energy was the change in the total energy when multiple atoms combined to form an integrated system relative to their isolated atomic states. A more negative E_b value indicated more favorable binding between the dopant and the host structure and was used to compare relative stability under the specified reference state. The calculated binding energy describes the interaction of dopant atoms with pre-existing vacancies under the adopted reference state.

The dielectric tensor of each relaxed structure was calculated using density functional perturbation theory (DFPT) [56]. Starting from the ground-state electronic structure, the first-order correction to the Kohn-Sham equation under a perturbing potential was obtained using the variational principle. The changes in charge density caused by small atomic displacements and their feedback effects were calculated, after which the force-constant and dynamical matrices were constructed. The dielectric tensor is written as:

$$\epsilon_{ij} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{pmatrix} (i, j \in \{x, y, z\}) \quad (2)$$

The in-plane component is defined as $\epsilon_{\parallel} = \frac{\epsilon_{xx} + \epsilon_{yy}}{2}$, and the out-of-plane component is defined as $\epsilon_{\perp} = \epsilon_{zz}$. In this case, the averaged static dielectric constant over the three directions is $\epsilon_0 = \frac{\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}}{3}$, which comprises the electronic contribution (ϵ_{∞}) and the ionic contribution (ϵ_{ion}). Electronic band structures were calculated along symmetry-adapted high-symmetry paths, and the total and projected densities of states (PDOS) were evaluated using Gaussian smearing with a width of 0.05 eV. For the candidate systems, the Heyd-Scuseria-Ernzerhof (HSE06) screened hybrid functional was additionally employed to obtain a more accurate description of the band structures.

2.2. ALIGNN architecture and model evaluation

In this work, we employed the open-source ALIGNN [51] framework, a GNN architecture that performed message passing on both an atomistic graph and its corresponding atomistic line graph. ALIGNN takes crystal structures as input, represents atoms as nodes in the atomistic graph, and represents neighboring atom pairs as edges. In the line graph, the edges of the atomistic graph are converted into nodes, and two bonds that share a central atom are connected to encode bond-angle information [50], as illustrated in Fig. 1. The material structure was first converted into an atomistic graph, in which each atom was represented as a node and the chemical bonds between atoms were represented as

edges. Each node was assigned nine input features according to its atomic species: element category, electronegativity, group number in the periodic table, covalent radius, number of valence electrons, first ionization energy, electron affinity, block in the periodic table, and atomic volume [48,51]. The initial edge feature was the interatomic bond length r , which was expanded using a Radial Basis Function (RBF). During construction of the line graph, each node represented an edge of the atomistic graph, namely a bond between two atoms. If two bonds connected to the same atom in the atomistic graph, an edge was established between the corresponding nodes in the line graph. Bond-angle information was thereby encoded as an edge feature of the line graph. During feature updating, edge-gated graph convolution (EGCN) updated the node and edge features, while a gating mechanism dynamically adjusted the importance of each edge.

The model architecture contained two ALIGNN layers and two EGCN layers, with a hidden feature dimension of 128. Continuous bond lengths and bond angles were expanded using 80-dimensional and 40-dimensional radial basis functions, respectively, and were then mapped into a common 128-dimensional latent space. After graph convolution, global average pooling generated a structure-level representation, and a fully connected regression layer output the dielectric constant. More details of the model workflow and key parameters are provided in the Supplementary Information. The ALIGNN implementation used in this study was based on the PyTorch deep learning framework and mainly combined Deep Graph Library (DGL) and PyTorch Geometric (PyG) [57, 58].

A database of dielectric properties and structures was constructed for 648 doped systems and was divided into training, validation, and test sets in a ratio of 80%:10%:10%. The Adam optimizer minimized the mean squared error, and a One Cycle strategy adjusted the learning rate. Model performance was evaluated using the coefficient of determination R^2 , root mean square error (RMSE), and mean absolute error (MAE), which were calculated as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (3)$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (4)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - \hat{y}_i| \quad (5)$$

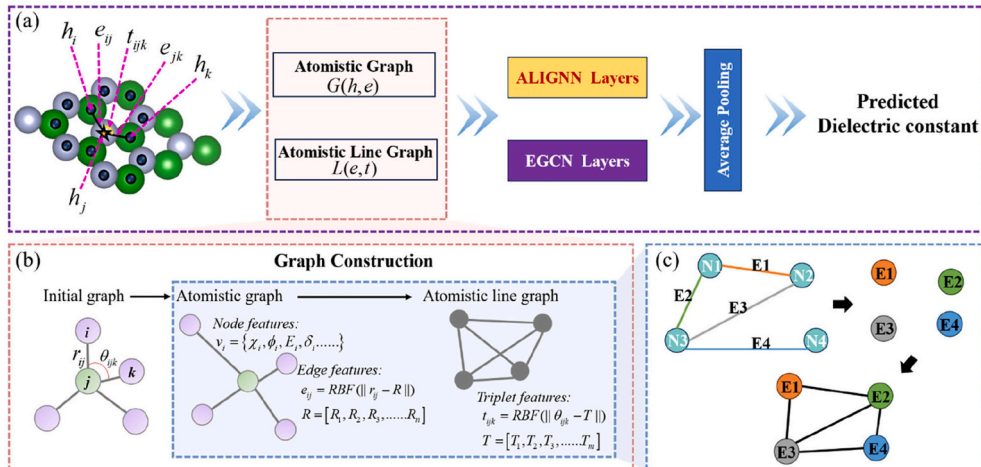


Fig. 1. Workflow of the ALIGNN model for predicting the dielectric constant of doped h-BN. (a) Overall prediction pipeline of the ALIGNN model. (b) Construction workflow of atomistic graph and atomistic line graph. (c) Schematic diagram of line graph transformation from original graph.

Here, y_i was the actual dielectric constant, $\hat{y}_i$ was the predicted dielectric constant, and n was the number of samples used for training.

2.3. Eliminating the contribution of the vacuum in the dielectric response

The dielectric constant of a monolayer obtained directly from a periodic supercell is affected by the thickness of the vacuum layer. The response of a supercell containing a large vacuum region therefore could not be regarded directly as an intrinsic material value. To remove the vacuum dilution effect, we use the 2D polarizability to analyze dielectric modulation. The in-plane and out-of-plane components of the 2D polarizability (α^{2D}) can be related to the dielectric tensor of the periodic supercell (ϵ^{SC}) as [59]:

$$\frac{\alpha_{\parallel}^{2D}}{\epsilon_v} = L(\epsilon_{\parallel}^{SC} - 1) \quad (6)$$

$$\frac{\alpha_{\perp}^{2D}}{\epsilon_v} = L\left(1 - \frac{1}{\epsilon_{\perp}^{SC}}\right) \quad (7)$$

where ϵ_v is the vacuum permittivity, L is the length along the z-direction separating the cell images. The 2D polarizability does not require an assumed effective thickness and is therefore unaffected by the ambiguity associated with the physical boundary assigned to the monolayer. It measures the induced dipole response per unit area and consequently provides a more accurate description of the dielectric response of an atomically thin material. The 2D polarizability is commonly converted to a quantity with dimensions of length and denoted as $\chi^{2D} = \alpha^{2D} / 4\pi\epsilon_v$. We also calculate the static dielectric constants of representative structures by normalizing the supercell dielectric response using their effective thicknesses. Further details can be found in Section 1.3 of the Supplementary Information.

3. Results and discussion

3.1. Structural stability

Fig. 2(a) and (b) show the top and side views of pristine monolayer h-BN, respectively. After relaxation, the B and N atoms retained a regular honeycomb network, each atom remained threefold coordinated, and

the monolayer preserved a stable planar structure. Before introducing dopant atoms, we geometrically relaxed h-BN containing a B vacancy or an N vacancy, as shown in Fig. 2(c) and (d). Table 1 lists the characteristic interatomic distances around the vacancies.

In pristine h-BN, the B-N bond length was 1.45 Å, and the nearest N-N and B-B distances were both 2.51 Å. After a boron vacancy (V_B) was formed, the adjacent B-N bond contracted to 1.40 Å, while the N-N distance across the vacancy increased to 2.73 Å. These values differed slightly from the previously reported values of 1.44 and 2.61 Å [60], but the trend remained consistent. By contrast, a nitrogen vacancy (V_N) left the B-N distance at 1.45 Å but shortened the B-B distance to 2.27 Å. These optimized values were close to the previously reported values of 1.44 and 2.31 Å [60]. The two vacancy types exhibited opposite local relaxation behavior, indicating that B and N vacancies form distinct local coordination environments. The optimized structures showed no buckling of the monolayer along the z direction, and the vacancy-induced changes were concentrated in the in-plane reconstruction near the defect. The overall monolayer structure of h-BN remained intact and provided a stable host environment for subsequent dopant incorporation.

Each of the 13 dopant elements was introduced into h-BN by substituting either a B atom or an N atom, followed by structural relaxation. The relaxed local geometries in Table 2 show that the equilibrium bond length between a dopant and its nearest host atom differs for the same dopant at different substitution sites. Comparison of the bond lengths after doping indicates that dopant size strongly affects local structural expansion and bonding. Elements with smaller atomic radii tend to form shorter bonds. Because the atomic radius of C was close to those of B and N, the C-B and C-N bond lengths formed after doping remained close to the pristine h-BN value of 1.45 Å. Sn produced the longest dopant-B bond at the N site (1.85 Å), whereas its dopant-N

Table 1

Characteristic interatomic distances in pristine and monolayer h-BN with vacancy.

Distance between atoms	h-BN	B vacancy	N vacancy
B-N	1.45 Å	1.40 Å	1.45 Å
N-N	2.51 Å	2.73 Å	—
B-B	2.51 Å	—	2.27 Å

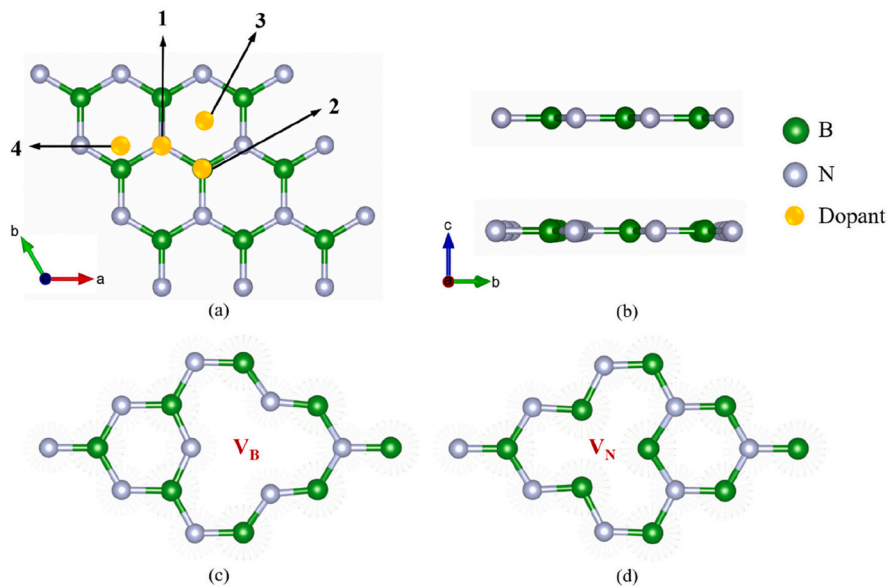


Fig. 2. Relaxed structures of pristine and monolayer h-BN with vacancy. (a) Top and (b) side view of monolayer h-BN. Relaxed structures containing (c) a B vacancy and (d) an N vacancy.

Table 2

Atomic distances in doped monolayer h-BN after structural relaxation.

Doped atom	N Site	B Site
	$d_{\text{(Dop-B)}}$	$d_{\text{(Dop-N)}}$
Ag	1.81 Å	1.82 Å
Au	1.82 Å	1.83 Å
C	1.49 Å	1.41 Å
Co	1.69 Å	1.66 Å
Cu	1.73 Å	1.70 Å
Fe	1.70 Å	1.66 Å
Ge	1.74 Å	1.68 Å
Pd	1.78 Å	1.78 Å
Pt	1.79 Å	1.80 Å
Rh	1.75 Å	1.75 Å
Si	1.72 Å	1.61 Å
Sn	1.85 Å	1.76 Å
Ti	1.81 Å	1.73 Å

bond at the B site was 1.76 Å. This compresses neighboring atoms and indicates potentially unstable structural characteristics. Within the same period, transition metals such as Fe ($3d^6 4s^2$) and Co ($3d^7 4s^2$) or Pd ($4d^{10}$) and Ag ($4d^{10} 5s^1$) showed relatively small differences in bond length after doping, indicating that periodic orbital structure also plays an important role in coordination behavior. Despite differences in dopant species and atomic radius, the bonding patterns still followed the constraints of the hexagonal h-BN lattice as closely as possible. After local structural adjustment and relaxation, the systems became stable without severe lattice distortion. The four representative structures in Fig. 3(c) likewise show that the larger Si and Ti atoms induce more pronounced local changes in bond lengths and angles, but these distortions do not destabilize the monolayer structure.

Fig. 3(a) compares the binding energy of 13 single-dopant configurations at B and N substitution sites. The binding energy details are presented in Table S1 of the Supplementary Information. All dopants had negative binding energy at B sites, whereas Pd, Ge, and Sn had

positive values at N sites, indicating relatively weak binding. For every element, the binding energy of the B-site configuration was more negative than that of the corresponding N-site configuration. This result indicates that the dopants bind more strongly to a pre-existing B vacancy than to a pre-existing N vacancy. C@B had the most negative binding energy among all single-dopant configurations, indicating the strongest binding to a pre-existing B vacancy under the adopted reference state. Based on the stability analysis of the single-dopant configurations, the nonmetallic elements C, Si, Ge, and Sn were selected to construct two-dopant substitutional configurations. These configurations included single-species configurations containing two identical dopants and co-doped configurations containing two different dopant species. The two dopants occupied either two B sites (B-B) or one B and one N site (B-N). The binding energy calculations for combinations of identical and different atoms can be found in Eq. (1) and Eq. (2) of the Supplementary Information. Except for the two-Sn doping configurations, which became highly unstable due to the large atomic size of Sn, all other structures exhibited favorable binding stability. The binding energy was consistently more negative when both dopants occupied B-B sites than when they occupied mixed B-N sites, as illustrated in Fig. 3(b). In addition, we examined three-dopant configurations involving C, Si, and Ge. We found that the structural strength decreased monotonically with increasing atomic radius of the Group IV dopants. The trend can be attributed to the larger atomic radius introducing greater local lattice distortion and longer bond lengths, which weaken the overall binding strength.

3.2. Dielectric constant analysis

To validate our computational approach, we first calculated the dielectric constants of pristine monolayer h-BN and compared them with the results reported by Laturia et al. [61]. The close agreement supports the reliability of our DFPT calculations. Details of the calculation and comparison are provided in Section 1.3.1 of the Supplementary

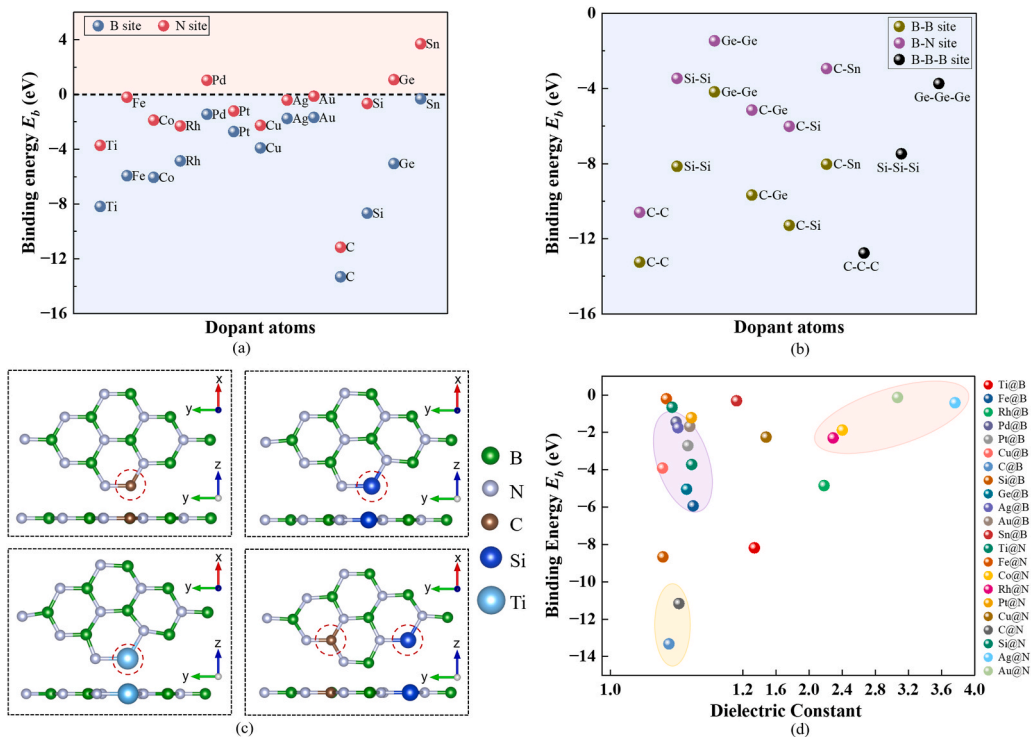


Fig. 3. Binding energy and dielectric response of doped monolayer h-BN. Binding energy of (a) single-dopant substitutional configurations at B or N site and (b) multi-dopant substitutional configurations at B-B sites, B-N sites, and B-B-B sites. (c) Representative relaxed structures. (d) Relationship between binding energy and dielectric constant.

Information. We then calculated and analyzed the binding energy and dielectric constants of h-BN doped with the 13 dopant species considered in this work. In Fig. 3(d), the dielectric constant axis is enlarged nonlinearly to distinguish the densely distributed data points in the range of 1.0–1.2. The configurations with the most negative binding energy were mainly C-doped systems and were concentrated in the low dielectric region. Systems in which Rh, Co, and other dopants occupied N substitution sites achieved higher dielectric constants while retaining intermediate binding stability. Fig. 4(a) decomposes the static dielectric constants of representative doped systems into electronic and ionic contributions and presents the in-plane and out-of-plane components of the 2D polarizability. More details regarding the dielectric constant and polarizability can be found in Table S5 of the Supplementary Information. Pristine h-BN and almost all doped structures exhibited higher in-plane than out-of-plane dielectric responses. This feature is consistent with the continuous in-plane B–N bonding network of 2D h-BN and its finite atomic layer thickness in the out-of-plane direction. The electronic contribution dominated in both directions, while the ionic contribution was generally smaller. This behavior results from the weak interlayer vdW interaction, which restricts ionic motion along the interlayer direction and allows the electronic cloud response to dominate. The increase in the total static dielectric constant is primarily driven by the enhanced electronic polarization, while the additional contribution from lattice polarization varies with the dopant element and its site occupation.

To establish a structure-property dataset for ML, we calculated 648 doped h-BN configurations. The distribution characteristics of the dataset grouped by different elements are presented in Fig. S3 of the Supplementary Information. Every structure in the dataset was geometrically relaxed to obtain its most stable atomic arrangement and ensure an accurate description of the doped structure. The dataset included single-species configurations and co-doped configurations containing nonmetal dopants (C–Si, C–Ge, C–Sn), as well as multiple doping positions corresponding to the four sites in Fig. 2(a). The doping concentration of some elements was adjusted by replacing n ($n = 1, 2$, or 3) B or N atoms. ALIGNN was trained to map the structural representations to the calculated dielectric properties. The input structures, which varied in dopant species, substitution sites, concentrations, and local geometries, naturally gave rise to different attributed graphs and distinct node and edge feature combinations. These structural differences then led to diverse local subgraphs, message-passing pathways,

and learned embeddings. The orientationally averaged static dielectric constant before vacuum normalization was used as a common scalar label for model training, establishing a consistent regression target across configurations with different local symmetries. Further discussion of the relationship between the label and the 2D polarizability is presented in Section 1.3.3 of the Supplementary Information. Fig. 4(b) shows that the data distribution spans both sides of the pristine reference value of 1.8862, demonstrating that doping can tune the dielectric properties of h-BN over a wide range. However, because the direction and magnitude of dielectric tuning were initially unknown, the sample distribution was imbalanced. Low and intermediate dielectric samples outnumbered those with extremely high dielectric constants, and only a small number of configurations represented the high value region. Nevertheless, the dataset included variations in elemental species, substitution site, and doping concentration and therefore provided a basis for learning nonadditive structure-dielectric relationships.

3.3. ALIGNN prediction and application

Fig. 4(c) compares the values predicted by ALIGNN with the first-principles results. The learning rate curve and loss function curve of the model are presented in Fig. S4 of Supplementary Information. The Pearson correlation coefficient (r), R^2 , RMSE, and MAE values for the training and test sets are summarized in Table 3. In addition, we performed five-fold cross-validation to further assess the model robustness, and the corresponding results are also included in the table. The model captures the linear trend of the dielectric constant well, as reflected by the high Pearson correlation coefficients obtained for both the training and testing sets. For unseen test structures, the correlation decreases only moderately. Relative to the target range of approximately 1–8, this error level indicates that the model can distinguish low, intermediate, and high dielectric responses and can preliminarily rank candidate structures. ALIGNN acts as an effective surrogate model within the present chemical and structural space. The residual distribution, with most training and test samples showing residuals close to zero, reveals the sources of model error. The larger errors occurred mainly in sparsely sampled regions. Further details of the cross-validation are provided in Fig. S5 of the Supplementary Information.

After a doped structure was provided as input, the surrogate model predicted its dielectric constant within a very short time, averaging approximately 0.07 s. By comparison, a DFT calculation required

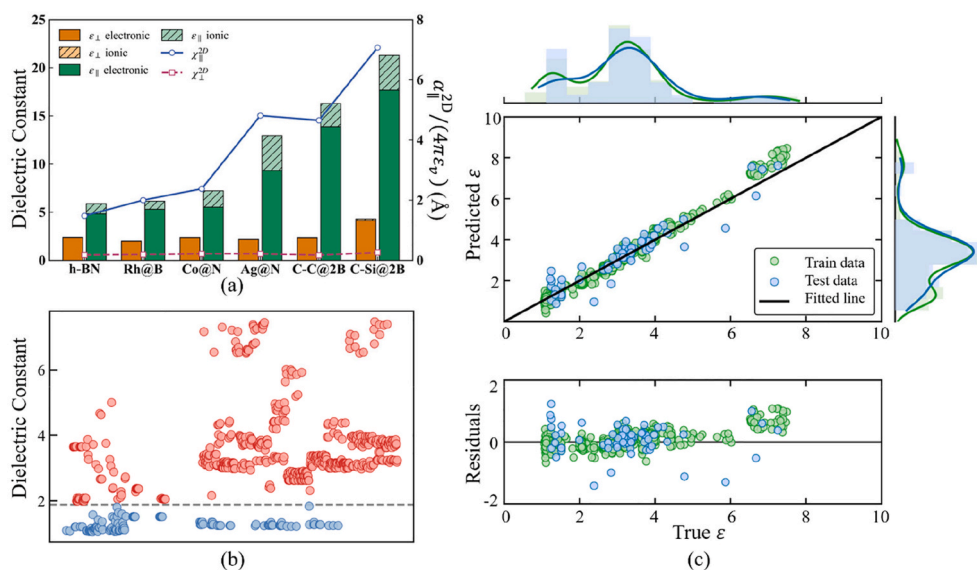


Fig. 4. Dielectric dataset and ALIGNN performance. (a) Electronic and ionic contributions to the in-plane ($\epsilon_{\parallel}$), out-of-plane ($\epsilon_{\perp}$), and 2D polarizability of representative structures. (b) Distribution of dielectric constant in the dataset. (c) Comparison between ALIGNN predicted dielectric constant and first-principles values with the residual distribution.

Table 3

Model performance metrics on the training set, testing set and 5-fold cross-validation.

Dataset	Pearson r	R^2	RMSE	MAE
Training set	0.993	0.964	0.271	0.197
Testing set	0.942	0.876	0.477	0.345
5-fold cross-validation	0.872 ± 0.033	0.734 ± 0.055	0.739 ± 0.086	0.425 ± 0.036

approximately 10 min per material on average and was therefore considerably more time-consuming. Before large-scale theoretical calculations of doped h-BN, the model can predict and screen the dielectric constants of candidate structures, reducing computational resources and time. To evaluate the model from a screening perspective, we further examined its ranking performance on the fixed test set. As shown in Fig. S6, the ALIGNN predictions generally reproduce the variation in the DFPT-calculated dielectric constants across the test samples. The predicted and DFPT values exhibited a Spearman rank correlation coefficient of 0.936. Moreover, nine of the ten configurations with the highest DFPT dielectric constants were recovered among the top ten candidates ranked by ALIGNN. These results indicate that, within the dopant, concentration, and configurational space represented by the present dataset, ALIGNN can provide a useful preliminary ranking of candidate structures. The model is therefore expected to reduce the number of candidates requiring subsequent DFPT dielectric-response calculations.

To understand the local information on which the model focuses in an atomic structure, we extracted the final feature vectors output by the EGCN and ALIGNN layers and mapped their norms to the corresponding atomic positions to obtain atomic representation-intensity maps. The atomic feature maps reveal that the model captures spatial variations in local structural environments during the learning process. In pristine h-BN, the model assigned larger feature magnitudes to B atoms, as shown on the left of Fig. 5(b). The inherent electronegativity difference between B and N induces persistent charge polarization. N atoms with higher electronegativity tend to capture valence electrons, leading to distinct atomic representation intensities at the intrinsic B and N sites, and this feature can be accurately captured by the ALIGNN model. After dopants were introduced, the larger feature magnitudes gradually concentrated on the dopants and their nearest-neighbor coordination environments. Fig. 5(a) presents atomic feature maps of h-BN containing one, two, and three substitutional C atoms at B sites. The doping ratios

were 5.56%, 11.11%, and 16.67%, and the dielectric constants before normalization were 1.10, 3.65, and 1.09, respectively. Although C doping can reduce the dielectric constant of h-BN, consistent with the previously reported experimental result [28], the analysis showed that the dielectric response did not vary monotonically with concentration. The atomic feature maps also show that host atoms of the same species have different intensities depending on their positions relative to the defect. This finding indicates that the model distinguishes structural environments not only by elemental species but also through bond lengths, bond angles, and local connectivity.

It is noteworthy that many C-Si co-doped configurations at different B sites produced high dielectric responses. The different spatial arrangements of the C and Si dopants resulted in variations in the dielectric response. Fig. 5(c) shows the C-Si@2B structure, which exhibits pronounced dielectric enhancement and was identified from the calculated DFPT database as a particularly promising high- k candidate based on its overall dielectric characteristics. The dielectric modulation is primarily evaluated using the 2D polarizabilities, as reported in Table 4. The in-plane and out-of-plane 2D polarizabilities of C-Si@2B are approximately 4.78 and 1.50 times the corresponding values of pristine h-BN, respectively. In the low- k doping space, three Si atoms formed Si-Si bonds in 3Si@3B, as shown in Fig. 5(d). The electric-dipole response of this nonpolar bond under an external electric field is weaker than that of a B-N bond, reducing the overall polarizability of the

Table 4

Two-dimensional polarizability of candidates.

Material	$\chi_{ }^{2D}$ ($\text{\AA}$)	$\chi_{\perp}^{2D}$ ($\text{\AA}$)
h-BN	1.48	0.18
C-Si@2B	7.07	0.27
3Si@3B	0.05	0.12

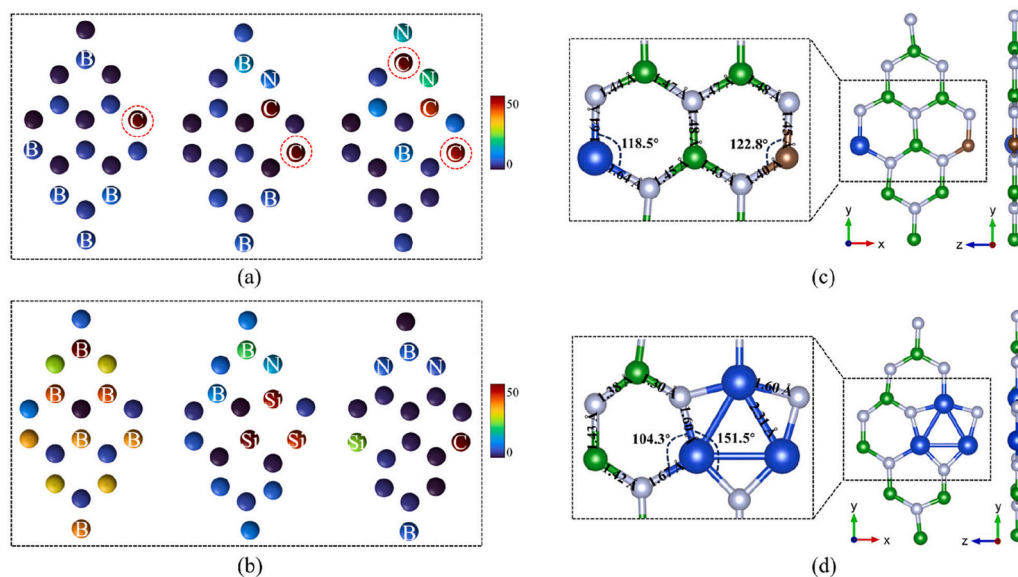


Fig. 5. ALIGNN atomic feature maps and representative doped structures. (a) Atomic feature maps for monolayer h-BN with increasing numbers of substitutional C dopants. (b) Atomic feature maps of pristine h-BN, 3Si@3B and C-Si@2B configurations from left to right, elemental symbols mark the six atoms with the highest representation intensities in each map. Relaxed structures of (c) C-Si@2B and (d) 3Si@3B.

material. Both components of its 2D polarizability are substantially lower than those of pristine h-BN. For comparison with conventionally reported dielectric constants, we also calculated the thickness-normalized dielectric constants using Eqs. (10) and (11) in the Supplementary Information. C-Si@2B had in-plane and out-of-plane dielectric constants of 21.29 and 4.29, respectively, and an averaged static dielectric constant of 15.62, supporting further investigation of C-Si@2B as a potential 2D high- k dielectric. For 3Si@3B, the corresponding dielectric constants were 1.15 and 1.56, respectively, with an averaged static dielectric constant of 1.29.

From the atomic feature maps, Si atoms at inequivalent substitution sites exhibit different representation intensities, indicating that the model distinguishes their local bonding environments in the 3Si@3B structure. For the C-Si@2B co-doped structure, C dopants yield substantially larger dielectric representation intensities relative to Si atoms. The observed differences in representation intensity are consistent with the electronic-structure trends revealed by our band-structure and PDOS calculations. The atomic feature maps explain model behavior and make the conventional black-box prediction more transparent by providing qualitative insight into the learned local structural representations. They help clarify the basis of the model decisions and provide a new perspective for revealing how specific doping strategies affect dielectric properties. The configuration space of doped systems must simultaneously consider elemental species, concentration, and site arrangement. The trained ALIGNN model represents these coupled variables through a unified atomic structure and can prioritize candidates for recalculation, thereby reducing the computational burden of indiscriminate enumeration.

3.4. Microscopic mechanisms of dielectric constant tuning

3.4.1. Ionic polarization

The total static dielectric response consists of electronic and ionic polarization, which may change differently for the same dopant substitution. The ionic contribution is particularly important under low-frequency or static electric fields. The ionic dielectric tensor is expressed as follows [62]:

$$\epsilon_{ij}^{\text{ion}} = \frac{4\pi}{\Omega} \sum_n \frac{S_{n,ij}}{\omega_n^2} \quad (8)$$

Here, Ω is the unit-cell volume, $S_{n,ij}$ is the oscillator strength tensor of the n -th phonon mode, constructed from products of mode effective charge components, and ω_n is the frequency of that infrared-active optical phonon mode. The mode effective charges are determined by the atomic Born effective charge tensors $Z_{\kappa,ij}^*$ and the mass-weighted phonon eigenvectors, where κ indexes the atoms. Larger mode effective charges and lower infrared-active optical phonon frequencies generally enhance the ionic polarization response, with other factors held constant. The Born effective charge tensor is expressed as follows:

$$Z_{ij}^* = \begin{pmatrix} Z_{xx} & Z_{xy} & Z_{xz} \\ Z_{yx} & Z_{yy} & Z_{yz} \\ Z_{zx} & Z_{zy} & Z_{zz} \end{pmatrix} (i, j \in \{x, y, z\}) \quad (9)$$

It characterizes the ionic polarization response under an external electric field. It quantitatively describes the contribution of lattice vibrations to dielectric polarization, and its magnitude directly reflects the strength of polarization.

We found that the total static dielectric constant increased when Rh substituted either a B or an N site. However, the ionic dielectric contribution decreased from 0.27 in pristine h-BN to 0.25 in Rh@B and increased in Rh@N, as shown in Table 5. In Rh@B, the magnitudes of the Born effective charges of B and N atoms around the substitution site were generally smaller than the original values, consistent with the slight decrease in the ionic dielectric contribution. In Rh@N, the Born effective charges of neighboring atoms increased markedly, thereby enhancing the ionic polarization response.

The lattice dielectric response depends not only on Born effective charges but also on infrared-active phonon frequencies [63]. For vibrations with similar mode effective charges, a lower frequency generally indicates a weaker restoring force and a larger ionic displacement induced by the field, resulting in a stronger contribution to the ionic dielectric constant. The calculated optical-mode frequencies of Rh@N and C-Si@2B decreased, indicating optical-phonon softening. Relative to the lowest-frequency mode of h-BN at 194 cm^{-1} , Rh@N exhibited a low-frequency mode at 125 cm^{-1} together with a pronounced increase in the ionic dielectric constant. The softening was more marked in C-Si@2B, where a low-frequency mode appeared at 54 cm^{-1} and the ionic dielectric contribution increased more strongly, producing a more pronounced dielectric enhancement than in the singly doped systems. Local strain caused by dopant incorporation softens certain optical phonons, promotes lattice polarization, and increases the ionic polarization contribution.

3.4.2. Electronic polarization

The electronic dielectric constant ϵ_{∞} is a macroscopic measure of electron-cloud polarization under an external electric field. To investigate doping-induced changes in the electronic response, we first calculated the band structure and PDOS of pristine h-BN, as shown in Fig. 6 (a). The horizontal red dashed line denotes the Fermi level. Pristine h-BN has a band gap of approximately 4.65 eV, exhibiting wide-band-gap insulating character. This value is consistent with the previously reported band gaps for monolayer h-BN [64,65]. The PDOS indicates that the valence-band edge is dominated by N-2p states, whereas the conduction-band edge mainly originates from B-2p states, consistent with the polar character of the B-N bonds. The introduction of different impurity atoms leads to distinct changes in the band gap.

The electronic structures of C-Si@2B and 3Si@3B proposed above were further evaluated using the HSE06 hybrid functional. Spin polarization was included for the 3Si@3B system, as its neutral supercell contains an odd number of valence electrons. C-Si@2B exhibits a band gap of approximately 0.71 eV, displaying its semiconducting nature. As shown in Fig. 6(b), the C-2p and Si-3p states overlap with the N-2p states

Table 5
Born effective charge tensors and ionic dielectric constants.

Material	Z_{ij}^B (e)	Z_{ij}^N (e)	$ Z_{ij}^B $	$ Z_{ij}^N $	$\epsilon_{\text{ion}}^{\text{SC}}$
h-BN	$\begin{pmatrix} 2.71 & 0.00 & 0.00 \\ 0.00 & 2.71 & 0.00 \\ 0.00 & 0.00 & 0.28 \end{pmatrix}$	$\begin{pmatrix} -2.71 & 0.00 & 0.00 \\ 0.00 & -2.71 & 0.00 \\ 0.00 & 0.00 & -0.28 \end{pmatrix}$	3.84	3.84	0.27
Rh @ B	$\begin{pmatrix} 2.71 & 0.00 & 0.00 \\ 0.00 & 2.44 & 0.00 \\ 0.00 & 0.00 & 0.23 \end{pmatrix}$	$\begin{pmatrix} -2.55 & 0.00 & 0.00 \\ 0.00 & -2.85 & 0.00 \\ 0.00 & 0.00 & -0.25 \end{pmatrix}$	3.65	3.83	0.25
Rh @ N	$\begin{pmatrix} 3.08 & 0.00 & 0.00 \\ 0.00 & 2.67 & 0.00 \\ 0.00 & 0.00 & 0.26 \end{pmatrix}$	$\begin{pmatrix} -3.87 & 0.00 & 0.00 \\ 0.00 & -2.79 & 0.00 \\ 0.00 & 0.00 & -0.11 \end{pmatrix}$	4.08	4.77	0.43

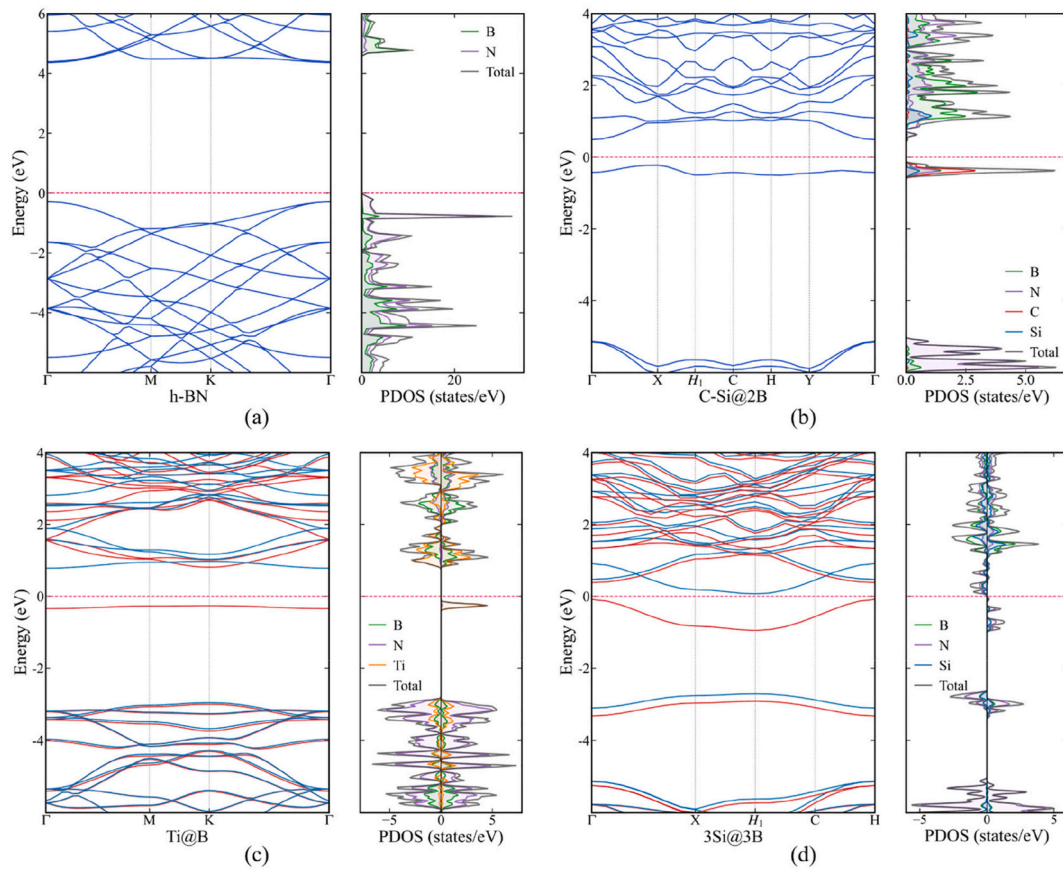


Fig. 6. Band structures and projected densities of states (PDOS) of (a) pristine h-BN, (b) C-Si@2B, (c) Ti@B, and (d) 3Si@3B. The red and blue curves represent the spin-up and spin-down bands, respectively, and the horizontal red dashed line denotes the Fermi level.

near the valence-band edge, while the Si-3p and B-2p states overlap near the conduction-band edge. This overlap indicates orbital hybridization between the dopants and the h-BN lattice and is consistent with the local distortion shown in Fig. 5(c). Substitution of adjacent B sites by C and Si produces bond angles of 118.5° and 122.8° around Si and C, respectively, compared with the ideal value of 120° in the hexagonal lattice. The resulting change in the local bonding environment alters the orbital interactions between the dopants and the neighboring B and N atoms, as reflected by the overlapping and broadened PDOS features. These structural and electronic changes introduce states near the band edges, reduce the band gap, and lower the energy required for electronic excitation. The electron cloud therefore responds more readily to an external electric field, resulting in the increased dielectric constant.

The low-*k* 3Si@3B configuration exhibits a distinctly different spin-dependent electronic structure, as illustrated in Fig. 6(d). The red and blue curves represent the spin-up and spin-down bands, respectively. The 3Si@3B system exhibits semiconducting behavior in both spin channels, with band gaps of approximately 0.47 eV for the spin-up channel and 2.77 eV for the spin-down channel. Weakly dispersive bands appear near the Fermi level, indicating that their energies vary only slightly with the wave vector. The corresponding PDOS exhibits sharp peaks concentrated within narrow energy ranges, with major contributions from Si and N atoms. These features indicate that the associated electronic states are mainly concentrated around the doped region and its neighboring atoms. Fig. 5(d) shows that the three Si atoms occupy adjacent B sites and form a local cluster, causing the surrounding bond angles to deviate substantially from 120°. The bond-angle distortion induced by Si aggregation weakens the extended B-N (sp^2) hybridization network and changes the band-edge hybridization from a broad delocalized distribution to localized coupling dominated by Si-N interactions. The spatial distribution, orbital overlap, and transition

characteristics of the band-edge states all affect the electronic response. The discrete and localized Si-N derived states in 3Si@3B are less favorable for long-range redistribution of the electron cloud across the lattice, thereby weakening the electronic polarization and resulting in a lower macroscopic dielectric constant. Despite its semiconducting behavior in both spin channels, the 3Si@3B configuration may have limited insulating stability, and its leakage characteristics require further verification.

Additionally, spin-polarized calculations were performed for all transition-metal (TM)-doped configurations, with different initial local magnetic moments tested to determine their converged magnetic states. The h-BN systems doped with Ti, Fe, and Cu exhibit finite magnetic moments, whereas the other TM-doped systems remain nonmagnetic. Further details of the converged total magnetic moments and local magnetic moments on the transition-metal atoms are summarized in Table S3 of the Supplementary Information. From the binding-energy analysis in Section 3.1, Ti@B was identified as the relatively most stable system among the transition-metal-doped configurations, with the most negative binding energy. We then analyzed its spin-dependent electronic structure. The Ti-doped system exhibits semiconducting behavior in both spin channels, with band gaps of approximately 1.07 eV for the spin-up channel and 3.74 eV for the spin-down channel (Fig. 6(c)). This spin-dependent electronic structure, together with its finite magnetic moment, indicates that the Ti-doped system is a magnetic semiconductor. Notably, a sharp Ti-dominated peak appears near the Fermi level in the spin-up channel, indicating a localized impurity state introduced by Ti doping. Its pronounced spin asymmetry reflects unequal occupation of the two spin channels and accounts for the finite magnetic moment of the system. These changes in the electronic structure are accompanied by slight increases in both the in-plane and out-of-plane 2D polarizabilities, indicating that Ti doping enhances the

polarization response in both directions.

4. Conclusion

This work establishes a framework that combines first-principles calculations with ALIGNN to investigate the dielectric properties of doped h-BN. A structure-dielectric property database containing 648 relaxed configurations was constructed by systematically considering 13 dopant species, different substitution sites, doping concentrations, and co-doping combinations. The binding-energy analysis shows that the examined dopants bind favorably to pre-existing B vacancies, with C@B exhibiting the strongest binding. For the two-dopant systems, binding to configurations containing two pre-existing B vacancies is stronger than binding to configurations containing one B vacancy and one N vacancy. The ALIGNN model used in this work simultaneously incorporates atomic species, interatomic distances, and bond angles to learn the nonlinear relationship between dopant species, sites, concentrations, local configurations, and dielectric response. The trained ALIGNN model achieves an R^2 of 0.876 on the test set, effectively learns the nonlinear relationship between local doping environments and dielectric response. It provides an efficient and interpretable surrogate tool for prioritizing doped h-BN configurations for subsequent first-principles evaluation across the high-dimensional doping design space. We visualize the atom-resolved latent dielectric representation intensities inside the doped structures using ALIGNN. After doping, the larger feature intensities shift from the uniform h-BN framework to the dopants and their neighboring environments, indicating that local connectivity is important structural information for the model when evaluating dielectric response. C-Si@2B exhibits significantly enhanced polarizability, with its in-plane 2D polarizability reaching approximately 4.78 times that of pristine h-BN, making it the prominent high-dielectric candidate in the present structural set. In contrast, 3Si@3B maintains a comparatively low polarizability, showing potential low-dielectric characteristics. The dielectric response depends not only on dopant species and concentration but also on substitution sites, atomic arrangements, and local bonding. The mechanism analysis shows that the dopant-induced local strain affects Born effective charges and the softening of optical phonon modes. Orbital hybridization caused by C-Si co-doping increases electronic polarizability, and the combined enhancement of electronic and lattice responses ultimately produces a large static dielectric constant. By contrast, the local Si-Si cluster formed in 3Si@3B weakens orbital coupling in the continuous B-N network and increases electronic-state localization, thereby limiting the overall polarization response. The combined first-principles and ML framework proposed here provides a transferable approach for rapid prediction and bidirectional tuning of h-BN and offers a theoretical basis and technical support for doping studies of 2D dielectric materials.

CRedit authorship contribution statement

Yuhui Guo: Writing – original draft, Methodology, Investigation, Formal analysis. **Zikang Guo:** Writing – review & editing, Methodology. **Shenghong Ju:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **Bingyang Cao:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtphys.2026.102262>.

Data availability

Data will be made available on request.

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